Chapter 3

DIELECTRIC RELAXATION OF SOME DISUBSTITUTED BENZENE AND ANILINE DERIVATIVES UNDER STATIC AND HIGH FREQUENCY ELECTRIC FIELDS

DIELECTRIC RELAXATION OF SOME DISUBSTITUTED BENZENE AND ANILINE DERIVATIVES UNDER STATIC AND HIGH FREQUENCY ELECTRIC FIELDS

1. INTRODUCTION

During the last few years the investigation of dielectric relaxation phenomena has provided an important approach to explore the structural behaviour of complex organic polar molecules in different nonpolar solvents [1,2]. The concept of dielectric relaxation mechanism may be explained in terms of the rate process involving the rotation of a dipolar molecule from one equilibrium position to the other under an electric field of Giga hertz frequency. The information about different energy parameters can be obtained from the measured dielectric relaxation data as a function of weight fraction ω_j of a polar solute in a nonpolar solvent [3] at different temperatures.

In course of derivation of a standard formula to estimate the dipole moment μ_s of a polar solute under the static electric field, Ghosh et al [4] and Guha et al [5] obtained a relation of μ_s of a polar solute (j) dissolved in a nonpolar solvent (i) from Debye's equation [6]. Although, the atomic polarisation in most of the polar-nonpolar liquid mixtures very oftetn lies between 1 and 1.15 times the electronic polarisation, it is assumed that the Debye model, they are equal in magnitudes to each other. The method usually involves the static experimental parameter X_{ij} in terms of the measured relaxation data like dielectric constant ϵ_{oij} and refractive index n_{Dij} of a polar-nonpolar liquid mixture (ij) for different ω_j's. The variation of X_{ij} with ω_j may be linear or parabolic in nature as shown in Figure 1, whose linear coefficient is conveniently used to estimate the static μ_s of a polar solute at a given temperature.

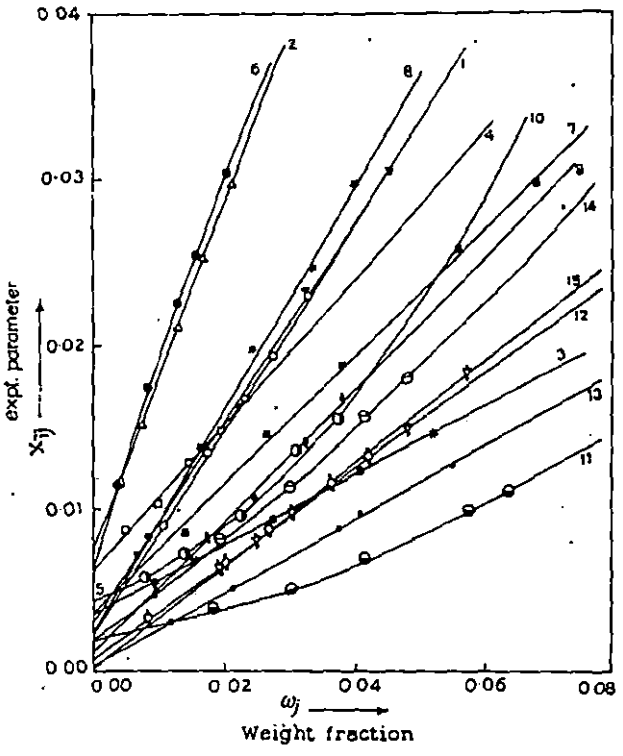

Figure 1. Represents plot of experimental parameter (X_{ij}) against ω_j.

1. for *o*-chloro nitrobenzene in C_6H_6.
2. for *o*-chloro nitrobenzene in CCl_4.
3. for 4-chloro 3-nitrobenzo trifluoride in C_6H_6.
4. for 4-chloro 3-nitrobenzo trifluoride in CCl_4.
5. for 4-chloro 3-nitro toluene in C_6H_6.
6. for 4-chloro 3-nitro toluene in CCl_4.
7. for *m*-amino benzo trifluoride in C_6H_6.
8. for *o*-nitro benzo trifluoride in C_6H_6.
9. for *m*-nitro benzo trifluoride in C_6H_6.
10. for *o*-choloro benzo trifluoride in C_6H_6.
11. for 2-chloro 6-methyl aniline in C_6H_6.
12. for 3-chloro 2-methyl aniline in C_6H_6.
13. for 3-chloro 4-methyl aniline in C_6H_6.
14. for 4-chloro 2-methyl aniline in C_6H_6.
15. for 5-chloro 2-methyl aniline in C_6H_6.

