

Dielectric characterization studies of lower order alcohols with n-propyl amine

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ABSTRACT

The dipole moment of the 1:1 complexes of lower order alcohols with n-propyl amine at 301K have been determined by using Huysken's method based on the Onsager theory. The dipolar increments of the systems were computed from the bond angle data available from molecular orbital theory. The enhancement of the dipole moment confirms the hydrogen bonding between all the systems.

Key words: H-bonding, dipole moment, Huyskens, Onsager theory, Dipolar increment

INTRODUCTION

Dielectric characteristics of the alcohol - amine complexes can give the expensive information concerning structure of liquids, complex formations etc., The complexes leads to an increases the polarity of the alcohol - amine complexes and hence to increase the dipole moment of the complex. The dipole moment of the hydrogen bonded complexes from the proton donor - acceptor in an inert solvent investigated by the mixed solvent techniques [1-5]. The changes in the dipole moment of acid - base arises due to the bond formation. From the determination of dipole moment of the complex indicates the type of the complexes like donor-acceptor, charge transfer, and polarization [6-11]. The dipole moment of complexes is higher than the sum of the dipole moments of the alcohol and amine components. It corresponds to leads to charge reorientation along the OH...N bond. The present work identified the nature of the alcohols - amine complexes by the dielectric measurements.

MATERIALS AND METHODS

In the present investigation the following samples of AR grade methanol, ethanol, butanol, pentanol, propyl amine were used. The samples were purified and dried before use. Solutions of these materials were prepared by accurately weighing amounts of solute in 10cm³ volumetric flasks. AR grade carbon tetrachloride was used as solvent for the dielectric measurements of ternary liquid mixtures. The dielectric constants were measured from capacity measurement using dipole meter RL09 supplied by Toshniwal, India operated at 220 V and working with an heterodyne principle with an oscilloscope null indication. It has a measuring frequency 300 KHz. The samples were placed in a cell containing a co-axial brass cylinder and the cell was immersed in water by means of precision thermostat with an accuracy of $\pm 0.1^\circ\text{C}$ supplied by Concord Instruments Pvt. Ltd., Chennai. The scale of the dipole meter is calibrated using the standard liquids. The refractive indices of the solutions under investigations were determined using Abbe's refractometer. Densities were measured using 5 ml specific gravity bottle. The temperatures for the measurements were maintained at 301K by thermostatically with an accuracy $\pm 1^\circ\text{C}$.

DIPOLE MOMENT OF 1:1 COMPLEX BY HUYSKENS METHOD

Considering the ternary mixture of polar components A (-OH group) and B (-NH₂ group) in a non-polar solvent, the relative orientations of A and B be different incessantly due to the mobility of the liquid phase. Assuming that the

time interval is small sufficient to consider the orientation is unchanging, the dipole moment of the solution may be written as

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

Where N_{ij} is the number of ij ensembles. Huyskens et al [11] showed that the Eq. (1) can be written as

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

Here $\langle \mu_{0j}^2 / j \rangle$ is the mean square of the B molecule in the square of the total dipole moment of the components. For

propyl amine as proton donor B, j is taken as 1 and $\langle \mu_{0j}^2 / j \rangle$ is practically μ_b^2 and $\frac{\langle \mu_{ij}^2 - \mu_{0j}^2 / j \rangle}{i}$

The quantity represents the mean square of the A molecule in the square of the total dipole moment of the components.

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

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

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

Here 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 Ω^2 from Frohlich [7] Equation.

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

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

$$\langle \mu_{ab}^2 - \mu_b^2 \rangle \frac{C_A}{C_B} + \mu_b^2 \Omega = \left[\frac{9KT}{4\pi N_A} \right] \left[\frac{1}{C_B} \right] \left(\frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{\epsilon_0(n_D^2 + 2)^2} \right) - \frac{C_s}{C_s} \left(\frac{(\epsilon_s - n_{DS}^2)(2\epsilon_s + n_{DS}^2)}{\epsilon_s(n_{DS}^2 + 2)^2} \right) \quad (7)$$

The experimental values of density, refractive index, dielectric constant and experimental quantity (Ω_B) for different concentrations of the systems were measured given in table 1. Using least square fitting method, C_A/C_B is plotted against Ω . From the slope and intercept (figure 1- 4) gives values of μ_{ab} and μ_b are obtained.

