

CHAPTER -8

DOUBLE RELAXATION PHENOMENA OF MONOSUBSTITUTED ANILINES IN BENZENE UNDER HIGH FREQUENCY ELECTRIC FIELD

DOUBLE RELAXATION PHENOMENA OF MONO-SUBSTITUTED ANILINES IN BENZENE UNDER HIGH FREQUENCY ELECTRIC FIELD

8.1. Introduction

In recent years, single or double relaxation phenomenon of polar liquid molecules in nonpolar solvents under high frequency (hf) electric field attracted the attention of a large number of workers [1,2]. The study often provides the valuable information on the shape, size and structure, in addition to solute — solvent or solute — solute molecular associations in terms of relaxation time τ and dipole moment μ estimated by any conventional method [3,4]. The stability or unstability [5] of the molecules towards dielectric relaxations, is, however, inferred from such study. τ_1 and τ_2 of the double relaxation method, τ_j from the ratio of slopes of the individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's in the limit $w_j = 0$. and μ_j 's from the linear coefficient β 's of either $\chi'_{ij}-w_j$ or hf conductivity $\sigma_{ij}-w_j$ curves shed more light on the structural aspects of such dielectropolar liquid molecules [6].

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity ϵ^*_{ij} together with the low frequency or static and optical frequency relative permittivities ϵ_{oij} and $\epsilon_{\infty ij}$ of isomers of methoxy substituted anilines (anisidines) and methyl substituted anilines (toluidines) in benzene under 2.02, 3.86 and 22.06 GHz electric field for different w_j 's were measured by Srivastava and Chandra [7] at 35°C. The analytical grade ortho-, para toluidines and para-anisidines were supplied by M/S. Riedel (Germany) and the others were of M/S. BDH (London). The liquids were further purified by repeated fractional distillations and their physical constants like density ρ . viscosity η and refractive indices n_{Dij} were carefully checked in agreement with the literature values before use. The purpose of the study [7] was to detect the possible existence of solute — solvent (monomer) and solute – solute (dimer) molecular associations in the mixtures of various concentrations.

Nowadays, the usual trend is to study the dielectric relaxation processes in terms of hf complex dielectric orientational susceptibility χ_{ij}^* rather than hf complex conductivity σ_{ij}^* or hf relative permittivity ϵ_{ij}^* . ϵ_{ij}^* includes within it all types of polarisations while σ_{ij}^* is associated with transport of bound molecular charges. Hence it is more reasonable to work with χ_{ij} 's as they have direct link with the orientational polarisations [8]. Moreover, the present method of study in S.I unit is superior because of its unified, coherent and rationalised nature.

The dielectric susceptibilities like real $\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{\infty ij})$, imaginary $\chi''_{ij} = \epsilon''_{ij}$ parts of complex susceptibility $\chi_{ij}^* = (\epsilon_{ij}^* - \epsilon_{\infty ij})$ and the low frequency susceptibility $\chi_{oij} = (\epsilon_{oij} - \epsilon_{\infty ij})$ which is real, were derived from the measured relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$ in each system for different ω_j 's of the respective solute [7]. The experimental results of χ_{ij} 's for different ω_j 's thus collected together are placed in Table 8.1 for use. 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_{oij} involved with ϵ_{oij} and $\epsilon_{\infty ij}$ is available. The use of n_{Dij}^2 for $\epsilon_{\infty ij}$ [7] may often introduce additional error in the calculation. Nevertheless the data presented in Table 8.1 are accurate upto 5% for χ''_{ij} and 2% for χ'_{ij} and χ_{oij} respectively.

The polar liquids like monosubstituted anilines often possess two or more τ 's in GHz electric field for the rotation of their flexible polar groups to the parent molecules and the whole molecule itself [9]. Bergmann et al [10] devised a graphical method to obtain double relaxation times τ_1 and τ_2 and hence weighted contributions c_1 and c_2 towards dielectric dispersions for some complex polar liquid molecules. The method is based on plotting the measured values of ϵ' , ϵ'' , ϵ_0 and ϵ_{∞} at various frequencies ω on a semicircle in a complex plane. A point was then selected on the chord through two fixed points on the semicircle drawn in consistency with the experimental data. Bhattacharyya et al [11], subsequently modified the above procedure to get the same with the

experimental values measured only at two different frequencies of GHz range.

Thus the object of the present paper is to detect the double relaxation times τ_1 and τ_2 due to rotations of the flexible parts and the whole molecules using χ_{ij} 's based on a single frequency measurement technique [7,12-13]. The aniline derivatives are thought to absorb electric energy strongly nearly at 10 GHz electric field. The parameters measured at 2.02, 3.86 and 22.06 GHz electric field may yield considerable τ_1 and τ_2 in comparison to 10 GHz electric field. Moreover, the present system of study in terms of new physical parameters, like χ_{ij} 's seems to yield a better insight into the relaxation phenomena of polar liquid molecules in nonpolar solvents. This study further tempted us to see how far χ_{ij} 's and σ_{ij} 's with w_j measurement yield the μ 's. The aspect of molecular orientational polarisation, is, however, achieved by introducing χ_{ij} 's because $\epsilon_{\infty ij}$ which includes the fast polarisation always appears as a subtracted term in Bergmann's equations [10]. Thus in order to exclude the fast polarisation processes and to avoid the clumsiness of algebra the established symbols of dielectric terminologies and parameters like $\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{\infty ij})$, $\chi''_{ij} = \epsilon''_{ij}$ and $\chi_{oij} = (\epsilon_{oij} - \epsilon_{\infty oij})$ of Table 8.1 are used to write the Bergmann's equations [10].

$$\chi'_{ij} / \chi_{oij} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad (8.1)$$

$$\chi''_{ij} / \chi_{oij} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (8.2)$$

assuming two separate broad dispersions for which the sum of c_1 and c_2 is unity. Eq. (8.1) and (8.2) are now solved to get.

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega (\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (8.3)$$

when the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} of Eq. (8.3) are plotted for

different w_j 's of a polar liquid at any given frequency ω of the applied electric field, a straight line results with intercept $-\omega^2\tau_1\tau_2$ and slope $\omega(\tau_1+\tau_2)$, as shown in Figure 8.1. The intercept and slope of Eq.(8.3) are, however, obtained by linear regression analysis made on the measured susceptibilities of different w_j 's of the monosubstituted anilines in C_6H_6 of Table 8.1 to get τ_1 and τ_2 as shown in the 7th and 8th columns of Table 8.2 extracted from the data of Table 8.1. The reliability of the data are checked through chisquares values. In absence of reliable τ_j values, the ratio of individual slopes of variation of χ''_{ij} and χ'_{ij} with w_j 's at $w_j \rightarrow 0$, as seen in Figures 8.2 and 8.3; were conveniently used to evaluate τ_j to compare with those of Murthy et al [14] of Figure 8.4 and Gopalakrishna's method [15].

