

**FLUID STRUCTURE OF LIQUID MIXTURES CONTAINING ASSOCIATIVE  
MOLECULES BY DIELECTRIC AND SPECTROSCOPIC STUDIES**

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Synopsis of the research work entitled **“FLUID STRUCTURE OF LIQUID MIXTURES CONTAINING ASSOCIATIVE MOLECULES BY DIELECTRIC AND SPECTROSCOPIC STUDIES”**.

## INTRODUCTION

Hydrogen bond (HB), in general, is an interaction of the type  $X - H \cdots Y$  in which the  $X - H$  bond length of the HB donor increases upon the HB formation. Consequently, the  $X - H$  stretching frequency exhibits a red shift in the vibrational spectra (i.e., a decrease in the  $X - H$  stretching frequency). However, certain HBs show a blue shift in the  $X - H$  stretching frequency and a decrease in the  $X - H$  bond length. Such HBs are often termed as blue shifting hydrogen bonds. Blue-shifting HBs are typically observed in systems involving electron-rich molecules, like aromatic molecules, halogenated species [1] and are a resultant of the hyper conjugation and re hybridization phenomena [2, 3]. However, the fine interplay between these two effects makes prediction of blue-shifting hydrogen bonds difficult as was shown by a wonderful observation of a red shift in the proton donating functional group of halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) upon complex formation with acetone [4].

In the present work, highly self associative primary alcohols are dissolved in some polar/non-polar liquids and molecular interactions / H- bonds in these liquid solutions are investigated. In most of the literatures [5-9], they have studied the molecular interactions through spectroscopic techniques, dielectric relaxation studies separately. But in this present investigation, the cumulative results of FTIR spectroscopy and  $^{13}\text{C}$  NMR studies are taken into account to study the molecular interactions happening in polar-polar and polar-non polar binary solutions. In addition the dielectric relaxation studies have been carried out to study the impact of these molecular interactions on the dielectric parameters in binary solutions.

The variations of dielectric parameters in these solutions have been explained through the results of FTIR and  $^{13}\text{C}$  NMR spectroscopic techniques.

**Chapter 1** deals with a brief introduction about the nature of hydrogen bonds in liquid solutions. An overview of various studies like Fourier Transform Infra Red (FTIR),  $^{13}\text{C}$  NMR and dielectric spectroscopy, used by the researchers for studying the molecular interactions in a system of interest has been presented in this chapter. A previous work on molecular interaction studies based on the above mentioned techniques has been provided. In addition, the scope of the present investigation has been included at the end of this chapter.

In **chapter 2** deals with theoretical backgrounds of the various methods used in the present research work. Since the basic concepts behind the instrumentation techniques (FTIR,  $^{13}\text{C}$  NMR), and also time domain reflectometric technique have been in elaborated. In addition that, the various dielectric theories of static and dynamic permittivity etc., has been discussed in this chapter. The formulae used for the calculation of dielectric parameters have been explained.

**Chapter 3** deals with the Spectroscopic (FTIR and  $^{13}\text{C}$  NMR) and time domain reflectometry (in the frequency range from 10 MHz to 25 GHz) studies have been carried out on the binary solutions of acetonitrile (AN) with ethylene glycol (EG). The presence of EG-EG multimers of various orders in neat EG has been confirmed by spectroscopic studies. AN-EG association through the formation of  $\text{C}\equiv\text{N}\cdots\text{H}-\text{O}, \text{C}\equiv\text{N}\cdots\text{H}-\text{C}(\text{EG})$  and  $(\text{EG})\text{C}-\text{O}\cdots\text{H}-\text{C}(\text{AN})$  hydrogen bonds have been identified using spectral studies. The principal relaxation process of the heteromolecular entities that involve higher order alcohol association in ethylene glycol rich solutions is found to be relatively slower than that in acetonitrile rich solutions in which lower order alcohol association involves in heterointeraction. The angular correlation among the dipoles appears to be described more

precisely when the experimental  $\epsilon_{\infty}$  values rather than  $\epsilon_{\infty} = n^2$  are used for the calculation of  $g^{eff}$ .

**Chapter 4** deals with the H-bond interactions of methyl cellosolve (MCS) with chlorobenzene (CBZ) have been studied using FTIR spectroscopy and Time Domain Reflectometry (TDR) studies.  $(MCS)O - H \cdots \pi (CBZ)$ ,  $(MCS)O - H \cdots Cl (CBZ)$ ,  $(MCS - CH_2)C - H \cdots \pi (CBZ)$ ,  $(MCS - CH_2)C - H \cdots Cl (CBZ)$  H-bond interactions may exist in the MCS-CBZ binary solutions. The shifts in the  $\nu(C - O - C)$  and  $\nu(C - OH)$  stretching bands on mixing are due to the proximity effect arising out of the involvement of  $CH_2$ , and both  $CH_2$  and  $O - H$  hydrogens, respectively, in heteromolecular H-bond. The role of molecular interactions and molar volumes become relatively less significant in determining the relaxation times of the solutions. Instead, the viscosity plays a more dominant role in determining the relaxation times of the MCS-CBZ solutions. Parallel orientation of dipoles is favored in MCS rich solutions while in CBZ rich solutions the dipoles prefer antiparallel alignment. The excess values of the dielectric constant and free energy show negative and positive deviations, respectively

