

Chapter 5

**SINGLE-FREQUENCY
MEASUREMENT OF
DOUBLE-RELAXATION TIMES
OF MONO-SUBSTITUTED
ANILINES IN BENZENE**

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1. INTRODUCTION

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

Bergmann *et al* [8] devised a graphical technique in order to obtain τ_1 and τ_2 to represent relaxation times of the flexible part attached to the parent molecule and the molecule itself respectively. The corresponding contributions c_1 and c_2 towards dielectric relaxations in terms of τ_1 and τ_2 were also found for some complex molecules. The method is based on plotting the normalized experimental points involved with the measured data of the real ϵ' , the imaginary ϵ'' of the complex dielectric constant ϵ^* , the static dielectric constant ϵ_0 and the optical dielectric constant ϵ_∞ at various frequencies ω on a semicircle in a complex plane. A point was then selected on the chord through the two fixed points on the semicircle in consistency with all the experimental points. Bhattacharyya *et al* [9] subsequently modified the above procedure to get τ_1 , τ_2 , c_1 and c_2 with the experimental values measured at two different frequencies.

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

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

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

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

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

Some of the disubstituted aniline and benzene derivatives had already been studied in detail by the new approach suggested by Saha *et al* [10]. Ten out of 12

highly non-spherical disubstituted anilines and benzenes were found to exhibit the double-relaxation phenomena as their flexible parts are not rigidly fixed in relation to the parent ones.

We, therefore, thought to study the available solution data of ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of mono-substituted anilines like anisidines and toluidines in their *ortho*, *meta* and *para* forms for their various concentrations as measured by Srivastava and Suresh Chandra [12] at different frequencies of 2.02, 3.86 and 22.06 GHz electric fields at 35°C to obtain τ_1 and τ_2 based on the new approach of Saha *et al* [10]. Highly non-spherical molecules like mono-substituted anilines are also expected to possess the double-relaxation phenomena by showing τ_1 and τ_2 . Although they are strongly of non-Debye type in their relaxation behaviour, it is found, in the present investigation, that they do not exhibit the effect of double-relaxation phenomena at all frequencies of the electric field. When the available data [12] were extended to 9.945 GHz (about 3 cm wavelength), which is supposed to be the most effective dispersive region for such polar molecules, all of them, on the other hand, showed the double-relaxation phenomena of reasonable τ_1 and τ_2 [13]. However, out of 18 systems, as shown in tables and figures, eight systems like *o*- and *m*-anisidine and *p*-toluidine at 3.86 and 22.06 GHz together with *o*- and *m*-toluidine at 2.02 and 3.86 GHz are found to show τ_1 and τ_2 . Only *p*-anisidine is an exception. It shows mono-relaxation behaviour at all frequencies. This sort of mono-relaxation behaviour may equally well be explained by considering a distribution of relaxation times, namely a single broad dispersion. Only τ_2 values of the compounds showing mono-relaxation are, however, obtained from the slopes of the straight line equations (such as (15), see later) of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ with $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ having zero intercepts.

The relaxation times τ , since accurate values for mono-substituted anilines are not available, are also estimated from the slopes of K''_{ij} versus K'_{ij} . They may be called the most probable relaxation time τ_0 of the three isomers of

anisidine and toluidine. τ_0 is often given by $\tau_0 = (\tau_1 \tau_2)^{1/2}$ where τ_1 and τ_2 convey their usual meanings. c_1 and c_2 in terms of τ_1 and τ_2 are also calculated from Fröhlich's equations [11] as well as by our graphical technique. The dipole moments μ_1 and μ_2 of these three isomers of anisidine and toluidine are finally estimated from the slope β of their concentration variation of UHF conductivities K_{ij} , at $w_j \rightarrow 0$ and in terms of the estimated τ_1 and τ_2 in order to establish the conformational structures of those compounds under investigation.

