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FTIR studies of hydrogen bonding interaction between the hydroxyl and carbonyl liquids

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ABSTRACT

The intermolecular hydrogen bonding interaction between p-chlorophenol and amyl acetate has been investigated by FT-IR spectroscopy. This article mainly reports the results of p-chlorophenol with carbon tetrachloride solution and in the presence of amyl acetate. The spectroscopic characteristics of OH….O complexes are specified. Also, the formation constant for 1:1 and 1:2 complexes at 25^{o} C were evaluated by the methods of Nash, Whetsel-Kagaraise and Becker. The free energy of 1:1 and 1:2 complexes were obtained from the formation constant values. The formation constant and free energy values indicate that existence of 1:1 and 1:2 complexes.

Key words: p- chlorophenol, Amyl acetate, Formation constant, Free energy, Dipole moment derivatives.

INTRODUCTION

Hydrogen bonding appears in a great variety of solution, being responsible, among others, for conformational properties, molecular packing in crystals, as well as for biological activity in many physiologically important systems. We have been interested in probing into the nature of intermolecular hydrogen bonding systems using FT-IR spectroscopy [1].

Amyl acetate [2] used as a flavoring agent in paints and liquor solvents, and in the preparation of penicillin also called banana oil. p-chlorophenol [2] is used as an intermediate for synthesis of insecticide, herbicides, preservative, antisepses, and disinfectants, dyes, aromatic compounds and other organic chemicals, solvent for extracting sulfur and nitrogen compound from coal.

Hydrogen bonding [3] is important because of the effects they have on the properties of compounds. If hydrogen boding is possible between solute-solvent, solute-(solute-solvent) mixed solvent, this property increase solubility and other results in large or even in infinite solubility. There is evidence that the double and triple bond aromatic rings, and cyclopropane rings can form hydrogen bonds with polar functional group. But these bonds are very weak.

Hydrogen bonding [4-9] is formed between functional group and an atom or group of atoms in the same or different molecules. It can exist in the form of solid and liquid phase or in solutions. Hydrogen bonding can be detected in many ways but the most important way is by the infrared spectroscopy. In many cases, there is some functional group are free and some are hydrogen bonded. In such cases two IR bands appear. IR spectroscopy can also distinguish between inter- and intra- molecular hydrogen bonding are investigated by an increase in concentration.

Inter molecular hydrogen bonding can be affected by the dilution or temperature while intra molecular hydrogen bonds are unaffected**.** In the present work identify the solute – solvent interactions of p-chlorophenol with amyl acetate by the FT-IR measurements.

MATERIALS AND METHODS

Out line

FT-IR spectroscopic investigations were carried out for a binary (p-chlorophenol+Ccl_4) and ternary (p-chlorophenol+amylacetate+Ccl_4) liquids at 25^o C.

Infrared Spectroscopy

Hydrogen bonding has a considerable influence on the stretching vibrational frequency of OH in p-chlorophenol and the IR spectroscopic measurements were carried out in that range. Temperature changes or dilution of p-chlorophenol significantly change the spectrum due to changes in association between the carbonyl and hydroxyl liquids. IR spectroscopy in this range can be effectively used to given quantitative interpretation on the association of p-chlorophenol.

In IR spectroscopic investigation the attenuation of the infrared radiation passes through the sample is measured. The intensities of the incoming radiation I_o and of the transmitted radiation after passing through the sample I are measured as a function of the wave number $(\bar{\nu})$ of the radiation. The ratio of I to I_o give the transmittance T. Using reflection and scattering are neglected, so the transmittance T is directly related to the absorbance A;

$$A'(\bar{\nu}) = -\log_{10} T(\bar{\nu}) = -\log_{10} \frac{I(\bar{\nu})}{I_o(\bar{\nu})} \qquad \ldots(1)$$

The wave number $(\bar{\nu})$ is the reciprocal of the wavelength λ. It is proportional to the frequency.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{C} \qquad \ldots(2)$$