The theoretical weighted contributions c_1 and c_2 due to estimated τ_1 and τ_2 from Eq. (8.3) were worked out from Fröhlich's equations [16] and are placed in Table 8.3 in order to compare them with the experimental ones from the intercept of the least squares fitted curves of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} against w_j from Figures 8.5 and 8.6 in the limit $w_j = 0$. The values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j = 0$ together with arbitrary curve of $1/\phi \log(\cos \phi)$ against ϕ in degrees shown elsewhere [17] are further used to obtain symmetric and asymmetric distribution parameters γ and δ as seen in Table 8.3 to conclude the symmetric relaxation behaviour of such molecules. Symmetric relaxation time τ_s from γ and characteristic relaxation time τ_{cs} from δ and ϕ are further estimated in order to compare both τ_s and τ_{cs} with τ_1 , τ_2 and τ_j in Table 8.2.

The dipole moments μ_1 and μ_2 by both hf susceptibility and conductivity measurement techniques are, however, worked out from linear coefficient β 's of $\chi'_{ij} - w_j$ and $\sigma_{ij} - w_j$ curves of Figures 8.3 and 8.7 in terms of b_1 , b_2 involved with the estimated τ_1 , τ_2 by double relaxation method. The μ_1 and μ_2 thus obtained are placed in Table 8.4 to see how far they are affected by the orientational polarisation and bound molecular charge in connection with χ_{ij} 's and σ_{ij} 's respectively. The estimated μ_1 and μ_2 by both the methods are finally

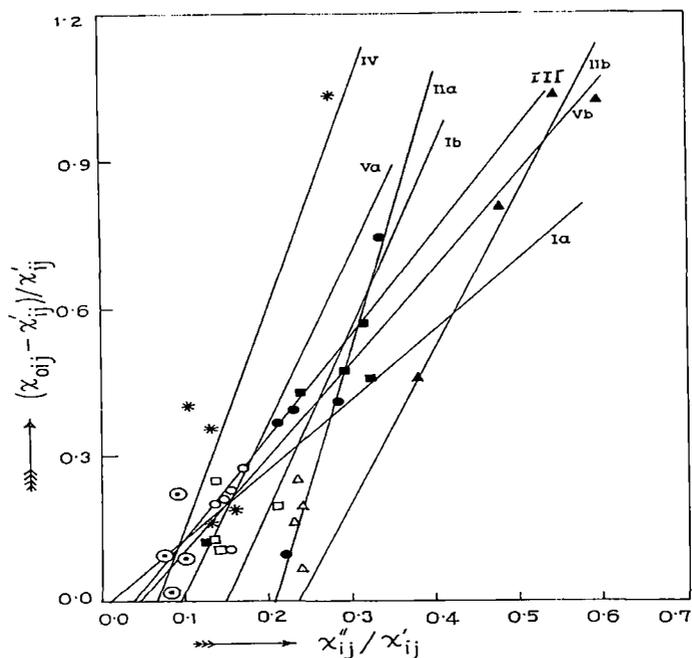


Figure 8.1: Linear variation of $(\chi'_{0ij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} of monosubstituted anilines in benzene at 35° C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

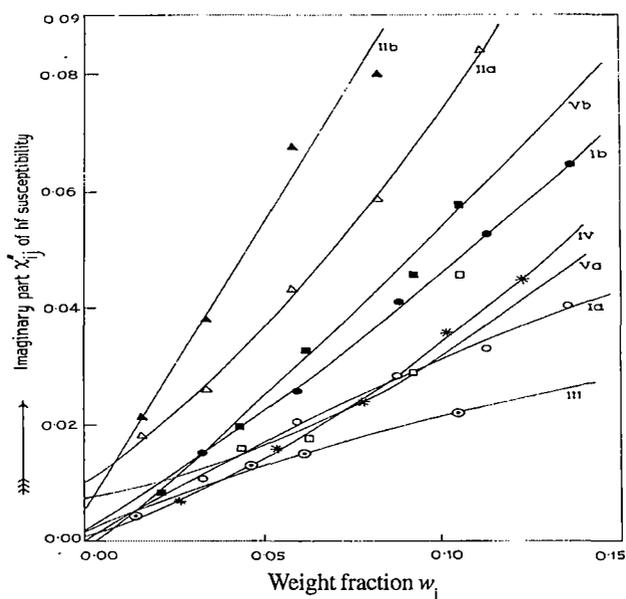


Figure 8.2: Variation of imaginary part of hf susceptibility χ''_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35° C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

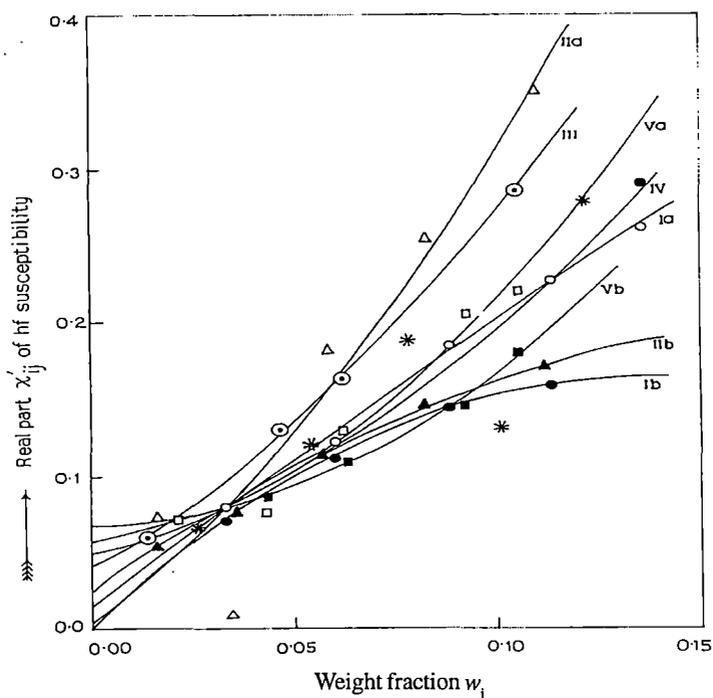


Figure 8.3: Variation of real part of hf susceptibility χ'_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35^o C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

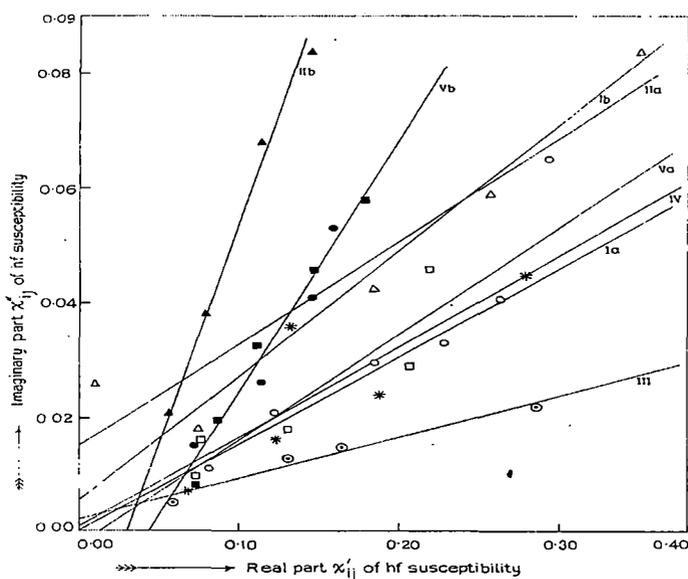


Figure 8.4: Linear plot of imaginary part of hf susceptibility χ''_{ij} against real part χ'_{ij} of monosubstituted anilines in benzene at 35^o C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

