

Chapter 4

**HIGH FREQUENCY AND STATIC
RELAXATION PARAMETERS OF
SOME POLAR MONOSUBSTITUTED
ANILINES IN BENZENE**

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1. INTRODUCTION

The dielectric relaxation behaviour of disubstituted benzenes and anilines in a nonpolar solvent is very interesting, because they usually show the double relaxation phenomena under high frequency (hf) electric fields¹. Monosubstituted anilines, on the other hand, possess either single or double relaxation times (τ_j 's) at three different hf electric fields of Giga hertz (GHz) range². But they always showed double relaxation times at 9.945 GHz electric field, which seems to be the most effective dispersive region for such polar molecules³. They were also found to obey the symmetric relaxation behaviour under such electric field³.

An attempt is, therefore, made to get the dimensionless dielectric relaxation parameters like real κ'_{ij} , imaginary κ''_{ij} parts of complex dielectric constant κ^*_{ij} , as well as static and infinite frequency-dielectric constants κ_{0ij} and $\kappa_{\infty ij}$ of solution (ij) as shown in Table 1, from the measured³ permittivities of ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ respectively, of three isomers of anisidines and toluidines at 35°C under 9.945 GHz electric field at different weight fractions w_j 's of solute (j). The purpose of such consideration is to get static dipole moment μ_s at any stage of dilution as well as the relaxation times (τ_j 's) and hence hf dipole moments (μ_j 's) derived from hf conductivities σ_{ij} 's as functions of κ'_{ij} and κ''_{ij} at different w_j 's.

The ratio of individual slopes of the concentration variation of the imaginary σ''_{ij} and the real σ'_{ij} parts of complex hf conductivity σ^*_{ij} as well as the slope of linear variation of σ''_{ij} with σ'_{ij} were simultaneously used⁴ to estimate τ_j 's of a polar liquid. The τ_j obtained by the former method provides a significant improvement over the latter one⁵, as it eliminates the polar-polar interaction in the solution. It is better to use the ratio of slopes of concentration variations of κ''_{ij} and κ'_{ij} instead of $\sigma''_{ij} - w_j$ and $\sigma'_{ij} - w_j$ curves to get τ_j because κ'_{ij} and κ''_{ij} can be obtained directly from experimental measurements of ϵ'_{ij} and ϵ''_{ij} .

But, the variation of k''_{ij} with w_j is not always linear with a constant intercept^{6,7}. In this paper, a comparison of static μ_s from the slope of $x_{ij} - w_j$ curve and hf μ_j in terms of τ_j using hf conductivities of solution under 9.945 GHz electric field is also made with μ_2 and μ_1 due to rotations of the whole as well as the flexible part attached to the parent ring of the molecule from the dielectric relaxation parameters of Table 1 obtained by careful graphical interpolation of measured data⁸ used earlier³. The comparison of all these seems to be an interesting phenomenon only to see how far they agree.

Table 1 : Experimental dielectric relaxation parameters of three isomers of anisidines and toluidines at 35°C under 9.945 GHz electric field for different weight fractions w_j 's of solutes.

System with Sl. No. and molecular wt.	Weight fraction	Real part of permittivity	Dielectric loss factor	Static permit- tivity	Infinite frequency permittivity	Dimensionless dielectric constants			
						$K'_{ij} \times 10^{-12}$	$K''_{ij} \times 10^{-10}$	$K_{oj} \times 10^{-12}$	$K_{eij} \times 10^{-12}$
M_j , kg	W_j of solute	(ϵ'_{ij}) F.m ⁻¹	(ϵ''_{ij}) F.m ⁻¹	(ϵ_{oj}) F.m ⁻¹	(ϵ_{eij}) F.m ⁻¹				
1. o-anisidine in C ₆ H ₆ $M_j = 0.123$ kg	0.0326	2.3104	0.0148	2.336	2.239	0.2609	0.1672	0.2638	0.2529
	0.0604	2.3520	0.0244	2.404	2.247	0.2656	0.2756	0.2715	0.2538
	0.0884	2.4064	0.0340	2.459	2.255	0.2718	0.3840	0.2777	0.2547
	0.1135	2.4416	0.0400	2.538	2.262	0.2758	0.4578	0.2867	0.2555
	0.1361	2.4672	0.0512	2.588	2.267	0.2786	0.5783	0.2923	0.2560
2. m-anisidine in C ₆ H ₆ $M_j = 0.123$ kg	0.0160	2.2720	0.0234	2.315	2.235	0.2566	0.2643	0.2615	0.2524
	0.0336	2.3040	0.0390	2.384	2.241	0.2602	0.4405	0.2693	0.2531
	0.0579	2.3904	0.0618	2.477	2.246	0.2700	0.6980	0.2798	0.2537
	0.0823	2.4544	0.0744	2.553	2.253	0.2772	0.8403	0.2883	0.2545
	0.1109	2.5344	0.1056	2.675	2.261	0.2862	1.1927	0.3021	0.2554
3. p-anisidine in C ₆ H ₆ $M_j = 0.123$ kg	0.0319	2.3104	0.0252	2.373	2.237	0.2609	0.2846	0.2680	0.2527
	0.0597	2.3904	0.0474	2.442	2.246	0.2700	0.5354	0.2758	0.2537
	0.0848	2.5088	0.0642	2.539	2.250	0.2834	0.7251	0.2868	0.2541
	0.1106	2.5376	0.0840	2.638	2.262	0.2866	0.9487	0.2929	0.2555
	0.1396	2.6272	0.1086	2.745	2.269	0.2967	1.2266	0.3100	0.2563
4. o-toluidine in C ₆ H ₆ $M_j = 0.107$ kg	0.0137	2.2752	0.0162	2.301	2.241	0.2570	0.1830	0.2600	0.2531
	0.0459	2.3648	0.0408	2.392	2.250	0.2671	0.4608	0.2702	0.2541
	0.0622	2.4032	0.0570	2.457	2.255	0.2714	0.6438	0.2775	0.2547
	0.1048	2.5376	0.0900	2.577	2.264	0.2866	1.0165	0.2911	0.2557
	0.0264	2.3136	0.0150	2.337	2.243	0.2613	0.1694	0.2639	0.2533
5. m-toluidine in C ₆ H ₆ $M_j = 0.107$ kg	0.0538	2.3552	0.0342	2.413	2.248	0.2660	0.3863	0.2725	0.2539
	0.0781	2.4576	0.0402	2.470	2.252	0.2776	0.4540	0.2790	0.2543
	0.1015	2.3840	0.0618	2.526	2.258	0.2692	0.6980	0.2853	0.2550
	0.1225	2.5280	0.0732	2.591	2.262	0.2855	0.8267	0.2926	0.2555
	6. p-toluidine in C ₆ H ₆ $M_j = 0.107$ kg	0.0213	2.3100	0.0102	2.319	2.237	0.2609	0.1152	0.2619
0.0428		2.3040	0.0204	2.367	2.244	0.2602	0.2304	0.2673	0.2534
0.0616		2.3904	0.0276	2.413	2.249	0.2700	0.3117	0.2725	0.2540
0.0916		2.4704	0.0384	2.483	2.254	0.2790	0.4337	0.2804	0.2646
0.1048		2.4960	0.0582	2.523	2.260	0.2819	0.6573	0.2850	0.2553

