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DIELECTRIC STUDIES OF THE TERNARY MIXTURES OF AMINES WITH DECANOL IN CARBON TETRACHLORIDE SYSTEMS

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ABSTRACT

The hydrogen bonded complexes involving primary amines (propyl amine, butyl amine and pentyl amine) and decanol in carbon tetrachloride were studied at 301k. The dipole moment of the complex obtained from the dielectric measurements using by Huysken's method based on Onsager theory. The dipolar increment and enthalpy changes during fond formation were evaluated from the complex dipole moment. The results were interpreted in terms of interactions. The $\Delta\mu$ and ΔH_B values indicate the interaction due to polarization only.

KEYWORDS: Dielectric constant, H-bonding, dipole moment, dipolar increment, Enthalpy.

INTRODUCTION

Decanol and primary amines like propyl amine, butyl amine and pentyl amine have been found to be important due to the various applications like industrial, chemical and pharma also act as an excellent proton donor.[1-2] Dielectric data about the mixtures are important due to understanding the nature of intermolecular interactions, hydrogen bonding, solute – solvent etc.,[3-7] The molecular interaction occurs due to redistribution of electrons density mainly depends upon following interaction namely electrostatic, polarization and charge transfer. The electrostatic interaction does not contribute to the dipole moment of the complex where as the polarization interaction change in the dipole moment value depends upon charge redistribution. The charge transfer interaction, charge migration parallel to H-bonded axis results in large change dipole moment. Many workers[8-10] have studied the complexes of alcohols and amines in recent years using dielectric methods. The present investigation

reports the results of molecular interactions between decanol and amines using dielectric data which may provide useful information about the molecular interaction between the components.

MATERIALS AND METHODS

The AR grade decanol, propyl amine, butyl amine, pentyl amine and carbon tetrachloride were used in present investigation with purity 99.99% after purified with standard procedure. Solutions of these materials were prepared by accurately weighing appropriate amounts of solute in $10cm^3$ volumetric flasks. AR grade carbon tetrachloride was used as solvents for the dielectric measurements of ternary liquid mixtures.

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

Refractive index of the pure and ternary 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 higher frequency have been measured ($\varepsilon\infty=n_D^2$).
The dielectric constants has been measured using dipole meter RL09 supplied by Toshniwal, India operated at 220 volts and It was operating 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 ±0.1°C supplied by Concord Instruments Pvt. Ltd., Chennai. The scale of the dipole meters calibrated using the standard liquids of carbon tetrachloride, benzene, and acetone.

DETERMINATION OF DIPOLE MOMENT OF THE COMPLEXES

Considering the ternary mixture of polar components a hydroxyl group and B amine group in a carbon tetrachloride as solvent, the relative orientations of A and B vary continuously due to the mobility of the liquid phase. Assuming that the time interval is short enough to consider the orientation as fixed, the dipole moment of the solution may be written as

$$D=\left[\frac{9KTX10^{39}}{4\pi N_a}\right]X\left[\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2}\right]-\frac{C_S}{C_s^o}\left[\frac{(\varepsilon_s-n_s^2)(2\varepsilon+n_s^2)}{\varepsilon_s(n_s^2+2)^2}\right] \quad \ldots\ldots (1)$$

C_B is the actual concentration of the base, whereas C_S is the actual concentration of the solvent in the solution, C°_S its concentration in the pure state and the subscript S refers to the pure solvent. So, one can write $D=\sum_i \mu_i^2 C_i$. In studying hydrogen bond formation by a substance B dissolved at a concentration c_B in a non-polar solvent the following experimental function may be considered.

$$\Omega_B = \frac{D}{C_B} \quad \text{..... (2)}$$

If the substance B exhibits self-association,

$$\Omega_B = \frac{\mu_i^2 C_i}{C_B} = <\mu_i^2 / i> \quad \text{..... (3)}$$

When substances A and B are dissolved in a non-polar solvent at the formal concentrations C_A and C_B, if these compounds form only hydrogen bonded complexes of 1:1 stoichiometry, one can write

$$C_A=C_a+C_{ab}= C_a(1+KC_b) \text{ and } C_B=C_b+C_{ab}= C_b(1+KC_b) \text{ .....(4)}$$

Here C_a, C_b andC_{ab} are the actual concentration of the entities and K is the equilibrium constant for complex formation. Then,

$$D= \mu_a^2 C_a + \mu_b^2 C_b + \mu_{ab}^2 C_{ab} \text{ ..... (5)}$$

Dividing by C_B and taking the equilibrium constant into account this can be written as

$$D= \mu_a^2 C_a + (\mu_{ab}^2 - \mu_b^2)\frac{1}{1+(KC_b)}\frac{C_A}{C_B} \text{ .....(6)}$$

Consider the case where $KC_b>>1$, this is obtained when $C_B - C_A >> K^{-1}$, under these circumstances the equation (2) can be reduced to

$$\Omega_b = \mu_b^2 + (\mu_{ab}^2 - \mu_b^2)\frac{C_A}{C_B} \quad \text{..... (7)}$$

The plots may draw between Ω_b with C_A/C_B. From the plots obtained the dipole moment of the base and complexes. Under these circumstances, it can readily shown that the vector equation can be written the following algebraic equation.

