

Dielectric studies of H-bonded complexes of substituted Benzaldehyde with alcohols

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Abstract: The dipolar complexation involving substituted Benzaldehyde and three alcohols namely 1-Butanol, Iso-butanol, and P-cresol in a non-polar CCl_4 were determine at 303k. The dipole moment of the complex are calculated from the dielectric data using by Huysken' s method based on Onsager theory .The dipolar increment were obtained from the bond angle data. The result were interpreted the nature of complexation.

Keywords: Dielectric Parameters, H-bonding, Huysken s' method, Anisaldehyde, O-Chlorobenzaldehyde, Dipolar increment.

I. Introduction

The dipolar complexation involving substituted benzaldehyde and three alcohols namely 1-butanol, iso-butanol, and p-cresol in a non- polar CCl_4 were determined a 303k. The dipole moment of the complex are calculated from the dielectric data using by Huysken method based on onsager theory. The dipolar increments were obtained from the bond angle data. The result were interpreted the nature of complex Benzaldehydeare important industrial chemicals and are widely used as perfume and flavoring compounds and it is also used in the preparation of certain aniline(1). Alcohols have found in various application and widely use in industry and excellent proton donors (2). Dielectric studies about binary mixtures are important to understand the intermolecular interactions and hydrogen bonding(3-7).The hydrogen bonded complexes a redistribution of electrons density mainly depend upon three types of interaction namely electrostatic, polarization and charge transfer interaction .The electrostatic interaction does not contribute to the dipole moment of the complex where as the polarization interaction change in the dipole moment value depend upon charge redistribution. The charge transfer interaction , charge migration parallel to H-bonded axis results in large change dipole moment. Several researchers (8-14) 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 aldehydes with alcohols using dielectric methods which may provide useful information about the formation of complex in the mixture

II. Materials and method

2.1 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 the pycnometer 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 $\pm 0.15K$.

2.2 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 ($\epsilon_\infty = n_D^2$)

2.3 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 Where c_0 = capacitance of air, c_1 = capacitance of standard liquids, c_x = capacitance of test liquids ϵ_r = dielectric constant of standard liquid

III. Theory

Using the onsager theory the dipole moment of a liquid containing polar liquid solute and non-polar solvent is given by.

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

Where

ϵ = relative permittivity of the solution

n_D =refractive index of the solution

ϵ_s = relative permittivity of the solvent

n_{D_s} =refractive index of the solvent

C_S =is the actual concentration of the solvent in mol lit⁻¹

N_A =Avogadro number

K =Boltzmann constant

C_B is the actual concentration of the base, whereas C_S is the actual concentration of the solvent in the solution,

C_S^0 its concentration in the pure state and the subscript S refers to the pure solvent. So, one can write

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

The experimental values of dielectric constant, refractive index, density were studied and given in the tables (1).

Using least square fitting method C_A/C_B versus plotted a graph from the intercept of the curve, the values of μ_{ab} and μ_b were calculated.

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

Anisaldehyde + 1-Butanol+CCl₄					
X₂	ε₁₂	Refractive Index	Density	Ca/Cb	Ω_B
0.03	2.392	1.456	1.414	0.5	14.48
0.05	2.429	1.455	1.406	0.25	8.91
0.07	2.464	1.454	1.390	0.16	6.95
0.09	2.497	1.453	1.378	0.12	5.94
0.11	2.525	1.452	1.370	0.1	5.25
0.13	2.565	1.451	1.362	0.08	4.95
0.15	2.627	1.449	1.352	0.07	5.02

Anisaldehyde +Iso -butanol+CCl₄					
X₂	ε₁₂	Refractive Index	Density	C_a/C_b	Ω_B
0.03	2.444	1.449	1.414	0.5	20.65
0.05	2.469	1.448	1.406	0.25	11.46
0.07	2.520	1.447	1.390	0.16	9.07
0.09	2.581	1.446	1.378	0.12	8.09
0.11	2.637	1.445	1.370	0.1	7.41
0.13	2.666	1.444	1.362	0.08	6.61
0.15	2.729	1.443	1.352	0.07	6.40

Anisaldehyde +P-cresol+CCl₄					
X₂	ε₁₂	Refractive Index	Density	C_a/C_b	Ω_B
0.03	2.490	1.461	1.418	0.5	21.07
0.05	2.546	1.4615	1.416	0.25	12.67
0.07	2.566	1.462	1.414	0.16	8.92
0.09	2.632	1.4625	1.408	0.12	7.93
0.11	2.678	1.463	1.406	0.1	7.02
0.13	2.742	1.4635	1.404	0.08	6.65
0.15	2.798	1.464	1.402	0.07	6.27

