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Dielectric Studies of H-Bonded Complexes of P-Bromoacetophenone with Alcohols

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Abstract: Dielectric constants of the binary mixtures of P-bromoacetophenone with alcohol such as in (1-Propanol, 1-Butanol, 1-Pentanol) in carbon tetra chloride were measured at 303 K. Make use of these measurements to calculate the dipole moment for Huysken's model based on Onsager's theory. Dipolar increment has been calculated for all the studied systems from the bond angle available from molecular orbital studies. The results have been used to interpret the molecular interaction.

Keywords: Dielectric Parameters, H-bonding, P-bromoacetophenone, Huysken's method, Dipolar increment.

I. INTRODUCTION

Aromatic ketones and their derivatives have great analytical and pharmaceutical applications. The dielectric studies about binary polar liquid mixtures provide valuable information regarding intermolecular interactions and the consequent structural rearrangement of molecules in solution. The homogeneous and heterogeneous interactions in binary mixtures using dielectric measurements have been studied and reported by several researchers. [1-2]. Alcohols have been the subject of extensive practical and theoretical investigations in the study of intermolecular hydrogen bonding [3]. Due to the presence –OH group in the molecule, these compounds can be strongly influenced by the intermolecular hydrogen bond formation. The present investigation is chosen to study the effect of ketone molecule when mixed with various alcohols that may influence dielectric parameters. The alcohols (1-Propanol, 1-Butanol, 1-Pentanol) of their binary mixtures with p-bromoacetophenone, as common component, were calculated at 303K. From these information, various derived parameters such as density, refractive index, dielectric constant were computed. The variations in these parameters with composition of the binary mixtures reveal extent of intermolecular interactions between the component molecules. In view of the significance mentioned, an effort have been made to explain the molecular interactions in the mixtures of various alcohols with P-bromoacetophenone respectively and to study the nature of complexes formed. Several researchers [4-9] have studied the complexes of alcohols and phenols with aldehydes, ketones, esters in recent years using dielectric methods. The present work is concerned with the determination of the hydrogen bonding between substituted ketone with alcohols using dielectric methods which may provide useful information about the formation of complex in the mixture.

II. MATERIALS AND METHOD

A. Measurement of density

The density of the pure liquid and liquids mixture were determined using a specific gravity bottle volume of 5 ml was calibrated with freshly prepared double distilled water. A digital electronic balance were used to measured density. For all the measurement, temperature were controlled by circulating water through an ultra-thermostat with an accuracy $\pm 0.15K$.

B. Measurement of refractive index

Refractive index of the pure and binary liquid mixture was measured by Abbe's refractometer. From the measured values of the refractive index of the dielectric constant at infinite dilution or dielectric constant at article frequency have been measured ($\epsilon_\infty = n_D^2$)

C. Measurement of Dielectric constant (ϵ_0)

Dipole meter is an instrument that is uses to measure the dielectric constant of liquids. In the equipment a particular circuit has been developed for audio oscillator that produce stabilized wave. In this experiment dielectric cell is standardized using reference liquid having known dielectric constant by immersing the dielectric cell assembly in to reference liquid then experimental liquid whose dielectric constant has to be determine. Is immersed into liquid resulting in change in frequency. From the resulting shift capacitance of cell in unknown of liquid is calculated(c) Dielectric constant of unknown liquid is calculated using the relation

$$\epsilon_0 = 1 + \frac{(c_0 - c_x)}{(c_0 - c_r)} (\epsilon_r - 1)$$

Where c_0 = capacitance of air, c_r = capacitance of standard liquids, c_x = capacitance of test liquids

ϵ_r = dielectric constant of standard liquid

III. THEORY

Huysken's [10] had developed a method to obtain the overall dipole moment of a system of solute-solvent mixture. The method is well suited for ternary mixtures of two polar components A(donor) and B(acceptor) in an apolar solvent in the liquid phase. Using Onsager theory [11] the overall dipole moment [M] of a solution containing polar substances and an apolar solvent (subscript-s) is given by

$$D = \left[\frac{9KT \times 10^{39}}{4\pi N_a} \right] X \left[\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} \right] - \frac{C_s}{C_s^0} \left[\frac{(\epsilon_s - n_s^2)(2\epsilon_s + n_s^2)}{\epsilon_s(n_s^2 + 2)^2} \right] \quad \text{----- (1)}$$

where

ϵ_0 – relative permittivity of the solution

n_D – refractive index of the solution

ϵ_s – relative permittivity of the solvent

n_s - refractive index of the solvent

If the concentration of proton acceptor is much greater than the concentration of proton donor for the complex in the solution, such that

$$C_B - C_A \gg K^{-1} \quad \text{----- (2)}$$

Where K is the equilibrium constant of 1:1 complexation and if the non – interacting Solvent has zero dipolar moment then eqn (2) reduces to

$$\Omega_b = \mu_b^2 + (\mu_{ab}^2 - \mu_b^2) \frac{C_A}{C_B} . \quad \text{----- (3)}$$