2. THEORETICAL FORMULATIONS OF c_1 AND c_2 IN TERMS OF τ_1 AND τ_2 BASED ON THE SINGLE FREQUENCY METHOD

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

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

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

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

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

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

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

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

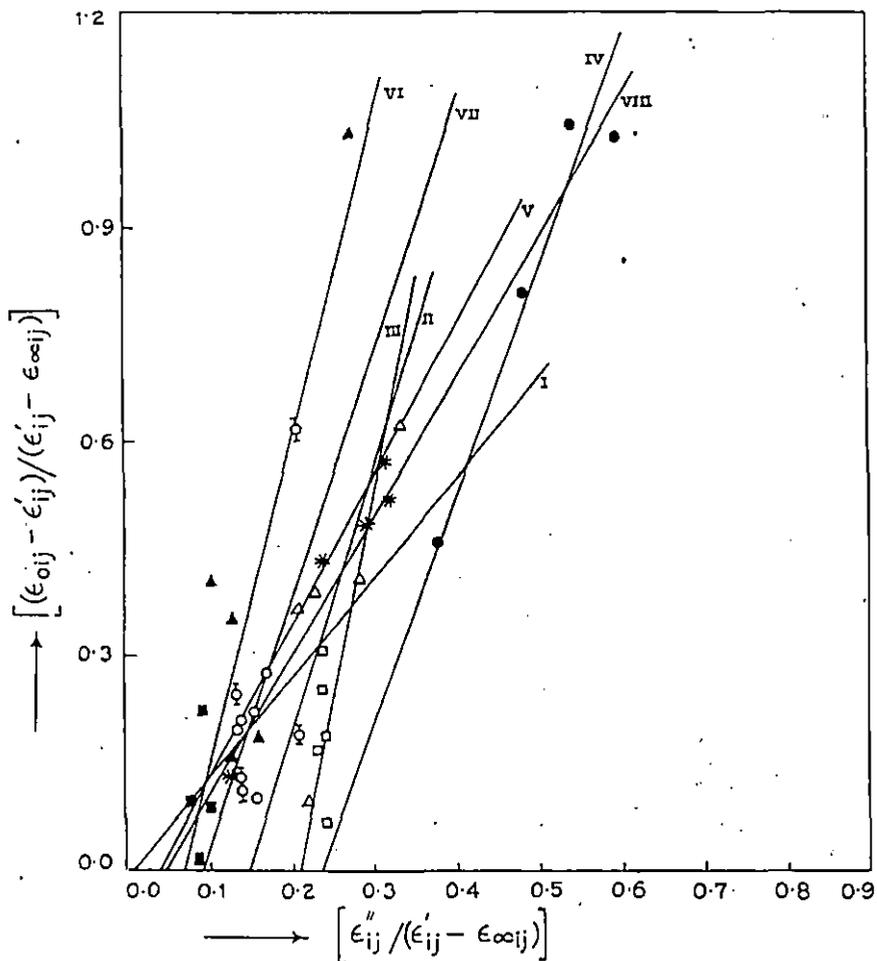


Figure 1. Variation of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ at 35°C for different weight fraction w_j (table 1): (I) *o*-anisidine at 3.86 GHz (○); (II) *o*-anisidine at 22.06 GHz (△); (III) *m*-anisidine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

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

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

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

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

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

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

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

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

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

The Fröhlich parameter A as shown in table 2 for polar solutes exhibiting the double-relaxation phenomena are used to evaluate both x and y of equations (3)

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

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

and (4) in terms of ω and the small limiting relaxation time $\tau_s = \tau_1$ by the following equations [11]:

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

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

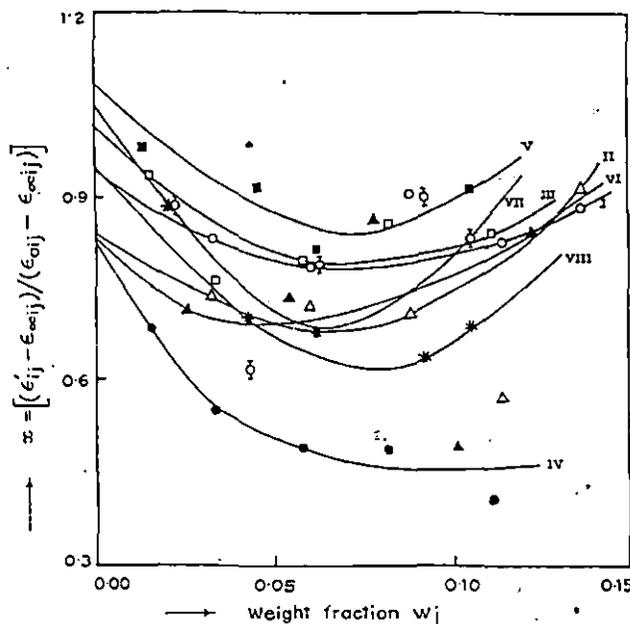


Fig. 2. Plot of $(\epsilon'_{ij} - \epsilon_{\alpha ij}) / (\epsilon_{0ij} - \epsilon_{\alpha ij})$ against weight fraction w_j for the polar-non-polar liquid mixture at 35°C (Table 2): (I) o-anisidine at 3.86 GHz (O); (ii) o-anisidine at 22.06 GHz (Δ); (III) m-anisidine at 3.86 GHz (\square); (IV) m-anisidine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

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

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

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

from the slope and intercept of equation (7) for each solute, when substituted on the right-hand sides of equations (1) and (2), suggest the limiting values of x and y as obtained from figures 2 and 3 at infinite dilution.

3. ESTIMATED μ_1 AND μ_2 FROM UHF CONDUCTIVITY K_{ij} IN TERMS OF τ_1 AND τ_2

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

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

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

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) w_j$$

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

$$\left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \text{..... (11)}$$

where M_j is the molecular weight of a polar solute, N is Avogadro's number, k

is the Boltzmann constant, the local field $F_{ij} = \frac{1}{9} (\epsilon_{ij} + 2)^2$, becomes

$F_i = \frac{1}{9} (\epsilon_i + 2)^2$ and the density $\rho_{ij} \rightarrow \rho_i$ the density of the solvent at $w_j \rightarrow 0$.

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

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

or

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

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

$$\mu_j = \left(\frac{3M_j k T \beta}{N \rho_f F_i \omega b} \right)^{1/2} \dots\dots\dots (13)$$

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

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

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

4. RESULTS AND DISCUSSION

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

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

The correlation coefficients r for each curve were also calculated to confirm their linearity. Some of the coefficients were found to be negative only due to their negative slopes, as is evidenced from table 1. The percentage of error involved in the calculation was found for each curve. The slope and intercept of equation (7) for each straight line were, however, used to determine τ_1 and τ_2 for each compound as shown in table 1. Although equation (7) is based on assumption