Absorption bands in IR spectra are mainly caused by changes between different vibrational states of bonds in molecules. The frequency range, where a given bond absorbs, is influenced by the strength of the bond and masses which take part in the bond. The absorbance of a band is measure of the number of molecules which undergo a change in their vibrational states upon IR radiation. The number of molecules affected increase with increasing path length as well as increasing concentration of the absorbing component dependent is described by Beer's – Lamberts law,

$$A'(\bar{\nu}) = \alpha'(\bar{\nu}) Cd \qquad \ldots(3)$$

α' is the absorbance coefficient, which is usually by calibration. When both the sample thickness d and the absorbance α' are known, the concentration of the absorbing component is determined from experimental absorbance data.

When the integrated form of Beer's – Lamberts law is used, the corresponding band absorbance A has to be determined from integration over the range of the band.

$$A = \int_{\nu_1}^{\nu_2} A'(\bar{\nu})\, d\nu = \left[\int_{\nu_1}^{\nu_2} \alpha'(\bar{\nu})\, d\nu \right] cd \qquad \ldots(4)$$

α' is the integrated band absorbance coefficient.

The quantitative evaluation of bands is difficult when these bands are caused by the components, which are not available as pure substances. In such cases the absorbance coefficient α' cannot be measured by then calibration. That difficulty can be overcome by determining the absorbance coefficient α' from spectroscopic data at different stoichiometric concentration of the absorbing components. Details can be given below.

Equipment and Operation

The FT-IR spectroscopic experiments carried out with Nicolet Avatar -360 series with a resolution 2 cm^{-1}. All spectra were recorded with a minimum of 1250 scans. The sample cell was a special design, where the optical unit was embedded in a copper block with a jacket of thermostating for the liquid. The temperature of the cell was maintained at 25^o C. The optical unit was equipped with NaCl windows.

The distance between the windows and the sample thickness'd' was varied using PIFE spaces, but cell thickness was constant throughout all measurements. Accurate measurements of the sample thickness are needed for the evaluation of spectroscopic results.

The path length of the cell was determined the interference pattern of the IR radiation, when the sample thickness was below 1mm. For larger values, the thickness of the spacers was measured with a slide gauge. The probe component of the spectrometer was purged with dried air to avoid absorbance of radiation by humidity. Because, the spectrometer was single beam apparatus, the so called background I_o before the intensity I of radiation transmitted by the sample was measured.

The spectrum of the p-chlorophenol–carbon tetrachloride mixtures includes, in addition to the bands of p-chlorophenol, which are of interest here, bands which are due to the solvent. The absorbance $A'_{A,mix}$ of the p-chlorophenol and the $A'_{S,mix}$ of the solvent.

$$A'_{mix} = A'_{A,mix} + A'_{S,mix} \quad ...(5)$$

The absorbance of the solvent $A'_{S,mix}$ was calculated from the absorbance of the pure solvent $A'_{S,}$ taking into account the dilution of the solvent in the mixture.

$$A'_{A,mix} = A'_{mix} - \frac{C_{s,mix}}{C_{s,pure}} A'_{S,pure} \quad \ldots(6)$$

The molarity of the sample C is calculated from the property of the sample and densities of the pure liquids, neglecting any excess volume. The error introduced by that assumption is negligible with decreasing the p-chlorophenol concentration. The ratio $\frac{C_{s,mix}}{C_{s,pure}}$ approaches unity and

$$\lim_{C \to 0} A'_{A,mix} = A'_{mix} - A'_{S,pure} = -\log_{10} \frac{I_{mix}}{I_{pure}} \quad \ldots(7)$$

Equation (7) shows that at low p-chlorophenol concentration, the spectrum of the sample p- chlorophenol obtained directly through collecting intensities of the radiation transmitted by the pure solvent and by the mixture sample, In that case, the background spectrum not required. From the FT-IR spectra, evaluate the various spectral parameter details given below.

Formation constant

The formation constant values determined from the following methods following methods are used for determination of formation constant of 1:1 complexes

Nash Method (N)

Nash Method [10] used to find equilibrium constant for the 1:1 complex using following relation

$$K_{11} = \frac{[AB]}{[A][B]} \quad \ldots(8)$$

Where [AB] is the concentration of the 1:1 complex [A] and [B] are the initial concentration of the donor and acceptor respectively.