In **chapter 5**, H-bond interactions between ethyl acetate (EAC) and methyl cellosolve (MCS) have been investigated using FTIR and dielectric studies. FTIR studies show the presence of  $(EAC - CH_3 \text{ and/or } CH_2)C - H \cdots O$  (ether linkage and/or hydroxyl oxygen of MCS) and the  $(MCS - CH_3 \text{ and/or } CH_2)C - H \cdots O$  (ester linkage and/or carbonyl oxygen of EAC) H-bonds. A doublet of  $\nu(C = O)$  appears in MCS rich solutions while singlet is noticed in EAC rich solutions. The relaxation time of pure MCS is smaller than the value for solutions with  $X_2 = 0.8, 0.9$ . Relatively larger deviation of  $g_f$  from unity is observed in EAC rich solutions.

In **chapter 6**, deals with the FTIR and time domain reflectometric spectroscopic studies on the methyl cellosolve with bromobenzene: the FTIR spectrum of binary solutions of various mole fractions of MCS with BBZ and pure spectrum have been recorded at room temperature.  $(MCS)O - H \cdots Br$  and  $\pi(BBZ)$ ,  $(MCS \text{ methyl and/or methylene})C - H \cdots Br$  and  $\pi(BBZ)$  and  $(BBZ \text{ aryl})C - H \cdots O$  (hydroxyl and/or ether)MCS heterointeractions have been identified from the FTIR spectral studies. Time domain reflectometric (TDR) studies carried out on the MCS-BBZ solutions in the frequency range 10 MHz – 30 GHz at 298K reveal that corrective Kirkwood correlation factor ( $g_f$ ) may provide appropriate information about the strength of heterointeractions in the BBZMCS solutions as compared to FTIR spectral studies

In **chapter 7**, FTIR spectra of neat acetonitrile (AN), pentanol (PEN) and their binary solutions at different composition range have been recorded at room temperature.  $(PEN)O - H \cdots N(AN)$ ,  $(PEN \text{ methyl and/or methylene})C - H \cdots N(AN)$  and  $(AN \text{ methyl})C - H \cdots O$  (hydroxyl)PEN heterointeractions have been identified from the FTIR spectral studies. The results arrived out of the FTIR spectral studies and time domain reflectometry studies on the acetonitrile (AN) - pentanol (PEN) binary solutions have been elaborated in this work. The non linear variation in static dielectric constant of mixtures may form with hetero interaction between constituent mixtures. The self associative polymeric nature of alcohols is well known and in the investigated system, the dielectric loss peak of pure *PEN* appearing in the low frequency range reveals the existence of *PEN – PEN* multimers. The  $g^{\text{eff}}$  value of pure *PEN* is 2.24 which is greater than unity similar to the results reported by Begum et al in their investigation of various compounds with alcohols and the  $g^{\text{eff}} > 1$  was discussed as the parallel orientation of alcohol dipoles. The parallel orientation continues in the *PEN* rich solution of concentration  $X_2 = 0.9$  also whose  $g^{\text{eff}}$  value is 1.08 and this

molecular orientation suddenly turns antiparallel with the increase in  $AN$  concentration in the  $X_2 = 0.8$  to  $0.1$  solutions.

**Chapter 8.** The FTIR spectroscopy and dielectric studies on the binary solutions of 1-pentanol with toluene/octane have been presented in this chapter. From the results of experimental FTIR spectra, the following heterointeractions have been predicted:  $(PEN)O - H \cdots \pi(TOL)$ ,  $(PEN \text{ methyl})C - H \cdots \pi(TOL)$  and  $(PEN \text{ methylene})C - H \cdots \pi(TOL)$ . and  $(TOL \text{ aryl and methyl})C - H \cdots O - H (PEN)$  in the binary solutions of 1-pentanol with toluene, and in the binary solutions of 1-pentanol with octane both the methyl and methylene hydrogens are found to involve in H-bond interaction with the hydroxyl oxygen of 1-pentanol. But, the H-bond interaction of 1-pentanol with octane is more stronger than that with toluene. In addition the non-linear variation of static permittivity values with the mole fraction of  $PEN(X_2)$  plot supplements the existence of heterointeractions suggested from the results of FTIR spectroscopy. The dielectric loss peak of pure pentanol lies within experimental frequency, which exhibits the polymerization in nature, the relaxation process of pentanol decrease in binary solutions, which may dissociation and association of pentanol in toluene in the formation of hydrogen bond between constituent mixtures.

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