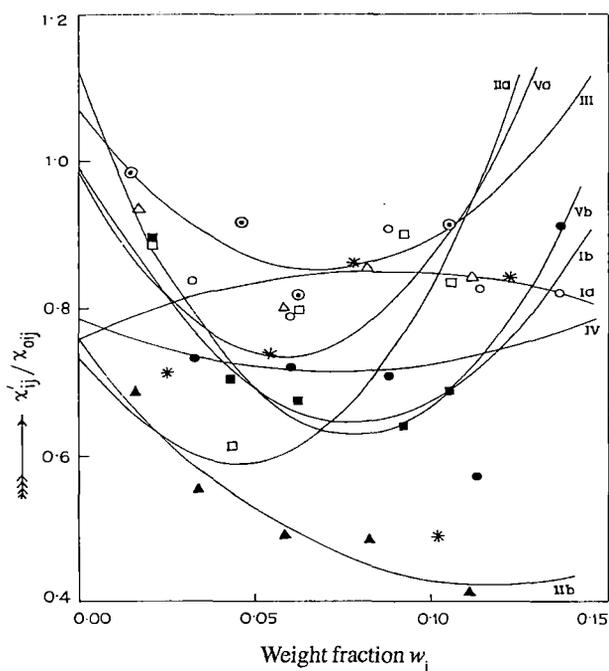


Figure 8.5: Plot of χ'_{ij}/χ'_{0ij} against weight fraction w_j of monosubstituted anilines in benzene at 35° C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

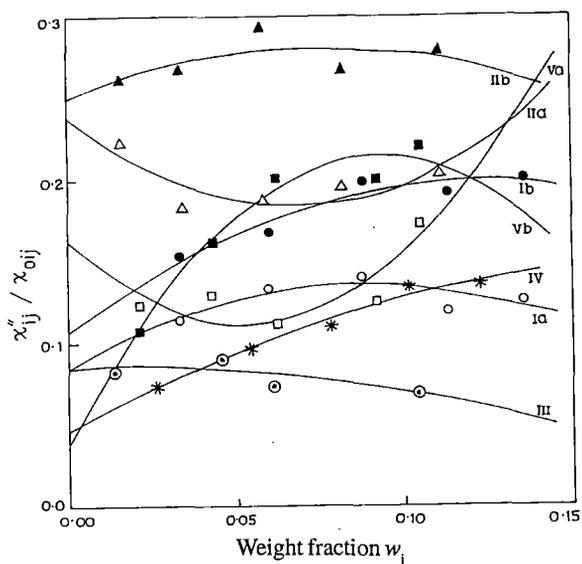


Figure 8.6: Plot of χ''_{ij}/χ''_{0ij} against weight fraction w_j of monosubstituted anilines in benzene at 35° C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

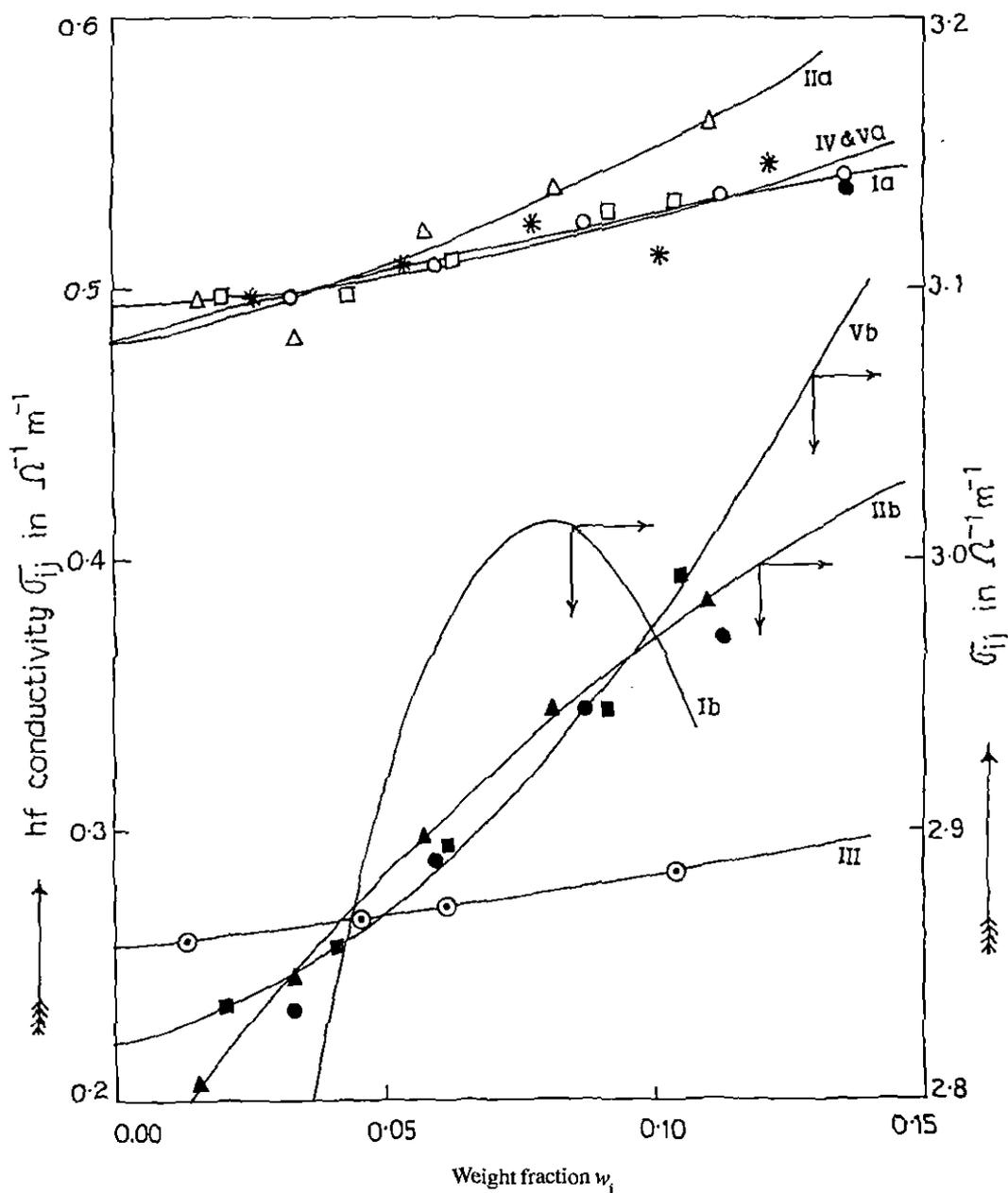


Figure 8.7: Plot of total hf conductivity σ_{β} against weight fraction w_j of monosubstituted anilines in benzene at 35° C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—),
 (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—),
 (III) o-toluidine at 2.02 GHz (—⊙—), (IV) m-toluidine at 3.86 GHz (—*—),
 (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

Table 8.1 : Real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity ϵ^*_{ij} , static and optical frequency hf relative permittivities ϵ_{oij} and $\epsilon_{\infty ij}$ together with real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dielectric orientational susceptibility χ^*_{ij} along with low frequency susceptibility χ_{oij} which is real for some monosubstituted anilines in benzene under different electric field frequencies at 35° C for various concentrations.