Whetsel and Kagaraise Method

Whetsel and Kagaraise Method [11] utilize to determine the formation constant for the 1:1 and 1:2 complexes, Let us consider the systems in which the equilibrium exists

$$A + B \Leftrightarrow AB \quad \ldots(9)$$

$$AB + B \Leftrightarrow AB_2 \quad ...(10)$$

The equilibrium constant 1:1 and 1:2 can be defined as the following relation

$$K_{11} = \frac{[AB]}{[A][B]} \quad ...(11)$$

$$K_{12}=\frac{[AB_2]}{[AB][B]} \quad \ldots(12)$$

Where $[AB]$ and $[AB_2]$ refer to the concentrations of 1:1 and 1:2 complexes. Widom et al., have shown that

$$[AB]=\frac{p}{(1+2k_{12}b)} \quad \ldots(13)$$

and

$$[AB_2]=\frac{(p\text{-}AB)}{2} \quad \ldots(14)$$

p and b can be determined from the absorbance of hydroxyl group of proton donor by the method of Widom et al [12]. $[AB]$ and $[AB_2]$ can be calculated for the various assumed value of $K_{12.}$ for individual solutions from equations (13) and (14).

Becker's Method

Becker's Method [13] also used to calculate the equilibrium of p-chlorophenol – amyl acetate by the hydrogen bond formation can be represented as

$$A\text{-}H+B \Leftrightarrow A\text{-}H\ldots..B \quad \ldots(15)$$

Where A-H is p-chlorophenol monomer B is oxygen electron donor of amyl acetate and A-H…B is hydrogen bonded complex. In the case of A-H is p-chlorophenol monomer, B is an O – electron donor of amyl acetate and A-H…B is hydrogen bonded complex. In the case where electron donor is present in excess over p-chlorophenol concentration,

$$K_{11}=\frac{C_m^o\text{-}C_m}{C_m C_A^o} \quad \ldots(16)$$

Using Becker's[14] procedure, the formation constant was determined from the monomer band absorbency

$$K_{11}=\frac{A^o\text{-}A}{ACA^o} \quad \ldots(17)$$

Where A^o is the monomer absorbency for carbon tetrachloride solution containing C_m^o moldm^{-3} of p-chlorophenol and A is the absorbency of the same band for the solution with p-chlorophenol C_m^o and acceptor concentration C_A^o.

Free energy of 1:1 and 1:2 complexes

The free energy [15] changes find using the following relation

$$\Delta G_{11}=-RT \ln K_{11} \quad \ldots(18)$$

and

$$\Delta G_{12}=-RT \ln K_{12} \quad \ldots(19)$$

where R, T and K represent the universal gas constant respectively.

Integrated intensity and dipole moment derivatives

The integrated intensity [16] of the complexes C=O and OH were calculated by using equation

$$A=\left(\frac{\pi}{2}\right)(\text{half width})\,\alpha_{max} \quad \ldots(20)$$

α_{max} is the absorption coefficient at the band maximum . The exact calculation of the band area is very tedious for some cases, impossible to owing to free and bonded bands. The method mentioned above suitable for present

investigation. The integrated intensity values and assuming that the vibration is pure stretching mode, the change in the bond moment on stretching mode was calculated from the relation [17, 18]

$$A=10^{-3}X\left[\frac{N_o\pi}{3mc^2}\right]\left[\frac{d\mu}{dr}\right]^2 \qquad \ldots(21)$$

A_s represents the integrated intensity involved in the reaction. The rate of change of dipole moments with respect to the bond distance was calculated for amyl acetate with p-chlorophenol. The values of the rate of change of dipole moment with length of the complexes and free C=O are given in table 3.