with μ_2 and μ_1 as obtained elsewhere³. This study further observes the effect of inductive and mesomeric moments of polar groups of the molecules as well as the frequency of the alternating electric field on μ_j 's in comparison to μ_s . Moreover, the present method of study in terms of modern internationally accepted units and symbols appears to be superior because of its unified, coherent and rationalised nature.

As is evident from Table 2, hf μ_j 's of the polar liquids were computed in terms of τ_j and the slopes (β 's) of $\sigma_{ij} - w_j$ curves of Fig. 1 under 9.945 GHz electric field at 35°C. τ_j being an important parameter for obtaining μ_j of polar liquid estimated from the ratio of slopes of individual variation of σ_{ij}'' and σ_{ij}' with w_j . The nature of variations of $\sigma_{ij}'' - w_j$ and $\sigma_{ij}' - w_j$ curves are presented in Figs 2 and 3, respectively. In place of using τ_j from the ratio of the slopes of $\sigma_{ij}'' - w_j$ and $\sigma_{ij}' - w_j$ curves, one may use the linear slope of $\sigma_{ij}'' - \sigma_{ij}'$ curve to get τ_j and hence μ_j as suggested by Murthy et.al.⁵. All the μ_j 's and τ_j 's from both the methods are reported in Table 2.

The static dipole moment μ_s under static or low frequency electric field was also calculated from the linear coefficient of $X_{ij} - w_j$ curve of Fig. 4 for each polar-nonpolar liquid mixture. The correlation coefficient r of the linear curve as well as the % error are presented in Table 3 alongwith μ_s and coefficients a_0 , a_1 of $X_{ij} - w_j$ curve. The theoretical dipole moment μ_{theo} 's from available bond angles and bond moments³ are found to be deviated from static μ_s 's and hf μ_j 's, because of the existence of the inductive and mesomeric moments of the different polar groups in them. As the variation of μ_s compared to μ_j is very little, conformational structures of the polar molecules are predicted by μ_{cal} values, which are in agreement with μ_s from the reduced bond moments of the substituent groups by a factor μ_s/μ_{theo} presented in Table 3 and illustrated in Fig.5.