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. 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 proton donor C_a formal concentration is

kept constant, $C_b \gg C_a$. The values of μ_b and μ_{ab} were obtained from figure 1 to figure 4. 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 . The values of θ_a and θ_b are non 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 . (Figure 2)

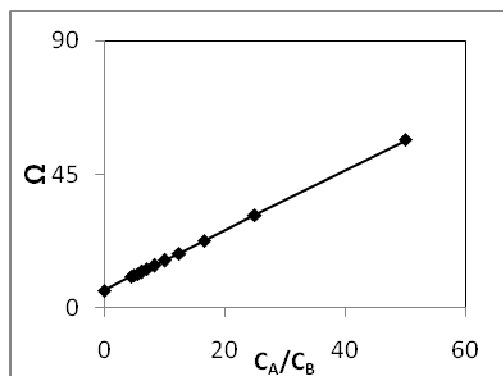
The mean value of $\langle \cos \Phi \rangle$ was found to be zero for O-H...N which means that all rotamers around the axis of the bond are equally possible

$$\Delta\mu = \mu_{ab} - (\mu_a + \mu_b) \quad (8)$$

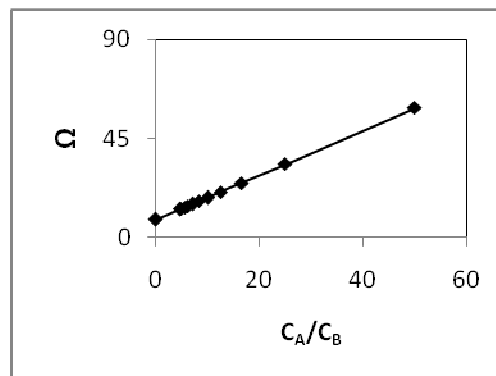
Equation (8) is used to calculate the dipolar increment $\Delta\mu$. These calculated values are given in table 2 for the four systems. It was observed that if the charge transfer interactions carrying charge from the proton acceptor to the proton donor takes place, the redistribution will, reach the panther end of the molecules resulting in a very large variation in the dipole moment of the complex.

Table-1 Values of dielectric constant, refractive index, density and experimental quantity of propyl amine with the formal concentration of alcohols

Methanol					Ethanol				
C_B (mole/lit)	ϵ_0	n_D	d gm/cm ³	Ω	C_B (mole/lit)	ϵ_0	n_D	d gm/cm ³	Ω
0.01	2.765	1.417	1.095	56.6	0.01	2.818	1.423	1.088	58.9
0.02	2.807	1.409	1.094	31.2	0.02	2.914	1.422	1.081	33.3
0.03	2.849	1.402	1.092	22.6	0.03	3.012	1.421	1.073	24.8
0.04	2.891	1.395	1.091	18.4	0.04	3.113	1.42	1.065	20.6
0.05	2.934	1.387	1.09	15.9	0.05	3.216	1.419	1.058	18
0.06	2.978	1.38	1.089	14.2	0.06	3.321	1.418	1.05	16.4
0.07	3.022	1.373	1.088	13	0.07	3.429	1.417	1.043	15.2
0.08	3.066	1.366	1.086	12.1	0.08	3.539	1.416	1.035	14.3
0.09	3.111	1.358	1.085	11.5	0.09	3.651	1.415	1.028	13.7
0.10	3.156	1.351	1.084	10.9	0.10	3.765	1.414	1.021	13.2
0.11	3.202	1.344	1.083	10.5	0.11	3.882	1.413	1.013	12.8
Propanol					Butanol				
0.01	2.807	1.423	1.088	58.1	0.01	2.8	1.423	1.089	57.5
0.02	2.892	1.422	1.081	32.5	0.02	2.879	1.423	1.081	31.8
0.03	2.979	1.422	1.074	23.8	0.03	2.959	1.422	1.074	23.3
0.04	3.068	1.421	1.066	19.6	0.04	3.041	1.422	1.066	19.1
0.05	3.158	1.42	1.059	17.1	0.05	3.124	1.421	1.059	16.5
0.06	3.251	1.419	1.051	15.5	0.06	3.208	1.42	1.052	14.9
0.07	3.345	1.419	1.044	14.2	0.07	3.294	1.42	1.045	13.7
0.08	3.441	1.418	1.037	13.4	0.08	3.382	1.419	1.037	12.8
0.09	3.538	1.417	1.029	12.7	0.09	3.471	1.418	1.03	12.1
0.10	3.638	1.416	1.022	12.2	0.10	3.562	1.418	1.023	11.6
0.11	3.739	1.416	1.015	11.7	0.11	3.654	1.417	1.016	11.2