RESULTS AND DISCUSSION

The fig.1 shows the FT-IR spectra of p-chlorophenol in carbon tetrachloride at 25^oC between 3000 and 3800cm$^{-1,}$ It is in the range of the hydroxyl stretching vibration, these spectra strongly influenced by H-bonding. The OH band of p-chlorophenol molecules in associated species absorbs at lower wave numbers as hydrogen bonding leads to a weakening of the OH band.

In highly diluted solutions, the monomer form of frequency 3610cm^{-1} of p-chlorophenol is predominant. At higher p-chlorophenol concentrations additional bands of frequency 3400 cm^{-1} are observed which are due to H-bonded p-chlorophenol molecules. The increase of the p-chlorophenol concentration the oligomer band becomes predominant and intensity of the free –OH band increase. No frequency shift is observed this indicate there is no solute – solvent interaction.

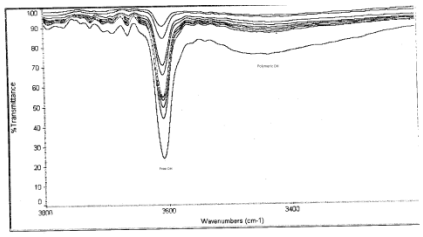

Fig.1 p-chlorophenol + carbon tetrachloride system (Hydroxyl region 3800-3200cm^{-1})

The quantitative interpretation of the IR spectroscopic data of p-chlorophenol solution studies on the accurate evaluation of the signal of the p-chlorophenol monomers. The requirement limits the range of stoichiometric p-chlorophenol concentration which are studied roughly to about 0.03 < 0.5 M. At lower p-chlorophenol concentration, the signal of the monomer is too small, at higher p-chlorophenol concentration; the overlap with oligomer band becomes too strong.

The fig.2 shows the FT-IR spectra of p-chlorophenol with amyl acetate in carbon tetrachloride at 25^oC between 3000 and 3800cm$^{-1,}$ i.e. in the range of the hydroxyl stretching vibration and 1500 and 1750 cm^{-1}. i.e. in the range of the carbonyl stretching vibration. The carbonyl absorption (C=O) spectra of 0.06 mole/liter solution of amyl acetate in carbon tetrachloride contains various amount of p-chlorophenol.

In the absence of p-chlorophenol, 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 and new band appear at the frequency of 1711. This behavior indicates the existence of 1:1 and 1:2 complexes.

As the concentration of p-chlorophenol increases, the free OH band intensities also increase. The formation constant were evaluated the following methods using FT-IR measurements. Details described below.

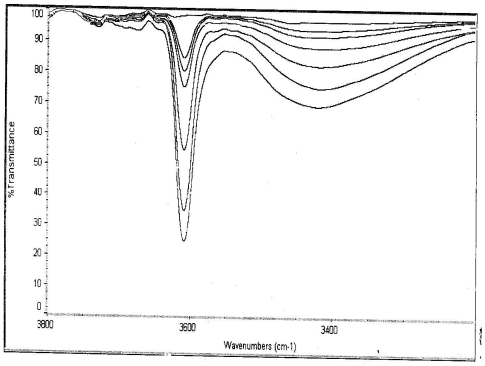

Fig.2 p-chlorophenol+ amyl acetate + carbon tetrachloride system (Hydroxyl region 3800-3200cm^{-1})

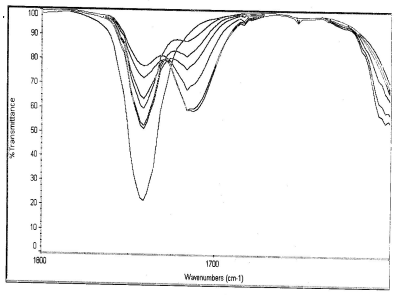

Fig.3 p-chlorophenol + amyl acetate + carbon tetrachloride system (carbonyl region 1800-1600cm^{-1})

The reciprocal of the donor concentration is plotted (Fig. 4) 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 hydroxyl band. The required data regarding intensities of the band characteristics of 1:1 complex are given in table 1.

