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**Formation Constant and Free Energy Values of 1:1 Complexes of
1-Bromohexane, 1-Bromodecane, 1-Bromooctane with
O-Nitro Phenol In CS_2**

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ABSTRACT

Molecular interaction has been studied by FTIR spectroscopy of 1-bromodecane, 1-bromohexane, 1-bromooctane with o-nitro phenol in carbon disulphide (CS_2) at room temperature. Formation constant and free energy values has been calculated from absorbance of the FTIR spectrum. The result about elucidate proton donating ability of o- nitro phenol.

KEYWORDS: FT-IR; formation constant; free energy;

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1. INTRODUCTION:-

Molecular interaction is huge in the field of molecular biology, chemistry, physics and material design because of importance of these interactions¹, scholars have paying their attention to these interactions. The scholars carried out the task of studying the molecular interactions in binary and ternary solutions²⁻¹⁴ These measurements are used to identify the nature of complexes and to evaluate formation constants of the complex formed by AB and AB₂ complexes Quing Liu et al.¹⁵ investigated infrared spectroscopy studies in 20 different pure organic solvents through the solute-solvent. FTIR investigation of the properties of organic compounds is of great value in understanding the nature of molecular interaction between the molecules keeping both the industrial and scientific interests¹⁶. In present study is expected to provide better understanding of solute- solute interactions of 1-Bromodecane, 1-Bromohexane, 1-Bromooctane and O-nitro phenol in Carbon di sulphide using FTIR spectroscopic measurement. To elucidate the effect of medium and role of specific solute-solute interactions on the stability of 1:1 complex formation donor to acceptor

2. EXPERIMENTAL

2.1 MATERIAL

1-Bromodecane, 1-Bromohexane, 1-Bromooctane, O- Nitro phenol, with purity >99% (spectroscopic grade) were purchased from precession scientific company in Coimbatore and used without any further purification. AR grade Carbon disulphide. The physical parameters of all the chemicals used in this study were checked against their literature values.

2.2. RECORDING OF FT-IR SPECTRA

SHIMADZU series FT-IR spectrometer was used in the present study with double beam operation. The scanning range of frequency is 4000 – 400 cm⁻¹. The accuracy of measurement with this instrument is ± 0.01 cm⁻¹. The cell used in a variable path length NaCl end plates. The thickness of cell was maintained at 0.05cm for all measurements. Distilled samples of 1- Bromodecane, 1-Bromohexane, 1-Bromooctane and O-nitro phenol were used. The instrument scans the spectra 50 times in minute.

3. CALCULATION

3.1 FORMATION CONSTANT AND FREE ENERGY OF THE 1:1 COMPLEX

NASH METHOD

In this method at lower concentration of alcohol the influence of the higher order complexes on the absorption spectrum of the base is neglected. The concentration A, B and AB involved in the

interaction are assumed to be obeying Beer's law at a given frequency characteristic of the 1:1 complex.^{17,18} Here one assumes that the existence of a chemical equilibrium of the form.



Where B is a donor molecule and A is an acceptor. For purposes of orientation, one assumes that only A and AB absorb in the wavelength region of interest and for temporary mathematical convenience, it is taken that the concentration of A is to be very small relative to that of B. the equilibrium constant appropriate to reaction (1) is given in concentration units by

$$K_c = \frac{C_{ab}}{C_a C_b} \quad (2)$$

Where C_{ab} is the formation constant of the complex AB and C_a and C_b are the formal concentrations of A and B per centimeter of the path (A) is given by

$$A = \epsilon_a C_a + \epsilon_{ab} C_{ab} \quad (3)$$

Where ϵ_a and ϵ_{ab} are the molar absorptivities of species A and AB respectively. In the absence of complexing agent B, the total absorbance per centimeter is given by

$$A^0 = \epsilon_a C_a^0 \quad (4)$$

Where C_a^0 is the initial concentration of A. If one divides equation (3) by equation (4) and substitutes for C_{ab} from equation (2).

$$\frac{A}{A^0} = \frac{C_a}{C_a^0} \left[1 + \frac{\epsilon_{ab}}{\epsilon_a} k C_b \right] \quad (5)$$

By introducing conservation of species A

$$C_a^0 = C_a + C_{ab} \quad (6)$$

And invoking equation (2) on second time one finds

$$\frac{C_a}{C_a^0} = (k C_b + 1)^{-1} \quad (7)$$

When equation (7) is substituted into equation (5) which results

$$\frac{A}{A^0} = \left[1 + \frac{\epsilon_{ab}}{\epsilon_a} k C_b \right] / (1 + K C_b) \quad (8)$$

For convenience, let one defines

$$\frac{A}{A^0} = Z \quad (9)$$

$$\frac{k \epsilon_{ab}}{\epsilon_a} = \alpha \quad (10)$$

$$\text{and } C_b = \frac{1}{Y} \quad (11)$$

Then the equation (8) becomes

$$Z = \frac{(1 + \alpha/Y)}{(1 + k/Y)} \quad (12)$$

Equation (12) may be solved explicit for obtain

$$Y = \frac{(kz-\alpha)}{(1-Z)} \quad (13)$$

When now one defines

$$X = \frac{1}{(1-Z)} \quad (14)$$

And substitutes equation (14) into equation (13) a linear equation results

$$Y = X(k-\alpha)-k \quad (15)$$

The physical significance of the equation (15) is quite clear. When the reciprocal of the donor concentration is plotted against the reciprocal of one minus the absorbance ratio value and a straight line should result if 1:1 complex formation occurs. The intercept of this line is the negative of the formation constant and the slope is related to the molar absorptivity of the complex.