O-Chlorobenzaldehyde + 1-Butanol + CCl ₄					
X ₂	ε ₁₂	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	1.4505	1.356	0.25	12.17
0.07	2.515	1.45	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	0.1	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

O-Chlorobenzaldehyde +P-cresol+CCl ₄					
X ₂	ε 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	1.4625	1.416	0.16	8.22
0.09	2.586	1.463	1.412	0.12	7.00
0.11	2.648	1.4635	1.408	0.1	6.54
0.13	2.694	1.464	1.404	0.08	6.01
0.15	2.748	1.4645	1.400	0.07	5.72

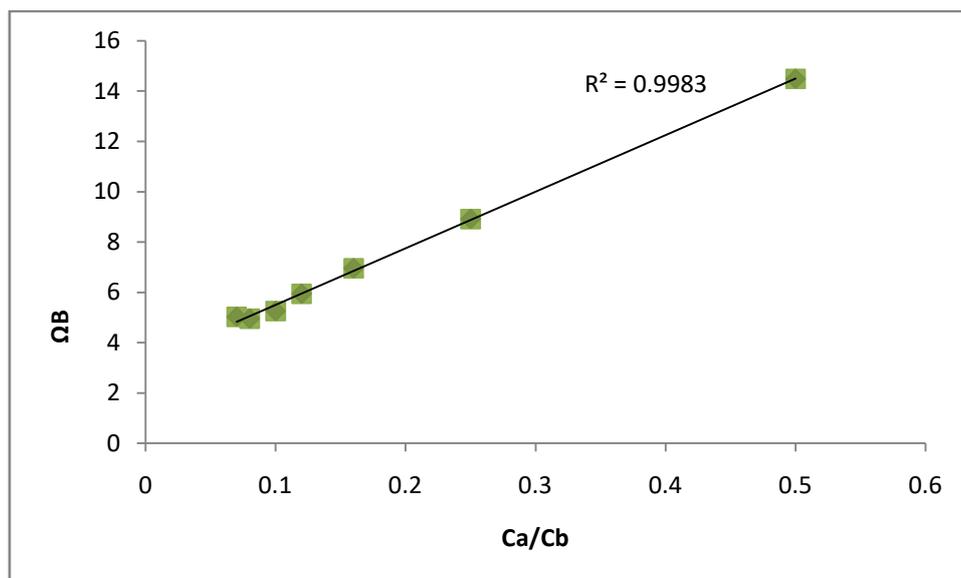


