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Research Article

DIELECTRIC STUDIES OF H-BONDED COMPLEXES OF P-CHLOROACETOPHENONE WITH ALCOHOLS

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ABSTRACT

Molecular interactions have been studied from the formation of H-bonded complex between P-Chloroacetophenone in carbon tetra chloride with alcohol such as Butanol, Iso-butanol, P-Cresol. The first two are the aliphatic alcohols whereas the remaining one is aromatic alcohol. The dipole moment of 1:1 complexes of the above said alcohols with P-Chloroacetophenone in carbon tetra chloride are computed by experimentally measured quantities like that density, refractive index and dielectric constants using 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. This investigation shows that in all the studied systems of dipole moments of the complexes are reported and the observed enhancement of dipole moment of the complexes are discussed.

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INTRODUCTION

Because of its significance in quite different spheres of chemistry and biology hydrogen bonding has long been the focus of interest in liquid state physics [1-3]. Dielectric studies on the binary mixtures provides information about the intermolecular interactions in the mixture due to the dipole-dipole interactions and hydrogen bonding. The dielectric investigations of 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. [4-7]. Aromatic ketones such as acetophenone and their derivatives have great pharmaceutical and analytical applications. Alcohols have been the subject of extensive practical and theoretical investigations in the study of intermolecular hydrogen bonding [8]. Due to the presence of 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 (butanol, isobutanol, p-cresol) of their binary mixtures with p-chloroacetophenone, as common component, were measured at 303K. From these data, 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 importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of various alcohols with P-Chloroacetophenone respectively and to study the nature of complexes formed. Several researchers have studied the complexes of alcohols and phenols with aldehydes, ketones, esters in recent years using dielectric methods. The present work is aimed to study the hydrogen bonding with between substituted ketones with alcohols using dielectric methods which may provide useful information about the formation of complex in the mixture.

MATERIALS AND METHOD

Measurement of density

Density values of liquid and liquids mixture were measured using a double armed pycnometer which has a bulb volume of 5 ml pycnometer was calibrated with freshly prepared double distilled water. A digital electronic balance were used to measured density. For all the measurement, temperatures were controlled by circulating water through an ultra-thermostat with an accuracy $\pm 0.15K$.

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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 (n_D)

Measurement of Dielectric constant (ϵ)

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

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 .

Theory

Huyskens [9] 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 [10] the overall dipole moment [M] of a solution containing polar substances and an apolar solvent (subscript-s) is given by

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

where

- ϵ – 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

$$C_B - C_A \gg K^{-1}$$

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

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

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 α and β respectively, If α and β 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

$$\mu = (\mu_{ab}^2 - \mu_a^2 \sin^2 \alpha - \mu_b^2 \sin^2 \beta - 2\mu_a \mu_b \sin \alpha \sin \beta \cos \phi)^{1/2} - \mu_a \cos \alpha - \mu_b \cos \beta$$

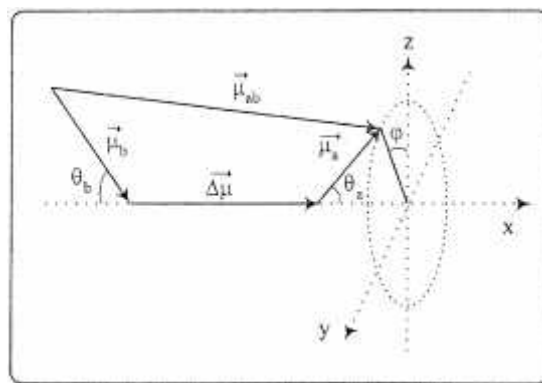


Fig. 1 Dipole moments μ_{ab} , μ_a and μ_b of the complex and of the partners, dipole increment μ

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

P-Chloroacetophenone +1-Butanol+CCl4					
X_2	ϵ	Refractive Index	Density	C_a/C_b	Ω_B
0.03	2.418	1.451	1.360	0.5	17.97
0.05	2.495	1.450	1.356	0.25	12.17
0.07	2.515	1.450	1.352	0.16	8.68
0.09	2.587	1.449	1.348	0.12	8.01
0.11	2.615	1.448	1.344	0.10	6.90
0.13	2.683	1.447	1.334	0.08	6.67
0.15	2.743	1.446	1.328	0.07	6.43

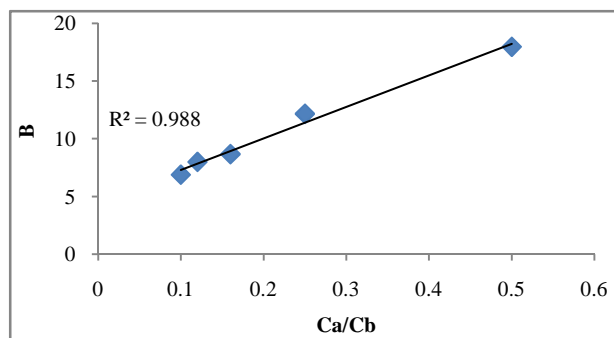


Fig. 2 The plot of C_a/C_b versus Ω_B for P-Chloroacetophenone + 1-Butanol + CCl_4