3.2 FREE ENERGY

The free energy.^{18,19} function provided the measure of chemical affinity under conditions of constant temperature and pressure energy changes in a chemical reaction can be defined as,

$$\Delta G = G_{(\text{product})} - G_{(\text{Reaction})} \quad (1)$$

Where $\Delta G=0$, there is no network obtainable, the system is in a stable of equilibrium. When ΔG is positive, network must be put in to the system to effect the reaction can proceed spontaneously with accomplishment of the network. The larger amount of this work that can be accomplished the further removed is the reaction from equilibrium. For this reason $-\Delta G$ as often been called the during force of the reaction.

Using the formation constant, obtained in the present investigation, the free energy (ΔG) were calculated for the systems under consideration with the relation.

$$\Delta G = -RT \ln K_{11} \quad (2)$$

Where R is gas constant.

The absolute temperature 298K and K_{11} is formation constant. The free energy of the bond formation obtained at 25°C for the system and values are given in table 5.9.

4. RESULT AND DISCUSSION

The FTIR spectral has been present for binary and ternary complexes in fig carbonyl bands in the range is (1215 - 1589). From ternary complexes proton acceptor fixed from 0.03 mol l⁻¹ proton donor (o-nitro phenol) concentration from 0.03-0.11mol l⁻¹ by changing concentration increases increasing concentration Fig (1-3). Absorbance values given in table (1-3). from this data reveal that the existence of 1:1 complex formation carbonyl group.

The association between donor (o- nitro phenol) A and acceptor (1-Bromodecane, 1-Bromohexane, 1-Bromooctane) B complex AB can be represented by the equilibrium

$A+B \leftrightarrow AB$, if only 1:1 complexes are present. The formation constant (K) for the 1:1 complex is calculated with the help of Nash(1960) method this interaction are assumed to be obeying Beer's law at a given characteristic frequency of the 1:1 complex. The physical significance of Y from Nash method. Reciprocal of donor concentration ($Y = [A]^{-1}$) is plotted against the reciprocal of one minus absorbance ratio ($A/\overset{\circ}{A}$) at X axis. It gives a straight line for 1:1 complex formation. The intercepts of plot are shown in plot (1-3).

Free energy has been calculated according to equation 2 with help of formation constant. Free energy values increase in the order 1-bromohexane < 1-bromooctane < 1-bromodecane. This change indicate that proton donating ability of proton donor varies of o-nitro phenol.

5. CONCLUSION:-

Results reveal that proton donation ability of O-nitro phenol proton accepting ability is linearly increasing. 1-Bromooctane greater than 1-Bromodecane but 1-Bromodecane greater than 1-Bromohexane.

6. REFERENCE:-

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Fig 1. FT-IR Spectra of o-nitro phenol with 1-Bromohexane in CS₂ system

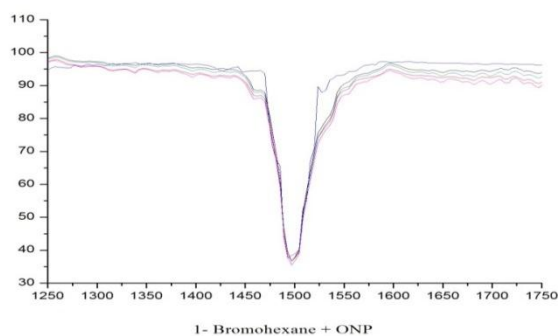


Fig 2. FT-IR Spectra of o-nitro phenol with 1-Bromooctane in CS₂ system

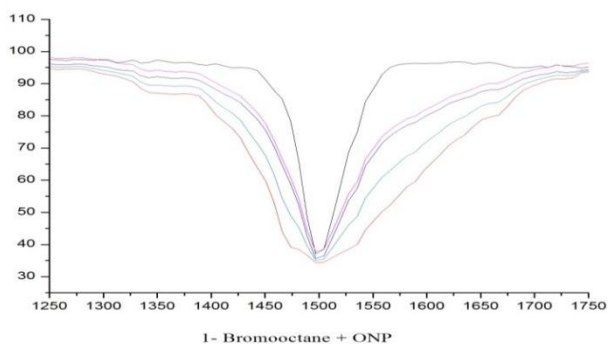


Fig 3. FT-IR Spectra of o-nitro phenol with 1-Bromodecane in CS₂ system

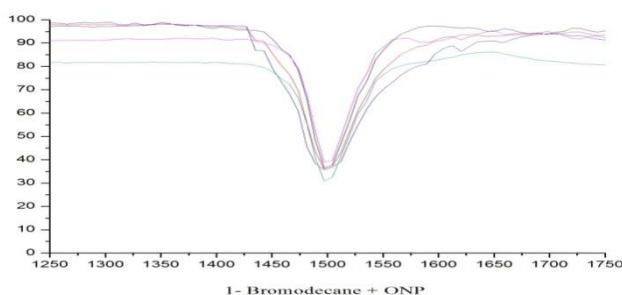


Table:- 1 o-nitro phenol with 1-Bromohexane in CS₂ system of C-N Stretching vibration and carbonyl absorbance.