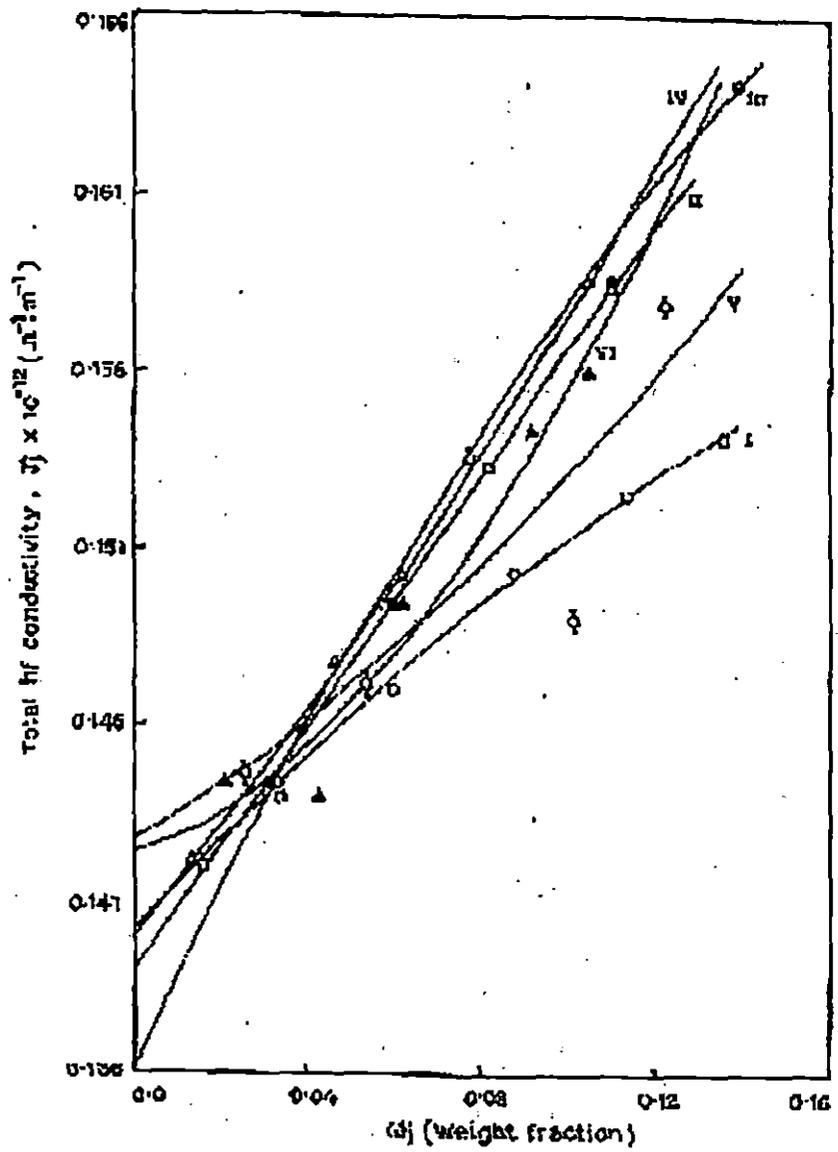


Fig. 1 — The variation of total conductivity σ_j with different W_j 's of solutes under 9.945 GHz electric field at 35°C [(I) o-anisidine (—○—), (II) m-anisidine (—□—), (III) p-anisidine (—●—), (IV) o-toluidine (—△—), (V) m-toluidine (—○—), (VI) p-toluidine (—▲—)]

Table 2 : Reports ratio of slopes of $(\sigma''_{ij}-w_j)$ and $(\sigma'_{ij}-w_j)$ curves at $w_j \rightarrow 0$ linear slope of $((\sigma''_{ij}-\sigma'_{ij}))$ curve, computed relaxation time τ_j and hence μ_j for both the methods and reported μ_2 and μ_1 in C.m from double relaxation method.

System with Sl.No. and molecular wt. M_j in kg. of solute	Ratio of slopes $x/y =$ $\frac{(d\sigma''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\sigma'_{ij}/dw_j)_{w_j \rightarrow 0}}$	Slope of $(\sigma''_{ij}-\sigma'_{ij})$ curve Eq.(5)	Cor- relation coeff- icient (r)	%of Error	Estimated $\tau_j \times 10^{12}$ in sec. from		Slope $\beta \times 10^{-12}$ in $\sigma''_{ij}-w_j$ of curve	Computed $\mu_j \times 10^{30}$ in c.m. from		Reported $\mu \times 10^{30}$ in c.m	
					Eq.(6)	Eq.(5)		Eq.(6) &	Eq.(5) &	(μ_2) &	(μ_1)
1.o-anisidine in C_6H_6 $M_j=0.123$ kg.	$(1.3024 \times 10^{11}) /$ (1.7179×10^{10}) $=7.5813$	4.5290	0.988	0.71	2.11	3.53	0.1302	5.38	5.38	31.11	6.40
2.m-anisidine in C_6H_6 $M_j=0.123$ kg.	$(1.7305 \times 10^{11}) /$ (5.2415×10^{10}) $=3.3015$	3.3521	0.993	0.40	4.85	4.77	0.1732	6.33	6.33	24.57	7.55
3.p-anisidine in C_6H_6 $M_j=0.123$ kg.	$(2.6210 \times 10^{11}) /$ (4.7768×10^{10}) $=5.4869$	3.8143	0.983	0.99	2.92	4.20	0.2621	7.58	7.71	52.74	9.00
4.o-toluidine in C_6H_6 $M_j=0.107$ kg.	$(1.4076 \times 10^{11}) /$ (5.0973×10^{10}) $=2.9380$	3.5123	0.997	0.31	5.45	4.56	0.1500	5.44	5.47	29.87	7.70
5.m-toluidine in C_6H_6 $M_j=0.107$ kg.	$(7.3263 \times 10^{10}) /$ (3.7452×10^{10}) $=1.9562$	2.9025	0.783	11.69	8.18	5.51	0.0732	4.13	3.89	17.07	5.20
6.p-toluidine in C_6H_6 $M_j=0.107$ kg.	$(4.3247 \times 10^{10}) /$ (4.2379×10^9) $=10.2048$	4.4801	0.929	4.12	1.57	3.57	0.0428	2.82	2.88	18.54	4.03

Table 3 : Coefficients a_0, a_1 in the equation $X_{ij} = a_0 + a_1 w_j$, correlation coefficient (r), % of error in fitting technique, static dipole moment μ_s in coulomb-metre, theoretical dipole moment μ_{theo} from bond angles and bond moments, reduced bond moments of substituent groups, μ_{cal} from reduced bond moments of anisidines and toluidines under static electric field at 35°C.