We derived [7] a formulation to obtain the dipole moment μ_j of a polar solute under high frequency (hf) electric field where the orientation polarisation plays an important role. In order to get μ_j by the above procedure one should know the measured relaxation time τ_j from other source [8]. Later on, Murthy et al [9] suggested that the simultaneous determination of τ_j and $\mu_j$could, however, be possible without any prior knowledge of either. τ_j of any polar liquid can thus be obtained by using the slope of the linear plot of the imaginary K''_{ij} part and the real K'_{ij} part of the hf complex conductivity K^*_{ij}. One can estimate μ_j of polar

solute from the slope β of the concentration variation of the total hf conductivity K_{ij} of the polar-nonpolar liquid mixture. Saha and Acharyya [10] also observed that the fitted curves of K''_{ij}-K'_{ij} for different ω_j's for Some interesting protic polar liquids vary linearly in nonpolar solvent. The variations of K''_{ij} and K'_{ij} with ω_j's may not be linear in higher concentrations [11] for all liquid mixtures. This fact at once suggested the use of the ratio of the individual slopes of K''_{ij}–ω_j and K'_{ij}–ω_j curves at $\omega_j \to 0$, which may be a better representation for $(dK''_{ij}/dK'_{ij})_{\omega j \to 0}$ to evaluate τ_j [9]. The corresponding μ_j is then obviously determined from the slope of K_{ij}–ω_j curve (Figure 2) at a given temperature.

We have applied the above procedures to get τ_j's and hence μ_j's of some disubstituted benzene and aniline derivatives with the measured dielectric relaxation data [12-14]. Similarly, we have determined μ_s under the static or low frequency electric field. They have been shown in Tables 2 and 1 respectively.

Table 1. Values of coefficients a_0, a_1, a_2 in the equation $X_{ij} = a_0 + a_1\omega_j + a_2\omega_j^2$.% error in fitting technique, calculated correlation coefficient r, μ_j in D(static) and those from bond angles and bond moments.

System with sl.no and molecular wt. M_j in gm.	Coefficients a_0, a_1, a_2 in eq. $X_{ij} = a_0 + a_1\omega_j + a_2\omega_j^2$			Correlation coefficient (r)	% error in fitting technique	μ_s in D (static) from eq. (6)	μ_{theo} in D from bond angle and bond moments
	a_0	a_1	a_2				
(1) o-chloro nitro benzene in C_6H_6 M_j = 157.5 gm	0.00227	0.6266	–	0.9981	0.11	4.16	5.28
(2) o-chloro nitro benzene in CCl_4 M_j = 157.5 gm	0.00755	1.0447	–	0.9993	0.04	4.00	5.28
(3) 4-chloro 3-nitro benzo tri-fluoride in C_6H_6 M_j = 225.5 gm	0.00367	0.2110	–	0.7664	12.44	2.89	3.78
(4) 4-chloro 3-nitro benzo tri-fluoride in CCl_4 M_j = 225.5 gm	0.00637	0.4432	–	0.9972	0.17	3.12	3.78

Table 1. (Cont'd)

System with sl.no and molecular wt. M_j in gm.	Coefficients a_0, a_1, a_2 in eq. $X_{ij} = a_0 + a_1\omega_j + a_2\omega_j^2$			Correlation coefficient (r)	% error in fitting technique	μ_s in D (static) from eq. (6)	μ_{theo} in D from bond angle and bond moments
	a_0	a_1	a_2				
(5) 4-chloro 3-nitro toluene in C_6H_6 $M_j = 171.5$ gm	0.00320	0.6103	–	0.9977	0.14	4.28	5.58
(6) 4-chloro 3-nitro toluene in CCl_4 $M_j = 171.5$ gm	0.00648	1.3221	-7.4488	0.9987	0.08	4.70	5.58
(7) *m*-amino benzo trifluoride in C_6H_6 $M_j = 161.05$ gm	0.00374	0.3889	–	0.9976	0.14	3.31	2.48
(8) *o*-nitro benzo trifluoride in C_6H_6 $M_j = 191.04$ gm	0.00268	0.6725	–	0.9988	0.07	4.74	6.18
(9) *m*-nitro benzo trifluoride in C_6H_6 $M_j = 191.04$ gm	0.00129	0.4012	–	0.9976	0.14	3.67	3.74
(10) *o*-chloro benzo trifluoride in C_6H_6 $M_j = 180.5$ gm	0.00461	0.1247	4.732	0.9923	0.46	1.99	3.98
(11) 2-chloro 6-methyl aniline in C_6H_6 $M_j = 141.52$ gm.	0.00231	0.0733	1.1011	0.9951	0.30	1.35	1.85
(12) 3-chloro 2-methyl aniline in C_6H_6 $M_j = 141.52$ gm	0.00105	0.2929	–	0.9996	0.02	2.70	2.48
(13) 3-chloro 4-methyl aniline in C_6H_6 $M_j = 141.52$ gm	0.00052	0.2277	–	0.9994	0.03	2.40	2.20
(14) 4-chloro 2-methyl aniline in C_6H_6 $M_j = 141.52$ gm	0.00226	0.2809	1.0847	0.9998	0.01	2.64	3.06
(15) 5-chloro 2-methyl aniline in C_6H_6 $M_j = 141.52$ gm	0.00053	0.3139	–	0.9991	0.06	2.80	2.83