The dipolar increment obtained using the relations

$$\Delta\mu = \mu_{ab} - \mu_a - \mu_b \text{ ..... (8)}$$

Equ (8) are used to find the dipolar increment Δμ. These values are given in Table 2 for all the systems. It was observed[11] 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.

ENTHALPY CHANGES DURING BOND FORMATION OF 1:1 COMPLEXES

The similar nature observed for the complexes there are some correlation between the dipole increment and the enthalpy changes ΔH_b. the relations of Δμ from the enthalpy of the bond ΔH_b is given by.

$$\Delta\mu = \frac{A(-\Delta H_b) + [B + C(-\Delta H_b)]\exp[A_1 + B_1(-\Delta H_b)]}{1 + [A_1 + B_1(-\Delta H_b)} \quad \text{..... (9)}$$

The equation was tested for more than one hundred OH..O complexes including some OH. N complexes. The above equation may be modified for the calculation of $-\Delta H_b$ from the known Δμ. If it is expressed in Debye and $-\Delta H_b$ in $KJmol^{-1}$, the numerical values of the constants as follows.

For OH. O bond A=0.028, A_1=-6.5, B=3.20, B_1=0.085, C=0.075

For OH. N bond A=0.0074, A_1=-7.765, B=4.41, B_1=0.172 C=0.045.

The equations 1 to 9 were used find the complex dipole moment, dipole moment of base, dipolar increment and enthalpy changes during the bond formation and reported the table 1 to 2.

RESULTS AND DISCUSSION

The values of dielectric constant (ε), refractive indices (n) and density(d) of the donor (decanol) with acceptor (propyl amine, butyl amine and pentyl amine) in carbon tetrachloride were measured with varying concentration of the proton donor (C_B) are recorded in table.1. The dipole moment of the donor – acceptor complex were determined using Huyskens method based on Onsager theory. The carbon tetrachloride used as a mixed solvent. These are closely agreed with the results from solution data. The proton donor C_a formal concentration is kept constant $C_b >> C_a$. The values of μ_b and μ_{ab} are obtained figure 1. The dipolar increment determined from relation (8) when a proton donor of dipole moment μ_a forms a 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 as θ_a and θ_b. If the values of θ_a and θ_b differ from 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) Thus when the experimental value Ω_b is plotted against the ratio C_A/C_B, one can obtain a straight line with intercept μ_b^2 and slope $(\mu_{ab}^2 - \mu_b^2)$. The appearance to higher order complexes A_2B, A_3B etc, generally provokes curvature of line. The experimental quantity Ω_b is calculated for various concentrations such as C_A/C_B value varying from 0.0 to 0.1 for each system. The plot of Ω_b versus C_A/C_B for all the systems studied is drawn; the readings and plots are given in tables 1 and fig. 1. The dipole moment of the complexes obtained by Huyskens method and dipole moment of the base are given in table 2. It reveals that the dipole moment of the complexes determined is not equal to the sum of the magnitude of the dipole moment of the components. The μ_b values determined from the graph agree closely with the reported literature value. The experimental values of the density, refractive index, dielectric constant and experimental quantity (Ω_B) for different concentrations for the system studies here are given in table 1. Using least square fitting method C_A/C_B is plotted against Ω_B. From the slope and intercept of the plot (Figure 1) gives the values of μ_{ab} and μ_b. Displacement of electrons further removed from the hydrogen bond can remain important, as shown by theoretical calculations. For the rotation isomers, this can lead to small deviations between the directions of $\vec{\Delta\mu}$ and that of the hydrogen bond. However, these effects practically vanish when leading with the mean direction of $\vec{\Delta\mu}$ for the various rotation positions. In a good approximation one can therefore assume that $\vec{\Delta\mu}$ has the direction of the hydrogen bond itself. It is reasonable to except that the magnitude of this value should reveal the nature of hydrogen bonding.