Where,

μ_b – dipole moment of proton acceptor

μ_{ab} – dipole moment of 1:1 complex

One can obtain the dipole moment of the acceptor from the intercept of the plot Ω_B

Versus (C_A/C_B) and μ_{ab}^2 can be determined from the slope. In general it can be taken that if higher order complexes like AB_2 , A_2B etc. are present then the plot is no longer a straight line and curved upwards. This serves as a criterion for choosing the proper concentration C_A and C_B of the proton donor and proton acceptor for 1:1 complexation.

When a proton donor of dipole moment μ_a forms hydrogen 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 by angles θ_a and θ_b respectively, If θ_a and θ_b differ from zero, one can

define azimuthal angle ϕ which describes the rotation position of μ_b around the hydrogen bond with respect to the plane formed by this bond and μ_a . The formation of H-bond is accompanied by the dipole moment of the molecules involved in H-bonding and the displacement of electron. As a consequence the dipole vector of the complex is different from the vector sum may be given by the expression

$$\Delta\mu = (\mu_{ab}^2 - \mu_a^2 \sin^2 \theta_a - \mu_b^2 \sin^2 \theta_b - 2\mu_a \mu_b \sin \theta_a \sin \theta_b \cos \phi)^{1/2} - \mu_a \cos \theta_a - \mu_b \cos \theta_b \quad \text{---- (4)}$$

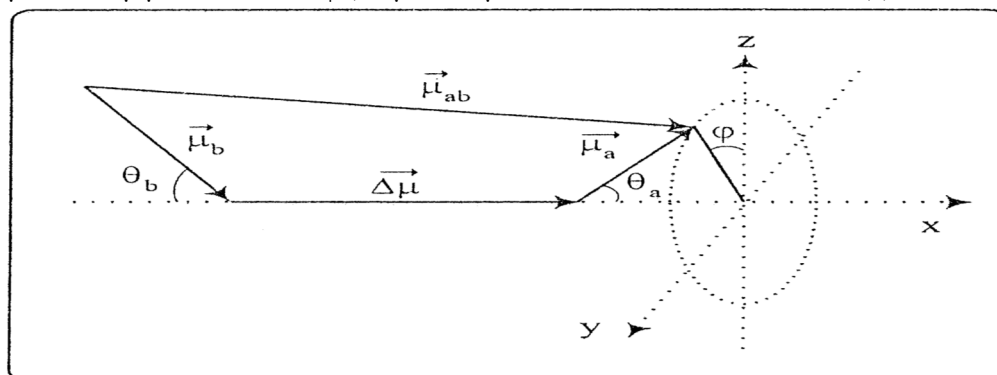


Fig. 1. Dipole moments μ_{ab} , μ_a and μ_b of the complex and of the partners, dipole increment $\Delta\mu$.

Tables: 1 variation of dielectric constant, refractive index, density and Ω_B with the formal concentration of different alcohols.

1-Propanol+P-bromoacetophenone+CCl₄

Concentration of base (C _B) Mol/lit	Dielectric constant (ε)	Density of solution (ρ) Kg/m ³	Refractive index of solution (n)	C _A /C _B	$\Omega_B \times 10^{39}$
0.06	2.7927	1.353	1.4994	8.3	132.0
0.08	2.8001	1.352	1.4772	6.3	100.2
0.1	2.853	1.351	1.4574	5.0	84.8
0.15	2.8679	1.35	1.4552	3.3	57.6
0.2	2.8887	1.35	1.4474	2.5	44.0
0.25	2.9305	1.349	1.4458	2.0	36.7
0.3	3.0243	1.348	1.4258	1.7	33.3
0.4	3.066	1.347	1.41582	1.3	25.9
0.45	3.1546	1.346	1.4134	1.1	24.7
0.5	3.2466	1.345	1.3974	1.0	23.7
0.55	3.1906	1.348	1.3872	0.9	20.6

