

## Dipole Moment Study of OH...N Complexes in Organic Liquids

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The dipole moment of 1:1 complexes of *p*-chloro phenol and 1-octanol with aniline, *o*-chloro aniline and *p*-chloro aniline in carbon tetra chloride were determined at 303 K. The dipolar increments of the systems were computed from the bond angle data available from molecular orbital theory. The enhancement of the dipole moment values confirms the hydrogen bonding between all the anilines.

**Key Words: H-Bonding, Anilines, Phenol, Dipole moment, Dipolar increment.**

### INTRODUCTION

Dielectric investigation of the solutes in an inert solvent can give the valuable information regarding structure, molecular complexes in solutions<sup>1-6</sup>. The formation of hydrogen bond leads to an increased the polarity of the A-H (proton donor) and hence to large dielectric constant and dipole moment. Huyskens *et al.*,<sup>7,8</sup> has developed the methods to determine the stereochemistries of hydrogen bonded complexes from the proton acceptor in an inert solvent. The dipole moment of the complex is a function of the relative strength of acid and base can be calculated. The dipole moment of the complexes higher than the sum of the individual components corresponds to charge redistribution along the A-H...B bond. In this paper, reporting the dipole moment of the 1:1 complexes of aniline, *o*-chloro aniline and *p*-chloro aniline with *p*-chloro phenol and 1-octanol.

### EXPERIMENTAL

The dielectric measurements at static frequency 300 kHz were made using a Toshniwal RL09 dipole meter and refractive index using Abbe's refractometer. The cell temperature was maintained at 30 °C by circulating water through glass jacket of the cell. The chemicals were purified by standard procedure and checked against the literature value.

**Theory:** Considering the ternary mixture of polar components A (-OH group) and B (-NH<sub>2</sub> group) in a non-polar solvent, the relative orientations of A and B vary continuously due to the mobility of the liquid phase. Assuming that the time interval

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is short enough to consider the orientation as fixed, the dipole moment of the solution may be written as

$$M^2 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} N_{ij} \mu_{ij} \quad (1)$$

where  $N_{ij}$  is the number of  $ij$  ensembles. Huyskens *et al.*,<sup>7</sup> showed that the eqn. 1 can be written as

$$M^2 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} N_{ij} \left( \frac{\mu_{ij}^2 - j \langle \mu_{0j}^2 \rangle}{i} \right) + n_B \langle \mu_{0j}^2 \rangle N_B \quad (2)$$

where  $\langle \mu_{0j}^2 \rangle$  is the mean square of the B molecule in the square of the total dipole moment of the entities. For anilines as proton donor B,  $j$  is taken as 1 and  $\langle \mu_{0j}^2 \rangle$  is practically  $\mu_b^2$ .

The quantity  $\frac{\mu_{ij}^2 - \mu_{0j}^2}{i}$  represents the mean share of the A molecule in the square of the total dipole moment of the entities.

$$n_A = \sum_{i=0}^{\infty} i N_{ij} / N_A \quad (3)$$

$$n_B = \sum_{i=0}^{\infty} i N_{ij} / N_B \quad (4)$$

$$\frac{M^2}{VN_A} = (\langle \mu_{ab}^2 \rangle - \mu_b^2) C_A + \langle \mu_b^2 \rangle C_B \quad (5)$$

where  $C_A$  and  $C_B$  are the formal concentration ( $\text{mol dm}^{-3}$ ) of the proton donor and proton acceptor, respectively.

From the knowledge of dielectric constant  $\epsilon_0$ , the refractive index  $n_D$  of the solution  $\epsilon_S$  and  $n_{DS}$  of the solvent. One can obtain a relation for  $M^2$  from Frohlich equation<sup>9</sup>.

$$M^2 = \frac{9Kt}{4\pi} \left( \frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\epsilon_0(n_D^2 + 2)^2} \right) - \frac{C_s}{C_s} \left( \frac{(\epsilon_S - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\epsilon_S(n_{DS}^2 + 2)^2} \right) \quad (6)$$

$C_s$  is the actual concentration of the polar solvent and  $\bar{C}_s$  is the concentration in its pure state. Substitute eqn. 6 in eqn. 5

$$\begin{aligned} (\langle \mu_{ab}^2 \rangle - \mu_b^2) \frac{c_a}{c_b} + \mu_b^2 \Omega_B = & \frac{9KT}{4\pi C_B} \left( \frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\epsilon_0(n_D^2 + 2)^2} \right) \\ & - \frac{C_s}{\bar{C}_s} \left( \frac{(\epsilon_S - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\epsilon_S(n_{DS}^2 + 2)^2} \right) \quad (7) \end{aligned}$$