(a) Methanol



(b) Ethanol

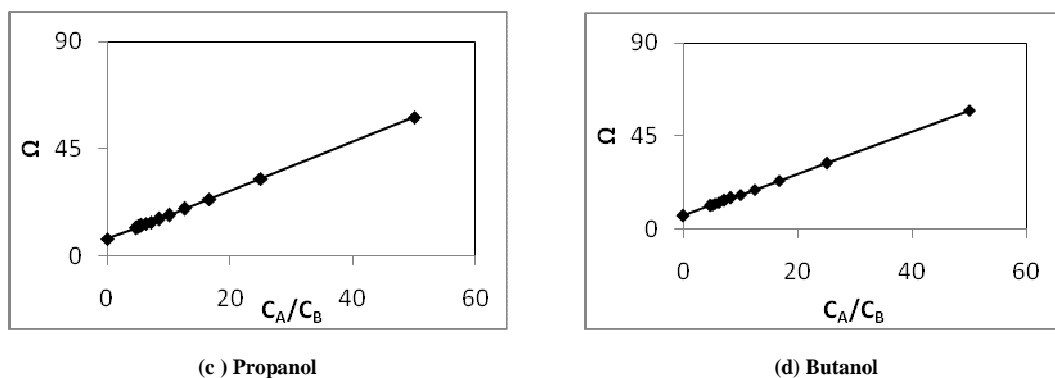


Figure 1 – Plots of C_A/C_B Vs Ω_B of alcohols with propyl amine complexes

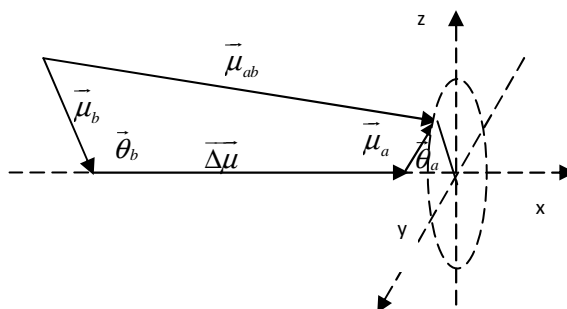


Figure 2 Dipole moment μ_a , μ_b and μ_{ab} and $\Delta\mu$

From the computed values of μ_{ab} and μ_b , the dipolar increments were obtained. This investigation reveals that the dipole moment is less than 0.40D for all the systems. It is clear that there was no contribution arising due to ionic structures, as would involve a very high value for $\Delta\mu$ ($>10D$). It was shown that about partial interaction moment observed experimentally arises due to the electronic interaction. Hence it may be concluded that only polarization interaction was one of the important contributing factors to the enhancement of dipole moment of the complexes studied here. The excess dipole moments for all the systems studied here are found to be small. 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. Hence it was concluded that the dipolar increment in all the systems was small due to the polarization interactions only but not due to the interactions.

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

Systems	μ_b (D)	μ_{ab} (D)	$-\Delta\mu$ (D)
Propyl amine (1.31 D) +			
Methanol	1.69	2.60	0.40
Ethanol	1.68	2.99	0.26
Propanol	1.67	2.82	0.16
Butanol	1.66	2.72	0.25

CONCLUSION

The dipolar increment values in the present investigations were small ($\Delta\mu < 0.40$). It is less than 2D for all the systems as indicated in the table 2. The results may be interpretive the charge transfer interaction and that higher order complexes may be AB, AB₂, A₂B, A₃B etc have got to succeed. Our results clearly indicate that intra molecular hydrogen bonds of alcohols are not broken by complexation of propyl amine. The dipole moment values of the complex and dipolar increment of the donor (alcohols) and acceptor (propyl amine) were obtained. These values indicate that an interaction occurs owing to the polarization interactions only and it is not due to charge transfer and other phenomenon. Dipole moment of propyl amine complex is increase in the order of methanol > ethanol > propanol > butanol.

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