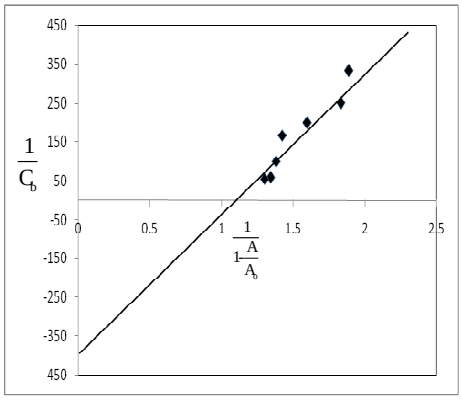

Fig. 4 Plots of 1/1-(A/A$_o$) versus 1/C$_b$

The values [A] could be obtained by the sum of [AB] and [AB_2] and from the initial concentration of A. Then the K_{11} , which could be obtained from the equation (11), should be plotted against the concentration of proton donor. This procedure should be repeated with different assumed values of K_{12}.

The values of K_{12} which correspond to the line of zero slope is considered to be best value and the intercept of this line gives the value of K_{11}.(Fig. 5) The formation constant expressed lit mol^{-1}.

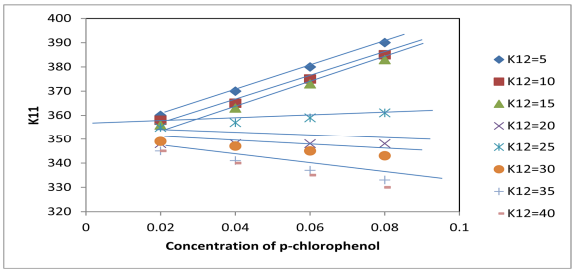

Fig. 5 Plots of Concentration of p-chlorophenol versus K_{11}

Spectroscopic characteristics for the monomer (free-OH) band of p-chlorophenol are given in table 1 Vibrational frequency of OH and half width of the band respectively. ε and B^o is the molar absorption co-efficient and the integrated absorption coefficient.

The spectroscopic parameters for OH…O hydrogen bonded complexes obtained in IR and equilibrium constant are reported in table .1. The hydrogen bonding between p-chlorophenol and amyl acetate can be represented by OH….O.

Table.1 Spectroscopic parameters for OH…..O hydrogen bonded complexes in IR

Donor	Acceptor	Monomer Frequency cm^{-1}	Chromophoric group cm^{-1}	$\Delta\nu$ cm^{-1}	$\nu_{1/2}$ cm^{-1}	ε cm^2mol^{-1}
p-chlorophenol	-	3610 3408	Free-OH Polymeric –OH	212	12	120
p-chlorophenol	amyl acetate	3610 3408 1741	Free-OH Polymeric –OH Carbonyl-C=O	225 30	22 18	112 154

Table 2 presents the formation constant and free energy change values of the hydrogen bonded complexes. The formation of 1:1 and 1:2 complexes of p-chlorophenol and amyl acetate in carbon tetrachloride confirmed.

Table.2 Equilibrium constant K (lit mol^{-1}) and free energy $(-\Delta G)$ $cal/mol^{-1}deg^{-1}$ of 1:1 and 1:2 complexes of p-chlorophenol and amyl acetate systems

Equilibrium constant K (lit mol^{-1})				free energy $(-\Delta G)$ $cal/mol^{-1}deg^{-1}$			
1:1 complex			1:2 complex	1:1 complex			1:2 complex
K (lit mol^{-1})			K (lit mol^{-1})	$(-\Delta G)$			$(-\Delta G)$
N	B	W- K	W-K	N	B	W- K	W- K
350	347	348	40	7.46	7.39	7.41	0.85

The mean dipole moment derivatives of the characteristic carbonyl band of 1:1 complexes are reported for OH…..O complexes. The dipole moment derivatives for the OH bands naturally are higher. However, it is not possible to calculate the exact values from the OH band intensities, because of the overlapping bands arising from self-association effects and two other symmetrical bands resulting from the H-bridge isomerism. However the degree of the interaction moment along the OH…O bond can be estimated from $\frac{d\mu}{dr}$.

