

DIPOLE MOMENT STUDIES OF HYDROXYL-CARBONYL COMPLEXES AT 301 K

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ABSTRACT

The dipole moment of the 1:1 complexes of benzaldehyde and *p*- benzaldehyde with phenol, *o*-chlorophenol, *m*-chlorophenol and *p*-chlorophenol at 303K have been determined by using Huysken's method based on the Onsager theory. The dipolar increments of the systems were computed from the experimental dipole moment of the complexes. The enhancement of the dipolar increment values confirms the hydrogen bonding between all the systems. The dipolar increment is negative indicate the predominant of polarization interaction taking place all the systems.

Keywords: Hydrogen bonding, Dipolar increment, hydroxyl-carbonyl complexes, Dipole moment, Dielectric constant.

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INTRODUCTION

Dielectric, refractive index, ultrasonic and Fourier transform infrared spectroscopy studies of the donor-acceptor complexes can give the valuable information regarding solute-solvent interactions, solute-solute interactions, structure, and molecular complexes in solutions.¹⁻¹⁰

The interactions takes place in donor – acceptor complexes leads to an increased the polarity of the proton donor and hence to increase dielectric constant also increases bond moment.¹¹ Huyskens *et.al.*¹² have establish the stereo chemistry 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, it is higher than the sum of the individual components corresponds to charge redistribution along the A-H....B bond.¹³

In this paper, reporting the dipole moment of the 1:1 complexes of carbonyls (benzaldehyde, *p*-chlorobenzaldehyde) with hydroxyl (phenol, *o*-chlorophenol, *m*-chlorophenol and *p*-chlorophenol) in inert solvent of carbon tetrachloride.

EXPERIMENTS

The permittivities were measured at 303 K by using Toshniwal RL09 type dipole meter at 300 KHz with accuracy of ± 0.002 . The refractive indices were measured by using Abbe's refractometer with accuracy ± 0.001 for sodium D line. The densities were obtained by 5 ml specific gravity bottle with accuracy ± 0.001 g/cm³. The hydroxyl solutes of phenol, *o*-chlorophenol, *m*-chlorophenol and *p*-chlorophenol, the carbonyl solutes of benzaldehyde and *p*-chlorobenzaldehyde, and solvent of carbon tetrachloride were used and purified by the standard procedure with purity 99.99%.

Dipole Moment of 1:1 Complex by Huyskens Method¹²⁻¹³

Considering the ternary mixture of polar components A (OH group) and B(C=O 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 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 showed that the Eq. (1) can be written as-

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

Where $\langle \mu_{0j}^2 / j \rangle$ is the mean square of the B molecule in the square of the total dipole moment of the entities. For benzaldehydes as proton donor B, j is taken as 1 and $\langle \mu_{0j}^2 / j \rangle$ is practically μ_b^2 and $\langle \mu_{ij}^2 - \mu_{0j}^2 / j \rangle$

i is the quantity represents the mean square of the molecule in the square of the total dipole moment of the entities.

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

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

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

Where C_A and C_B are the formal concentration (mol lit^{-1}) of the proton donor and proton acceptor respectively.

From the knowledge of dielectric constant ϵ_o , the refractive index n_D of the solution ϵ_s and n_{DS} of the solvent. One can obtain a relation for M^2 from Frohlich Eqn.-

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

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

$$(\langle \mu_{ab}^2 - \mu_b^2 \rangle) \frac{C_A}{C_B} + \mu_b^2 \Omega_B = \frac{9KT}{4\pi C_B} \left(\frac{(\epsilon_o - n_D^2)(2\epsilon_o + n_D^2)}{\epsilon_o (n_D^2 + 2)^2} \right) - \frac{C_s}{\bar{C}_s} \left(\frac{(\epsilon_s - n_{DS}^2)(2\epsilon_s + n_{DS}^2)}{\epsilon_s (n_{DS}^2 + 2)^2} \right) \quad (7)$$

The experimental values of the density, refractive index, dielectric constant and experimental quantity (Ω_B) for different concentrations for the system studies here are given in table-1. Using least square fitting method C_A/C_B is plotted against Ω_B is shown in fig.-1 to 2. From the slope and intercept of the plot (Fig.-1) values of μ_{ab} and μ_b were calculated.