The experimental values of the density, refractive index, dielectric constant and experimental quantity ( $\Omega_B$ ) for different concentrations for the system studies here are given in Table-1

TABLE-1  
VALUES OF DIELECTRIC CONSTANT, REFRACTIVE INDEX AND DENSITY OF ANILINE, *o/p*-CHLOROANILINE WITH THE FORMAL CONCENTRATION OF 1-OCTANOL AND *p*-CHLORO PHENOL

1-Octanol + aniline + CCl <sub>4</sub>					1-Octanol + <i>o</i> -chloro aniline + CCl <sub>4</sub>				
C <sub>B</sub> (mol/L)	$\epsilon_o$	n <sub>D</sub>	d (g/cm <sup>3</sup> )	$\Omega_B$	C <sub>B</sub> (mol/L)	$\epsilon_o$	n <sub>D</sub>	d (g/cm <sup>3</sup> )	$\Omega_B$
0.06	2.2545	1.440	1.57350	14.30	0.08	2.28002	1.437	1.5432	14.45
0.10	2.364	1.441	1.57319	17.52	0.10	2.32043	1.437	1.5324	14.97
0.15	2.3849	1.442	1.57236	12.65	0.20	2.34305	1.438	1.5273	8.30
0.20	2.4110	1.442	1.57156	10.56	0.40	2.38534	1.440	1.5081	4.89
0.25	2.4318	1.443	1.57022	9.02	0.50	2.45342	1.443	1.4965	4.86
0.30	2.4892	1.444	1.54525	8.97	0.60	2.50241	1.451	1.4852	4.34
0.40	2.6008	1.448	1.52677	8.67	0.70	2.54436	1.452	1.5742	4.16
0.50	2.7086	1.450	1.49932	8.49	–	–	–	–	–
1-Octanol + <i>p</i> -chloro aniline + CCl <sub>4</sub>					<i>p</i> -Chloro phenol + aniline + CCl <sub>4</sub>				
0.08	2.26016	1.437	1.5431	12.34	0.08	2.30435	1.436	1.5455	17.36
0.10	2.29156	1.437	1.5534	12.54	0.10	2.35045	1.437	1.5558	17.48
0.20	2.32304	1.438	1.5362	7.46	0.20	2.41145	1.438	1.5386	11.13
0.40	2.37556	1.440	1.5281	4.69	0.40	2.44265	1.439	1.5305	6.13
0.50	2.45434	1.443	1.5503	4.88	0.50	2.45305	1.441	1.5527	4.97
0.60	2.50161	1.451	1.5382	4.33	0.60	2.53505	1.448	1.5406	4.91
0.70	2.52787	1.452	1.5233	3.97	0.70	2.57095	1.454	1.6316	4.38
<i>p</i> -Chloro phenol + <i>o</i> -chloro aniline + CCl <sub>4</sub>					Chlorophenol + <i>p</i> -chloro aniline + CCl <sub>4</sub>				
0.08	2.2743	1.440	1.5448	12.83	0.06	2.3808	1.438	1.5890	32.88
0.10	2.3204	1.445	1.5222	12.80	0.10	2.4070	1.439	1.5782	21.62
0.15	2.3814	1.446	1.5190	11.73	0.15	2.4595	1.441	1.5679	16.90
0.20	2.4126	1.447	1.5024	9.94	0.20	2.5068	1.442	1.5658	14.45
0.25	2.4230	1.449	1.4924	8.07	0.25	2.6590	1.443	1.5620	16.26
0.40	2.5050	1.451	1.4862	6.56	0.30	2.7010	1.445	1.5603	14.44
0.50	2.5409	1.451	1.4880	5.82	0.40	2.8008	1.446	1.5594	12.67
0.60	2.5921	1.455	1.4840	5.33	0.50	2.8900	1.448	1.5592	11.36

Using least square fitting method  $C_A/C_B$  is plotted against  $\Omega_B$ . From the slope and intercept of the plot (Fig. 1) values of  $\mu_{ab}$  and  $\mu_b$  were calculated.

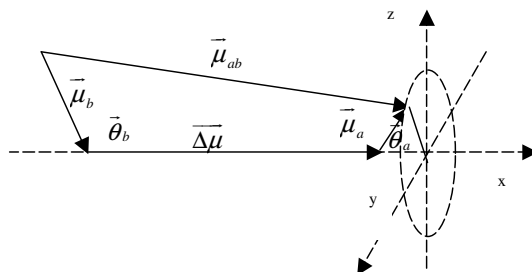


Fig. 1. Dipole moments  $\mu_{ab}$ ,  $\mu_a$  and  $\mu_b$  of the complex and of the partners-dipole increment  $\Delta\mu$

When a proton donor of dipole moment  $\mu_a$  forms a H-bond with a proton acceptor of dipole moment  $\mu_b$ , the direction of  $\mu_a$  and  $\mu_b$  with respect to A-H...B axis can be defined as  $\theta_a$  and  $\theta_b$ . If the values of  $\theta_a$  and  $\theta_b$  differ from zero, one can define the azimuth angle  $\Phi$ , which describes the rotation position of  $\mu_b$  around the hydrogen bond with respect to the plane formed by the bond and  $\mu_a$  (Fig. 1).

