# RED AND BLUE SHIFTED H-BONDS IN LIQUID MIXTURES: FTIR STUDIES, QUANTUM CHEMICAL CALCULATIONS AND DIELECTRIC STUDIES

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## SYNOPSIS

Molecular interactions are the attractive or repulsive forces between molecules in which chemical bonds are the connections between atoms in a molecule. The interaction includes both strong intramolecular interactions (covalent and ionic bonds) and weak intermolecular forces (dipole-dipole interactions, the London dispersion forces, and hydrogen bonding). Intramolecular forces are the forces that hold atoms together within *a* molecule. Intermolecular forces are forces that exist between molecules. Intermolecular forces are mainly responsible for the physical characteristics of the substance. The particles making up solids and liquids are held together by intermolecular forces**.**

The hydrogen bond, an important intermolecular interactions, is represented as X – H … Y, where the dots denote the H – bond. The donor is represented as X – H, while the acceptor can be an atom or an ion [1]. The $X$ and $Y$ are the electronegative elements (O, F and N) with $Y$ carrying one or more lone pairs. In some cases, X and Y are identical. Intensive researches also noticed that aromatic ring with its high electron density can act as proton acceptor in the interaction like $O{-}H{\cdots}\pi$ which has been observed in the interactions of benzene with water and methanol. The hydrogen bond may also exist between the $C-H$ as the proton donor and $Y$, an electronegative or electron rich region and is denoted by $C{-}H{\cdots}Y$ [2, 3]. The $X-H$ bond length changes upon the hydrogen bond formation. The X$-H{\cdots}Y$ and $C{-}H{\cdots}Y$ type of H – bonds are called as classical (red) and non-classical (blue) H – bonds. These two kinds of bonds show completely different characteristic features [4 – 16] which are given below.

This research work is on the study of red (Classical) and blue shifting (non-classical) H – bond interactions in binary liquids solutions using FTIR studies and DFT calculations. Dielectric studies has also been carried out. The investigated binary solutions are methylcellosolve(MCS)/dimethyl sulfoxide(DMSO)/N, N-dimethyl formamide (DMF) + acetylacetone (AcAc) and acetonitrile (AN) + acetylacetone/triethylene glycol(TEG).

A brief introduction on the H – bond interactions and, experimental and theoretical techniques employed in this work have been given in **chapters 1 and 2**.

The results of the FTIR spectroscopic studies in relation to the binary solutions of MCS/DMSO/DMF with AcAc at various mole fraction of MCS/DMSO/DMF or AcAc have been presented in **chapter 3**. The presence of MCS – AcAc H – bond interactions that are relatively weaker than the interaction forces stabilizing the MCS – MCS H – bonded multimers has been inferred from the blue shift of $\nu(O-H)$ band of MCS in MCS – AcAc binary solutions. The rapid suppression of the intensity of the bands due to the in-plane $O-H$ bending vibrations and the $O-H$ stretching vibrations of MCS with decrease in MCS concentration, indicates the dissociation of the higher order multimers into lower order multimer units which readily form H – bonds with AcAc. Neat liquid DMSO exists as monomer and dimer which is indicated by the substructure of $\nu(S=O)$ band which has been deconvoluted into four Gaussian peaks. In the DMSO – AcAc solutions, except the SS1 in which the mole fraction of AcAc is 0.2, the shifts suffered by the DMSO bands suggest the presence of DMSO open dimer – AcAc and DMSO monomer – AcAc complexes. The $\nu(S=O)$ band of both the monomer and dimer of DMSO undergo blue shift upon H – bond formation which is completely opposite to the usual red shift occurring on account of the participation the $S=O$ oxygen in heteromolecular H – bond. Red shift in most of the $\nu(C=O)$ bands of AcAc (*keto* as well as *enol*) and blue shift in the $\nu(C=O)$ band of DMF have been noticed in all the solutions. This is the indication that the heteromolecular H – bonds formed at the DMF $C=O$ oxygen are weaker than the hydrogen bonds with AcAc $C=O$ oxygen as H – bond acceptor. The existence of AcAc as monomers in neat liquid phase has been confirmed by the spectral features of spectrum of AcAc. Classical and non-classical H – bonds are found to be formed in MCS – AcAc, DMSO – AcAc and DMF – AcAc binary solutions and the strength of these H – bonds is greatly MCS/DMSO/DMF or AcAc concentration dependent. There is no clear sign that can be used to know the most favourable partner for AcAc to interact with.