The purpose of the present paper is to test the success of the methods developed earlier. The molecules, referred in Tables 1 and 2, are very important because they often show double relaxation times τ_1 and τ_2 due to their flexible parts attached to the parent rings as well as due to the whole molecules themselves at 9.945 GHz electric field which is supposed to be the most effective dispersive region

Table 2. The slope of $K''_{ij} - K'_{ij}$ curve, relaxation time (τ_j), dimensionless parameter (b) from eqs. (9) and (15) along with ratio of slopes of $K''_{ij} - \omega_j$ and $K'_{ij} - \omega_j$ equation at $\omega_j \to 0$, corresponding (τ_j) and (b) using eqs. (10) and (15), hf computed dipole moment μ_j from eq. (14) by two methods and μ_j due to Guggenheim method.

System with sl. no. and molecular wt. M_j in gm	Slope of $K''_{ij} - K'_{ij}$ curve	Relaxation time $\tau_j \times 10^{12}$ sec	Dimensionless parameter $b = \frac{1}{1+\omega^2\tau_j^2}$	Ratio of slopes of K''_{ij} & K'_{ij} with $\omega_j x/y =$ $\left(\frac{dK''_{ij}}{d\omega_j}\Big/\frac{dK'_{ij}}{d\omega_j}\right)_{\omega_j \to 0}$	Relaxation time $\tau_j \times 10^{12}$ sec	Dimensionless parameter $b = \frac{1}{1+\omega^2\tau_j^2}$	Computed μ_j in D $\overline{hf}$ method eq. (10) and eq. (14)	Computed μ_j in D hf method eq. (9) and eq. (14)	μ_j in D due to Guggenheim method (Reported)
(1) *o*-chloro nitro benzene in C_6H_6 M_j = 157.5 gm	1.3529	11.83	0.6469	3.9039/2.8865 = 1.3525	11.84	0.6465	4.39	4.39	4.35
(2) *o*-chloro nitro benzene in CCl_4 M_j = 157.5 gm	1.2729	12.58	0.6183	5.2884/4.1544 = 1.2729	12.58	0.6183	3.92	3.92	4.19
(3) 4-chloro 3-nitro benzo trifluoride in C_6H_6 M_j = 225.5 gm	1.3353	11.99	0.6407	1.4495/1.0897 = 1.3302	12.04	0.6388	2.86	2.86	2.97
(4) 4-chloro 3-nitro benzo trifluoride in CCl_4 M_j = 225.5 gm	0.9678	16.54	0.4838	1.5534/1.5827 = 0.9814	16.32	0.4905	2.83	2.85	3.17
(5) 4-chloro 3-nitro toluene in C_6H_6 M_j = 171.5 gm	1.0092	15.86	0.5048	2.6982/2.6692 = 1.0109	15.84	0.5054	4.35	4.35	4.49
(6) 4-chloro 3-nitro toluene in CCl_4 M_j = 171.5 gm	0.7871	20.44	0.3803	3.1254/3.9841 = 0.7844	20.41	0.3810	4.04	4.04	4.68
(7) *m*-amino benzo trifluoride in C_6H_6 M_j = 161.04 gm	1.3989	11.44	0.6620	2.2798/1.6297 = 1.3989	11.44	0.6620	3.34	3.34	3.51
(8) *o*-nitro benzo trifluoride in C_6H_6 M_j = 191.04 gm	1.3024	12.29	0.6293	3.9944/3.0553 = 1.3074	12.25	0.6308	4.95	4.95	4.96