Systems with Sl. no and molecular wt. M_j in kg. of solutes	Intercepts and slopes of X_{ij} - w_j Eq.		Correlation Coefficient (r)	% of error in fitting technique	$\mu_s \times 10^{30}$ and $\mu_{theo} \times 10^{30}$		Reduced bond moments $\times 10^{30}$ of			$\mu_{cal} \times 10^{30}$ in c.m.
	$a_0 \times 10^{-10}$	$a_1 \times 10^{-10}$			in c.m.		-OCH ₃ (c.m.)	-CH ₃ (c.m.)	-NH ₂ (c.m.)	
1. o-anisidine in C ₆ H ₆ $M_j = 0.123$ kg	0.0193	1.2196	0.9976	0.14	2.94	3.40	2.07	-	-3.36	2.94
2. m-anisidine in C ₆ H ₆ $M_j = 0.123$ kg	0.0211	1.9208	0.9988	0.07	3.69	5.50	1.61	-	-2.60	3.68
3. p-anisidine in C ₆ H ₆ $M_j = 0.123$ kg	0.0219	1.7353	0.9977	0.14	3.51	6.30	1.33	-	-2.16	3.49
4. o-toluidine in C ₆ H ₆ $M_j = 0.107$ kg	0.0158	1.5942	0.9981	0.13	3.13	4.63	-	0.83	-2.63	3.13
5. m-toluidine in C ₆ H ₆ $M_j = 0.107$ kg	0.0240	1.3430	0.9988	0.08	2.88	3.43	-	1.03	-3.25	2.88
6. p-toluidine in C ₆ H ₆ $M_j = 0.107$ kg	0.0230	1.2393	0.9996	0.02	2.76	5.13	-	0.66	-2.09	2.75

2. THEORETICAL FORMULATION TO ESTIMATE HF DIELECTRIC RELAXATION PARAMETERS

Under hf electric field of GHz range the dimensionless complex dielectric constant κ^*_{ij} is written as

$$\kappa^*_{ij} = \kappa'_{ij} - j\kappa''_{ij} \quad \dots\dots\dots (1)$$

where $\kappa'_{ij} = \epsilon'_{ij}/\epsilon_0 =$ real part of dielectric constant and $\kappa''_{ij} = \epsilon''_{ij}/\epsilon_0 =$ dielectric loss factor, respectively. ϵ'_{ij} and ϵ''_{ij} are the real and imaginary parts of complex

permittivity ϵ_{ij}^* having dimension of Farad meter⁻¹ (F.m⁻¹) and ϵ_0 = permittivity of free space = 8.854×10^{-12} F.m⁻¹. Hence, Murphy-Morgan⁹ relation for the complex hf conductivity σ_{ij}^* of a solution of w_j is given by

$$\sigma_{ij}^* = \omega \epsilon_0 \kappa_{ij}'' + j \omega \epsilon_0 \kappa_{ij}' \quad \dots\dots\dots (2)$$

where $\sigma_{ij}' = (\omega \epsilon_0 \kappa_{ij}'')$ and $\sigma_{ij}'' (= \omega \epsilon_0 \kappa_{ij}')$ are the real and imaginary parts of complex conductivity, and j is a complex number = $\sqrt{-1}$.

The total hf conductivity σ_{ij} , is, however, obtained from $\sigma_{ij} = \omega \epsilon_0 \sqrt{\kappa_{ij}''^2 + \kappa_{ij}'^2} \dots (3)$

Again, the imaginary part of hf conductivity σ_{ij}'' related to the real part of hf conductivity σ_{ij}' by

$$\sigma_{ij}'' = \sigma_{\infty ij} + (1/\omega\tau) \sigma_{ij}' \quad \dots\dots\dots (4)$$

where $\sigma_{\infty ij}$ is the constant conductivity in the limit of $w_j=0$ and τ is the relaxation time of a polar unit.

Differentiating Eq. (4) with respect to σ_{ij}' one gets

$$d\sigma_{ij}''/d\sigma_{ij}' = 1/\omega\tau_j \quad \dots\dots\dots (5)$$

In higher concentration region, the variation of the individual σ_{ij}'' and σ_{ij}' with w_j may not be linear due to polar-polar interactions, it is better to use the following relation to get τ_j as :

$$\begin{aligned} (d\sigma_{ij}''/dw_j)_{w_j \rightarrow 0} / (d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0} &= 1/\omega\tau_j \\ \text{or, } x/y &= 1/\omega\tau_j \quad \dots\dots\dots (6) \end{aligned}$$

Under hf alternating electric field, it is also observed experimentally that $\sigma_{ij}'' \cong \sigma_{ij}$

Hence Eq. (4) becomes $\sigma_{ij} = \sigma_{\infty ij} + (1/\omega\tau_j)\sigma_{ij}' \quad \dots\dots\dots (7)$

$$\text{or, } \beta = \frac{1}{\omega\tau_j} \left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} \quad \dots\dots\dots (8)$$

where β = slope of $\sigma_{ij} - w_j$ curve at $w_j \rightarrow 0$, i.e.