Systems with serial number & molecular weight M_j	Frequency (f) in GHz	Weight fraction w_j of solute	Measured dielectric relative permittivities				Dimensionless dielectric orientational susceptibilities		
			ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}	χ_{oij}
	(a) 3.86	0.0326	2.32	0.011	2.336	2.239	0.081	0.011	0.097
		0.0604	2.37	0.021	2.404	2.247	0.123	0.021	0.157
		0.0884	2.44	0.029	2.459	2.255	0.185	0.029	0.204
		0.1135	2.49	0.033	2.538	2.262	0.228	0.033	0.276
		0.1361	2.53	0.041	2.588	2.267	0.263	0.041	0.321
II o-anisidine in benzene $M_j = 0.123$ kg	(b) 22.06	0.0326	2.31	0.015	2.336	2.239	0.071	0.015	0.097
		0.0604	2.36	0.026	2.404	2.247	0.113	0.026	0.157
		0.0884	2.40	0.041	2.459	2.255	0.145	0.041	0.204
		0.1135	2.42	0.053	2.538	2.262	0.158	0.053	0.276
		0.1361	2.56	0.065	2.588	2.267	0.293	0.065	0.321
II	(a) 3.86	0.0160	2.31	0.018	2.315	2.235	0.075	0.018	0.080
		0.0336	2.25	0.026	2.384	2.241	0.009	0.026	0.143
		0.0579	2.43	0.043	2.477	2.246	0.184	0.043	0.231
		0.0823	2.51	0.059	2.553	2.253	0.257	0.059	0.300
		0.1109	2.61	0.084	2.675	2.261	0.349	0.084	0.414
m-anisidine in benzene $M_j = 0.123$ kg	(b) 22.06	0.0160	2.29	0.021	2.315	2.235	0.055	0.021	0.080
		0.0336	2.32	0.038	2.384	2.241	0.079	0.038	0.143
		0.0579	2.36	0.068	2.477	2.246	0.114	0.068	0.231
		0.0823	2.40	0.080	2.553	2.253	0.147	0.080	0.300
		0.1109	2.43	0.115	2.675	2.261	0.169	0.115	0.414

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Systems with serial number & molecular weight M_j	Frequency (f) in GHz	Weight fraction w_j of solute	Measured dielectric relative permittivities				Dimensionless dielectric orientational susceptibilities		
			ϵ'_{ij}	ϵ''_{ij}	ϵ_{nij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}	χ_{nij}
III	2.02	0.0137	2.30	0.005	2.301	2.241	0.059	0.005	0.060
o-toluidine		0.0459	2.38	0.013	2.392	2.250	0.130	0.013	0.142
in benzene		0.0622	2.42	0.015	2.457	2.255	0.165	0.015	0.202
$M_j = 0.107$ kg		0.1048	2.55	0.022	2.577	2.264	0.286	0.022	0.313
IV	3.86	0.0264	2.31	0.007	2.337	2.243	0.067	0.007	0.094
m-toluidine		0.0538	2.37	0.016	2.413	2.248	0.122	0.016	0.165
in benzene		0.0781	2.44	0.024	2.470	2.252	0.188	0.024	0.218
$M_j = 0.107$ kg.		0.1015	2.39	0.036	2.526	2.258	0.132	0.036	0.268
	(a) 3.86	0.1225	2.54	0.045	2.591	2.262	0.278	0.045	0.329
		0.0213	2.31	0.010	2.319	2.237	0.073	0.010	0.082
		0.0428	2.32	0.016	2.367	2.244	0.076	0.016	0.123
		0.0616	2.38	0.018	2.413	2.249	0.131	0.018	0.164
V	(b) 22.06	0.0916	2.46	0.029	2.483	2.254	0.206	0.029	0.229
p-toluidine in benzene		0.1048	2.48	0.046	2.523	2.260	0.220	0.046	0.263
$M_j = 0.107$ kg		0.0213	2.31	0.009	2.319	2.237	0.073	0.009	0.082
		0.0428	2.33	0.020	2.367	2.244	0.086	0.020	0.123
	(b) 22.06	0.0616	2.36	0.033	2.413	2.249	0.111	0.033	0.164
		0.0916	2.40	0.046	2.483	2.254	0.146	0.046	0.229
		0.1048	2.44	0.058	2.523	2.260	0.180	0.058	0.263

Table 8.2 : Intercept and slope of linear equation of $(\chi_{oij}'' - \chi_{ij}') / \chi_{ij}'$ against χ_{ij}'' / χ_{ij}' , correlation coefficient (r) and chisquare values, estimated relaxation times τ_1 and τ_2 due to rotation of flexible polar group and whole molecule, measured τ_j from Eq (8.16) and (8.17), reported τ (Gopalakrishna) symmetric and characteristic relaxation times τ_s and τ_{es} of Eq. (8.11) and (8.13), of some monosubstituted anilines in benzene at 35°C under different GHz electric field frequencies.

Systems with serial number & Molecular weight (M_j)	Frequency (f) in GHz	Intercept and slope of Eq. (8.3)		Correlation coefficient (r) and chisquares values involved in Eq. (8.3)		Estimated relaxation times τ_1 and τ_2 in p.sec		Measured τ (ps) ^a	Ratio of slopes of $\chi_{ij}'' - w_j$ & $\chi_{ij}' - w_j$ curves at $w_j \rightarrow 0$	Relaxation times			
		Intercept (c)	Slope (m)	(r)Chisquares		τ (ps) ^b	τ (ps) ^c			τ_s (ps)	τ_{es} (ps)		
				(r)	Chisquares								
I. o-anisidine in benzene $M_j = 0.123$ kg	(a) 3.86	0.0179	1.4360	0.3032	0.07	0.52	58.73	6.29	0.1891	7.80	5.25	0.92	471.52
	(b) 22.06	0.5406	3.6741	0.8277	0.23	1.11	25.41	1.59	0.1601	1.15	1.56	0.90	—
II. m-anisidine in benzene $M_j = 0.123$ kg	(a) 3.86	1.1404	5.5485	0.9999	0.15	8.82	220.07	7.61	0.2188	9.02	8.05	12.30	90.52
	(b) 22.06	0.7318	3.1447	0.9803	0.02	1.83	20.87	5.55	0.5413	3.91	4.41	2.33	14.80
III. o-toluidine in benzene $M_j = 0.107$ kg	2.02	0.0773	2.0910	0.2402	0.02	2.97	161.86	5.70	0.1536	12.11	4.97	17.06	—

^aMeasured by the slope of χ_{ij}'' against χ_{ij}' using Eq. (8.16).

^b From the ratio of individual slopes.