Table 2. *(Cont'd.)*

System with sl. no. and molecular wt. M_j in gm	Slope of $K''_{ij} - K'_{ij}$ curve	Relaxation time $\tau_j \times 10^{12}$ sec	Dimension less parameter $b = \frac{1}{1+\omega^2\tau_j^2}$	Ratio of slopes of K''_{ij} & K'_{ij} with $\omega_j x/y =$ $\left(\frac{dK''_{ij}}{d\omega_j}\Big/\frac{dK'_{ij}}{d\omega_j}\right)_{\omega_j \to 0}$	Relaxation time $\tau_j \times 10^{12}$ sec	Dimension less parameter $b = \frac{1}{1+\omega^2\tau_j^2}$	Computed μ_j in D		μ_j in D due to Guggenheim method (Reported)
							$\overline{hf}$ method eq. (10) and eq. (14)	hf method eq. (9) and eq. (14)	
(9) *m*-nitro benzo trifluoride in C_6H_6 M_j = 191.04 gm	1.0808	14.81	0.5309	1.7707/1.6472 = 1.0749	14.90	0.5360	3.51	3.50	3.67
(10) *o*-chloro benzo trifluoride in C_6H_6 M_j = 180.5 gm	1.5263	10.49	0.6997	1.9986/1.2983 = 1.5394	10.40	0.7033	3.17	3.18	3.38
(11) 2-chloro 6-methyl aniline in C_6H_6 M_j = 141.52 gm	2.5150	6.37	0.8635	1.3675/0.5430 = 2.5184	6.36	0.8637	2.10	2.10	2.32
(12) 3-chloro 2-methyl aniline in C_6H_6 M_j = 141.52 gm	2.1337	7.50	0.8199	2.1142/0.9913 = 2.1327	7.51	0.8196	2.68	2.68	3.02
(13) 3-chloro 4-methyl aniline in C_6H_6 M_j = 141.52 gm	1.4769	10.84	0.6856	1.2657/0.8571 = 1.4767	10.84	0.6857	2.27	2.27	2.61
(14) 4-chloro 2-methyl aniline in C_6H_6 M_j = 141.52 gm	1.3252	12.08	0.6372	1.7350/1.3094 = 1.3250	12.08	0.6372	2.7	2.7	3.28
(15) 5-chloro 2-methyl aniline in C_6H_6 M_j = 141.52 gm	1.2122	13.21	0.5950	1.6288/1.3436 = 1.2122	13.21	0.5950	2.79	2.79	3.10

for them [15,16]. The molecules are planar and have the property of cyclic delocalisation of π-electrons on each carbon atom. The non-polar solvent C_6H_6 unlike CCl_4, is also a cyclic and planar compound and has three double bonds and six p-electrons on six carbon atoms. Hence π-π interaction or resonance effect combined with inductive effect known as the mesomeric effect may play a vital role in the measured relaxation data.

Hence, a special attention is to be paid to the contributions of the available bond angles and bond moments due to the different substituent groups in the parent rings of the molecules in calculating theoretical dipole moment μ_{theo} (last column of Table 1). But μ_{theo} thus calculated for some molecules are found to be deviated from the measured μ_s (Table 1) because of the existence of the inductive and the mesomeric moments in different groups. Of these, the latter effect for these compounds have significant values as illustrated in Figure 3.

Moreover, μ_j's as obtained from τ_j's by the hf method under 9.945 GHz electric field are compared with μ_s. It seems to be interesting to observe the frequency dependence of μ_j.

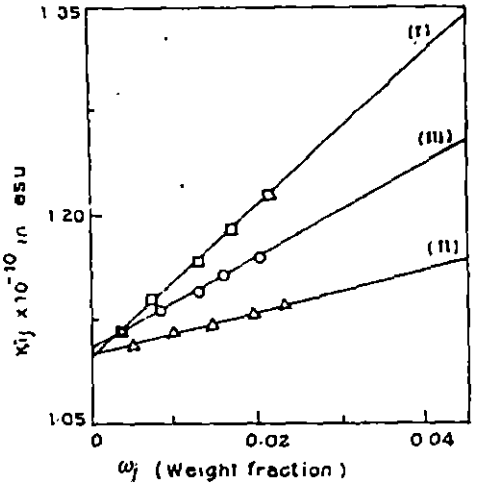

Figure 2. Represents the plot of $K_{ij} \times 10^{-10}$ against ω_j.