Table 1: Variation of experimental value of dielectric constant(ε), refractive index (n) and density (kg/m^3) mean square dipole moment of decanol – amine complexes at 301K

C_B	ε	n	ρ	Ω_B	ε	n	ρ	Ω_B	ε	n	ρ	Ω_B
0.1	2.76	1.417	1.088	56.3	3.63	1.423	1.102	118.8	3.31	1.428	1.11	94.1
0.2	2.81	1.409	1.081	31.3	3.68	1.416	1.094	62.4	3.36	1.421	1.102	50.0
0.3	2.85	1.402	1.073	22.7	3.73	1.408	1.087	43.8	3.41	1.414	1.094	35.4
0.4	2.89	1.395	1.066	18.3	3.78	1.401	1.079	34.4	3.46	1.406	1.087	28.2
0.5	2.93	1.387	1.058	15.8	3.83	1.394	1.072	28.8	3.5	1.399	1.079	23.6
0.6	2.98	1.38	1.051	14.2	3.88	1.387	1.064	25.1	3.55	1.392	1.072	20.7
0.7	3.02	1.373	1.043	13.0	3.93	1.379	1.056	22.5	3.6	1.384	1.064	18.7
0.8	3.07	1.366	1.036	12.2	3.99	1.372	1.049	20.6	3.65	1.377	1.057	17.2
0.9	3.11	1.358	1.028	11.5	4.04	1.365	1.042	19.0	3.7	1.37	1.049	16.0
1	3.16	1.351	1.021	11.0	4.09	1.358	1.034	17.8	3.75	1.363	1.042	15.1
1.1	3.2	1.344	1.014	10.5	4.15	1.351	1.027	16.9	3.8	1.355	1.034	14.3

Table 2: The dipole moment of the complex (μ_{ab}), cis (μ_{cis}), dipole increment ($\Delta\mu$) and enthalpy changes (ΔH_B)

Decanol – amine	Dipole moment complex	$\Delta\mu$	ΔH_B
Propyl amine	2.87	0.70	8.51
Butyl amine	2.95	0.65	7.37
Pentyl amine	3.00	0.40	4.54

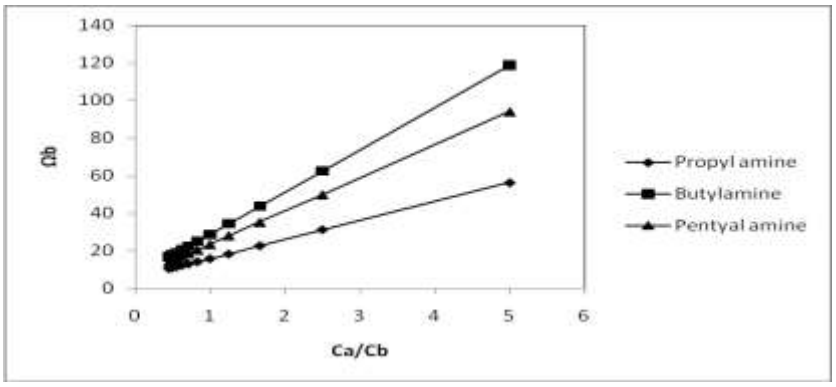

Fig 1: Plots of C_A/C_B with Ω_B of donor – acceptor complexes

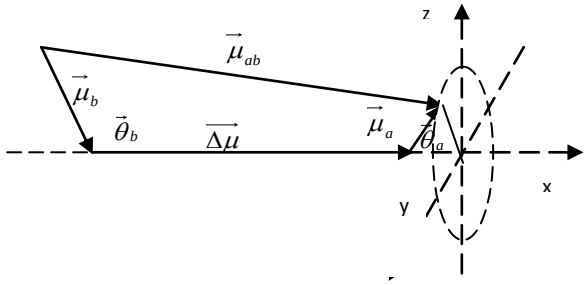

Fig.2 Dipole moment μ_a. μ_b and μ_{ab} and $\Delta\mu$

From the computed values of μ_{ab} and μ_b, the dipolar increments were obtained using the relation (8). From our results $\Delta\mu$ < 1.49D for all the systems, It is clear that there is no contribution arising due to ionic structures, as would involve a very high value for $\Delta\mu$ (>10D). It was shown that about 50% of the interaction moment observed experimentally arises due to the electronic interaction. Hence it may be concluded that only polarization interaction is the other important contributing factor to the enhancement of dipole moment of the complexes studied here. The excess dipole moments for all the systems studied are found to be small, which is in agreement with the values reported by many authors[11-15] for the mixtures of decanol with amines. The plot of (C_A/C_B) with Ω_B is straight line which indicates that the formation of a 1:1 complex. Hence it is concluded that the dipolar increment in all the systems is small due to the polarization effect only and it is not due to charge transfer or other phenomenon.

CONCLUSIONS

Dipolar increment in all the systems is $\Delta\mu$ >1D due to the polarization interactions only and it is not due to charge transfer and other phenomenon. The dipolar increment ($\Delta\mu$) values in the present investigations are $\Delta\mu$ <1D. It is less than 1D for all the systems as indicated in the table (2) our results may be interpretive the charge transfer interaction and that higher order complexes may be AB_2, A_2B, A_3B etc must prevail. Obviously the intra molecular hydrogen bond of alcohols is not broken by complication of amine. The dipole moment of the complex and dipolar increment is donor (decanol) and acceptor (Propyl amine > butyl amine > Pentyl amine. Dipole moment of decanol complex is increase in the order of Propyl amine > butyl amine > Pentyl amine.

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