IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 9, Issue 4 Ver. III (Jul. – Aug. 2017), PP 42-47
www.iosrjournals.org

Dipole Moment Studies of H-Bonded Complexes of Anilines with Alcohol

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Abstract: *The dielectric was determined by using the mixtures of anilines and ethanols. The complexes of hydrogen bonding formed by the mixtures of 2-butoxy ethanol, 2-methoxy ethanol, ethanol with aniline, o-chloro aniline, p-chloro aniline at* 30^0 *C by Huysken's method. The dipolar increment of the systems are computed and the values of dipole moment confirms the hydrogen bonding of all the systems.*

Keywords: *H-Bonding, 2-butoxy ethanol, 2-methoxy ethanol, ethanol, Aniline, o-chloroaniline, p-chloroaniline, Dipole moment, Dipolar increment.*

Date of Submission: 10-07-2017 Date of acceptance: 05-08-2017

I. Introduction

Dielectric investigation of the solutes in an inert solvent can give the valuable information regarding structure, molecular complexes in solutions. Understanding the mutual interactions of amides with hydroxyl groups is important in relation to the conformational stability of proteins[1]. The dipole moment of the complex is a function of the relative strength of acid and base can be calculated. Alcohols are excellent proton donors[2]. In hydrogen bonded complexes, a redistribution of electron density can occur due to three types of interactions namely, electrostatic, polarization and charge – transfer interaction. The interaction due to electro static effects does not contribute significantly to the dipole moment of the complex, but the polarization effect results in a significant change in the dipole moment value due to appreciable charge distribution. In the event of charge transfer interaction, charge migration parallel to the H-bonded axis will yield a large change in the dipole moment. Thus, the experimental determination of dipole moment of the complexes serves as an indication of the nature of the interaction involved in the formation of the complexes. The most important characteristics of the hydrogen bond are the increase in the distance of OH accompanied by an enhancement of the bond moment $\Delta\mu$. The determination dipole moment will indicate the type of the complex since the dipolar increment is a function of the excess molar polarization Δp. The dipole moment of the complexes higher than the sum of the individual components corresponds to charge redistribution along the A-H…..B Bond. Several researchers[3-5] have studied the complexes of alcohols, phenols with ketones and amines in recent years using dielectric methods. In this paper, reporting the dipole moment of the 1:1 complexes of aniline, o-chloro aniline and p-chloro aniline with ethanol, 2-butoxy ethanol and 2-methoxy ethanol. In this work we have undertaken the investigation of complex formation involving aniline – ethanol in non-polar solvent based on Onsager's method[10].

II. Experimental Method

The dielectric measurements were taken by using static frequency 300kHz by Toshniwal RL09 type dipole meter using standard liquids the meter was calibrated. The refractive indices were measured at the same temperature using Abbe's refractometer. 10ml specific gravity bottle was used for determined densities and a SHIMADZU – ATY224 digital balance is used.

Considering the ternary mixture of polar components A(-OH group) and B($-NH_2$ group) in a non- polar solvent, the relative orientations of A and B vary continuously due to the mobility of the liquid phase. Huyskens et al.,[6,7] developed methods to obtain the overall dipole moment of a system of solute- solvent mixtures. The method well suited for ternary mixtures of two polar components A(donor)and B(acceptor) in an apolar solvent in liquid phase, where a great mobility is envisaged. Using the Onsager theory[10] , Assuming that the time interval is short enough to consider the orientation as fixed, the dipole moment of the solution may be written as

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

where N is the number of ij ensembles. Huyskens et al.,[7]showed that eqn. 1 can be written as

$$M^2 = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} N_{ij}\left[\frac{\mu_{ij}^2 - j<\mu_{oj}/j>}{i}\right] + n_B < \mu_{oj}^2 / j > N_B \qquad (2)$$

Where $<\mu_{oj}/j>$ 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 $<\mu_{oj}/j>$ is practically μ_b^2.

