Dielectric studies of H-bonded complexes of 1-Decanol with o-Fluorobenzaldehyde and p-Fluorobenzaldehyde in CarbontetraChloride system

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ABSTRACT : *The dielectric studies of the polar binary mixture of 1- decanol with o-Fluorobenzaldehyde, p-Fluorobenzaldehyde in carbon tetrachloride were experimentally studied at 303k. The dipole moment of the complexes has been determined by Huyskens and Debye's polarization based on the Onsager theory. The enhancement of the dipole moment indicates the formation of 1:1 complexes. The result is used to discuss the molecular interaction.*

Keywords

Dielectric parameters, H- bonding, Huyskens method, o-Fluorobenzaldehyde, p-Fluorobenzaldehyde, dipolar increment.

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1. Introduction

The dielectric study of binary mixture provides a very sensitive tool for detecting molecular interaction. Benzaldehyde and its derivatives have shown antitumor activity mice [1-2]. They are also important intermediaries for the processing of perfume and flavoring compounds and in the preparation of certain aniline dyes. Alcohols are excellent proton donors. Several author (3- 6) have studies the complex of phenols and alcohols with ketones, ester, amides, aldehydes, and amines in recent years using dielectric methods. The review of Davie's [7]. Zenger's - Huysken's and Huysken's [8], Muller et al [9] can be cited in emphasizing the importance of this type complex. It was generally inferred that in a given medium ΔPK_a is an important factor governing the nature of the complex and particular difference are observed between the families of complex. Mayappan et al [10] investigated the mechanism of complex formation in phenol - ketone / aldehyde system .A survey of the literature shown that a few works[11-14] that enhancement of the dipole moment does not explained by electrostatic induction moment as it was not clear that whether the interaction arises due to polarization or change transfer with this inview the present investigation aimed at studying the dielectric behavior of binary mixture of o-fluorobenzaldehyde, p-fluorobenzaldehydand,1-decanol which may provide useful information about the formation of complex in the mixture.

2. Experimental

2.1 Materials

Theo Fluorobenzaldehyde,pFluorobenzaldehyde, 1-Decanol compounds were purified by standard procedures and checked against their literature value.

2.2 Dielectric constant (ε_0)

Dipole meter is an adaptable instrument that is used 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 determining as taken and assembly is immersed into liquid resulting in change in frequency. From the resulting shift capacitance of cell in unknown of liquid is calculated (c_x). Dielectric constant of unknown liquid is calculated.

2.3 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 optical frequency have been measured ($\varepsilon_\infty = n_D$)

2.4. 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 was used in the density measurement. For all the measurement, temperature was controlled by circulating water through an ultra-thermostat (CONCORD) with an accuracy $\pm$ 0.15K. The uncertainty in dielectric constant, refractive index and density measurement was within $\pm$ 0.0001 $\pm$0.001 and $\pm$ 0.0001gcm$^{3.}$.

Using the limiting polarization method [15] the dipole moment of the solute (μ_b) in a non-polar solvent can be calculated from the relation

$$\mu_b = \sqrt{\frac{9K}{4\pi N}} \left[(P_{2\infty} - R_D) \, T \right]^{1/2} \qquad (1)$$

Where K is the Boltzmann constant, N is Avogadro's number is the absolute temperature $P_2\infty$ is the molar polarization at infinite dilution and R_D is mole fraction of the solute

$$R_D = \left(\frac{n_2^2 - 1}{n_2^2 - 2} \right) \frac{M_2}{d_2} \qquad (2)$$

Here n_2, d_2 and M_2 are the refractive index, density and molecular weight of the solute.

3. Dipole moment of the complex by Huysken's method

The dielectric constant ε and the refractive index for the sodium line n_D of a ternary solution with formal concentrations C_A of proton donor and C_B proton acceptor of base in CCl_4 solution are measured first .The quantity Ω_B is then computed from the experiment data [16]

$$\Omega_B = \frac{9KTX\,10^{39}}{4\pi N_A}\frac{1}{C_B}\left[\frac{(\varepsilon - n_D^2)(2\varepsilon + n_D^2)}{\varepsilon(n_D^2 + 2)^2} - \frac{C_s}{C_s^0}\frac{(\varepsilon_s - n_{Ds}^2)(2\varepsilon_s + n_{Ds}^2)}{\varepsilon_s(n_{Ds}^2 + 2)^2}\right] \quad (3)$$

C_s^0 Is the formula concentration of the solvent in the pure sate and C_S its actual concentration in the pure subscripts refer to the pure solvent.

Ω_B for different $C_A\backslash C_B$ along the x-axis and ΩB along the Y-axis. Intercept of the curve in the Y- axis gives $(\mu_{ab}{}^2 - \mu_b{}^2)$

If the internal index of refraction of the dissolved entities can be approximated as n_D the theories of Onsager [17] and Froehlich [18]

This serves as a criterion for choosing the proper centration of C_A and C_B of the proton donor and proton acceptor for 1:1 complexation. If the formal concentration C_A of the proton acceptor is far greater than the formal concentration C_B of the proton donor such that.