FTIR spectral studies has been carried out on the binary solutions of AN with AcAc has been analyzed in **chapter 4** in view of investigating the interacting nature of AN in the presence of AcAc molecules. In the binary solutions, the stretching vibrarions of AN masked by the AcAc vibrational movements. The AN dimers dissociate into monomers even in the binary solution in which the concentration of AcAc is 0.2 mole fraction that is one fourth of the AN concentration. The formation of the 1:1 complex between AN and AcAc in all the solutions has been identified

which resulted in more or less the same absorption position of the $\nu(C \equiv N)$ band in all the solutions. The shift of the AN methyl stretching vibrational bands show that the non-classical H – bond formed by AN with AcAc is relatively weaker than that existing between two AN molecules. At the same time, the red shift in the $\nu(C \equiv N)$ band in the solutions shows that the H – bond formed by the $C \equiv N$ nitrogen with the $CH_3/\ CH_2/O-H$ hydrogen of AcAc is stronger than that formed by the $C \equiv N$ nitrogen with the $CH_3$ hydrogen of another AN molecule.

**Chapter 5** presented the interaction of acetonitrile with triethylene glycol as revealed by the FTIR spectral studies. Pure triethylene glycol exist simultaneously as multimers of various orders in liquid phase. In its binary solution with acetonitrile, the combination of multimers present in neat triethylene glycol appears to be preserved but $C \equiv N \cdots H(CH_2/H-O)$ and $(AN\ methyl)H \cdots O(TEG\ C-O-C)$ heteromolecular H – bonds are found to be formed in all the solutions. The strength of these interactions depends on the concentration of acetonitrile/triethylene glycol.

Theoretical studies on the heteromolecular H – bonded structures of AcAc+ AN/DMSO discussed in **chapter 6**. The $(AcAc)\ methyl\ C-H \cdots N \equiv C(AN)$ H-bond is the dominant interaction among the $(AcAc)\ methyl\ C-H \cdots N \equiv C(AN)$, $(AN)C-H \cdots O=C(AcAc)$, $(AN)C-H \cdots O-C(AcAc)$ H-bonds in the stable configurations.The $O-H$ hydrogen of AcAc participates only in the strong intramolecular H-bond with $C=O$ oxygen. The $(AcAc)O-H \cdots O=C(AcAc)$ intramolecular interaction ranks first among all the delocalization interactions as suggested by the second order perturbation energy profile. The H – bond interaction forced between DMSO and AcAc enhances the stability of the 2:1 (DMSO:AcAc) complex in comparison with the stability of DMSO dimer but reduces the stability of the 1:1 complexes. The LP3 is found to interact with extremely larger delocalization energy than the other two lone pair of electrons of $S=O$. The intramolecular H – bond interaction of AcAc is drastically weakened if the heteromolecular H – bond is a the $C=O$ oxygen.

Dielectric studies carried out on the ANAcAc and DMSOAcAc binary solutions by employing TDR technique were analyzed in **chapter 7**. The relaxation time value profile confirms the non-associative nature of AcAc. Antiparallel alignment exists in AN/DMSO rich solutions while parallel orientation is preferred in AcAc rich solutions. From the $g_f$ values, it is obvious that non-classical H – bond interactions exist between AN/DMSO and AcAc which are relatively weaker than the non-classical H – bonds existing between AN/DMSO dimers as suggested by the

positive $\Delta F^E$ values. The deviation of excess dielectric constant $\varepsilon^E$ from ideal behaviour qualitatively the same if the volume fraction dependency is considered instead of mole fraction but quantitatively a large change occurs.

**In chapter 8**, the results of dielectric studies on the binary solutions of MCS, the highly associative molecule, with ACACT at different mole fractions of MCS/ACACT were reported. The relaxation time of MCS slowly decreases when its concentration is decreased. The rate at which the τ value decreases is more in MCS rich solutions than in ACACT rich solutions. The formation of heteromolecular H – bonds is more favoured in MCS rich solutions. The $g^{eff}$ values indicate that the heteroassociated molecular dipoles have parallel angular correlation. The excess dielectric permittivity $\varepsilon^E$ values have been calculated using the four formulae available in literature. All the four have qualitatively yield the same trend of deviation of $\varepsilon^E$ values from the ideal values.

AcAc is an important tautomeric compound whose interaction behaviour with other organic molecules has not been reported much in literature. In the present work, its interacting nature with some molecules has been studied using FTIR studies, DFT calculations and dielectric studies. The outcome of this work may serve as the basic scientific data for the future work.

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