^cBy Gopalakrishna's method [15]

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Systems with serial number & Molecular weight (M_j)	Frequency (f) in GHz	Intercept and slope of Eq. (8.3)		Correlation coefficient (r) and chisquares values involved in Eq. (8.3)		Estimated relax- ation times τ_1 and τ_2 in p.sec		Measured τ (ps) ^a	Ratio of slopes of $\chi''_{ij}-w_j$ & $\chi'_{ij}-w_j$ curves at $w_j \rightarrow 0$	Relaxation times				
		Intercept (c)	Slope (m)			(r)Chisquares					τ	τ	τ_s	τ_{cs}
											(ps) ^b	(ps) ^c	(ps)	(ps)
(IV) m-toluidine in benzene $M_j=0.107$ kg	3.86	0.2938	4.5092	0.8469	0.51	2.73	183.29	6.53	0.3792	15.64	7.05	2.23	1181.3	
(V) p-toluidine in benzene $M_j = 0.107$ kg	(a) 3.86	0.3149	3.4446	0.6480	0.30	3.88	138.22	7.64	0.2116	8.73	7.65	8.15	—	
	(b) 22.06	0.0821	1.9151	0.9408	0.03	0.32	13.51	3.19	46.1743	333.30	5.53	2.11	—	

^aMeasured by the slope of χ''_{ij} against χ'_{ij} using Eq. (8.16).

^b From the ratio of individual slopes.

^cBy Gopalakrishna's method [15]

Table 8.3 : Frohlich's parameter A, χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} values estimated from Frohlich's equations (8.6) and (8.7) with estimated τ_1 and τ_2 and those obtained from Figures 8.5 and 8.6 at $w_j \rightarrow 0$, weighted contributions c_1 and c_2 from Frohlich's method and those by graphical technique together with symmetric and asymmetric distribution parameters γ and δ of some monosubstituted anilines in benzene at 35°C under different electric field frequencies in GHz range.

Systems with serial number	Frequency (f) in GHz	Frohlich parameter (A)	Estimated values of χ'_{ij}/χ_{oij} & χ''_{ij}/χ_{oij} of Frohlich's equations (8.6) and (8.7)		Weighted contributions c_1 & c_2 from Eqs. (8.4) and (8.5)		Estimated values of χ'_{ij}/χ_{oij} & χ''_{ij}/χ_{oij} from Figures 8.5 and 8.6 at $w_j \rightarrow 0$		Weighted contributions c_1 and c_2 from graphical technique		Symmetric distribution parameter γ	Asymmetric distribution parameter δ
I. o-anisidine in C_6H_6	(a) 3.86	4.7269	0.8829	0.2001	0.7491	0.4053	0.7613	0.0859	0.7073	0.1637	0.7089	0.0757
	(b) 22.06	3.1308	0.5893	0.3646	0.5200	1.0893	1.0006	0.1086	1.0380	-0.1801	-0.0724	—
II. m-anisidine in C_6H_6	(a) 3.86	3.2169	0.4811	0.3650	0.4496	1.5081	0.7527	0.2389	0.7712	0.4485	0.3155	0.2688
	(b) 22.06	2.4340	0.5534	0.4063	0.4816	0.9439	0.7468	0.2508	0.7699	0.2181	0.2969	0.2910
III. o-toluidine in C_6H_6	2.02	3.9982	0.7936	0.2699	0.6755	0.6212	1.0700	0.0841	1.0498	0.1133	-0.4921	—
IV m-toluidine in C_6H_6	3.86	4.2068	0.6401	0.3049	0.5826	1.2450	0.7858	0.0475	0.7903	-0.0213	0.8230	0.0393
V p-toluidine in C_6H_6	(a) 3.86	3.5730	0.6509	0.3320	0.5727	1.0167	0.9901	0.1639	0.9769	0.2657	-0.0661	—
	(b) 22.06	3.7429	0.7992	0.2766	0.6685	0.5943	1.1134	0.0399	1.1208	-0.0233	-0.8078	—

Table 8.4 : Linear coefficient 'β's, correlation coefficient (r) and % of error of $\chi'_{ij} - w_j$ and $\sigma_{ij} - w_j$ curves of Figure 8.3 and 8.7, estimated dipole moments μ_1 and μ_2 for rotations of flexible polar groups and whole molecule by susceptibility and conductivity measurement techniques, dimensionless parameters b_1 and b_2 together with theoretical dipole moment μ_{theo} obtained from bond angles and bond moments, reported μ (Gopalakrishna) of some monosubstituted anilines in benzene at 35° C under different electric field frequencies.

Systems with serial number and molecular weight (M_j) in kg.	Frequency (f) in GHz	Linear coefficient of $\chi'_{ij} - w_j$ & $\sigma_{ij} - w_j$ curves of Figs. 8.3 and 8.7	Correlation coefficient (r) and % of errors involved in $\chi'_{ij} - w_j$ and $\sigma_{ij} - w_j$ curves		Dimensionless parameters		Estimated dipole moment $\mu \times 10^{30}$ C.m from hf susceptibility and conductivity measurement		Theoretical $\mu \times 10^{30}$ in C.m from bond angles and bond moments	$\mu \times 10^{30}$ in C.m from Gopalakrishnas method.
			(r)	% of error	b_1	b_2	μ_1	μ_2		
					$\frac{1}{1+\omega^2\tau_1^2}$	$\frac{1}{1+\omega^2\tau_2^2}$				
I. o-anisidine in C_6H_6 $M_j = 0.123$	(a) 3.86	1.9358 0.4890	0.9980 0.9984	0.12 0.10	0.9998	0.3304	5.07 5.50	8.81 9.56	3.40	5.03
	(b) 22.06	2.4031 17.3978	0.9102 0.9316	5.18 5.98	0.9769	0.0747	5.71 13.88	20.66 50.19		
II. m-anisidine in C_6H_6 $M_j = 0.123$	(a) 3.86	1.8788 0.4623	0.9417 0.9508	3.41 2.89	0.9563	0.0339	5.10 5.46	27.10 29.01	5.50	6.33
	(b) 22.06	1.8214 2.5571	0.9934 0.9963	0.40 0.22	0.9396	0.1068	5.07 5.42	15.03 16.08		
III. o-toluidine in C_6H_6 $M_j = 0.107$	2.02	1.4840	0.9966	0.23	0.9986	0.1917	4.14	9.45	4.63	5.37
		0.1981	0.9981	0.13			4.51	10.30		

Contd...

Systems with serial number and molecular weight (M_j) in kg.	Frequency (f) in GHz	Linear coefficient of $\chi'_{ij}-w_j$ & $\sigma_{ij}-w_j$ curves of Figs. 8.3 and 8.7	Correlation coefficient (r) and % of errors involved in $\chi'_{ij}-w_j$ and $\sigma_{ij}-w_j$ curves		Dimensionless parameters		Estimated dipole moment $\mu \times 10^{30}$ C.m from hf susceptibility and conductivity measurement		Theoretical $\mu \times 10^{30}$ in C.m from bond angles and bond moments	$\mu \times 10^{30}$ in C.m from Gopalakrishnas method.
			(r)	% of error	b_1	b_2	μ_1	μ_2		
					$\frac{1}{1+\omega^2\tau_1^2}$	$\frac{1}{1+\omega^2\tau_2^2}$				
IV. m-toluidine in C_6H_6 $M_j=0.107$	3.86	0.5720	0.8479	8.48			2.57	11.69	3.43	4.90
		0.1265	0.8732	7.16	0.9956	0.0482	2.61	11.87		
V. p-toluidine in C_6H_6 $M_j=0.107$	(a) 3.86	0.4791	0.9755	1.46			2.36	8.22	5.13	5.00
		0.1638	0.9825	1.04	0.9912	0.0818	2.98	10.38		
	(b) 22.06	0.0109	0.9819	1.08			0.35	0.75		
		0.3762	0.9864	0.81	0.9980	0.2221	1.88	3.99		

compared with reported μ 's (Gopalakrishna) and μ_{theo} 's from bond angles and bond moments of polar groups of the parent polar molecules to support their conformations. The slight disagreement between measured μ_j 's and μ_{theo} 's invites the existence of inductive, mesomeric and electromeric effects suffered by polar groups, in addition to weak molecular associations between the polar molecules.