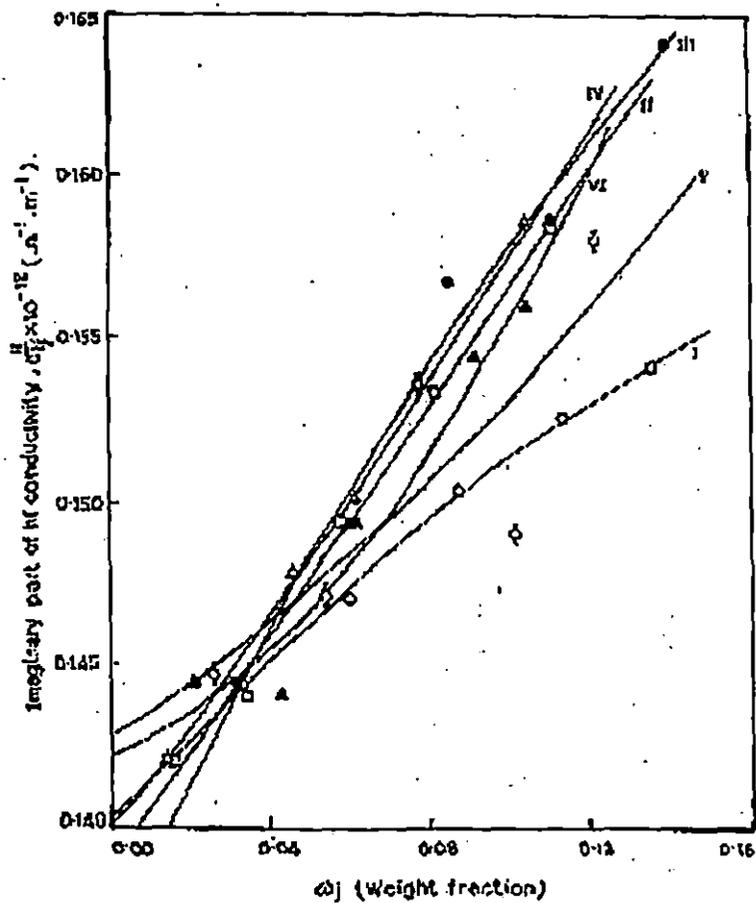


Fig. 2 — The plot of imaginary part of conductivity σ''_{ij} with fractions W_j 's of anisidines and toluidines at 35°C under 9.945 GHz electric field

[(I) o-anisidine (—○—), (II) m-anisidine (—□—), (III) p-anisidine (—●—), (IV) o-toluidine (—△—), (V) m-toluidine (—◇—), (VI) p-toluidine (—▲—)]

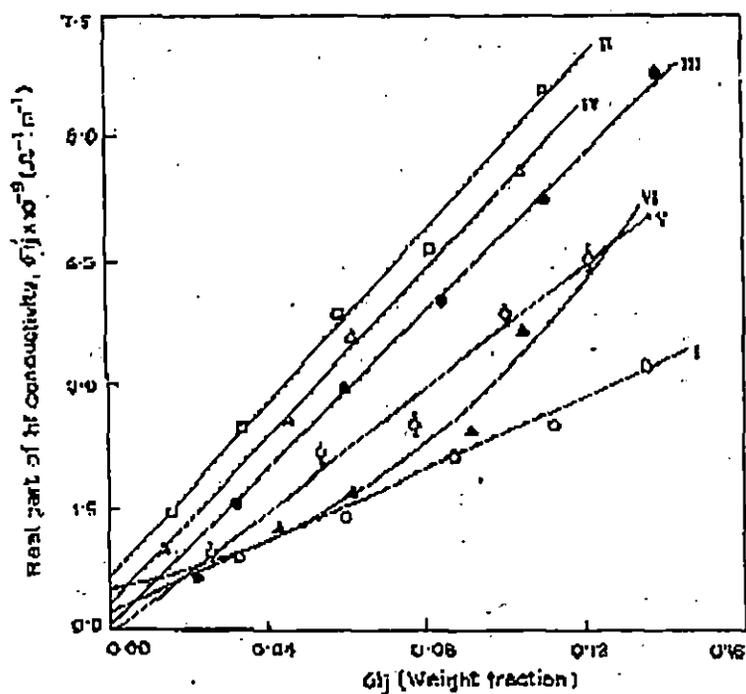


Fig. 3 — The variation of real part of conductivity σ'_{ij} against W_j 's of solute at 35°C under 9.945 GHz electric field [(I) o-anisidine (—○—), (II) m-anisidine (—□—), (III) p-anisidine (—●—), (IV) O-toluidine (—△—), (V) m-toluidine (—○—), (VI) p-toluidine (—▲—)]