1-Butanol+P-bromoacetophenone+CCl₄

Concentration of base (C _B) Mol/lit	Dielectric constant (ε)	Density of solution (ρ) Kg/m ³	Refractive index of solution (n)	C _A /C _B	$\Omega_B \times 10^{39}$
0.06	3.0124	1.464	1.5026	8.3	50.7
0.08	3.0198	1.463	1.4804	6.3	38.6
0.1	3.0727	1.462	1.4606	5.0	32.9
0.15	3.0876	1.461	1.4584	3.3	22.4
0.2	3.1084	1.461	1.4506	2.5	17.2
0.25	3.1502	1.46	1.449	2.0	14.4
0.3	3.244	1.459	1.429	1.7	13.2
0.4	3.2857	1.458	1.419	1.3	10.3
0.45	3.3743	1.457	1.4166	1.1	9.9
0.5	3.4663	1.456	1.4006	1.0	9.6
0.55	3.4103	1.459	1.3904	0.9	8.2

1-Pentanol+P-bromoacetophenone+CCl₄

Concentration of base (C _B) Mol/lit	Dielectric constant (ε)	Density of solution (ρ) Kg/m ³	Refractive index of solution (n)	C _A /C _B	Ω _B X10 ³⁹
0.06	3.11341	1.476	1.5149	8.3	53.8
0.08	3.12081	1.475	1.4927	6.3	40.8
0.1	3.17371	1.474	1.4729	5.0	34.7
0.15	3.18861	1.473	1.4707	3.3	23.6
0.2	3.20941	1.473	1.4629	2.5	18.1
0.25	3.25121	1.472	1.4613	2.0	15.1
0.3	3.34501	1.471	1.4413	1.7	13.7
0.4	3.38671	1.47	1.4313	1.3	10.7
0.45	3.47531	1.469	1.4289	1.1	10.2
0.5	3.56731	1.468	1.4129	1.0	9.9
0.55	3.51131	1.471	1.4027	0.9	8.5