8.2. Weighted contributions c_1 and c_2 for τ_1 and τ_2

By putting $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$ the Eqs. (8.1) and (8.2) are solved to get

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (8.4)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (8.5)$$

provided $\alpha_2 > \alpha_1$. The theoretical values of c_1 and c_2 towards dielectric relaxations were, however, obtained from Eqs. (8.4) and (8.5) with the help of Fröhlich's following theoretical equations [16].

$$\chi'_{ij}/\chi_{oij} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) \quad (8.6)$$

$$\chi''_{ij}/\chi_{oij} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \quad (8.7)$$

in terms of the measured τ_1 and τ_2 as presented in Table 8.2 from Eq. (8.3) of double relaxation method.

The theoretical c_1 and c_2 as entered in Table 8.3 are compared with the experimental ones obtained from the intercept of fitted parabolic curves of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} against w_j of Figures 8.5 and 8.6 in the limit $w_j=0$ and Eqs. (8.4)

and (8.5). The curves in Figures 8.5 and 8.6 drawn by the regression analysis of polynomial fitting, are thought to yield the accurate values of χ' / χ_{oj} and $\chi''_{ij} / \chi_{\text{oj}}$ in the limit $w_j = 0$ in comparison to earlier study of graphical extrapolation technique based on personal judgement. The Fröhlich parameter $A = \ln(\tau_2/\tau_1)$ are placed in Table 8.3 for each compound at different frequencies.

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

The molecules under present investigation appear to behave like nonrigid ones at 2.02, 3.86 and 22.06 GHz electric field having either symmetric or asymmetric distribution parameters γ and δ involved in the Eqs. (8.8) and (8.9)

$$\frac{\chi^*_{ij}}{\chi_{\text{oj}}} = \frac{1}{1+(j\omega\tau_s)^{1-\gamma}} \quad (8.8)$$

$$\frac{\chi^*_{ij}}{\chi_{\text{oj}}} = \frac{1}{(1+j\omega\tau_{cs})^\delta} \quad (8.9)$$

The former one (Eq. 8.8) is associated with symmetric relaxation time τ_s and the latter one (Eq. 8.9) with characteristic relaxation time τ_{cs} . Separating the real and imaginary parts of Eqs. (8.8) and (8.9) and rearranging them in terms of $\chi'_{ij} / \chi_{\text{oj}}$ and $\chi''_{ij} / \chi_{\text{oj}}$ at $w_j \rightarrow 0$ of Figures 8.5 and 8.6 γ and τ_s were obtained from :

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[(1 - \chi'_{ij} / \chi_{\text{oj}}) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{\text{oj}}} \right] \quad (8.10)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{(\chi'_{ij} / \chi''_{ij}) \cos\left(\frac{\gamma\pi}{2}\right) - \sin\left(\frac{\gamma\pi}{2}\right)} \right]^{1/(1-\gamma)} \quad (8.11)$$

Similarly δ and τ_{cs} can be had from Eq. (8.9):

$$\tan(\varphi\delta) = \frac{(\chi''_{ij}/\chi_{oij})w_j \rightarrow 0}{(\chi'_{ij}/\chi_{oij})w_j \rightarrow 0} \quad (8.12)$$

$$\text{and } \tan \varphi = \omega\tau_{cs} \quad (8.13)$$

As φ can not be evaluated directly an arbitrary theoretical curve between $1/\varphi \log(\text{Cos } \varphi)$ against φ in degrees was drawn elsewhere [17] from which

$$\frac{1}{\varphi} \log(\text{Cos } \varphi) = \log \left[\frac{\chi'_{ij}/\chi_{oij}}{\text{Cos } \varphi\delta} \right] / \varphi\delta \quad (8.14)$$

can be known. The known values of $(1/\varphi) \log(\text{Cos } \varphi)$, is used to know φ from $1/\varphi \log(\text{Cos } \varphi) - \varphi$ curve. With known φ Eqs. (8.12) and (8.13) were used to obtain δ and τ_{cs} respectively. τ_s and τ_{cs} so evaluated are entered in Table 8.2 to compare with τ_j 's by Murthy et al [14], freshly calculated Gopalakrishna [15] and τ_1, τ_2 by double relaxation methods. Estimated γ and δ are shown in Table 8.3.

8.4. Theoretical Formulation to obtain hf dipole moment μ_j :

(A) hf susceptibility method

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity ϵ^*_{ij} are related by :

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

$$\epsilon'_{ij} - \epsilon_{\infty ij} = \left(\frac{1}{\omega\tau} \right) \epsilon''_{ij}$$

$$\chi'_{ij} = \left(\frac{1}{\omega\tau} \right) \chi''_{ij} \quad (8.15)$$

$$\text{and } (d\chi''_{ij}/d\chi'_{ij}) = \omega\tau \quad (8.16)$$

χ''_{ij} 's are expected to vary linearly with χ'_{ij} [14] as seen in Figure 8.4. The slope of linear equation of χ''_{ij} and χ'_{ij} was used to get τ_j from Eq. (8.16).

But the variations of χ''_{ij} with χ'_{ij} in Figure 8.4 are not strictly linear, the ratio of individual slopes of variations of χ''_{ij} and χ'_{ij} with w_j 's in Figures 8.2 and 8.3 is a better representation of Eq. (8.16) to get τ_j where the polar-polar interactions are supposed to be eliminated. Thus

$$\left(\frac{d\chi''_{ij}}{dw_j}\right)_{w_j \rightarrow 0} / \left(\frac{d\chi'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \omega\tau_j \quad (8.17)$$

The imaginary part χ''_{ij} of χ^*_{ij} is [17-19]

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_{ij} + 2)^2 w_j \quad (8.18)$$

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

$$\left(\frac{d\chi''_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \cdot \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_{ij} + 2)^2 \quad (8.19)$$

From Eqs. (8.17) and (8.19) one obtains

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

$$\mu_j = \left[\frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_{ij}(\varepsilon_{ij} + 2)^2 b} \right]^{1/2} \quad (8.20)$$

where ε_0 is the permittivity of free space = 8.854×10^{-12} F.m⁻¹

β = linear coefficient of $\chi'_{ij} - w_j$ curves of Figure 8.3 at $w_j \rightarrow 0$