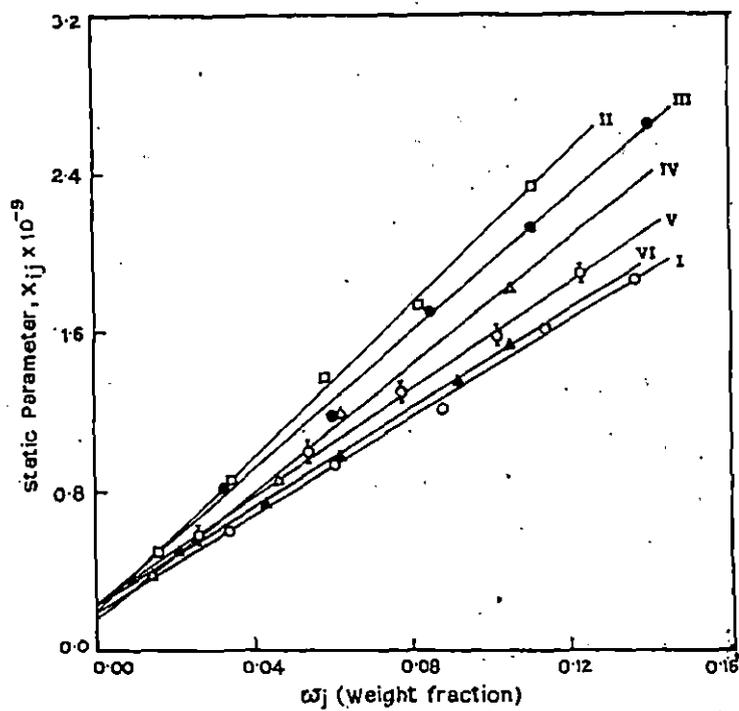


Fig. 4 — The linear variation of static experimental parameter X_{ij} for different H_j 's of anisidines and toluidines at 35°C [(I) o-anisidine (—○—), (II) m-anisidine (—□—), (III) p-anisidine (—●—), (IV) o-toluidine (—△—), (V) m-toluidine (—⊙—), (VI) p-toluidine (—▲—)]

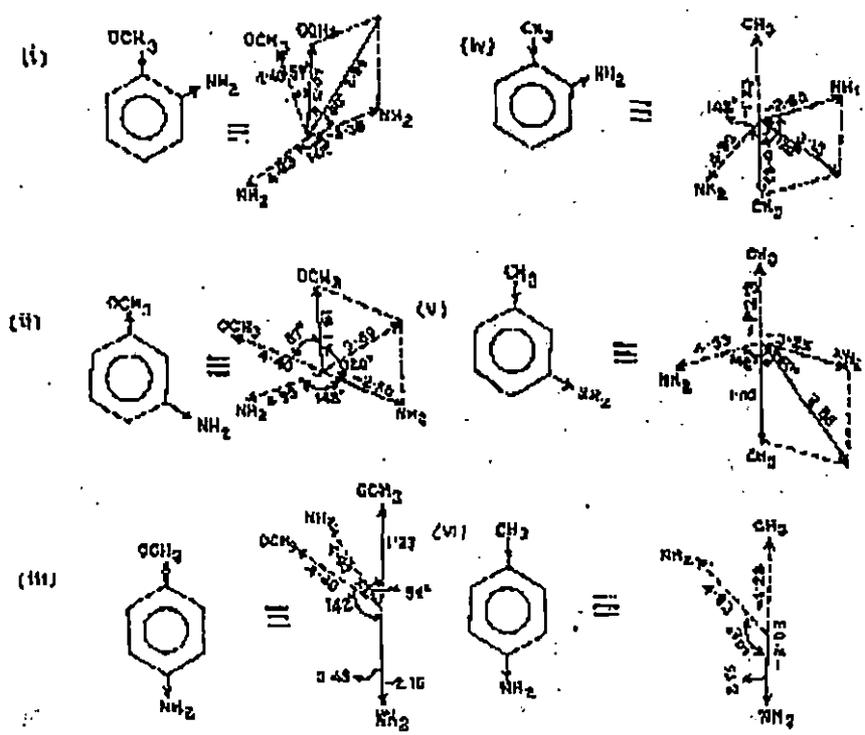


Fig. 5 — Conformational structures of isomers of anisidine and toluidine in terms of reduced bond moments ($\times 10^{-30}$ coulomb-metre) of their substituent groups [(I) o-anisidine, (II) m-anisidine, (III) p-anisidine, (IV) o-toluidine, (V) m-toluidine, (VI) p-toluidine]

$\left(\frac{d\sigma'_{ij}}{dw_j}\right)_{w_j \rightarrow 0}$ as presented in Table 2 for all the liquids under investigation.

The real part of hf conductivity σ'_{ij} at T, K is related with imaginary part of dielectric constant or dielectric loss¹⁰ of a given solution of w_j by

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 k_B T M_j} \left(\frac{\omega^2\tau}{1+\omega^2\tau^2} \right) (\epsilon_0 \kappa_{oij} + 2) (\epsilon_0 \kappa_{\infty ij} + 2) w_j \quad \dots\dots\dots (9)$$

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

$$\left(\frac{d\sigma'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{3\epsilon_0 k_B T M_j} \left(\frac{\epsilon_i + 2}{3}\right)^2 \left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right) \quad \dots\dots\dots (10)$$

Here, N=Avogadro's number, ρ_i = density of solvent, ϵ_i = dielectric permittivity of the solvent, M_j = molecular weight of solute and k_B = Boltzmann constant. All the parameters are, however, expressed in S.I. Units. From Eqs (8) and (10) one gets hf dipole moment μ_j from

$$\mu_j = \left(\frac{27\epsilon_0 k_B T M_j \beta}{N\rho_i (\epsilon_i + 2)^2 \omega b} \right)^{1/2} \quad \dots\dots\dots (11)$$

in terms of b, which is a dimensionless parameter, given by

$$b = \frac{1}{1+\omega^2\tau^2} \quad \dots\dots\dots (12)$$

All the μ_j 's in terms of β 's and b's involved with τ_j 's are, however, placed in Table 2, in order to compare with the static μ_s as presented in Table 3.