The quantity $\frac{\mu_{ij}^2 - \mu_{oj}/j>}{i}$ represents the mean share of the A molecule n^{th} square of the total dipole moment of the entities.

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

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

$$\frac{M^2}{VN_A} = (< \mu_{ab}^2 - \mu_b^2 > C_a + < \mu_b^2 > C_b) \qquad (5)$$

Where C_a and C_b are the formal concentration (mol dm^{-3}) of the proton donor and proton acceptor, respectively.

From the knowledge of dielectric constant ε_0, 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.9.

$$M^2 = \frac{9KT}{4\pi}\left[\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\varepsilon_0 (n_D^2+2)^2}\right] - \frac{C_S}{\bar{C}_S}\left[\frac{(\epsilon_S - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\varepsilon_S (n_{DS}^2+2)^2}\right] \qquad (6)$$

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

$$(< \mu_{ab}^2 - \mu_b^2 >)\frac{c_a}{c_b} + \mu_b^2\Omega_B = \frac{9KT}{4\pi C_b}\left[\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\varepsilon_0 (n_D^2+2)^2}\right] - \frac{C_S}{\bar{C}_S}\left[\frac{(\epsilon_S - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\varepsilon_S (n_{DS}^2+2)^2}\right] \qquad (7)$$

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.

Table 1: Values of Dielectric Constant, Refractive Index and Density of anliline, o-chloro aniline and p-chloro aniline with the formal concentration of ethanol

Ethanol +Aniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.8453	1.3724	1.622	1.97267	1.990045
0.1	3.4478	1.3823	1.624	7.11115	7.12905
0.2	2.7265	1.3823	1.690	10.38179	10.72939
0.3	2.8451	1.3823	1.702	21.7285	32.542273
0.4	2.9446	1.3822	1.61	37.7778	37.7883
0.5	2.7067	1.3823	1.680	42.98474	48.14875

Ethanol + o-chloroaniline in CCl_4 System

Mole Fraction of the Solute X2	Dielectric Constant of the Solution ε12	Refractive Index of the Solution n12	Density of the Solution d12	ΩB	μb2
0.05	2.4467	1.3723	1.649	1.19581	1.213170
0.1	2.8947	1.3723	1.658	4.88549	4.90279
0.2	2.7220	1.3724	1.691	10.71181	10.72939
0.3	2.5650	1.3724	1.677	16.33265	16.35025
0.4	2.6448	1.3724	1.667	28.6750	28.68544
0.5	2.5258	1.3724	1.669	35.4475	35.4578

Ethanol+ p-chloroaniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.4566	1.3724	1.644	1.21367	1.57421
0.1	2.5357	1.3723	1.616	3.25526	4.15875
0.2	2.5456	1.3723	1.664	8.60954	10.9680
0.3	2.4764	1.3723	1.584	14.3512	18.3276
0.4	2.6349	1.3723	1.611	28.3282	35.7997
0.5	2.6250	1.3724	1.613	41.0594	51.2271

Table 2: Values of Dielectric Constant, Refractive Index and Density of anliline, o-chloro aniline and p-chloro aniline with the formal concentration of 2-Butoxyethanol

2-Butoxyethanol +Aniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	1.4523	1.3938	1.6414	86.250	86.265
0.1	1.516	1.3934	1.6356	73.522	73.537
0.2	1.7076	1.3930	1.6256	6.3009	6.3009
0.3	1.9001	1.3926	1.6164	14.1287	14.1287
0.4	2.054	1.3822	1.6099	8.7835	8.735
0.5	2.407	1.3818	1.6005	5.7732	5.7886

2-ButoxyEthanol+ o-chloroaniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.1808	1.3739	1.6336	45.526	45.806
0.1	2.1914	1.3737	1.6293	20.050	20.069
0.2	2.2892	1.3724	1.6288	10.154	10.173
0.3	2.3387	1.3721	1.6214	6.1395	6.1587
0.4	2.3858	1.3715	1.5988	8.4579	8.477
0.5	2.4372	1.3710	1.5962	3.2321	3.055