Concentration	Free Band Absorbance	Inverse of the observed concentration	C-N Band Absorbance	$X = \frac{1}{1-\frac{A}{\lambda}}$
0.03	1.4621	33.4896	0.4109	0.7537
0.05	1.3617	19.9840	0.4064	0.7685
0.07	1.4302	14.2430	0.4106	0.7547
0.09	1.3177	11.1185	0.4130	0.7470
0.11	1.3030	9.0802	0.4212	0.7220

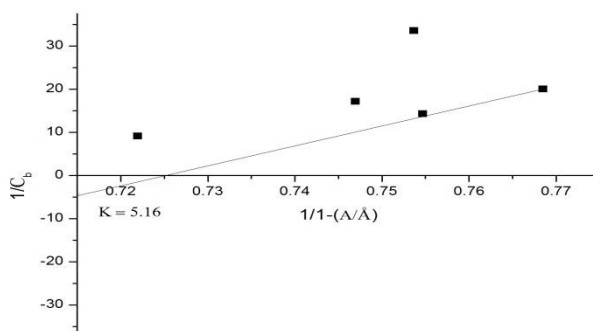
Table:- 2 o-nitro phenol with 1-Bromooctane in CS₂ system of C-N Stretching vibration and carbonyl absorbance.

Concentration	Free Band Absorbance	Inverse of the observed concentration	C-N Band Absorbance	$X = \frac{1}{1-\frac{A}{\lambda}}$
0.03	0.0278	33.2447	0.4083	0.7621
0.05	0.1097	19.9880	0.4370	0.6781
0.07	0.2410	14.2430	0.4247	0.7118
0.09	0.0308	11.0619	0.4382	0.6750
0.11	0.1053	9.0662	0.4134	0.7457

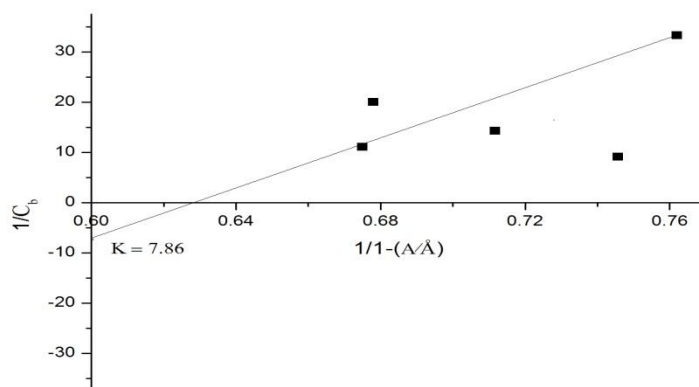
Table:- 3 o-nitro phenol with 1-Bromodecane in CS₂ system of C-N Stretching vibration and carbonyl absorbance.

Concentration	Free Band Absorbance	Inverse of the observed concentration	C- N Band Absorbance	$X = \frac{1}{1-\frac{A}{\lambda}}$
0.03	0.0278	32.7547	0.4225	0.7181
0.05	0.1097	19.9880	0.4132	0.7464
0.07	0.2410	14.2857	0.4162	0.7370
0.09	0.0358	11.234	0.4746	0.5926
0.11	0.1053	9.0801	0.4463	0.6580

Plot:- 1 o-nitro phenol with 1-Bromohexane system of C-N Stretching vibration and carbonyl absorbance.



Plot:- 2 o-nitro phenol with 1-Bromooctane in CS₂ system of C-N Stretching vibration and carbonyl absorbance.



Plot:- 3 o-nitro phenol with 1-Bromodecane in CS₂ system of C-N Stretching vibration and carbonyl absorbance.

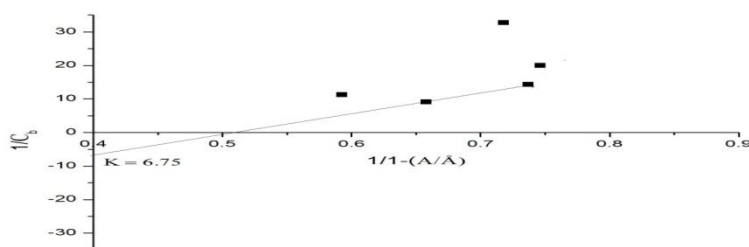


Table – 4 Formation constant and Free energy values of 1:1 complexes

System	Nash method	Free energy
	K ₁₁ lit mol ⁻¹	-ΔG ₁₁
O-nitro phenol+		
1-Bromohexane	5.16	4.07
1-Bromooctane	7.86	5.11
1-Bromodecane	6.75	4.73