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

System	Frequency in GHz	Slope $\beta \times 10^{10}$ of $K_{ij} - w_j$ equations	% error involved in calculation	Dimensionless parameters			Estimated dipole moments (in Debye)			Theoretical μ_j in D from bond angle and bond moment	Estimated μ_1 in D from $\mu_1 = \mu_2(C_1/C_2)^{1/2}$
				$b_0 = \frac{1}{1+\omega^2\tau_0^2}$	$b_1 = \frac{1}{1+\omega^2\tau_1^2}$	$b_2 = \frac{1}{1+\omega^2\tau_2^2}$	μ_0	μ_1	μ_2		
<i>o</i> -anisidine	2.02	0.1620	0.40	0.9942		0.8026	1.39	1.54			
	3.86	0.1786	0.41	0.9800	0.9998	0.3119	1.06	1.05	1.88	1.02	
	22.06	0.3870	1.01	0.9526	0.9769	0.0747	0.66	0.65	2.37	1.64	
<i>m</i> -anisidine	2.02	0.3347	0.18	0.9778		0.9269	2.01	2.07			
	3.86	0.2311	2.06	0.9596	0.9563	0.0339	1.22	1.22	6.49	1.65	
	22.06	2.2841	0.08	0.7758	0.9396	0.1068	1.78	1.62	4.81	3.44	
<i>p</i> -anisidine	2.02	0.3380	0.35	0.9930		0.9891	2.01	2.01			
	3.86	0.6473	0.09	0.9756		0.9601	2.03	2.04	1.89		
	22.06	2.8513	0.31	0.8400		0.6960	1.91	2.10			
<i>o</i> -toluidine	2.02	0.2097	0.26	0.9960	0.9986	0.1917	1.47	1.47	3.35		
	3.86	0.5507	0.37	0.9732		0.9508	1.74	1.76	1.39	3.49	
	22.06	1.3618	0.09	0.7597		0.4569	1.29	1.67			
<i>m</i> -toluidine	2.02	0.2359	0.39	0.9879		0.9835	1.56	1.57			
	3.86	0.4889	1.82	0.9737	0.9956	0.0482	1.64	1.63	7.38	1.03	
	22.06	0.9826	1.30	0.8167		0.5930	1.06	1.24		5.05	
<i>p</i> -toluidine	2.02	0.0906	0.21	0.9973		0.9685	0.97	0.98			
	3.86	0.1583	0.44	0.1873	0.9912	0.0818	2.13	0.93	3.23	1.54	
	22.06	1.2927	0.34	0.8602	0.9980	0.2221	1.19	1.10	2.34	2.48	

of the existence of τ_1 and τ_2 , the mono-relaxation behaviour showing only τ_2 for some compounds at different frequencies of the electric field may be equally explained by taking into account a single broad dispersion. The resulting equation (7) becomes, when $\tau_1 = 0$,

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

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

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

where $\tau_0 = 1/(2\pi f m)$. They are seen to correspond to the relation $\tau_0 = (\tau_1 \tau_2)^{1/2}$ approximately, which gives 5.53, 5.31, 44.06, 6.18, 21.93, 22.37, 23.16 and 4.32 ps respectively for the mono-substituted anilines showing the double-relaxation phenomena at different frequencies of the applied electric field. Some of these relaxation times are reasonably good. The estimated values of τ_1 , τ_2 and τ_0 are all given in table 1.

It is found in table 1 that *m*-anisidine, *m*- and *p*-toluidines at 3.86 GHz and *o*-toluidine at 2.02 GHz show considerably high values of τ_1 in the range 9-3 ps; while their τ_2 values are comparatively much larger in the range 220-138 ps. This fact confirms that, under such frequencies of alternating electric field, the

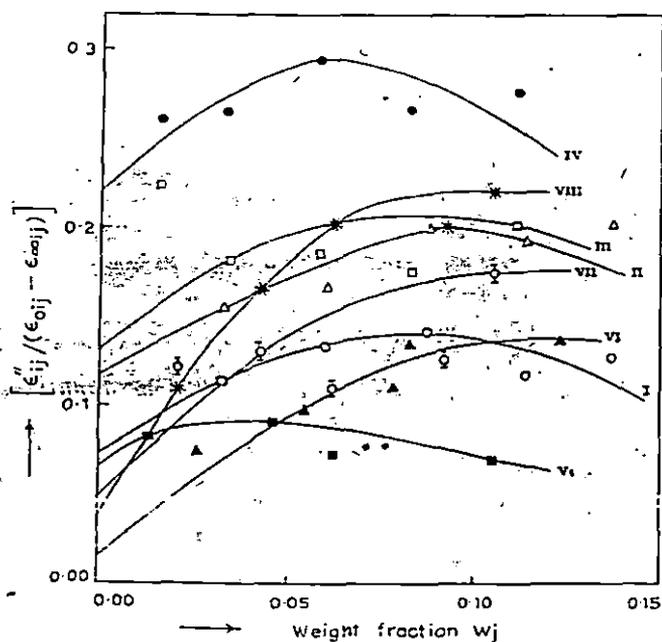


Figure 3. Plot of $\epsilon''_{ij}/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction w_j of polar solutes in dilute solutions at 35°C (table 2): (I) *o*-anisidine at 3.86 GHz (○); (II) *o*-anisidine at 22.06 GHz (Δ); (III) *m*-anisidine at 3.86 GHz (□); (IV) *m*-anisidine at 22.06 GHz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