I. —□—□— for *o*-chloro nitro benzene in CCl_4.

II. —Δ—Δ— for 4-chloro 3-nitrobenzo trifluoride in CCl_4.

III. —O—O— for 4-chloro 3-nitro toluene in CCl_4.

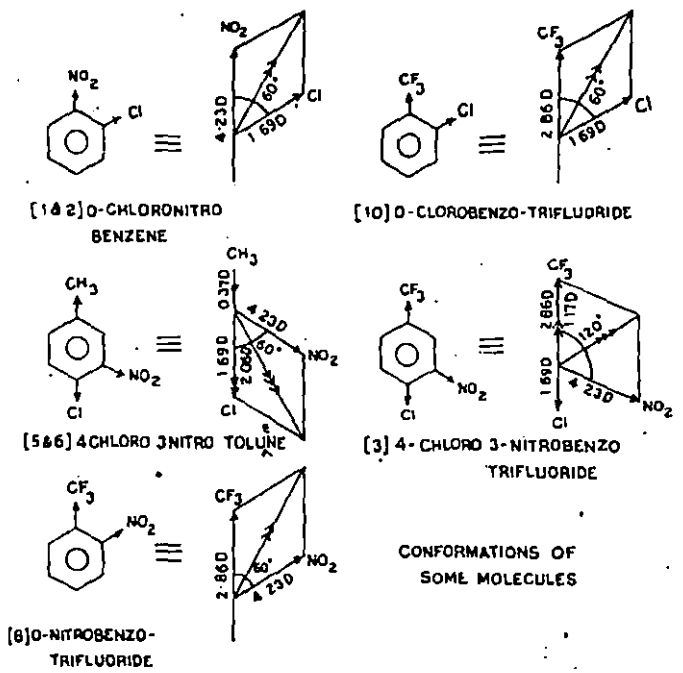

Figure 3. Conformations of some molecules

in comparison to static μ_s, although the variation of μ_j with temperature is also a significant one.

As evident from Table 1 and Figure 1, the least square fitted curves of X_{ij} vs ω_j, are linear for almost all liquids except 4-chloro 3-nitro toluene in CCl_4, o-chloro benzo trifluoride, 2-chloro 6-methyl aniline and 4-chloro 2-methyl aniline in C_6H_6 respectively. The latter systems, on the other hand, are found to be parabolic in nature. μ_s's are estimated from the linear coefficients (Table 1) of X_{ij} vs ω_j relations. They are then compared with μ_{theo} from bond angles and bond moments (last column of Table 1).

τ_j's in the hf electric field are evaluated from the slope of K''_{ij} against K'_{ij} curve. They are then used to calculate the dimensionless parameter b as presented in the 3rd and 4th columns of Table 2. τ_j's are also calculated from the ratio of slopes of fitted curves K''_{ij}–ω_j and K'_{ij}–ω_j together with b in terms of τ_j as shown in the 6th and the 7th columns of Table 2. The agreement of both the b's are, however, excellent. As a result, calculated μ_j's in terms of b's and slope of K_{ij}–ω_j curve are in conformity with each other. μ_j's thus estimated are compared with those due to Guggenheim method as reported elsewhere [15] and shown in the last column of Table 2 together with the μ_s placed in the 7th column of Table 1.

2. THEORETICAL FORMULATIONS

(i) Static dipole moment μ_s :

The well known Debye equation [6] for a polar-nonpolar liquid mixture of molar concentration c_j of a polar solute at a given temperature T°K is given by :

$$\frac{\epsilon_{oij}-1}{\epsilon_{oij}+2}-\frac{n^2_{Dij}-1}{n^2_{Dij}+2}=\frac{\epsilon_{oi}-1}{\epsilon_{oi}+2}-\frac{n^2_{Di}-1}{n^2_{Di}+2}+\frac{4\pi N\mu^2_s}{9kT}c_j \quad \text{.....(1)}$$

The symbols used in eq.(1) are of usual significance. c_j is again related to ω_j by

$$c_j = \rho_{ij}\omega_j/M_j, \qquad \text{.....(2)}$$

where M_j is the molecular weight of the polar solute and ρ_{ij} is the density of the solution. When the weight W_j of the solute of volume V_j is made to dissolve in the weight W_i of the solvent of volume V_i, the solution density ρ_{ij} is expressed by:

$$\rho_{ij} = \frac{W_i + W_j}{V_i + V_j} = \frac{\rho_i \rho_j}{\left(\frac{W_i}{W_i + W_j}\right)\rho_j + \left(\frac{W_j}{W_i + W_j}\right)\rho_i}$$

$$= \frac{\rho_i}{1-(1-\rho_i/\rho_j)\omega_j} = \frac{\rho_i}{1-\gamma\omega_j} = \rho_i(1-\gamma\omega_j)^{-1}, \qquad \text{.....(3)}$$

