

FT-IR Spectroscopic Studies of Donor-Acceptor (OH...N and OH...O) Complexes

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The complex formation of *p*-chlorophenol with amyl acetate, anisole and aniline in inert media of carbon tetrachloride making use of FT-IR measurements. The mixed solvent techniques have been used to study the frequency and intensity variations of the characteristic bands of inter molecular interacting systems for identifying and understanding the nature of the complexes. The formation constant values are obtained utilizing the Nash method.

Key Words: H-Bonding, FTIR, Formation constant, Free energy.

INTRODUCTION

The FT-IR studies of molecular interactions can give the valuable information regarding structure and properties of the molecules. Hydrogen bonding studies has attracted a great deal of interest as it gives a key to understanding the properties and structure of liquid phases¹⁻⁸. The types of specific molecular interactions which are distinguishable namely the hydrogen bonding and charge transfer interaction. Attempts to relate the frequency shifts to the bulk dielectric effects have been partly successful.

Bellamy and Williams⁹ proposed that the specific interactions with the solvents are responsible for the ways in which these spectral variation, frequency shifts, variation of band intensity and half width of vibrational bands. Caldow and Thomson^{10,11} calculated the individual contributions of dielectric and specific interaction effects. However no direct check on the validity of these results is available. Since the above conclusions based on indirect evidence, it would be worthwhile to determine directly the contribution of the various factors. Though this is very difficult, some progress can be made through a more systematic study of solute-solvent systems. In this case, the use of mixed solvents technique proposed by Bellamy and Hallan¹² can be used with considerable success. In addition, it is possible for one to vary the proton-donating or accepting properties of the given chromophore by which one can change the specific interaction properties in a systematic manner. Nash¹³ has made an extensive investigation on the specific interactions of the carbonyl stretching

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band using mixed solvent technique. They have also determined the formation of 1:1 complex. In the present investigation, a systematic study of the solvents on the characteristics carbonyl bands (C=O, C-O) of amyl acetate and anisole and NH₂ bands of aniline in mixtures of *p*-chloro phenol in carbon tetrachloride was taken in order to study the specific interaction and to determine the formation constant for 1:1 complexes using mixed solvent technique. The method of calculation essentially the same as given in detail by Nash¹³.

EXPERIMENTAL

Perkin-Elmer-1600 series FT-IR spectrometer equipped with sodium chloride optics was used in the present study with double beam operation. The scanning range of frequency was 4000-200 cm⁻¹ and it must be capable of measuring frequencies which was less than 10⁻⁴ cm⁻¹ and with high degree of accuracy. The sample cell was containing variable path length with sodium chloride end plates. The path length of the cell was maintained at 0.05 cm for all measurements, distilled pure samples of amyl acetate, anisole, aniline and *p*-chloro phenol were used. The temperature of the cell was maintained at 25 °C.

RESULTS AND DISCUSSION

In the case of *p*-chloro phenol + amyl acetate system, the carbonyl absorption (C=O) spectra of 0.06 mol/L solution of amyl acetate in carbon tetrachloride contains various amount of *p*-chlorophenol as shown in Table-1. In the absence of *p*-chloro phenol, characteristic carbonyl band has been observed at 1741 cm⁻¹. As more and more *p*-chlorophenol is added, the intensity of the original band decreases, while the half width slightly increases. This behaviour indicates the existence of 1:1 complex. As the concentration of *p*-chloro phenol increases, the free OH band intensities also increase.

TABLE-1
P-CHLORO PHENOL + AMYL ACETATE IN CARBON TETRACHLORIDE SYSTEM
C=O STRETCHING VIBRATIONAL AND HYDROXYL ABSORBANCES

Required concentration of <i>p</i> -chloro phenol (mol/L)	Free hydroxyl band absorbance	Inverse of the observed concentration 1/C _b	Carbonyl (1741 cm ⁻¹) band absorbance	$\frac{1}{1 - \frac{a}{a_0}}$
0.00	—	—	0.29330	—
0.02	0.03792	250.00	0.09855	1.508
0.04	0.04445	200.00	0.08980	1.441
0.06	0.05740	142.80	0.08375	1.399
0.08	0.06221	125.00	0.07592	1.349
0.10	0.07480	111.10	0.05250	1.218
0.12	0.09012	90.90	0.05150	1.214
0.14	0.11020	66.66	0.04820	1.196

In the case of *p*-chloro phenol + anisole system, the carbonyl absorption (C-O) band of 0.06 mol/L solution of anisole in carbon tetrachloride contains various amount of *p*-chloro phenol as shown in Table-2. In the absence of *p*-chloro phenol, characteristic carbonyl band was observed at 1247 cm^{-1} . As more and more *p*-chloro phenol is added, the intensity of the original band decreases, while the half width slightly increases. This behaviour indicates the existence of 1:1 complex. As the concentration of *p*-chloro phenol increases the free OH band intensities also increases.