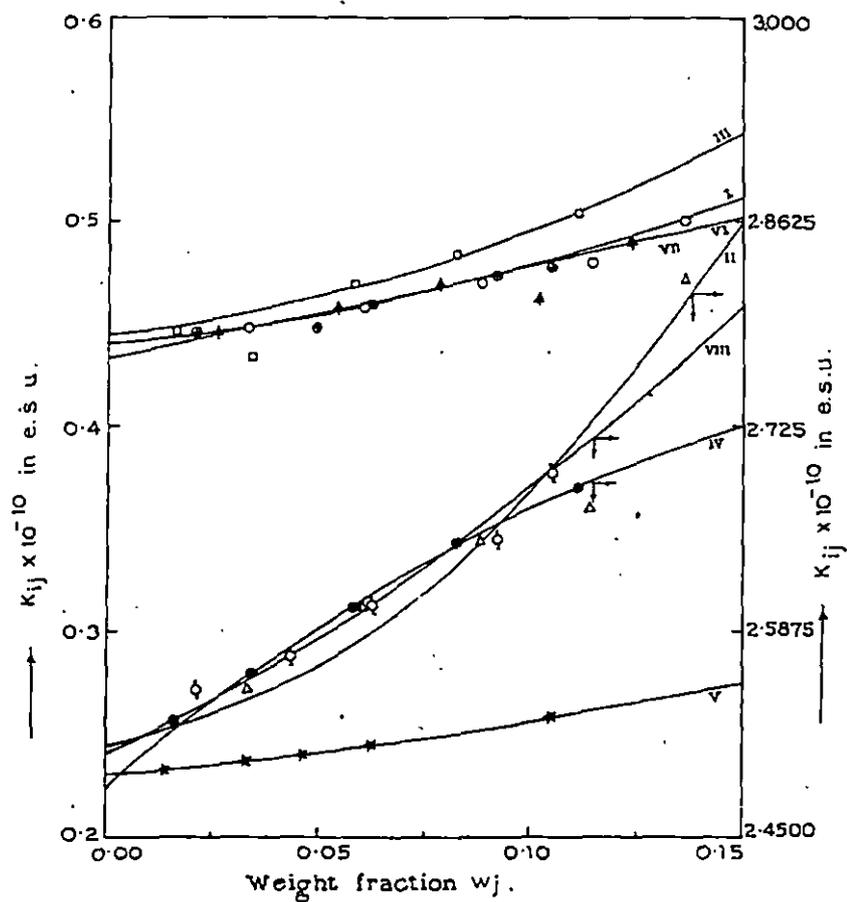


Figure 4. Concentration variation of ultra-high-frequency conductivity K_{ij} of mono-substituted anilines at 35°C: (I) *o*-anisidine at 3.86 GHz (○); (II) *o*-anisidine at 22.06 GHz (Δ); (III) *m*-anisidine at 3.86 GHz (□); (IV) *m*-anisidine at 22.06 GHz (●); (V) *o*-toluidine at 2.02 GHz (*); (VI) *m*-toluidine at 3.86 GHz (▲); (VII) *p*-toluidine at 3.86 GHz (⊕); and (VIII) *p*-toluidine at 22.06 GHz (◇).