RESULTS AND DISCUSSION

The values of dielectric constant, refractive indices and density measured with varying concentration of the proton donor C_b are recorded in table-1. The dipole moment of the donor and acceptor were determined by Huyskens method based on Onsager theory using carbon tetrachloride as solvent. These are closely agreed with the results from solution data. The formal concentration of the proton donor C_a is kept constant, $C_b \gg C_a$. The values of μ_b and μ_{ab} are obtained shown in fig.-1 and 2.

The dipolar increment determined from relation (8), when a proton donor of dipole moment μ_a forms an H-bond with a proton acceptor of dipole moment μ_b , the direction of μ_a and μ_b with respect to A-H...B axis can be defined as θ_a and θ_b .

Table-1 : Variation of dielectric constant (ϵ_0) refractive index (n_D) density (ρ gm/cm³) and experimental quantity (Ω_B) with the concentration (C_B mole/lit) of hydroxyl-carbonyl complexes.

C_B	ϵ_0	n_D	ρ	Ω_B	C_B	ϵ_0	n_D	ρ	Ω_B
Phenol + benzaldehyde					Phenol+ <i>p</i> -chlorobenzaldehyde				
0.907	3.775	1.515	1.473	12.2	0.716	3.558	1.474	1.523	13.36
1.738	4.554	1.462	1.481	9.09	1.419	4.336	1.482	1.470	10.13
2.504	5.332	1.410	1.490	8.08	2.109	5.114	1.490	1.478	8.96
3.210	6.110	1.357	1.498	7.63	2.787	5.892	1.498	1.365	8.33
3.865	6.888	1.305	1.506	7.40	3.451	6.671	1.506	1.313	7.92
4.473	7.666	1.252	1.514	7.28	4.104	7.449	1.514	1.260	7.63
5.039	8.445	1.199	1.522	7.22	4.745	8.227	1.523	1.208	7.40
5.568	9.223	1.147	1.530	7.21	5.375	9.005	1.531	1.551	7.23
o-chlorophenol- benzaldehyde					o-chlorophenol- <i>p</i> -chlorobenzaldehyde				
0.893	3.625	1.476	1.534	11.15	0.708	3.408	1.477	1.542	11.94
1.713	4.254	1.488	1.500	7.957	1.402	4.036	1.488	1.508	8.727
2.468	4.882	1.499	1.467	6.928	2.084	4.664	1.500	1.475	7.547
3.167	5.510	1.511	1.433	6.424	2.754	5.291	1.511	1.441	6.918
3.814	6.138	1.522	1.400	6.152	3.411	5.921	1.523	1.408	6.501
4.416	6.766	1.534	1.366	5.978	4.056	6.549	1.534	1.374	6.210
4.978	7.395	1.545	1.333	5.879	4.690	7.177	1.545	1.341	5.987
5.502	8.023	1.556	1.299	5.817	5.313	7.805	1.557	1.307	5.795
<i>p</i> -chlorophenol+benzaldehyde					<i>p</i> -chlorophenol+ <i>p</i> -chlorobenzaldehyde				
0.893	3.655	1.475	1.532	11.41	0.708	3.438	1.475	1.540	12.32
1.713	4.314	1.484	1.497	8.268	1.402	4.096	1.485	1.505	9.079
2.468	4.972	1.494	1.462	7.235	2.084	4.754	1.494	1.470	7.928
3.167	5.630	1.503	1.427	6.762	2.754	5.412	1.504	1.435	7.291
3.814	6.288	1.513	1.392	6.494	3.411	6.071	1.513	1.400	6.894
4.416	6.946	1.522	1.357	6.350	4.056	6.729	1.523	1.365	6.599
4.978	7.605	1.532	1.322	6.257	4.690	7.387	1.532	1.330	6.385
5.502	8.263	1.541	1.287	6.215	5.313	8.045	1.542	1.295	6.203
<i>m</i> -chlorophenol- benzaldehyde					<i>m</i> -chlorophenol- <i>p</i> -chlorobenzaldehyde				
0.893	3.755	1.475	1.535	12.16	0.708	3.538	1.475	1.543	13.28
1.713	4.514	1.484	1.502	9.006	1.402	4.296	1.485	1.510	9.991
2.468	5.272	1.494	1.470	7.972	2.084	5.045	1.495	1.478	8.763
3.167	6.030	1.504	1.437	7.490	2.754	5.812	1.504	1.445	8.150
3.814	6.788	1.514	1.405	7.231	3.411	6.571	1.514	1.413	7.722
4.416	7.546	1.523	1.372	7.098	4.056	7.329	1.524	1.380	7.415
4.978	8.305	1.533	1.340	7.016	4.690	8.087	1.533	1.348	7.192
5.502	9.063	1.543	1.307	6.973	5.313	8.845	1.543	1.315	7.002