2-ButoxyEthanol+ p-chloroaniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.1623	1.3730	1.6380	43.1827	43.2039
0.1	2.191	1.3728	1.6369	20.204	20.225
0.2	2.3190	1.3725	1.6367	10.850	10.871
0.3	2.3209	1.3721	1.6318	5.9098	5.9313
0.4	2.3877	1.3712	1.6314	4.2856	4.307
0.5	2.4867	1.3701	1.6296	3.519	3.540

Table 3: Values of Dielectric Constant, Refractive Index and Density of anliline, o-chloro aniline and p-chloro aniline with the formal concentration of 2-Methoxyethanol

2-Methoxyethanol+Aniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.0453	1.489	1.6390	17.4628	17.477
0.1	2.1041	1.4791	1.6379	5.0332	5.048
0.2	2.1103	1.4770	1.6377	1.6405	1.655
0.3	2.223	1.4750	1.6372	0.5724	0.5874
0.4	2.2404	1.4730	1.6368	0.5192	0.5337
0.5	2.260	1.4710	1.6319	0.5195	0.5195

2-MethoxyEthanol+ o-chloroaniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.0472	1.4044	1.6408	11.518	11.518
0.1	2.1816	1.4042	1.6350	11.133	11.1452
0.2	2.2209	1.3940	1.6339	6.8657	6.8778
0.3	2.2397	1.3938	1.6329	3.9643	3.9764
0.4	2.3582	1.3936	1.6323	3.4717	3.4839
0.5	2.3780	1.3932	1.6303	2.4969	2.5096

2-MethoxyEthanol+ p-chloroaniline in CCl_4 System

Mole Fraction of the Solute X_2	Dielectric Constant of the Solution ε_{12}	Refractive Index of the Solution n_{12}	Density of the Solution d_{12}	Ω_B	μ_b^2
0.05	2.1163	1.4041	1.6408	22 .0359	22.0496
0.1	2.2317	1.3938	1.6350	18.572	18.5858
0.2	2.2602	1.3936	1.6329	7.8267	7.8403
0.3	2.3170	1.3932	1.6323	4.97234	4.9859
0.4	2.3877	1.3828	1.6329	3.9758	3.9894
0.5	2.4165	1.3823	1.6249	2.9092	2.9228

Table 4 : Dipole Moments of the Components and their 1: 1 Complexes and Dipolar Increments of the Complexes Ethanol+ Anilines

Systems	μ_a(D)	μ_b(D)	μ_{ab}(D)	$\Delta\mu$(D)
Ethanol+ Aniline+ CCl_4	1.5	3.2	8.17	9.92
Ethanol+ o-chloro aniline + CCl_4	1.8	2.6	7.9	6.24
Ethanol+ p-chloro aniline + CCl_4	3.1	2	7.07	6.18

Table 5 : Dipole Moments of the Components and their 1: 1 Complexes and Dipolar Increments of the Complexes 2-Butoxyethanol+ Anilines

Systems	μ_a(D)	μ_b(D)	μ_{ab}(D)	$\Delta\mu$(D)
2-Butoxyethanol + Aniline+ CCl_4	1.5	1.73	7.33	7.55
2-Butoxyethanol + o-chloro aniline + CCl_4	1.8	2	6.46	6.74
2-Butoxyethanol + p-chloro aniline + CCl_4	3.1	1.22	7.07	7.35

Table 6: Dipole Moments of the Components and their 1: 1 Complexes and Dipolar Increments of the Complexes 2-Methoxyethanol+ Anilines

Systems	μ_a(D)	μ_b(D)	μ_{ab}(D)	$\Delta\mu$(D)
2-Methoxyethanol + Aniline+ CCl_4	1.5	0.707	4.5	4.1
2-Methoxyethanol + o-chloro aniline + CCl_4	1.8	1.4	3.9	3.6
2-Methoxyethanol + p-chloro aniline + CCl_4	3.1	1.1	5.5	4.7

