Dielectric Studies of H-Bonded Complexes of Anilines with Alcohol

R. Priscilla[1], S. Balamuralikrishnan[2]

[1]Department of Physics, A.D.M. College for Women (Autonomous), Nagapattinam-611001, Tamil Nadu, India
[2]Department of Physics, Annamalai University, Chidambaram, Tamil Nadu, India

Abstract: *The Hydrogen-bonded complexes formed by aniline, o-chloro aniline, p-chloro aniline with ethanol at 303K have been determined by using Huysken's method based on the Onsager theory. The excess dipole moments of the complexes were obtained from bond angle data available from molecular orbital theory. The enhancement of the dipole moment values confirms the hydrogen bonding between all the anilines.*

Keywords: H-Bonding, Anilines, Ethanol, Dipole moment, Dipolar increment.

1. Introduction

The dipole moment μ_ABof the complex formed between the proton donor group A-H and acceptor group B. Dielectric investigation of the solutes in an inert solvent can give the valuable information regarding structure, molecular complexes in solutions[1-4]. 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.,[5,6] has developed the methods to determine the stereo chemistries 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. Alcohols are excellent proton donors. 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 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 ethanol. We have undertaken the investigation of complex formation involving aniline – ethanol in non-polar solvent based on Onsager's method[9].

2. Experimental

The dielectric measurements were measured at static frequency 300KHZ by Toshniwal RL09 type dipole meter. The dipole meter was calibrated using standard liquids. The cell temperature was maintained at 303K by circulating water through the glass jacket of the cell. The refractive indices were measured at the same temperature using Abbe's refractometer. Densities were determined using 10ml specific gravity bottle and a SHIMADZU – ATY224 digital balance. Chemicals are purified by standard procedure. The Physical parameters of all the chemicals were checked against their literature values.

2.1 Theory

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. Assuming that the time interval is short enough to consider the orientation as fixed, the dipole moment of the solution may be written as

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

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

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

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 practicallyμ_b^2.

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

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

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

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

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

International Journal of Scientific Engineering and Research (IJSER)
www.ijser.in
ISSN (Online): 2347-3878, Impact Factor (2014): 3.05

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.

$$M^2 = \frac{9KT}{4\pi}\left[\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\epsilon_0\,(n_D^2+2)^2}\right] - \frac{C_s}{\overline{C}_s}\left[\frac{(\epsilon_S - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\epsilon_S\,(n_{DS}^2+2)^2}\right] \quad (6)$$

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

$$(<\mu_{ab}^2 - \mu_b^2>)\frac{c_a}{c_b} + \mu_b^2\Omega_B = \frac{9KT}{4\pi C_b}\left[\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\epsilon_0\,(n_D^2+2)^2}\right] - \frac{C_s}{\overline{C}_s}\left[\frac{(\epsilon_S - n_{DS}^2)(2\epsilon_S + n_{DS}^2)}{\epsilon_S\,(n_{DS}^2+2)^2}\right] \quad (7)$$

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.

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

anliline + ethanol + ccl₄			
C_b(mol/L)	ε_0	n_D	d(g/cm3)	Ω_B
0.05	2.190	1.3835	1.702	51.4826
0.1	2.3645	1.3830	1.690	41.2239
0.2	2.482	1.3827	1.680	25.6635
0.3	2.583	1.3823	1.624	19.9598
0.4	2.645	1.3775	1.622	16.8201
0.5	2.722	1.3724	1.61	14.8857

o-chloro aniline+ ethanol + ccl₄				
C_b(mol/L)	ε_0	n_D	d(g/cm3)	Ω_B
0.05	2.4467	1.3743	1.691	45.0692
0.1	2.5259	1.3740	1.677	30.7997
0.2	2.565	1.3735	1.669	14.1231
0.3	2.6449	1.3730	1.664	10.7393
0.4	2.722	1.3724	1.658	9.0414
0.5	2.8949	1.3721	1.649	9.0112

p-chloro aniline + ethanol + ccl₄				
C_b(mol/L)	ε_0	n_D	D (g/cm3)	Ω_B
0.05	2.4567	1.3727	1.644	46.6407
0.1	2.4765	1.3720	1.636	24.3033
0.2	2.5357	1.3690	1.616	13.8182
0.3	2.5456	1.3687	1.613	9.3882
0.4	2.6250	1.3683	1.611	8.0310
0.5	2.6349	1.3678	1.584	6.5418