If the values of θ_a and θ_b differ from zero. One can define the azimuth angle Φ , which describes the rotation position of μ_b around the hydrogen bond with respect to the plane formed by the bond and μ_a (Fig.-3).

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.⁶⁻¹⁰

The dipolar increment is given by-

$$\Delta\mu = (\mu_{ab}^2 - \mu_a^2 \sin^2 \theta_a - \mu_b^2 \sin^2 \theta_b - 2\mu_a \mu_b \sin \theta_a \sin \theta_b \langle \cos \Phi \rangle)^{1/2} - \mu_a \cos \theta_a - \mu_b \cos \theta_b \quad (8)$$

From the computed values of μ_{ab} and μ_b , the dipolar increments were obtained using eqn.-8. These values are given in Table-2 for all the systems.

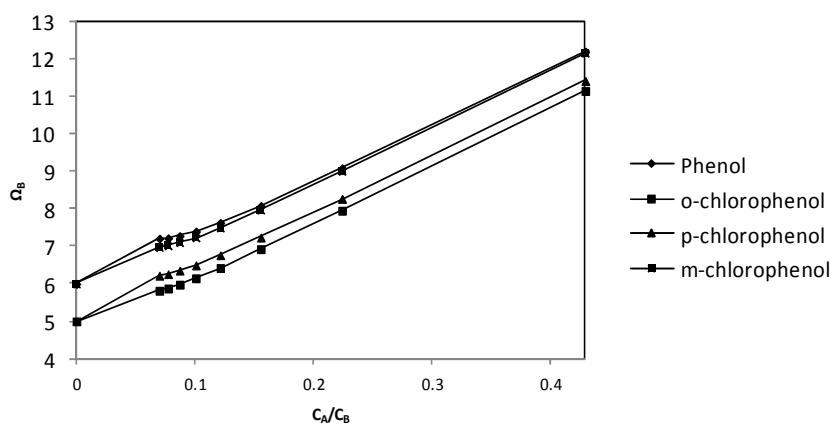


Fig.-1: Plots of C_A/C_B Vs Ω_B phenols with benzaldehyde in carbon tetrachloride systems.