Fig. 1. The plot of C_a/C_b versus Ω_B for Anisaldehyde + 1-Butanol + CCl₄

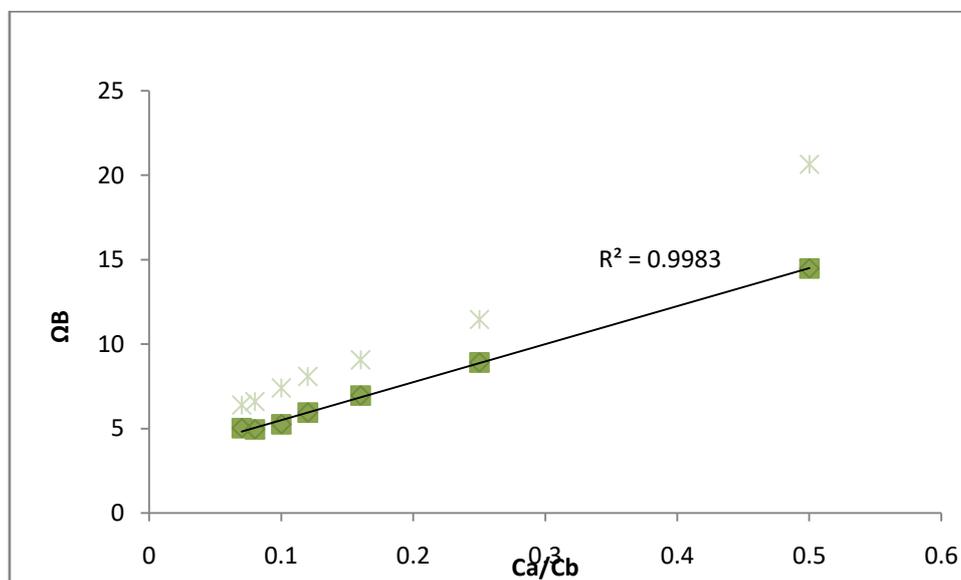


Fig. 2. The plot of C_a/C_b versus Ω_B for Anisaldehyde + Iso-butanol + CCl₄

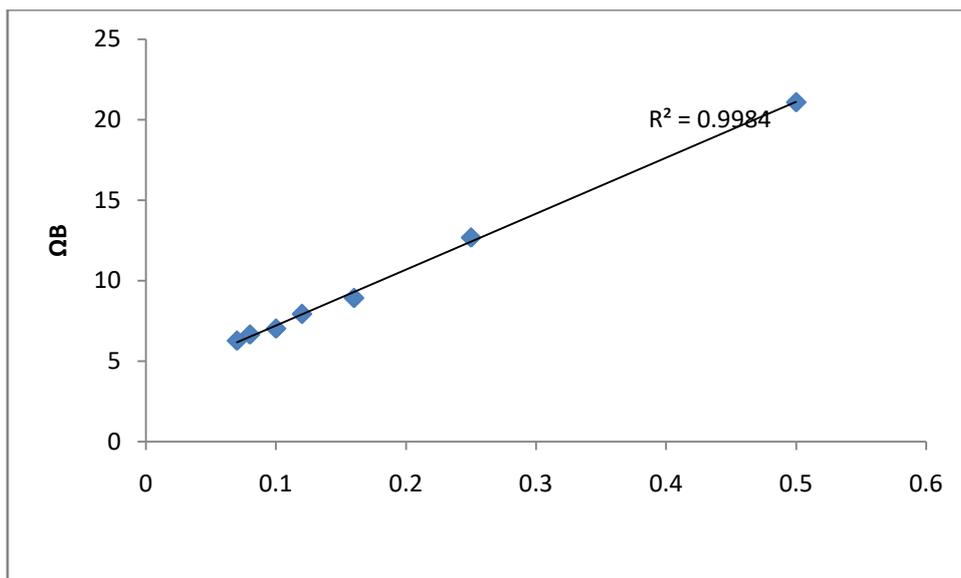


Fig. 3. The plot of C_a/C_b versus Ω_B for Anisaldehyde + P-cresol + CCl_4

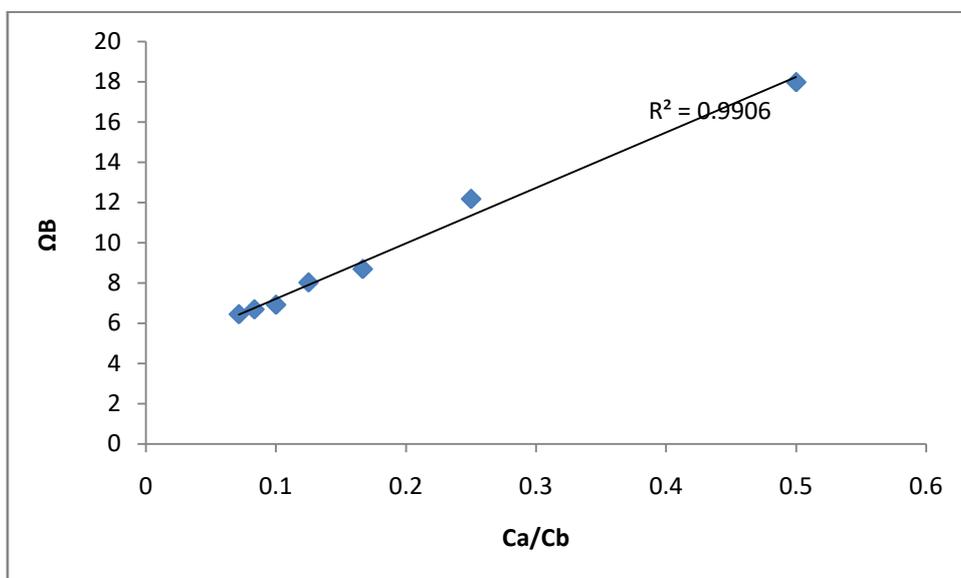


Fig. 4. The plot of C_a/C_b versus Ω_B for O-Chlorobenzaldehyde + I-Butanol + CCl_4

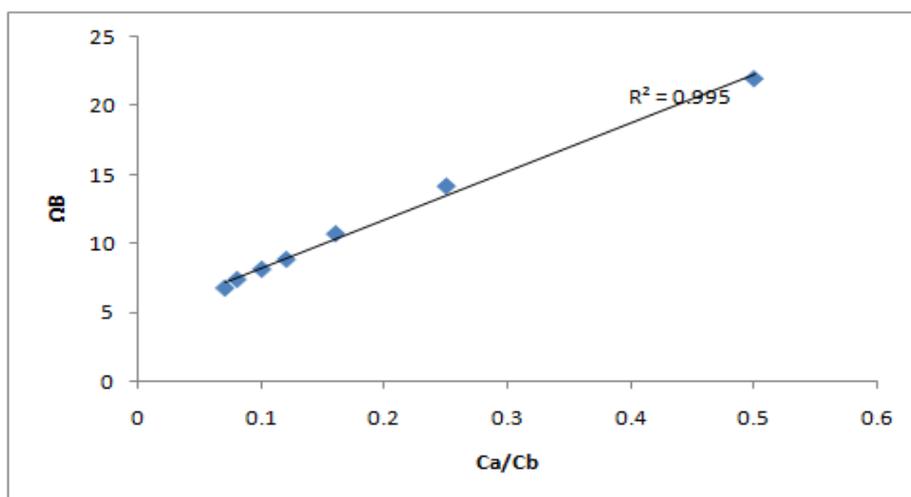


Fig. 5. The plot of C_a/C_b versus Ω_B for O-Chlorobenzaldehyde + Iso-butanol + CCl_4