Using least square fitting method C_a/C_b is plotted against Ω_B. From the slope and intercept of the plot (Fig. 1) values of μab and μ_b were calculated.
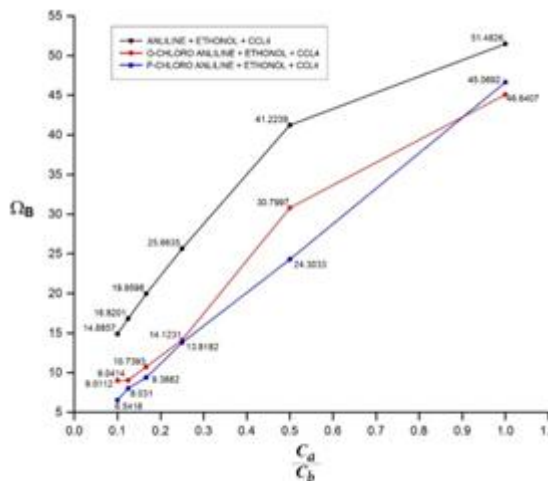
Graph

Figure 1: Dipole moments μ_{ab}, μ_a and μ_b of the complex and of the partners-dipole increment Δμ

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 μb with respect of A-H---B axis can be defined as θ_a and θb. 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. 1).

The mean value of $<\cos\varphi>$ was found to be zero for O-H---N which means that all rotamers around the axis of the bond are equally possible[10]

The dipolar increment is given by

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

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. The Values of θ_a and θ_b taken from the literature.

Table 2: Dipole Moments of the Components and their 1: 1 Complexes and Dipolar Increments of the Complexes

Systems	μ_a(D)	μ_b(D)	μ_{ab}(D)	Δμ(D)
Ethanol+ Aniline+ CCl₄	1.5	3.2	8.17	9.92
Ethanol+ o-chloro aniline + CCl₄	1.8	2.6	7.9	6.24
Ethanol+ p-chloro aniline + CCl₄	3.1	2	7.07	6.18

3. Results and Discussion

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. The formal concentration of the proton donor C_a is kept constant, $C_a \gg C_b$ the values of μ_b and μ_{ab} are obtained fig.1. 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 θ_a and θ_b. If the values of θ_a and θ_b differs from zero.

Similar results were reported by Malathiet al.[8] 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). Hence it may be concluded that only polarization interaction is the other important contribution 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 value reported byte excess dipole moments for all the systems studied are found to be small, which is in agreement with the values reported by Balamurali krishnan1 for the mixtures of alcohol with aniline's. Similar results were reported by Abdel-Nour, et al [3]. The plot of (C_a/ C_b) with M^2 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 [2,13] than 10D. Since $\Delta\mu$ is less than 10 D, it may be concluded that the complexation may be only due to redistribution of electrons due to polarization effects. The dipole moments for all systems are anliline> o-chloro aniline > p-chloro aniline in the order of 9.92D > 6.24 D > 6.18D > which again supports the above conclusion. On the basis of eqn.1 it is possible to calculate the above dipole moment values. It is inferred from Table 2 that the dipole moment for the halogen substituted acceptor complexes are greater than for the mono substituted acceptor complexes .But the case is reversed in halogen substitution of donor complexes. Similar conclusions were drawn7 for the mixture of alcohol with substituted piper dines. Similar results were also reported by Thenappan5 and Sabesan [14,15] 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.

4. 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.

References

[1] S. Balamuralikrishnan and A.U. Maheswari, J. Mol. Liq.,12, 419 (2006)

[2] Bauge& Smith, J ChemSoc,(1964) 4244

[3] K.N.A. El- Nour and S.LA. El-Messieh, J. Mol. Liq., 79, 235 (1999)

[4] P.H. Gore, P.A. Hopkins, R.J.W. Le Fevere, L. Radom and G.L.D. Ritehre, J. Chem. Soc. B, 12, 120 (1971)

[5] P.L. Huyskens and H.M. Vanbrabant-Govaerts, J. Mol. Struct., 84, 141 (1982)

[6] Huyskens P L, Siegel G C, Herrera F & Cappele Ph, J MolLiq, 44 (1990) 175

[7] R.S. Kumar, R. Sabesan and S. Krishnan, J. Mol. Liq., 95, 41 (2002)

[8] M. Malathi, R. Sabesan and S. Krishnan, J. Mol. Liq., 109, 11 (2004)

[9] OnsagarL, J. Am. Chem., 58, 1486 (1936)

[10] Sabesan R, Varadharajan R & Sargurumoorthy M, Indian J Pure & Appl Phys, 55B (1981) 353

[11] G.G. Siegel, F.Herrera, Ph. Cappelle and P.l. Huyskens, J. Mol. Liq., 44, 175 (1990)

[12] A. Singh, R. Misra, J.P. Shukla and M.C. Sexana, Indian J. pure Appl. Pys., 21, 228 (1983)

[13] Sobhanadri J, Satheesh V &Jeyaraj M, J Mol. Liq.64 (1995) 247

[14] M. Subnramanianand T. Thennappan, Indian J. Pure Appl. Phys., 39 417 (2001)

[15] T. Thenappanand M. Subramanian, Mater. Sci. Eng., 86B, 7 (2001)