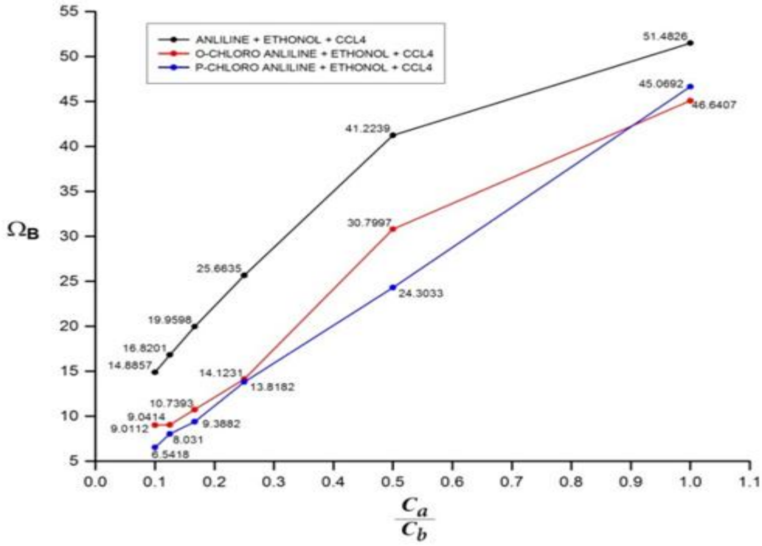

Fig.1 The formation of a 1: 1 complex aniline, o-chloro aniline and p-chloro aniline with the formal concentration (C_a/C_b) of ethanol with Ω_B.

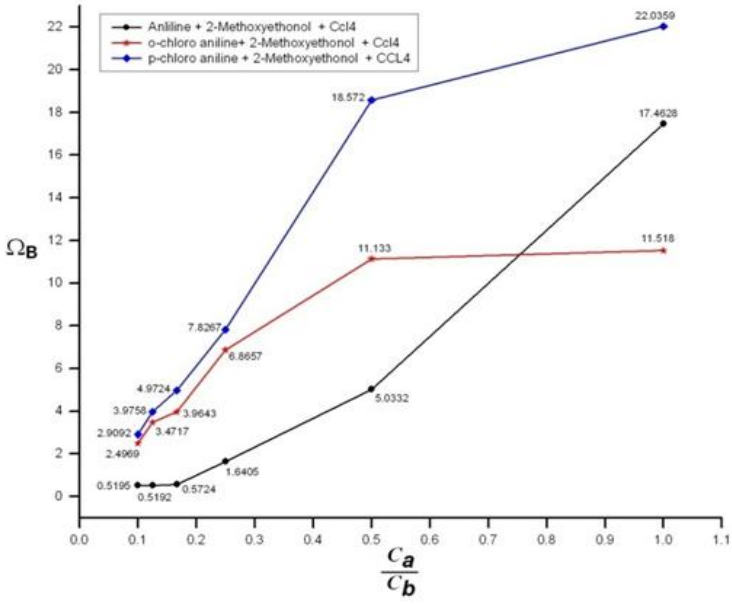

Fig.2 The formation of a 1: 1 complex aniline, o-chloro aniline and p-chloro aniline with the formal concentration (C_a/C_b) of 2- methoxyethanol with Ω_B.