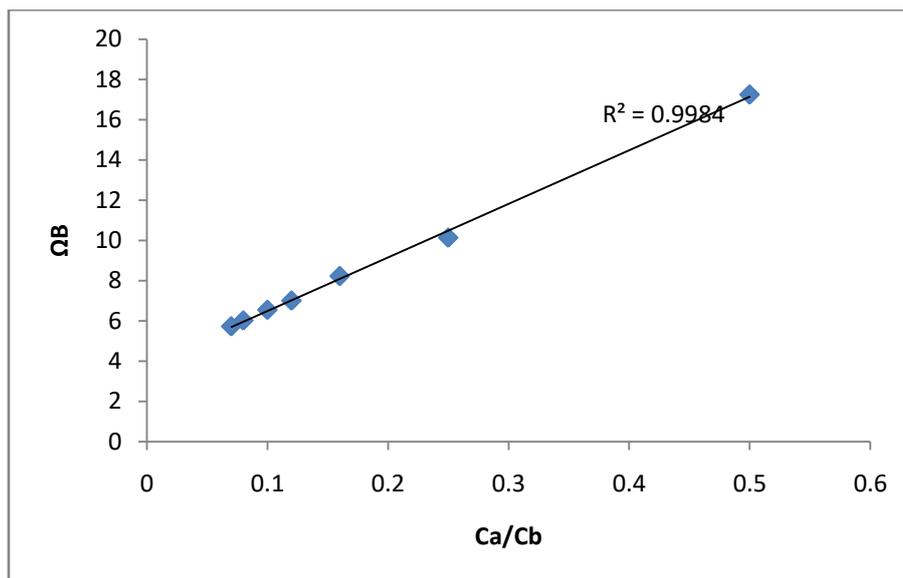


Fig. 6. The plot of C_A/C_B versus Ω_B for O-Chlorobenzaldehyde + P-cresol + CCl_4

IV. Results and discussion

The dipole moment of the proton donor μ_a is mixed with proton acceptor μ_b in a non-polar solvent a complex may be formed. The dipolar increment of $\Delta\mu$ determines the nature of interaction. From the change of concentration studied the plot of Ω_B with C_A/C_B in a straight line. Hence it can be taken as a indication for the formation of 1:1 complex. Computed values of $\Delta\mu$ are 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-Butanol+Anisaldehyde	1.66	1.76	4.84	4.29
Iso-Butanol+ Anisaldehyde	1.64	1.94	5.76	5.49
P-Cresol+Anisaldehyde	1.73	2.02	5.93	5.32
1-Butanol+ O-Chlorobenzaldehyde	1.66	2.02	5.25	2.65
Iso-butanol+ O-Chlorobenzaldehyde	1.64	2.12	5.92	3.28
P-Cresol+ O-Chlorobenzaldehyde	1.73	1.87	5.18	2.63

Calculation of dipolar increment.

If a single H- bond is formed between the partners, it can be presumed that $\Delta\mu$ has the direction of the hydrogen bond. The vector equation can be transformed in from.

The dipole increment is given by

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

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 $\mu_a, \mu_b, \mu_{ab}, \theta_a$ 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 and sometimes even negative. This explains the absence of charge transfer effects. If charge transfer effects excites, $\Delta\mu$ which exceed (15-16) than 10D. Therefore the complexation may be only due to the redistribution of electrons due to polarization effects. Similar results were reported by Thenappan (17) and Sabesan(18)

for the alcohol mixture. The values of $\Delta\mu$ decreases in the order Iso- butanol > P-cresol > 1-Butanol. This is probably due to steric effect. Similar conclusions were drawn for the mixture of Alcohols with ethyl methyl ketone(19-20). Hence it can be concluded that the complexation in the present study are is due to polarization effect.

V. Conclusion

In this paper, the dielectric properties of hydrogen bonded complexes formed by substituted aldehydes with alcohols namely, 1-Butanol, Iso-butanol, and P-Cresol in CCl_4 have been studied by computing the dipolar increment values for various concentrations at 303K. The investigation of dipolar increments shows presence of polarization effect in all the complexes. The linear graph between Ω_B and C_A/C_B shows 1:1 complex formation in all the mixtures.

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