Where $\gamma = (1 - \rho_i/\rho_j)$, ρ_i and ρ_j are the densities of the pure solvent and pure solute respectively, $\omega_i = \frac{W_i}{W_i + W_j}$ and $\omega_j = \frac{W_j}{W_i + W_j}$ are the weight fractions of the solvent and solute respectively, provided $\omega_i + \omega_i = 1$. Equation (1) with the help of eqs. (2) and (3) becomes [4,5]:

$$\frac{\epsilon_{oij} - n^2_{Dij}}{(\epsilon_{oij} + 2)(n^2_{Dij} + 2)} = \frac{\epsilon_{oi} - n^2_{Di}}{(\epsilon_{oi} + 2)(n^2_{Di} + 2)} + \frac{4\pi N\mu_s^2}{27\,kT}\frac{\rho_i}{M_j}\omega_j(1-\gamma\omega_j)^{-1}$$

$$\text{or} \quad X_{ij} = X_i + \frac{4\pi N\mu_s^2\rho_i}{27M_jkT}\omega_j + \frac{4\pi N\mu_s^2\rho_i}{27M_jkT}\gamma\omega_j^2 +$$

$$= X_i + R\omega_j + R\gamma\omega_j^2 + \qquad \text{.....(4)}$$

where X_{ij} and X_i are the static experimental parameters of the solution and solvent respectively in terms of the static dielectric relaxation parameters (e.g. the static dielectric constants ϵ_{oij}, ϵ_{oi} and refractive indices n_{Dij}, n_{Di} of solution and solvent respectively); and

$R = \frac{4\pi N\mu_s^2\rho_i}{27M_jkT}$. As evident from Table 1 and Figure 1, X_{ij} for most of the polar-nonpolar liquid mixtures, under our investigation, behave linearly with ω_j except in a few cases as mentioned above.

This at once indicates X_{ij} as a polynomial function of ω_j like

$$X_{ij} = a_0 + a_1\omega_j + a_2\omega_j^2 \qquad \text{..... (5)}$$

neglecting the higher powers of ω_j in eq. (4) as they contain the factors arising due to orientation effect, relative density effect, dipole-dipole interactions, associations etc., whereas a_1's in eq. (5) are free from all sorts of factors as supported by the experimental plots of X_{ij} with ω_j in Figure 1. Hence, equating the first power of ω_j from eqs. (4) and (5), one gets μ_s as

$$\mu_s = \left(\frac{27kTM_j}{4\pi N\rho_i}a_1\right)^{1/2} \qquad \text{..... (6)}$$

The estimated μ_s are then placed in the 7th column of Table 1 together with μ_{theo} due to bond angles and bond moments of the same Table 1 for comparison.

(ii) High frequency dipole moment, μ_j and the relaxation time τ_j :

The complex hf electrical conductivity K^*_{ij} is given by Murphy and Morgan [17] as:

$$K^*_{ij} = K'_{ij} + jK''_{ij} \qquad \text{..... (7)}$$

$K'_{ij} = \frac{\omega}{4\pi}\epsilon''_{ij}$ and $K''_{ij} = \frac{\omega}{4\pi}\epsilon'_{ij}$ are the real and imaginary parts of the complex hf K^*_{ij} of solution of weight fraction ω_j of a polar solute and $j = \sqrt{-1}$ is a complex number.

Now in the hf electric field, K''_{ij} is related to K'_{ij} by

$$K''_{ij} = K_{\infty ij} + \frac{1}{\omega\tau_j} K'_{ij}, \qquad \text{..... (8)}$$

where $K_{\infty ij}$ is a constant conductivity at infinite dilution. Equation(8) on differentiation with respect to K'_{ij} yields

$$(dK''_{ij}/dK'_{ij}) = 1/\omega\tau_j, \qquad \text{..... (9)}$$

which offers a convenient method [9] to estimate τ_j. Both K''_{ij} and K'_{ij} are the function of ω_j and hence for comparatively large concentrations they may not be linear [11].

In that case one can use the following relation

$$\left(\frac{dK''_{ij}}{dK'_{ij}}\right) = \left(\frac{dK''_{ij}}{d\omega_j}\right)_{\omega_j \to 0} \Big/ \left(\frac{dK'_{ij}}{d\omega_j}\right)_{\omega_j \to 0} = \frac{1}{\omega\tau_j}$$

or, $\qquad x/y = 1/\omega\tau_j, \qquad \text{..... (10)}$

to get τ_j of a polar solute where ω is the angular freqtuency $= 2\pi f$, f being the frequency of the applied electric field.