P-Chloroacetophenone +Iso-butanol+CCl ₄					
X ₂	12	Refractive Index	Density	C _A /C _B	Ω _B
0.03	2.469	1.4515	1.346	0.5	21.95
0.05	2.546	1.451	1.340	0.25	14.13
0.07	2.592	1.450	1.334	0.16	10.67
0.09	2.632	1.450	1.328	0.12	8.81
0.11	2.697	1.449	1.312	0.10	8.09
0.13	2.743	1.449	1.326	0.08	7.35
0.15	2.778	1.448	1.320	0.07	6.72

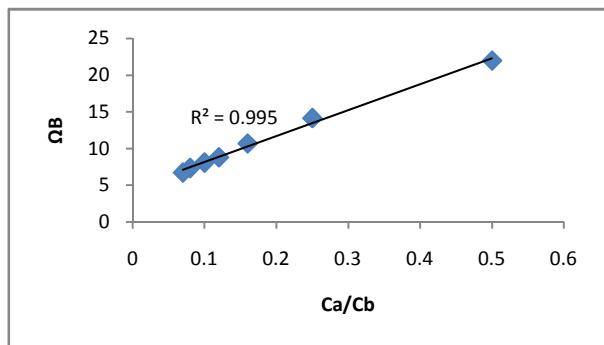


Fig. 3 The plot of C_A/C_B versus Ω_B for P-Chloroacetophenone +Iso-Butanol+CCl₄

P-Chloroacetophenone +P-cresol+CCl ₄					
X ₂	12	Refractive Index	Density	C _A /C _B	Ω _B
0.03	2.444	1.4615	1.424	0.5	17.25
0.05	2.484	1.462	1.420	0.25	10.13
0.07	2.541	1.462	1.416	0.16	8.22
0.09	2.586	1.463	1.412	0.12	7.00
0.11	2.648	1.463	1.408	0.10	6.54
0.13	2.694	1.464	1.404	0.08	6.01
0.15	2.748	1.464	1.400	0.07	5.72

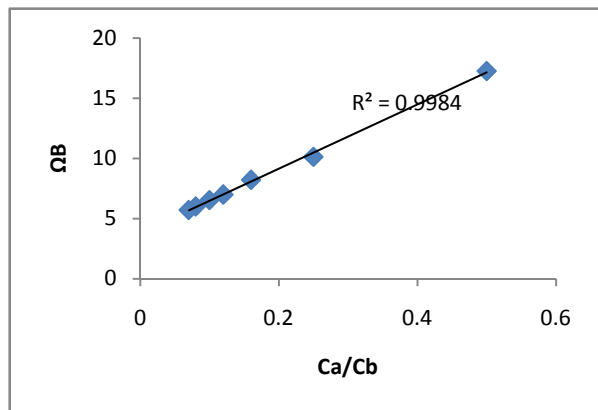


Fig. 4 The plot of C_A/C_B versus Ω_B for P-Chloroacetophenone +P-Cresol+CCl₄

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 (μ) value for all the systems is reported in Table 2.

The dipolar incremental studies shows the type of interaction formed between the proton donor and proton acceptor [11,12]. The dipolar increment is given in Table 2. The magnitude of μ

determines the nature of complexation. The complexation may be due to polarization effects or charge transfer effects.

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)	μ ⁺ (D)
1-Butanol + P-Chloroacetophenone	1.66	1.87	5.73	2.94
Iso-butanol + P-Chloroacetophenone	1.64	2.16	6.44	3.42
P-cresol + P-Chloroacetophenone	1.73	1.81	7.12	4.43

The dipolar increments (μ) reported for all studied systems are very low and negative. Our investigation shows that the value of μ does not even exceed 4D for all systems. It is observed that there is no contribution arising due to ionic structures, as it would involve a very high value of μ > 10D. It is clear that the negative value of μ is due to the redistribution of the charges by polarization effect. Sampathkumar were studied [13] for the mixture of phenols with substituted piperidines. Similar results were reported by Thenappan [14] Parthipan [15] and Sabesan [16] for alcohol mixtures. This is also supported by the fact that the plot of Ω_B versus C_A/C_B is linear. Hence it is clear that the order of the complexation is 1:1 in all the systems studied.

The obtained value of the dipole moment of the complex (μ_{ab}) is found to be more or less value for all the studied systems. This is probably due to steric effect. Similar conclusions were drawn for the mixture of alcohols with ethylmethylketone [17]. Therefore the greater tendency of complexation (P-cresol + P-Chloroacetophenone) system than the other two systems. Hence it can be concluded that formation of the complexes in the systems studied is only due to polarization effects and not due to charge transfer effects.

CONCLUSION

In this paper dielectric studies have been made on the ternary mixtures of equimolar concentrations of P-Chloroacetophenone with 1-Butanol, Iso-Butanol, P-cresol 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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