The integrated intensity and change in dipole moment for the various concentrations of amyl acetate complex systems referred to the values of pure carbonyl stretching in carbon tetrachloride as the standard are given in table 3.

The concentration of p-chlorophenol involved in the complex formation was obtained from the peak intensities of the free C=O and in various concentrations of p-chlorophenol in carbon tetrachloride.

Two bands appear which increased due to higher concentration, and bands get altered. It is possible to isolate the 1:1 and 1:2 complex in the cases. This means that no frequency shift occurs in these complexes. Such a result may be attributed to the accumulated effects such as steric factors, resonance, stabilization etc., which determine the electron density around proton accepting atom.

The integrated intensity and change in dipole moment of the C=O bond increase due to the bond formation. This results can be explained satisfactorily on the basis of polarization of the base on hydrogen bond formation and on the later model proposed by group is linked directly to the proton accepting atom, i.e. oxygen, the unshared electron pair on the acceptor atom takes part in the conjugation which reduce the electron density of acceptor atom. This may result in the weakening of the hydrogen bonding ability in amyl acetate.

The lower value for the C=O frequency in amyl acetate and high H-bonding ability can be present in the oxygen atom. This may result in the weakening of the hydrogen bonding ability amyl-acetate, The Value of $\frac{d\mu}{dr}$ for 1:1 complexes of the carbonyl and hydroxyl system studied here various from $1.4461X10^{-10}$ to $2.0369 X 10^{-10.}$ esu appearing in table 3.

Table 3 The dipole moment derivatives of various concentrations of p-chlorophenol with amyl acetate (c=o Vibrations of amyl acetate (1:1 complex)

Concentration of p-chlorophenol mol/lit	A_s X 10^7 $cm^2mol^{-1}sec^{-1}$	$\frac{d\mu}{dr}$ X 10^{10} esu cm^{-1}	$\frac{\left[\frac{d\mu}{dr}\right]}{\left[\frac{d\mu}{dr}\right]_{ccl_4}}$	$\frac{A_s}{[A_s]_{ccl_4}}$
0.00	2.0912	1.4461	1	1
0.02	2.2902	1.5133	1.0951	1.0464
0.04	2.6371	1.6239	1.2610	1.1229
0.06	2.9395	1.7145	1.4056	1.1855
0.08	3.2419	1.8005	1.5502	1.2450
0.10	3.5443	1.8826	1.6948	1.3018
0.12	3.8467	1.9612	1.8394	1.3562
0.14	4.1491	2.0369	1.9840	1.4085

Its one of the oxygen orbital is almost collinear with the OH…O. It will be in a most favorable position for maximum interaction between the OH bond and lone pair of electrons forming the atomic dipole minimized distances of 1.20A^o and 1.04 A^o for true and H-bonded on the maximum displacement of 0.025A^O along the O…O distance , one obtained as $\Delta\mu$ of about 0.03 to 0.15D owing to the polarization of the C=O. A similar or slightly higher value would also be expected for the induced moment for the OH bond. So a total $\Delta\mu$ about 0.25 to 3 D may explain by considering the vibration of the lone pair of the electrons together with the vibrations of the OH bond.

CONCLUSION

The FT-IR spectra were recorded for the p-chlorphenol with carbon tetrachloride, p-chlorophenol with amyl acetate in carbon tetrachloride systems. From these measurements, identify the nature of interactions. No frequency shift is observed in the p-chlorophenol in carbon tetrachloride. This at indicates there is no solute – solvent interaction. p-chlorophenol concentration is increases and amyl acetate keeping constant, intensity of the carbonyl band decreases and hydroxyl band increases also additional band is developed. This behavior indicates that there may be the 1:1 and 1:2 complexes formed. Determine the equilibrium constant of p-chlorophenol-amyl acetate complexes; from these values evaluate the free energy. These values confirmed that the existence of 1: 1and 1:2 complexes also determine the dipole moment derivatives. The increasing concentration of p-chlorophenol the dipole moment derivative also increases. These values indicate the interaction mainly due to the polarization only no charge transfer or other effects.

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