The mean value of  $\langle \cos \Phi \rangle$  was found to be zero for O-H...N which means that all rotamers around the axis of the bond are equally possible<sup>10</sup>

The dipolar increment is given by

$$\Delta\mu = (\mu_{ab}^2 - \mu_a^2 \sin^2 \theta_a - \mu_b^2 \sin^2 \theta_b - 2\mu_a\mu_b \sin \theta_a \sin \theta_b \langle \cos \Phi \rangle)^{1/2} - \mu_a \cos \theta_a - \mu_b \cos \theta_b$$

From the computed values of  $\mu_{ab}$  and  $\mu_b$ , the dipolar increments were obtained using eqn. 8. These values are given in Table-2 for all the systems. The values of  $\theta_a$  and  $\theta_b$  taken from the literature.

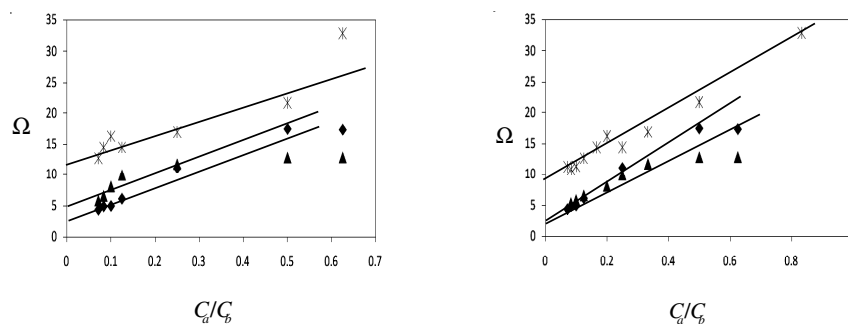
TABLE-2  
DIPOLE MOMENTS OF THE COMPONENTS AND THEIR 1:1 COMPLEXES  
AND DIPOLAR INCREMENTS OF THE COMPLEXES

Systems	$\mu_a$ (D)	$\mu_b$ (D)	$\mu_{ab}$ (D)	$\Delta\mu$ (D)
1-Octanol + aniline + CCl <sub>4</sub>	1.72	1.44	3.56	0.32
1-Octanol + <i>o</i> -chloro aniline + CCl <sub>4</sub>	1.70	1.75	4.20	0.71
1-Octanol + <i>p</i> -chloro aniline	1.72	2.90	4.23	0.80
<i>p</i> -Chloro phenol + aniline + CCl <sub>4</sub>	2.14	2.09	4.70	0.42
<i>p</i> -Chloro phenol + <i>o</i> -chloro aniline + CCl <sub>4</sub>	2.17	3.15	5.64	0.30
<i>p</i> -Chloro phenol + <i>p</i> -chloro aniline	2.20	1.43	4.11	0.38

## RESULTS AND DISCUSSION

It was observed<sup>11</sup> that if the charge transfer interactions carrying charge from the proton acceptor to the proton donor takes place, the redistribution will, reach the other end of the molecules resulting in a very large variation in the dipole moment of the complex. From present results where  $\Delta\mu < 0.8$  for all the systems. It is clear that there is no contribution arising due to ionic structures, as would involve a very high value for  $\Delta\mu (> 10D)$ . It was shown that about 50 % of the interaction moment observed experimentally arises due to the electronic interaction. Hence it may be concluded that only polarization interaction is the other important contributing factor to the enhancement of dipole moment of the complexes studied here.

The excess dipole moments for all the systems studied are found to be small, which is in agreement with the values reported by Balamuralikrishnan<sup>1</sup> for the mixtures of alcohol with aniline's. Similar results were reported by Malathi *et al.*<sup>11</sup>. The plot of  $(C_A/C_B)$  with  $\Omega_B$  is straight line which indicate the possibility for the formation of a 1:1 complex (Fig. 2). Hence it is concluded that the dipolar increment in all the systems is small due to the polarization effect only and it is not due to charge transfer phenomenon.

Fig. 2. Plots of  $C_A/C_B$  versus  $\Omega_B$ 

### Conclusion

Dipolar increment in all the systems is small. This indicates that the polarization interactions only and it is not due to charge transfer interactions.

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