3. STATIC RELAXATION PARAMETERS

Under static or low frequency electric field, μ_s of a polar liquid (j) in a non polar solvent (i) may be written from Debye's equation¹¹ as

$$\frac{(\epsilon_0 \kappa_{oij} - 1)}{(\epsilon_0 \kappa_{oij} + 2)} - \frac{(\epsilon_0 \kappa_{\infty ij} - 1)}{(\epsilon_0 \kappa_{\infty ij} + 2)} = \frac{(\epsilon_0 \kappa_{0i} - 1)}{(\epsilon_0 \kappa_{0i} + 2)} - \frac{(\epsilon_0 \kappa_{\infty ci} - 1)}{(\epsilon_0 \kappa_{\infty ci} + 2)} + \frac{N\mu_s^2}{3\epsilon_0 k_B T} c_j \quad \dots\dots\dots 13$$

where κ_{oij} ($= \epsilon_{oij} / \epsilon_0$) and $\kappa_{\infty ij}$ ($= \epsilon_{\infty ij} / \epsilon_0$) are the dimensionless static and infinite

frequency dielectric constants of solution c_j is the molar concentration given by $c_j = \rho_{ij} w_j / M_j$ and other symbols carry usual meaning^{4,12-13}.

A polar liquid of weight W_j and of volume V_j is mixed with a non-polar solvent of weight W_i and of volume V_i to get the solution density ρ_{ij} where

$$\rho_{ij} = \frac{\rho_i \rho_j}{\rho_j w_i + \rho_i w_j} = \rho_i (1 - \gamma w_j)^{-1} \quad \dots\dots\dots (14)$$

Here, weight fractions w_j and w_i of solute and solvent are given by

$$w_j = \frac{W_j}{W_i + W_j} \text{ and } w_i = \frac{W_i}{W_j + W_i} \text{ such that } w_i + w_j = 1, \gamma = \left(1 - \frac{\rho_i}{\rho_j}\right)$$

and ρ_i and ρ_j are densities of pure solvent and solute, respectively. Now Eq. (13) may be written as

$$\frac{(\kappa_{oij} - \kappa_{\alpha ij})}{(\epsilon_o \kappa_{oij} + 2)(\epsilon_o \kappa_{\alpha ij} + 2)} = \frac{(\kappa_{oi} - \kappa_{\alpha i})}{(\epsilon_o \kappa_{oi} + 2)(\epsilon_o \kappa_{\alpha i} + 2)} + \frac{N \rho_i \mu_s^2}{9 \epsilon_o^2 M_j k_B T} w_j (1 - \gamma w_j)^{-1}$$

$$\text{or } X_{ij} = X_i + \frac{N \rho_i \mu_s^2}{9 \epsilon_o^2 M_j k_B T} w_j + \frac{N \rho_i \mu_s^2}{9 \epsilon_o^2 M_j k_B T} \gamma w_j^2 \quad \dots\dots\dots (15)$$

Since, the left hand side of Eq. (15) is a function of w_j , the usual variatin of X_{ij} with w_j can, however, be represented by

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 \quad \dots\dots\dots (16)$$

Now, comparing the linear coefficients of w_j of Eqs. (15) and (16) one gets μ_s from

$$\mu_s = \left(\frac{9 \epsilon_o^2 M_j k_B T}{N \rho_i} \times a_1 \right)^{1/2} \quad \dots\dots\dots (17)$$

where a_1 is the slope of $X_{ij} - w_j$ curve. But μ_s from higher coefficients of Eqs.

(15) or (16), which are involved with different factors like solvent effect, relative density effect, solute-solute associations, etc. are not reliable. The estimated μ_s along with the slope α_1 are placed in Table 3 in order to compare with hf μ_j 's presented in Table 2.

4. RESULTS AND DISCUSSION

The hf dipole moments μ_j 's of all the isomers of anisidines and toluidines at different w_j 's of solutes from the measured data of Table 1 are calculated in terms of slope β of $\sigma_{ij} - w_j$ curve and τ_j estimated from Eqs (5) and (6) of the methods suggested. The variation of σ_{ij} with w_j 's of solutes are parabolic, having almost same intercept and slope as seen in Fig. 1. This is probably due to same polarity of the molecules as observed earlier³. They also meet at a point within $0.02 \leq w_j \leq 0.045$ indicating solute - solute (dimer) or solute-solvent (monomer) molecular associations under 9.945 GHz electric field³. τ_j 's of polar liquids were, estimated from the linear slope of $\sigma''_{ij} - \sigma'_{ij}$ curve⁵ as well as the ratio of slopes of individual variations of $\sigma''_{ij} - w_j$ and $\sigma'_{ij} - w_j$ curves of Figs 2 and 3. Both σ''_{ij} and σ'_{ij} are functions of w_j . Their variations with w_j 's were not linear as shown in Figs 2 and 3. The latter method appears to be a significant improvement over the other⁵, as it eliminates polar-polar interactions at $w_j \rightarrow 0$. The correlation coefficients (r's) and the % errors in measurement of τ_j 's from Eq. (4) were calculated and presented in Table 2. τ_j 's are found to agree well for both the methods and the % error involved in them are very low except m-toluidine, perhaps due to experimental uncertainty in the measurement of the relaxation parameters. It is interesting to note that unlike $\sigma'_{ij} - w_j$ curve, the variation of σ''_{ij} with w_j is identical with $\sigma_{ij} - w_j$ curve. This fact suggests the applicability of the approximation of $\sigma'' \cong \sigma_{ij}$ in Eq. (7). The plot of σ'_{ij} with w_j is, however, linear except p-toluidine in C_6H_6 when fitted with the measured data of κ''_{ij} for different w_j 's of solutes under 9.945 GHz electric field as displayed in Fig. 3. This type of behaviour reveals the fact that the data presented in Table 1 are very accurate. The μ_j 's as obtained from slope β of $\sigma_{ij} - w_j$ curves of Fig. 1 and the dimensionless

parameters b of Eq. (12) involved with τ_j measured by both the methods are shown in Table 2. The excellent agreement of μ_j 's in both cases implies that the method suggested is a correct one.