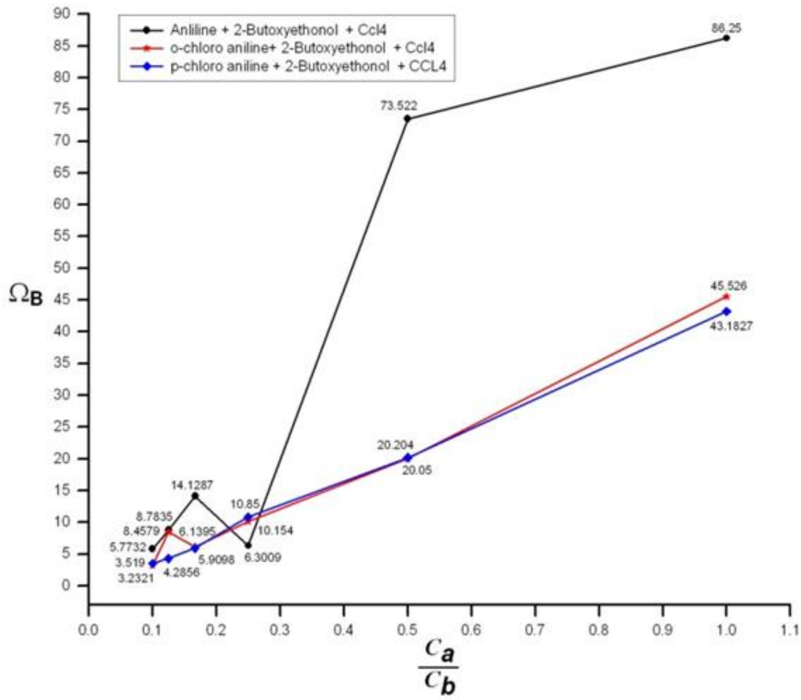

Fig.3 The formation of a 1: 1 complex aniline, o-chloro aniline and p-chloro aniline with the formal concentration (C_a/C_b) of 2- butoxyethanol with Ω_B.

III. Results And Discussion

Priscilla[12],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 values of dielectric constant, refractive indices and density measured with varying concentration of the proton donor C_b are recorded in Table 1 and Table 3.The dipolar increment determined from relation (8) when a proton donor of dipole moment μ_a forms a 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 $\theta_a$and θ_b . If the values of θ_a and θ_b differs from zero.Similar results were reported by Malathi et al.[9,15] The plot of (C_a/C_b) with Ω_B is straight line which indicate the possibility for the formation of a 1: 1 complex (Fig 2). The values reported by Balamuralikrishnan[1] for the mixtures of alcohol with aniline's. The plot of (C_a/ C_b) with Ω_B is straight line which indicates the possibility for the formation of a 1:1 complex. The values are small, sometimes even negative. This explains the absence of charge transfer effects. If charge transfer effect had been there, $\Delta\mu$ would have been greater[13] than 10D. Since $\Delta\mu$ is less than 10 D, it may be concluded that the complexion may be only due to redistribution of electrons due to polarization effects. The dipole moments for the system ethanol in anliline > o-chloro aniline > p-chloro aniline in the order of 9.92D > 6.24 D > 6.18D > the dipole moments for the system 2-methoxyethanol in p-chloro aniline > aniline > o-chloro aniline in the order of 4.7D > 4.1D >3.6D > and the dipole moments for the system 2-butoxy ethanol in aniline > p-chloro aniline > o-chloro aniline in the order of 7.55D >7.35 D > 6.74D > which again supports the above conclusion. It is inferred from Table 4 to Table 6. Similar conclusions were drawn for the mixture of alcohol with substituted piper dines. Similar results were also reported by Thenappan and Sabesan[14,] for alcohol mixtures. Hence it is concluded that the dipolar increment in all the systems is small due to the Polarization effect only and due to charge transfer phenomenon.

IV. Conclusion

- The dipole moments for the system ethanol in anliline > o-chloro aniline > p-chloro aniline in the order of 9.92D > 6.24 D > 6.18D > the dipole moments for the system 2-methoxyethanol in p-chloro aniline > aniline > o-chloro aniline in the order of 4.7D > 4.1D >3.6D > and the dipole moments for the system 2-butoxy ethanol in aniline > p-chloro aniline > o-chloro aniline in the order of 7.55D >7.35 D > 6.74D > which supports the 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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IOSR Journal of Applied Physics (IOSR-JAP) is UGC approved Journal with Sl. No. 5010, Journal no. 49054.

R.Priscilla. "Dipole Moment Studies of H-Bonded Complexes of Anilines with Alcohol." IOSR Journal of Business and Management (IOSR-JBM) 9.4 (2017): 42-47.