B. hf conductivity method

According to Murphy and Morgan [20] the real and imaginary parts of hf conductivity are related by :

$$\sigma_{ij}'' = \sigma_{\infty ij} + \frac{1}{\omega\tau} \sigma_{ij}' \quad (8.21)$$

where $\sigma_{ij}' = \omega\epsilon_0 \epsilon_{ij}''$ and $\sigma_{ij}'' = \omega\epsilon_0 \epsilon_{ij}'$ are the real and imaginary parts of hf complex conductivity σ_{ij}^* . $\omega = 2\pi f$ and f is the frequency of applied electric field in GHz range.

$$\left(\frac{d\sigma_{ij}''}{dw_j}\right)_{w_j \rightarrow 0} = \left(\frac{1}{\omega\tau}\right) \left(\frac{d\sigma_{ij}'}{dw_j}\right)_{w_j \rightarrow 0}$$

Since $\sigma_{ij}'' \simeq \sigma_{ij}$ where σ_{ij} the total hf conductivity $= \omega\epsilon_0 (\epsilon_{ij}'^2 + \epsilon_{ij}''^2)^{1/2}$

$$\text{One has } \left(\frac{d\sigma_{ij}'}{dw_j}\right)_{w_j \rightarrow 0} = \omega\tau\beta \quad (8.22)$$

where β is the linear coefficient of $\sigma_{ij}-w_j$ curve of Figure 8.7 in the limit $w_j = 0$.

Again, the real σ_{ij}' of hf complex conductivity σ_{ij}^* is [18,22]

$$\sigma_{ij}' = \frac{N\mu_j^2 \rho_{ij}}{27M_j k_B T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2}\right) (\epsilon_{ij} + 2) w_j \quad (8.23)$$

which on differentiation w.r. to w_j and at $w_j \rightarrow 0$ yields that

$$\left(\frac{d\sigma_{ij}'}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\mu_j^2 \rho_{ij}}{27M_j k_B T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2}\right) (\epsilon_{ij} + 2)^2 \quad (8.24)$$

From Eqs. (8.22) and (8.24) one gets

$$\mu_j = \left[\frac{27M_j k_B T \beta}{N \rho_{ij} (\epsilon_{ij} + 2)^2 \omega \tau} \right]^{1/2} \quad (8.25)$$

where β = linear coefficient of $\sigma_{ij} - w_j$ curve of Figure 8.7 at $w_j \rightarrow 0$. In both the Eqs. (8.20) and (8.25) we have

$$N = \text{Avogadro's number} = 6.023 \times 10^{23}$$

$$\rho_i = \text{density of solvent (C}_6\text{H}_6) = 865 \text{ kg. m}^{-3}$$

$$\epsilon_i = \text{relative permittivity of solvent C}_6\text{H}_6 = 2.253$$

$$M_j = \text{molecular weight of solute in kg.}$$

$$k_B = \text{Boltzmann constant} = 1.38 \times 10^{-23} \text{ J.mole}^{-1} \text{ K}^{-1}$$

$$b = \frac{1}{1 + \omega^2 \tau^2} = \text{dimensionless parameter involved with measured } \tau.$$

Dipole moment μ_1, μ_2 in terms of b_1, b_2 involved with estimated τ_1, τ_2 were computed from both the Eqs. (8.20) and (8.25) as well with the linear coefficient β 's of both, $\chi'_{ij} - w_j$ and $\sigma_{ij} - w_j$ curves of Figures 8.3 and 8.7. All μ_j 's are placed in Table 8.4 together with μ_{theo} 's and reported μ_j 's (Gopalakrishna) for comparison.

8.5. Results and Discussion

The least squares fitted straight line equations in terms of χ'_{ij}, χ''_{ij} and χ_{oij} of Table 8.1 were worked out for each system as shown graphically in Figure 8.1 at different w_j of solute in solvent benzene at 35°C under GHz electric field with the experimental points placed upon them. χ'_{ij} and χ''_{ij} are real and imaginary parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and χ_{oij} is the static or low frequency real dielectric susceptibility. They are, however, derived from measured [7] relative permittivities $\epsilon'_{ij}, \epsilon''_{ij}, \epsilon_{oij}$, and $\epsilon_{\infty ij}$ of Table 8.1. The correlation coefficients (r) and chisquare values placed in the 5th and 6th columns of Table 8.2 are estimated to show how far the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} of Eq (8.3) are correlated.

It is seen that r is low for o-anisidine at 3.86 GHz and o-toluidine at 2.02 GHz possibly for errors introduced in the measurement of ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. This fact is also confirmed by remarkable deviations of experimental data from linear curves of Figure 8.1. In order to locate the double relaxation phenomena accurate measurements of ϵ_{oij} and $\epsilon_{\infty ij}$ are essential. The refractive index n_{Dij} measured by Abbe's refractometer often yields $\epsilon_{\infty ij} = n_{Dij}^2$ [7] although Cole-Cole [3] and Cole-Davidson [21] plots give $\epsilon_{\infty ij}$ (1.0–1.15) times of n_{Dij}^2 . The intercepts and slopes of linear curves of Figure 8.1 are seen in the 3rd and 4th columns of Table 8.2, to get τ_1 and τ_2 due to rotation of flexible polar groups and end over end rotations of the whole molecules. τ_1 and τ_2 thus measured are presented in the 7th and 8th columns of Table 8.2. τ_2 's in Table 8.2 increases gradually from meta to ortho for anisidines at 22.06 GHz while the reverse is true at 3.86 GHz. But in case of toluidines τ_2 increases from para to ortho and to meta forms. This behaviour is, however, explained by the fact that C—NH₂ group is significantly influenced by GHz electric field. On the other hand τ_1 increases from ortho to meta forms for anisidines while it increases from meta to ortho and to para forms for toluidines. This behaviour, however, indicates that flexible parts of the molecules are loosely bound to the parent molecules [12, 13].

In absence of reliable τ_j 's of monosubstituted anilines the slopes of the least squares fitted straight line curves of χ''_{ij} against χ'_{ij} of Figure 8.4 as claimed by Murthy et al [14] were used to get τ_j from Eq. (8.16). They are placed in the 9th column of Table 8.2. The experimental points of Table 8.1 are found to deviate from linearity of Figure 8.4 due to solute - solute molecular interactions. The individual variations of χ''_{ij} and χ'_{ij} with w_j are not strictly linear as seen in Figures 8.2 and 8.3. This fact at once prompted one to use the ratio of slopes of the individual variations of χ''_{ij} and χ'_{ij} with w_j 's [17] entered in 10th column of Table 8.2 to evaluate τ_j from Eq. (8.17) at $w_j \rightarrow 0$. τ_j 's thus obtained are in close agreement with τ_1 from double relaxation and Gopalakrishna's [15] method and are placed in the 11th column of Table 8.2. τ_j for p-toluidine at 22.06

GHz shows large value probably for error introduced in ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$ measurements. The basic soundness of the latter method in getting τ_j is thus confirmed because the polar - polar interactions are fully avoided [22]. Moreover, it shows that hf susceptibility measurement yields microscopic τ where as double relaxation method gives both microscopic and macroscopic τ_1 and τ_2 as observed elsewhere [23].