Now, the real part of conductivity K'_{ij} of a polar-nonpolar liquid mixture at T^0K is given by [18].

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

$$\text{or } \left(\frac{dK'_{ij}}{d\omega_j}\right)_{\omega_j \to 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left(\frac{\omega^2\tau_j}{1+\omega^2\tau_j^2}\right) \qquad \text{..... (11)}$$

Here, the density ρ_{ij} and the local field F_{ij} of the solution become ρ_i and F_i $[= (\epsilon_i + 2)/3]^2$ where ρ_i, F_i, and ϵ_i are the density, local field and dielectric constant of solvent respectively.

Again, the total hf conductivity is approximated as

$$K_{ij} = K_{\infty ij} + \frac{1}{\omega\tau_j} K'_{ij} \qquad \text{..... (12)}$$

which on differentiation with respect to ω_j at $\omega_j \to 0$ gives

$$(dK'_{ij}/d\omega_j)_{\omega_j \to 0} = \omega\tau_j\beta \qquad \text{..... (13)}$$

where β = slope of $K_{ij} - \omega_j$ curves of which only o-chloronitro benzene, 4-chloro 3-nitro benzotrifluoride and 4-chloro 3-nitro toluene in CCl_4 are shown in Figure 2; others are reported elsewhere [7, 15]. Using eqs. (11) and (13) μ_j is written as

$$\mu_j = \left[\frac{27M_jkT}{N\rho_i(\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b}\right]^{\frac{1}{2}} \qquad \text{..... (14)}$$

where b is a dimensionless parameter and is given by

$$b = \frac{1}{1 + \omega^2\tau_j^2} \qquad \text{..... (15)}$$

The estimated b's in terms of τ_j's from eqs. (9) and (10) are finally used in eq. (14) to get μ_j as shown in Table 2 for disubstituted benzene and aniline molecules.

3. RESULTS AND DISCUSSIONS

The variation of the experimental dielectric parameters X_{ij}'s with different weight fractions ω_j's of polar solutes of all the disubstituted benzenes and anilines at 35°C are shown in Figure 1. They are, however, obtained by fitting the experimental X_{ij}'s with ω_j's in order to get a polynominal equation like $X_{ij} = a_0 + a_1\omega_j + a_2\omega_j^2$. The coefficients a_0, a_1 and a_2 in all the X_{ij}'s for disubstituted benzenes and anilines are shown in Table 1. Table 1 also shows that, for eleven out of fifteen systems, X_{ij}'s vary linearly with ω_j. The series expansion of X_{ij} in terms of ω_j based on five available experimental data [12-14] using ϵ_{oij} and ~~and~~ n^2_{Dij}, is highly convergent beyond linear terms for the very low values of ω_j i.e., $\omega_j << 1$.

However, the coefficients of ω_j^2 for the systems like 4-chloro 3-nitro toluene in CCl_4, o-chloro benzo trifluoride, 2-chloro 6-methyl aniline and 4-chloro 2-methyl aniline all in C_6H_6 are very significant. This type of behaviour may, perhaps, be due to polar-polar interactions of the solutes. The linear behaviour of all the systems including the four parabolic ones is confirmed by the correlation coefficients r which are found to lie within the range 0.7664 to 0.9998 as presented in the 5-th column of Table 1. The corresponding percentage of errors of r in fitting technique are also shown in the 6th column of the same Table 1. The errors are, however, very small indicating the soundness of the method adopted for evaluating μ_s. The only molecule like 4-chloro 3-nitro benzo trifluoride in C_6H_6 shows considerably large error, perhaps, due to the inherent experimental uncertainty in the measured data. The respective dipole moments μ_s are calculated from linear coefficient of X_{ij} vs ω_j curve i.e. from eq. (4) or eq. (5) and are placed in the 7th column of Table 1 together with those due to bond angle and bond moments in the 8th column of the same Table 1.

For all the compounds referred in Table 1, due to their aromaticity, the resonance effect combined with inductive effect known as mesomeric effect are important. The so called mesomeric moments have significant values. This is caused by the permanent polarisation of different substituent groups acting as pusher or puller of electron towards or away from p-electron of carbon atom attached to the parent rings.