TABLE-2
p-CHLORO PHENOL + ANISOLE IN CARBON TETRACHLORIDE SYSTEM C=O
 STRETCHING VIBRATIONAL AND HYDROXYL ABSORBANCE'S

Required concentration of <i>p</i> -chloro phenol (mol/L)	Free hydroxyl band absorbance	Inverse of the observed concentration $1/C_b$	Carbonyl (1247 cm^{-1}) band absorbance	$\frac{1}{1 - \frac{a}{a_0}}$
0.00	–	–	0.35077	–
0.02	0.02158	333.33	0.16480	1.8861
0.04	0.03292	250.50	0.15975	1.8305
0.06	0.04052	200.00	0.13082	1.5947
0.08	0.05185	166.60	0.10415	1.4223
0.10	0.07250	100.00	0.09647	1.3793
0.12	0.12921	58.82	0.08912	1.3406
0.15	0.13007	55.55	1.29730	1.2973

In the case of *p*-chloro phenol + aniline system, the vibrational N-H band spectrum of 0.1 mol/L solution of aniline in carbon tetrachloride contains various amount of *p*-chloro phenol. In the absence of *p*-chloro phenol, the characteristic N-H band observed at 3475 cm^{-1} . As more and more *p*-chloro phenol is added, the intensity of the original band decreases, while the half width slightly increases. This behaviour indicates the existence of 1:1 complex. As the concentration of *p*-chloro phenol increase the free OH band intensities also increases.

The intensity changes of carbonyl (C=O, C-O) and amine (NH_2) band can be used for determination of formation constant of the complexes. A factor which is directly connected with the complex is the formation constant which represents the energy of interaction. These constant gives an idea about the quantitative characteristic of bond formation, it is possible to predict accurately the position and nature of the spectra of the different species, *viz.*, the energy changed that is involved in the reaction. It is evident that this energy change depends upon the ability of the molecules to form the bond with a given proton donor or acceptor, this determining the energy of interaction. Hence the formation constants of the complexes taken for study are determined, using Nash method¹³. The reciprocal of the donor concentration is plotted against the reciprocal of one minus the absorbance ratio (acceptor) value a gives straight line should result 1:1 complex formation occurs. The intercept of this line is the negative of the formation constant and slope is related to the molar absorptivity

of the complex. The calculations have been carried out for the systems utilizing the spectral details of complexes carbonyl and N-H band. The required data regarding intensities of the band characteristics of 1:1 complex are given in Tables 1-3.

TABLE-3
p-CHLORO PHENOL + ANILINE IN CARBON TETRACHLORIDE SYSTEM -NH₂
STRETCHING VIBRATIONAL AND HYDROXYL ABSORBANCE

Required concentration of <i>p</i> -chloro phenol (mol/L)	Free hydroxyl band absorbance	Inverse of the observed concentration 1/C _b	Carbonyl (3475 cm ⁻¹) band absorbance	$\frac{1}{1 - \frac{a}{a_0}}$
0.00	–	–	0.35077	–
0.01	0.05478	166.60	0.08010	5.253
0.02	0.08059	100.00	0.07990	5.198
0.03	0.09030	83.30	0.07061	3.500
0.04	0.09959	76.92	0.06076	2.591
0.05	0.10080	71.42	0.05590	2.290
0.08	0.14055	52.63	0.04185	1.730
0.10	0.14660	40.28	0.03025	1.440

Fig. 1 gives the values of formation constants were found for all three systems and those values are given in Table-4. Using the formation constants, calculated the free energy.

$$\Delta G = RT \ln K$$

where R is gas constant, T is absolute temperature at 25 °C, K is formation constant. Formation constants (K) and free energy value of three systems are given in Table-4.

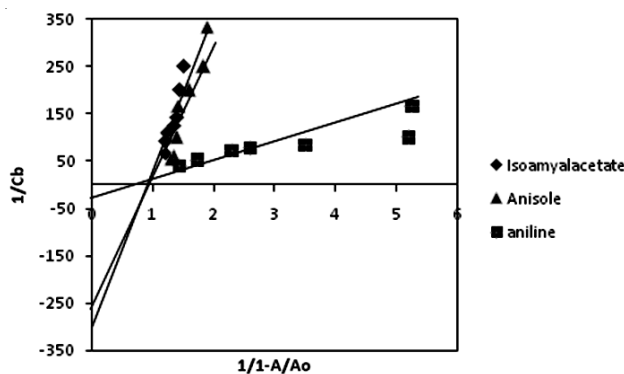


Fig. 1. Plots of $1/1 - a/a_0$ versus $1/C_b$

Conclusion

The Nash methods indicate the presence of 1:1 complexes in three systems. The formation constant values indicate that the system containing *p*-chloro phenol

TABLE-4
FORMATION CONSTANT AND EXCESS ENERGY OF VARIOUS DONORS-
ACCEPTOR IN CARBON TETRACHLORIDE SYSTEMS

<i>p</i> -Chloro phenol + acceptor in carbon tetrachloride system	Formation constant (K) (L/mol)	Free energy (-ΔG) (K cal/mol/deg)
Amyl acetate	260	3.372027
Anisole	250	3.347981
Aniline	26	1.984248

as donor, the interacting ability of the acceptor in the order of amyl acetate > anisole > aniline >. Extensive work on mixed solvent systems seems promising the study and in the development of generalized concept of molecular interactions.

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