These μ_j 's are again compared with the hf dipole moments μ_2 and μ_1 due to whole and the flexible part of the molecule attached to the parent ring as presented earlier³. μ_j 's are found to be in agreement with μ_1 , suggesting the fact that a part of the molecule is rotating under nearly 10GHz electric field⁴. The gradual increase of μ_j 's from o- to p-anisidines and from p- to o-toluidenes like μ_1 is probably due to the same polarity of the molecules as supported by the slopes (β 's) as observed earlier.³

The static or low frequency dipole moment μ_s at 35°C are computed from the linear coefficients α_1 of X_{ij} - w_j curves of Fig. 4. All the μ_s 's are entered in Table 3. The variation of X_{ij} with w_j is almost linear as evident from the correlation coefficient r and % error involved in getting the coefficients α_0 and α_1 which are placed in Table 3. The curves are found to increase with the addition of solute and show a tendency to meet at a common point on the ordinate axis at $w_j = 0$. This reveals the fact that static polarisability increases with w_j 's of solute and yields static experimental parameter X_1 of solvent C_6H_6 for all the polar liquids under investigation at infinite dilution. This indicates the basic soundness of the method adopted here as well as the reliability of the experimental data of X_{ij} involved with k_{0ij} and $k_{\infty ij}$ of the solutions. The μ_s 's are, however, little smaller than μ_j 's. They are seen to increase from o-to p-anisidines and p-to o-toluidines like μ_j 's establishing the fact that μ 's are very little influenced by the frequency of the applied alternating electric field of GHz range.

The theoretical dipole moments μ_{theo} 's of the polar molecules are calculated assuming their planar structures, from the vector addition of available bond moments of 4.40×10^{-30} , 1.25×10^{-30} , 4.93×10^{-30} in Coulomb-meter (C.m) for respective. $-OCH_3$ - CH_3 and $-NH_2$ groups, which make angles 57° , 180° and 142° with the C-atoms of parent benzene ring as placed in Table 3. μ_{theo} 's are

found to differ from μ_s probably due to existence of inductive and mesomeric moments of the substituent polar groups arising out of difference in electron affinity of two adjacent atoms. For all the polar compounds as referred to Tables 1-3 are planar ones and have the property of cyclic delocalized π -electrons on each carbon atom of the rings. The solvent C_6H_6 is also a cyclic and planar compound and has three double bonds and six p-electrons on its six carbon atoms. Hence due to their aromaticity, the resonance effect combined with inductive effect known as mesomeric effect are playing an important role among the substituent polar groups attached to the parent ring under static and hf electric field. The so called mesomeric moment is, however, caused by the permanent polarisation of different substituent groups acting as pusher or puller of electrons towards or away from p-electrons of C-atoms attached to the parent rings. Thus a special attention is to be paid to get the conformational structures of the molecules of Fig. 5 by μ_{cal} in terms of reduced bond moments by a factor μ_s/μ_{theo} in agreement with μ_s to take into account of the mesomeric effects in them. Similar effects may also be observed in those molecules in the hf electric field. They are not calculated because they were found not to depend strongly on the frequency (f) of the alternating hf electric field of 10 GHz.

5. CONCLUSIONS

A convenient method for the determination of τ_j of a polar liquid from the ratio of slopes of the individual variations of imaginary σ''_{ij} and real σ'_{ij} with w_j 's of solutes in a non-polar solvent is suggested in terms of measured data to avoid polar-polar interactions. The estimated τ_j when compared with the existing method using the slope of σ''_{ij} with σ'_{ij} for different w_j 's reveals the soundness of the method suggested. τ_j 's are reliable and claimed to be accurate up to $\pm 10\%$. The computed μ_j 's ($\pm 5\%$) in terms of the slopes β 's of σ_{ij} - w_j curves and τ_j 's are found to agree with the static μ_s excellently. The static μ_s as calculated from X_{ij} - w_j curves are used to test the accuracies of permittivities of ϵ_{oij} and $\epsilon_{\infty ij}$ measured in the static or low frequency electric field. The curves of X_{ij} with w_j vary linearly and have a tendency to meet at a common point in the ordinate

axis at $w_j = 0$, signifying the accuracy of the measured relaxation data once again. The % errors in terms of correlation coefficients r 's of $\sigma_{ij} - w_j$ and $X_{ij} - w_j$ curves are very easy, simple and straightforward to compute. The deviations of the static μ_s and hf μ_j from μ_{theo} as obtained from the available bond moments and bond angles of the substituent polar groups attached to the parent molecule imply the existence of mesomeric and inductive moments in the molecules. The comparison of μ_j with μ_2 and μ_1 obtained from double relaxation method provides an important information, that under the 10GHz electric field only a part of the molecule is rotating. Thus the present method of study in terms of measured dimensionless dielectric constants of Table 1 seems to give a new insight of the molecular interactions in relaxation phenomena.

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