Large τ_2 arises for the bigger size of rotating unit ($\tau_j T/\eta^j$) due to solvent environment around solute molecules. The distribution of τ between two extreme τ_1 and τ_2 values yields the symmetric and asymmetric distribution parameters γ and δ . They are, however, obtained from Eqs. (8.10) and (8.12) with $(\chi'_{ij}/\chi_{oij})_{\omega_j \rightarrow 0}$ and $(\chi''_{ij}/\chi_{oij})_{\omega_j \rightarrow 0}$ of Figures 8.5 and 8.6. The value of $(1/\phi) \log (\cos \phi)$ against ϕ in degree as shown elsewhere [17] is essential to know δ . Knowing ϕ , δ 's were obtained. γ and δ are entered in 12th and 13th column of Table 8.3.

The symmetric relaxation times τ_s from Eq. (8.11) in terms of γ of Eq. (8.10) are presented in the 13th column of Table 8.3. The close agreement of τ_s 's with τ_1 's and reported τ 's by freshly calculated from Gopalakrishna's method, indicates symmetric relaxation behaviour of such molecules in C_6H_6 . The agreement is however, poor in case of o-toluidine. The characteristic relaxation times τ_{cs} obtained from Eq. (8.13) for o-anisidine at 3.86 GHz, m-anisidine at 3.86 and 22.06 GHz and m-toluidine at 3.86 GHz as seen in 14th column of Table 8.2 shows high values as δ 's are found to be low. For other systems τ_{cs} and δ could not be found out as $(1/\phi) \log (\cos \phi)$ for them are positive. This fact rules out the applicability of asymmetric relaxation behaviour for such compounds.

The theoretical weighted contributions of c_1 and c_2 towards dielectric relaxations were obtained from Eqs. (8.4) and (8.5) by the measured τ_1 and τ_2 of Eq. (8.3) and χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} of Fröhlich's equations (8.6) and (8.7). The

6th and 7th columns of Table 8.3 contain c_1 and c_2 . The experimental c_1 and c_2 values were also obtained from $(\chi'_{ij} / \chi_{oij})w_{j \rightarrow 0}$ and $(\chi''_{ij} / \chi_{oij})w_{j \rightarrow 0}$ of the concentration variations of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} of Figures 8.5 and 8.6 by using Eqs. (8.4) and (8.5). They are presented in the 10th and 11th columns of Table 8.3 for comparison with the theoretical ones. Fröhlich's equations (8.6) and (8.7) are related to Fröhlich parameter A, where $A = \ln(\tau_2/\tau_1)$. Both the theoretical and experimental c_1 and c_2 as seen in Table 8.3 showed that $|c_1 + c_2| \approx 1$ establishing the validity of Eq. (8.3). It is interesting to note that experimental c_2 's are negative in case of o-anisidine and p-toluidine at 22.06 GHz and m-toluidine for the inertia of the flexible parts [23]. In Figures 8.5 and 8.6 it is also seen that the experimental points often do not lie on the smooth fitted curves probably due to solute - solute or solute-solvent molecular associations.

The dipole moments μ_1 and μ_2 of the flexible parts and the whole molecules were estimated from the linear coefficients β 's in the 3rd column of Table 8.4 of both $\chi'_{ij}-w_j$ and $\sigma_{ij}-w_j$ curves of Figures 8.3 and 8.7 and dimensionless parameters b_1 and b_2 involved with measured τ_1 and τ_2 from Eq. (8.3). The μ_1 and μ_2 thus obtained from Eqs. (8.20) and (8.25) are placed in the 8th and 9th columns of Table 8.4 for comparison. Correlation coefficients r 's and % of errors involved in the regression analysis in the 4th and 5th columns of Table 8.4 were made only to show how far χ'_{ij} 's and σ_{ij} 's are correlated with w_j 's. Both the χ'_{ij} 's and σ_{ij} 's with w_j in Figures 8.3 and 8.7 give reliable β to yield accurate μ_1 and μ_2 . It is seen in Figures 8.3 and 8.7 that almost all the curves show a tendency to be closer within the region $0.00 \leq w_j \leq 0.03$ indicating the same polarity of the molecules, in addition to solute-solvent (monomer) or solute-solute (dimer) molecular associations [6,22]. μ_1 and μ_2 in Table 8.4 from $\chi'_{ij}-w_j$ curves of Figure 8.3 are always smaller in magnitude than $\sigma_{ij}-w_j$ curves of Figure 8.7 as χ_{ij} 's are associated with orientational polarisation while σ_{ij} is more linked with the bound molecular charges. Theoretical dipole moments μ_{theo} 's of monosubstituted anilines as estimated elsewhere [17] in terms of available bond angles and bond

moments of polar groups $C \rightarrow NH_2$, $C \rightarrow OCH_3$, $C \rightarrow CH_3$ are entered in the 10th column of Table 8.4 to compare with the experimental μ_j 's. The contribution of inductive, mesomeric and electromeric moments of the substituent polar groups of the molecules towards the hf μ_j 's are, however, explained by the factor $\mu_j(\text{expt})/\mu_{j,\text{theo}}$ of values 1.49, 1.68, 0.93, 0.92, 0.89, 0.75, 0.46 and 0.07 of Ia, Ib, IIa, IIb, III, IV, Va and Vb respectively. The amount of bound molecular charge is judged from the difference $\Delta\mu_j$ between μ_j 's of hf σ_{ij} and χ'_{ij} respectively to contribute to hf σ_{ij} [8].

In absence of reliable μ_j 's Gopalakrishna's method [15] were reemployed. The close agreement between reported μ_j 's (Gopalakrishna) μ_1 and μ_{theo} 's confirms the basic soundness of the methods prescribed in getting hf μ_j in addition to the fact that a part of the molecule is rotating under GHz electric field.

8.6. Conclusions

The methodology so far presented in SI units with internationally accepted symbols of dielectric terminologies and parameters appears to be more topical, simple, straightforward and unique one to predict relaxation parameters as χ_{ij} 's are directly linked with molecular orientational polarisation. The significant and interesting equations to evaluate τ_j 's and μ_j 's in terms of χ_{ij} helps one to shed more light on the relaxation phenomena of complicated molecules. The simple straight line equation (8.3) provides with microscopic and macroscopic τ 's i.e. τ_1 and τ_2 . The method to evaluate τ_j from the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with ω_j is a better representation of the earlier method of Murthy et al as it eliminates polar-polar interactions in solution. The relative weight factors c_1 and c_2 by Fröhlich's and graphical method shows $|c_1 + c_2| \simeq 1$ confirming the applicability of the linear equation (8.3) to estimate τ_1 and τ_2 respectively for monosubstituted anilines. The close agreement of τ_j , τ_1 and τ_2 confirms the nonrigid character of the molecules under hf electric field in C_6H_6 .

μ_1 and μ_2 by hf susceptibility and conductivity methods establish the fact that different types of polarisations are associated with χ'_{ij} 's and σ_{ij} 's. The theoretical reasons of evaluating τ_1 's and μ_1 's in agreement of τ_j 's and μ_j 's from freshly calculated Gopalakrishna's method is really sound. Various types of molecular associations are inferred from usual departure of graphically fitted plots of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with w_j 's and conformational structure of the molecules in which the effect of inductive, mesomeric and electromeric moments of the polar groups of the molecule plays the prominent role.

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