flexible parts are loosely bound to the parent molecules. They, therefore, require longer times to accommodate their flexible parts towards dielectric relaxation as shown by c_2 values in table 2 being greater than unity. The other molecules like *o*-anisidine at 3.86 and 22.06 GHz and *m*-anisidine and *p*-toluidine at 22.06 GHz show very small values of τ_1 , often less than or equal to unity, while their τ_2 values are more or less consistent with the expected values that are often observed in the literature. However, *p*-anisidine shows the mono-relaxation behaviour at all frequencies by showing only τ_2 in agreement with τ_0 . Hence *p*-anisidine unlike *p*-toluidine appears to be highly rigid at all the experimental frequencies. The *o*- and *m*-anisidines at 2.02 GHz, *o*-toluidine at 3.86 and 22.06 GHz, *m*-toluidine at 2.02 and 22.06 GHz and *p*-toluidine at 2.02 GHz exhibit the mono-relaxation behaviour in yielding τ_2 values in agreement with our τ_0 values. They indicate their rigidity at those frequencies. When the dielectric relaxation data are extended to 9.945 GHz [13] it is really interesting to note that all these mono-substituted anilines show τ_1 and τ_2 in close agreement with the expected literature values. This fact establishes that an X-band microwave electric field is actually the most effective dispersive region for highly non-spherical polar molecules like mono- or disubstituted aniline and benzene respectively [10].

The c_1 and c_2 values were also calculated from the values of x and y in Fröhlich's equations (8) and (9) with $\tau_1 = \tau_s$ (table 1) and Fröhlich's parameter A , where $A = \ln(\tau_2/\tau_1)$. They are given in table 2 together with those values obtained from the graphical technique of determination of x and y from figures 2 and 3 at infinite dilution. The experimental x and y values on the left-hand sides of equations (1) and (2) as plotted with different w_j in figures 2 and 3 show the usual decrease in x while the latter increases with w_j in concave and convex ways respectively indicating the values of τ_1 and τ_2 as a function of concentration [5]. τ_1 and τ_2 , as obtained from the slope and intercept of equation (7) for a polar-non-polar liquid mixture are, therefore, fixed for a polar compound in consistency with the right-hand sides of equations (1) and (2). The values of c_1 by Fröhlich's method are found to be less than unity while c_2 values are greater

