

**CHAPTER-IV**

**SUMMARY**

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The concept of hydrogen bond has been found to be of great utility in understanding the structural characteristics of many chemical compounds and the life governing processes. In fact man himself is fabricated of H-bonding substances. We feed, clothe and house ourselves by H-bonding materials.

The importance of hydrogen bonding has been stressed in the introduction part of this dissertation. The review of the scientific literature is also presented in introduction.

The work described concerns with the nature of the investigation carried out in present work (Chapter II). The system studied were :

- a) Pure solvents-chloroform, acetonitrile and acetone.
- b) Pure solids-P-nitrophenol, P-toluidine, P-anisidine (by KBr pellets technique).
- c) P-nitrophenol, aniline, P-toluidine and P-anisidine in solution phase at different concentrations in above mentioned three solvents.
- d) [P-nitrophenol+aniline] (1:1) adduct-at different concentrations in three solvents.

- e) [P-nitrophenol+P-toluidine] (1:1) adduct at different concentrations in three solvents.
- f) [P-nitrophenol+P-anisidine] (1:1) adduct at different concentrations in three solvents.

The solvents chloroform, acetonitrile and acetone were deliberately chosen, as these have different dielectric constants. Amines used for the complexation with P-nitrophenol were the aniline and its derivatives. The proton donor i.e. P-nitrophenol was selected because it is known to possess intermolecular hydrogen bonding in pure state and has little tendency to have any possibility of intramolecular hydrogen bonding.

The experiments were carried out by taking standard samples and IR spectrographs were obtained. The detailed use is mentioned in this chapter. The IR spectra of nitrophenols and various amines were obtained and the results were presented in experimental section.

The results obtained for the various systems are incorporated in result section of chapter III. From the comparative study of -OH stretching and -NH stretching vibration frequencies in solids and their solutions in different solvents, it has been observed that the -OH

stretching vibration of para-nitrophenol in solid phase appears at  $3360\text{ cm}^{-1}$ , in 0.4 M solution of it in chloroform at  $3400\text{ cm}^{-1}$ , in 0.4M solution in acetonitrile at  $3320\text{ cm}^{-1}$  and in 0.4M solution in acetone at  $3200\text{ cm}^{-1}$ . It clearly indicates that in solid phase there is intermolecular association and the -OH stretching frequency goes on decreasing in solvents with increasing dielectric constant. It is observed that there is no considerable change in -NH stretching frequencies in solid phase and solution phase in different solvents in case of P-toluidine and P-anisidine; and also in case of aniline solutions in different solvents.

The verification of Beer's and Lambert's law is tested by studying the variation of absorbance as a function of concentration in case of P-anisidine solutions. ~~were plotted~~. All the plots of previously mentioned sample solutions were found to be straight lines passing through the origine. It indicated the validity of Beer's and Lambert's law. Although it was expected that in case of associative equilibria like in P-nitrophenol and acetone, Beer's and Lambert's law show deviations but in studied concentration range it obeys approximately.

The extinction coefficients of above mentioned samples were also calculated and it has been concluded that the extinction coefficient values of P-nitrophenol, aniline, P-toluidine and P-anisidine solution prepared in solvent acetonitrile always greater than that prepared in chloroform. It might be due to higher dielectric constant of acetonitrile than chloroform.

The IR spectra of complexes formed by combination of (1:1) mixture of P-nitrophenol (0.4M) and different amines (0.4M) (e.g. aniline, P-toluidine and P-anisidine) in three solvents (e.g. chloroform, acetonitrile and acetone) were obtained and after the scrutiny, the following observations emerged :

- a) In the complex formed between P-nitrophenol and aniline in chloroform solvent the disappearance of -OH stretching and -NH stretching peak indicates the presence of hydrogen bond between P-nitrophenol and aniline. The appearance of new band at  $3200\text{ cm}^{-1}$  confirms the presence of vibration of hydrogen bonded species.

In case of same complex in solvents acetonitrile and acetone no new band appeared because of hydrogen bonding. Thus tentatively it can be explained in terms of equilibria, either solute-solvent or acid-base which

are facilitated by the polar nature and comparatively higher dielectric constants of the solvents used.

- b) In the complex formed between P-nitrophenol and P-toluidine in solvent chloroform, the disappearance of -NH stretching peak suggested hydrogen bonding between the two. However very small effect on free -OH still exist.

In case of the same complex in solvents like acetonitrile and acetone there is hydrogen bond formation but the vibrations of the corresponding hydrogen bond are very weak. This further indicated a stronger bond having comparatively higher equilibrium constant. This in turn can be explained in terms of adduct (ionic) formation via acid-base equilibria.

- c) In the complex formed between P-nitrophenol and P-anisidine; in solvents chloroform, acetonitrile and acetone; free -OH exist as mentioned in point (b). The substitution of  $-OCH_3$  in place of  $-CH_3$  does not influence the stretching characteristics of the hydrogen bonded species but only the -NH bending vibrations are shifted to higher value. On the basis of inductive effect the  $-OCH_3$  is expected to weaken the hydrogen bond tendency however because of the para position of  $-OCH_3$  group the desired effect could not be observed. All these observations are neatly accounted in discussion part of this dissertation.

Thus, the present infrared spectroscopic investigations has enabled to gain useful information about hydrogen bonding in liquids, solution phase containing acidic and basic components and their complexes.

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