CB-CA>>k-1…………………….(.4

Where K is the equilibrium constant for 1:1 complexation Eq (4) is valid. Thus, for the experimentally observed values of ε_o, n_D, ε_s, and n_{Ds}, it is possible to obtain the values of

Table 1: Variation of dielectric constant, refractive index, density and Ω_B with the formal concentration of different aldehydes

o- Fluorobenzaldehyde + 1 Decanol + CCl_4					
X2	ε_{12}	Refractive index	C_a/C_b	Density	Ω_B
0.03	2.031	2.128	1.66	1.41	28.65
0.05	2.268	2.130	1.00	1.41	23.65
0.07	2.314	2.137	0.71	1.39	21.37
0.09	2.335	2.141	0.55	1.38	19.81
0.11	2.371	2.143	0.45	1.37	19.28
0.13	2.426	2.153	0.38	1.38	17.45
0.15	2.449	2.163	0.33	1.35	16.80

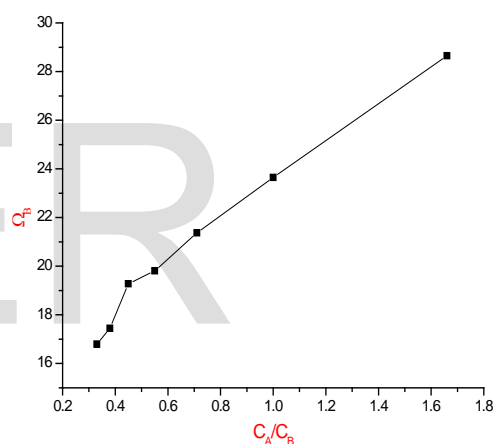| p - Fluorobenzaldehyde + 1 Decanol + CCl_4					
X_2	ε_{12}	Refractive index	Density	C_a/C_b	Ω_B
0.03	2.449	2.128	1.41	1.60	17.55
0.05	2.555	2.130	1.40	1.00	15.27
0.07	2.853	2.135	1.39	0.71	13.58
0.09	3.031	2.138	1.38	0.55	13.13
0.11	3.100	2.144	1.38	0.45	12.67
0.13	3.174	2.149	1.36	0.38	12.07
0.15	3.223	2.155	1.36	0.33	11.30

Figure.1; o - Fluorobenzaldehyde + 1 Decanol + CCl_4
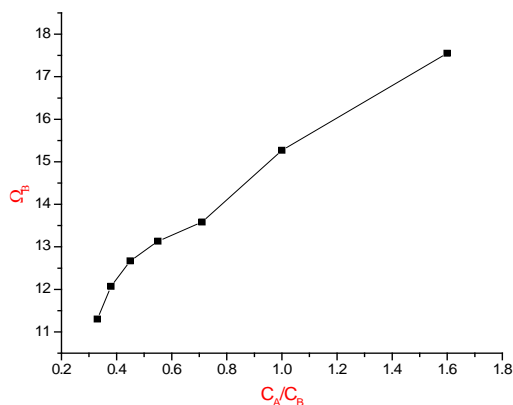
Figure.2: p- Fluorobenzaldehyde + 1 Decanol + CCl_4

4. RESULTS AND DISCUSSION:

The values of the density (ρ) refractive indices (n_D) dielectric constant (ε) and Ω_B for varying concentration of the proton donor are recorded in Table (1). The values of μ_{ab} and μ_b are obtained from the slope and the intercept of the straight line graph.

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

system	μ_a (D)	μ_b (D)	μ_{ab} (D)	$\Delta\mu$ (D)
1-Decanol+p-Fluorobenzaldehyde	2.06	3.16	2.78	1.41
1-Decanol+o-Fluorobenzaldehyde	3.31	3.80	5.3	3.87

The dipole moment of the donor and acceptor were determined by Huysken's method based on Onsager Theory using carbon tetrachloride as solvent. There are closely agreed with the result from solution data. The vectorial relation for the dipole moment of the complex and its partners and the dipolar increment as discussed by Huyskens [19] is given in Fig.

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

$$\Delta\mu=(\mu^2_{ab}-\mu^2_a\sin^2\theta_a-\mu^2_b\sin^2\theta_b-2\mu_a\mu_b\sin\theta_a\sin\theta_b\langle\cos\Phi\rangle)^{1/2}-\mu_a\cos\theta_a-\mu_b\cos\theta_b$$

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 μ_a in a non – polar solvent θ_a complex may be formed. The dipole moment may be enhanced by an amount $\Delta\mu$. The magnitude of $\Delta\mu$ determines the nature of complexation may be either due to polarization effects.

For the range of concentrations studied, the plot of ΩB with $C_A\backslash C_B$ is a straight line. This indicates the formation of a 1: 1 complex. Computed values of μ are reported in table 2. Values of $\Delta\mu$ are found to be positive. This explains the absence of change transfer effects. If charge transfer effect exist, then $\Delta\mu$ would have been greater than 10 D [20, 21]. Since $\Delta\mu$ is small and less than 10 D, the complexation may be only due to the redistribution of electron due to polarization effects. Similar conclusions were drawn [22] for the mixture of phenols with substituted piperidines. Similar results were reported by Thenappan [23] and Sabesan [24] for the alcohol mixtures.

5. References

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