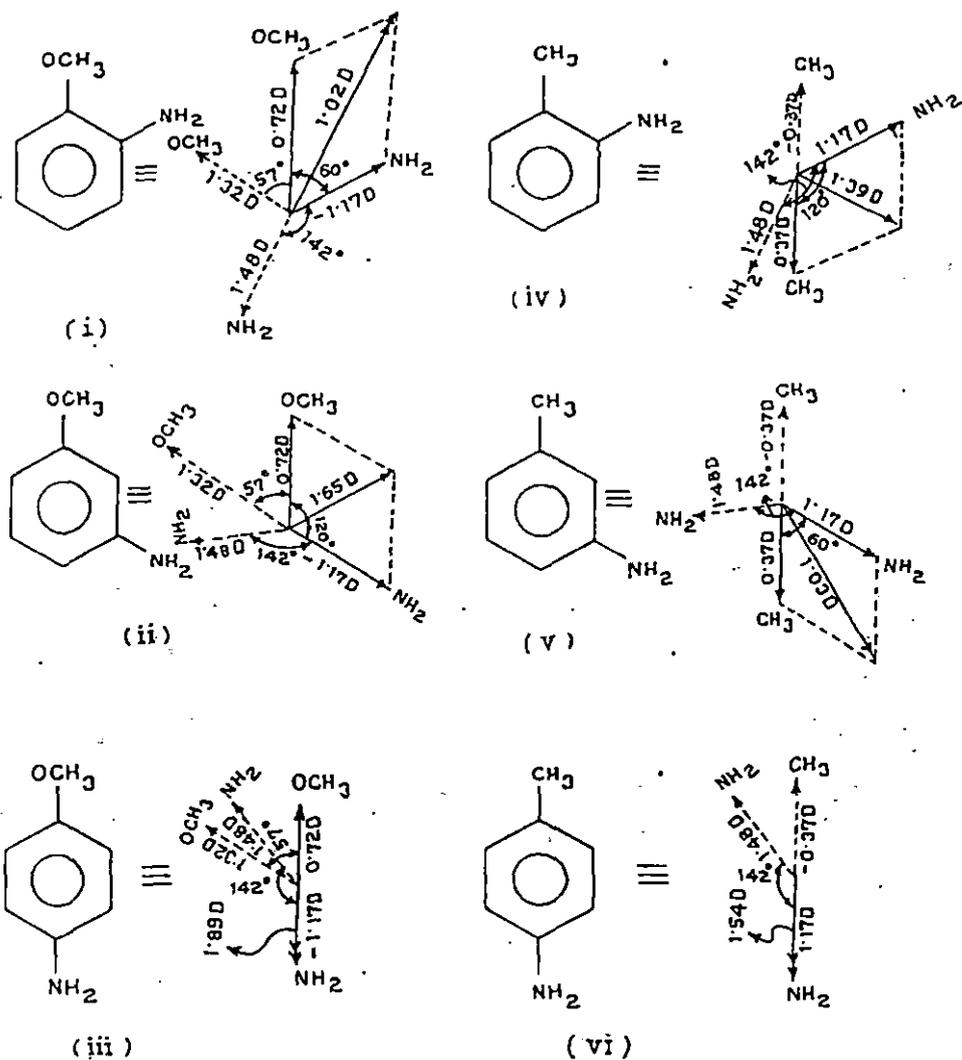


Figure 5. Conformational structures of anisidines and toluidines in *ortho*, *meta* and *para* forms: (i) *o*-anisidine, (ii) *m*-anisidine, (iii) *p*-anisidine, (iv) *o*-toluidine, (v) *m*-toluidine and (vi) *p*-toluidine.

than and nearly equal to unity. The graphical technique adopted here yields the opposite results by showing $c_1 \geq 1.0$ and c_2 very small, often becoming negative (table 2), probably due to inertia [10]. The values of c_1 and c_2 in table 2 suggest that the two double-relaxation phenomena are not equally probable.

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

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

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

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

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

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

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

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

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

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

An attempt was made to estimate from the available bond moments and bond angles the theoretical μ values of the polar liquids, assuming the molecules to be planar. The bond moments and bond angles of C \rightarrow OCH₃ in anisidine and C \leftarrow CH₃ in toluidine are 1.32 D, 0.37 D and 57°, 180° with respect to the benzene ring while those of C \rightarrow NH₂ are 1.48 D and 142° respectively [17]. The

conformational structures thus obtained by the vector addition method for anisidine and toluidine in their *ortho*, *meta* and *para* forms are displayed in figure 5. The estimated μ_j are given in table 3, with those of μ_1 where $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ assuming that the two relaxation phenomena are equally probable. The close agreement of μ values as shown in table 3 at once indicates that the method as suggested is a simple, straightforward and unique one.

5. CONCLUSION

The determination of slope and intercept of the derived linear equation (equation (7)) involved with a single UHF dielectric relaxation recording of a polar-non-polar liquid mixture at different w_j and at a given temperature in degrees Celsius is an analytical and reliable method by which to calculate τ_1 and τ_2 of the flexible part as well as of the whole molecule itself. The relative contributions c_1 and c_2 towards dielectric relaxations in terms of τ_1 and τ_2 can be calculated by using Fröhlich's equations. The graphical techniques used are also convenient tools to estimate c_1 and c_2 . The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 , and from the slope β of the concentration variation of K_{ij} of polar-non-polar liquid mixtures, throw much light on the structural conformation of a complex polar liquid under investigation. The methodology so far advanced seems to be a significant improvement over the existing ones in that it allows estimation of correlation coefficients between the data used and the percentage of error introduced in the obtained results. The procedure is thus simple, straightforward and requires less computational work than the existing methods, in which experimental data of a pure polar liquid at two or more electric field frequencies are usually needed.

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