But in solvent CCl_4 one of the C→Cl dipoles interacts with solutes, often to yield large μ_s in comparison to those in C_6H_6. μ_s and μ_{theo} as shown in Table 1, differ appreciably for some polar liquids like o-chloro nitrobenzene, 4-chloro 3-nitro toluene, o-nitro benzo trifluoride, o-chloro benzo trifluoride and 4-chloro 3 nitro benzo trifluoride probably due to mesomeric moments of the substituent groups for their close proximity (Figure 3). The reduction in bond moments evidently occurs in almost all polar liquids, except those containing - NH_2 group, by a factor μ_s/μ_{theo} lying in the range 0.7 to 0.8 to conform to the exact μ_s. The

other molecules exhibit μ_{theo} in close agreement with μ_s for their low mesomeric moments. They were already displayed and sketched elsewhere [7,15].

The relaxation time τ_j's in the hf method from the slope of K''_{ij}–K'_{ij} curves are calculated and compared with those due to the ratio of slopes of K''_{ij}– ω_j and K'_{ij}– ω_j curves as shown in Table 2. The μ_j's thus obtained are found to agree well with each other. This fact indicates that the latter procedure is more effective in calculating the μ_j's of polar solutes because in this case, not only polar-polar interaction is totally avoided, but also for wide range of concentraion of polar solute, the individual variation of K''_{ij} and K'_{ij} remain insignificant in determining τ_j. The dimensionless parameters b involved with τ_j are also calculated for both the cases. They are used to estimate μ_j of polar solutes in terms of slope β of K_{ij}– ω_j curve. The linear variation of hf conductivity K_{ij} with ω_j for disubstituted benzenes and anilines in benzenes were, however, investigated earlier and shown elsewhere [7,15]. Polar molecules like o-chloronitrobenzene, 4-chloro 3-nitrobenzo trifluoride, 4-chloro 3-nitro toluene dissolved in solvent CCl_4 are also found to vary linearly according to the following equations :

$K_{ij} \times 10^{-10} = 1.0973 + 5.4508\ \omega_j$,

$K_{ij} \times 10^{-10} = 1.0999 + 1.5781\omega_j$ and

$K_{ij} \times 10^{-10} = 1.1044 + 3.2769\ \omega_j$. They are shown graphically in Figure 2.

As evident from Tables 1 and 2, the respective static and hf dipole moments μ_s's and μ_j's of fifteen systems agree excellently, although μ_j's are slightly smaller than μ_s's. This fact reveals that dipole moments μ_j's are very little affected by the frequency of the applied electric field. It is also interesting to note that like disubstituted anilines, almost all disubstituted benzenes show close agreement of μ_s's and μ_j's with the dipole moments μ_l due to the flexible parts of the molecules [15]. This behaviour may be explained on the basis of the fact that under hf electric field, the probabilities of rotations of the flexible parts are greater than that of the whole molecules themselves because of their loose attachment with the parent molecules. Some of the disubstituted benzenes like

o-chloro benzo trifluoride, m-nitro benzo trifluoride, m-amino benzo trifluoride all in C_6H_6 as well as 4-chloro 3-nitro benzo trifluoride in bothC_6H_6 and CCl_4 show μ values in agreement with the dipole moments μ_2 due to end-over-end rotation of the whole molecule [15]. This is, perhaps, due to the more rigid attachment of the flexible parts with the parent molecules as evident from Tables [15] showing either μ_2 or μ_1 and μ_2 simultaneously having small values of μ_1. Finally, the estimated μ_j and μ_s are compared with those due to Guggenheim method and μ_{theo} due to bond angles and bond moments [15,7]. The agreement is excellent as shown in Tables 2 and 1 respectively.

4. CONCLUSION

Thus, we may conclude that the dielectric relaxation parameters canbe conveniently used for simultaneous determinations of the relaxation times and dipole moments in hf electric field together with static dipole moment. The estimated static dipole moment μ_s from the linear coefficient of experimental parameters X_{ij} against ω_j curve is a reliable one except in four cases where they are very little affected due to the presence of quadratic term of eq. (4). The percentage of errors calculated through the correlation coefficients r are also very low signifying the soundness of the method adopted here. The comparison of μ_s with hf dipole moment μ_j is necessarily an interesting phenomenon, although the errors in estimation of the latter are generally claimed to be ± 5% [9].

The μ_j's are usually affected by the rise in temperature but appears to be equal to those due to the flexible parts of the molecule. This at once indicates that a part of the molecule is rotating in the electric field of highly dispersive region of nearly 10 GHz.

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