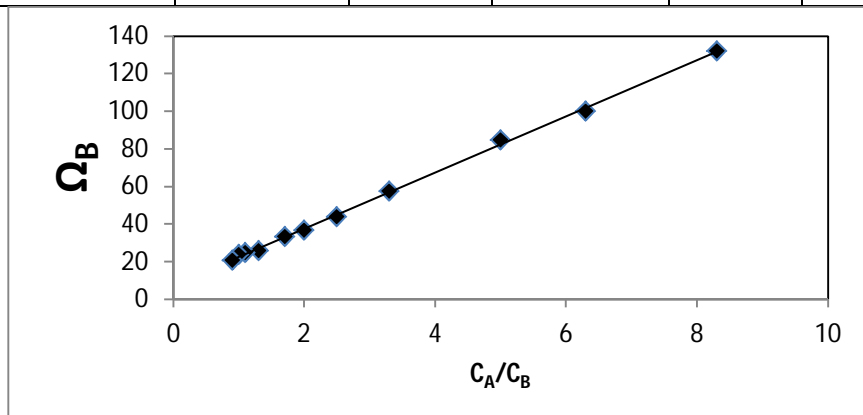


Fig. 2. The plot of C_A/C_B versus Ω_B for P-Bromoacetophenone + I-Propanol+CCl₄

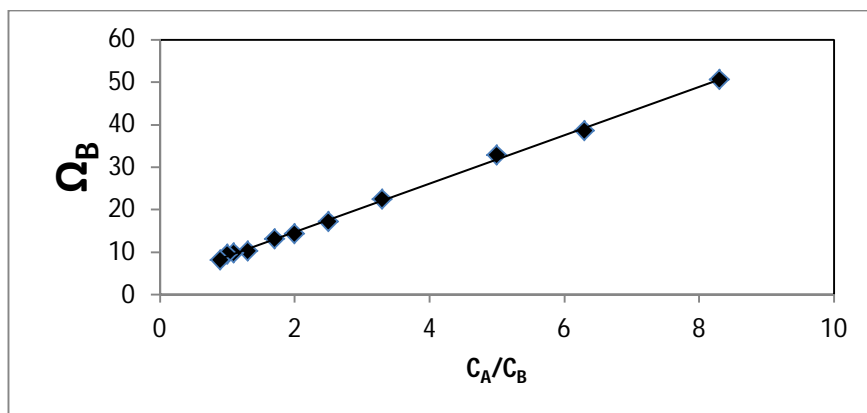


Fig. 3. The plot of C_A/C_B versus Ω_B for P-Bromoacetophenone + I-Butanol+CCl₄

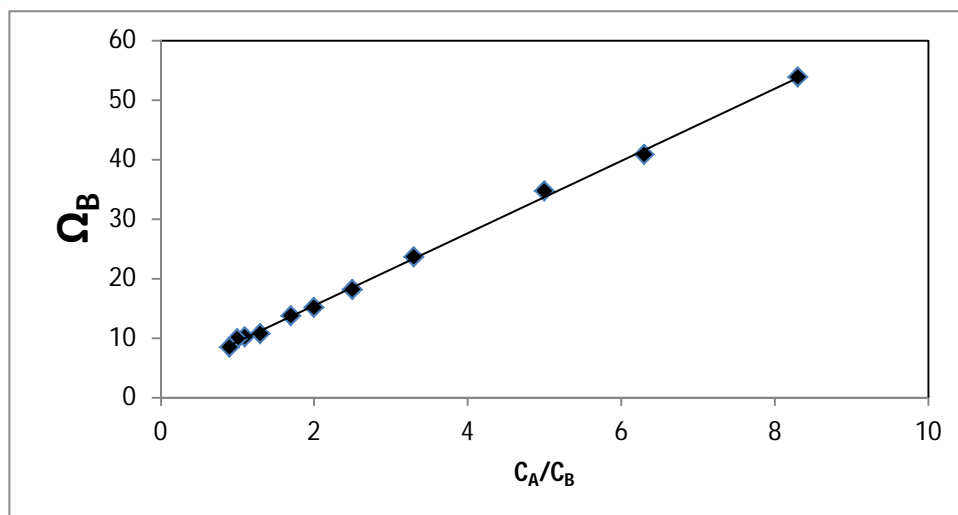


Fig. 4. The plot of C_A/C_B versus Ω_B for P-Bromoacetophenone +1-Pentanol+CCl₄

IV. RESULTS AND DISCUSSION

The values of density, dielectric constants and refractive indices measured at different concentrations of proton donor C_A are reported in Table 1. The formal concentration of the proton acceptor C_B is kept constant. The plots of Ω_B against C_A/C_B are given in Fig. 2-4. The dipolar increment ($\Delta\mu$) value for all the system is reported in Table 2.

TABLE:2 Dipole moment of the components and their 1:1 complex and dipolar increments of the complex system

Systems	μ_a (D)	μ_b (D)	μ_{ab} (D)	$\Delta\mu$ (D)
1-Propanol + P-Bromoacetophenone	1.66	6.5	4.70	3.48
1-Butanol + P-Bromoacetophenone	1.64	4.6	3.00	1.98
1-Pentanol + P-Bromoacetophenone	1.73	3.3	3.05	1.96

From the computed values of μ_{ab} and μ_b , the dipolar increments were obtained using eq(5).there values are given in Table 2 for all systems. The values of θ_a and θ_b were taken from the literature. When a proton donor of dipole moment μ_a, μ_b, μ_{ab} , θ_a and θ_b values are shown the Table 2. The Dipole moment may be enhanced by an amount $\Delta\mu$. The dipolar increment $\Delta\mu$ determines the nature of complexes in the system studied only due to polarization effects and not due to charge transfer effect. The values of $\Delta\mu$ are found to be small. This explains the absence of charge transfer effects. If charge transfer effects excites, $\Delta\mu$ which exceed(12) than 10D. Therefore the complexation may be only due to the redistribution of electrons due to polarization effects. Similar results were reported by Thenappan (13) and Sabesan(14) for the alcohol mixture. The values of $\Delta\mu$ decreases in the order 1-Propanol>1-Butanol>1-Pentanol. This is probably due to steric effect. Hence it can be concluded that the complexation in the present study are is due to polarization effect.

V. CONCLUSION

In this paper dielectric studies have been made on the ternary mixtures of equimolar concentrations of P-bromoacetophenone with1-Propanol, 1-Butanol, 1-Pentanol in non polar solvent CCl₄. From the study of the enhancement of dipole moment of the complexes, it is concluded that the complexation formed by the formation of the H-bond is only due to the polarization effect and not due to the charge transfer effect in all the systems studied.

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