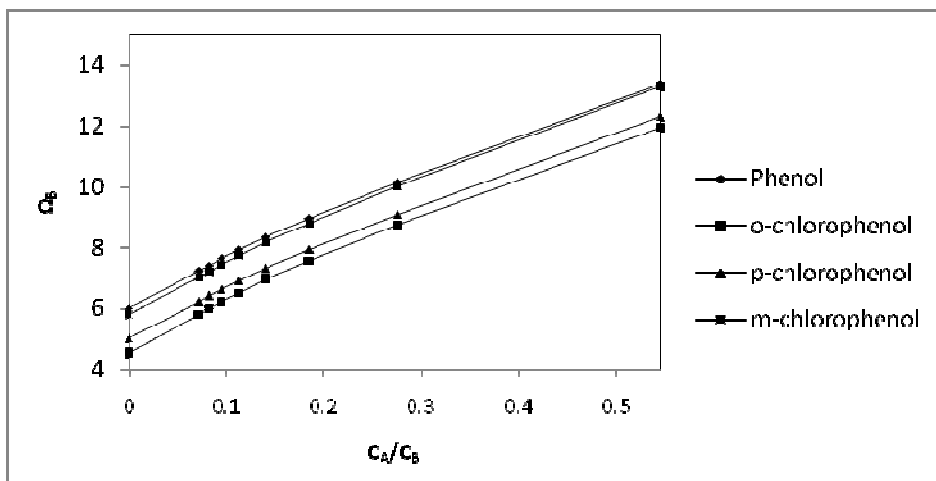


Fig.-2: Plots of C_A/C_B Vs Ω_B phenols with p-chlorobenzaldehyde in carbon tetrachloride systems.

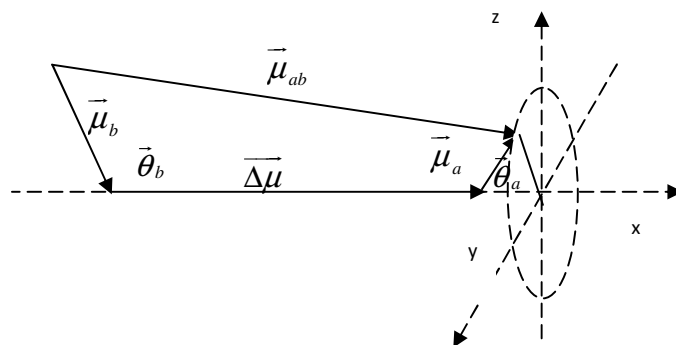


Fig.-3: Dipole moment μ_{ab} , μ_a and μ_b and $\Delta\mu$.

Table-2: Dipole moments of the components, 1:1 complexes and dipolar increments of the Hydroxyl - Carbonyl complexes.

S.No.	Solute	Solvent	μ_a	μ_b	μ_{ab}	$\Delta\mu$
1	phenol	benzaldehyde	1.7	2.45	2.47	-1.69
		p-chloro benzaldehyde	1.70	2.54	2.55	-1.69
2	o-chlorophenol	benzaldehyde	2.02	2.14	2.16	-2.00
		p-chloro benzaldehyde	2.02	2.24	2.26	-2.00
3	m-chlorophenol	benzaldehyde	2.10	2.25	2.27	-2.08
		p-chloro benzaldehyde	2.10	2.33	2.34	-2.09
4	p-chlorophenol	benzaldehyde	2.02	2.41	2.42	-2.01
		p-chloro benzaldehyde	2.02	2.49	2.50	-2.01

It was observed¹⁴⁻¹⁸ that if the charge transfer interactions carrying charge from the proton acceptor to the proton donor takes place, the redistribution will, reach the panther end of the molecules resulting in a very large variation in the dipole moment of the complex. From our results where $\Delta\mu < -2.08D$ 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 Balamuralikrishnan¹⁸⁻²⁰ for the mixtures of alcohol with aniline's. Similar results were reported by Abdel-Nour *et al.*¹⁴ The plot of (C_A/C_B) with Ω_B is straight lines which indicate the possibility for the formation of a 1:1 complex. 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.

CONCLUSIONS

Dipolar increment in all the systems is negative due to the polarization interactions only and it is not due to charge transfer and other phenomenon. The dipolar increment ($\Delta\mu$) values in the present investigations are $\Delta\mu < -2.08$. It is less than $2D$ for all the systems as indicated in the table-2, our results may be interpretive the charge transfer interaction and that higher order complexes may be AB_2 , A_2B , A_3B etc must prevail. Obviously the intra molecular hydrogen bond of phenol, *o*-chlorophenol, *m*-chlorophenol and *p*-chlorophenol are not broken by complexation of benzaldehyde and *p*-benzaldehyde. Dipole moment of benzaldehyde complex is less than the *p*-chlorobenzaldehyde, that indicates *p*-chlorobenzaldehyde is highly associative than benzaldehyde.

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