CHAPTER - 1

The dielectric constant is a characteristic quantity which can give considerable informations about the structural properties of polar fluids. The molecular dipole moment from the measured dielectric constant depends on the molecular interactions with their neighbours. The different models explaining these interactions, long range as well as short range are discussed. A review of the earlier work is also presented. The alignment of neighbouring dipoles governs the structure and properties of associated liquids, which could be studied by dielectric methods. The Kirkwood-correlation factor \( g \) is a measure of the short range intermolecular forces that lead to dipole-dipole interaction. Statistical mechanical model of Fronlich is briefly outlined. The problem of self association in liquids is explained. The various possible multimer configurations are discussed. The interaction between the polar solute and a non-polar solvent is considered by a modification of the Kirkwood-Frohlich correlation factor \( g' \) which takes care of the interaction of the solute molecules. Values of \( g' \) are reported for 1-propanol, 2-propanol, tert-butanol, 1-pentanol, 2-pentanol, 1-octanol and 2-octanol in benzene at temperatures 298K, 308K and 318K. The temperature dependence of \( g' \) is discussed.
The isodielectric behaviour of all alcohols taken for investigation is reported. The significance of the existence of a critical number density is recognised for the first time. Results are interpreted in the light of the existing theories of the fluid structure of these alcohols. The concept of significant structure theory is invoked to explain the angular correlation parameter \( G \) of the solute domains and that of the solvent domain \( S \). Winklemann's expression for the excess free energy of mixing due to the dipolar interaction is used to calculate \( \Delta F^E \) for monoalcohols at 298K, 308K and 318K and the results are interpreted.

CHAPTER - 2

Dielectric relaxation measurements provide a different approach to the study of H-bonding. At very high frequencies the dipolar molecules do not attain equilibrium with the applied field, energy is absorbed and dielectric constant decreases. The dielectric relaxation time \( \tau \) is defined as the time in which the polarization is reduced to \((1/e)\) times the original value. The Debye's theory, describing the dielectric relaxation of liquids is discussed. It is an established fact that for systems in condensed phase, a range of relaxation times is exhibited rather than a single relaxation time. In associated liquids, three regions of relaxation times are identified theoretically.
The experimental set up of the X-band microwave bench used for the study of $\varepsilon'$ and $\varepsilon''$ is described. Cole-Cole and Higasi methods are used to determine the relaxation times of monoalcohols at varying concentrations and at different temperatures. Measured values of density, refractive index, dielectric constants and viscosity are reported. The free energy of activation due to dielectrics and viscosity are determined and the results are discussed. The significance of our results of dielectric relaxation and the complementary study of linear correlation factor in relation to fluid structure is analysed.

CHAPTER - 3

The role of ultrasonics in determining the fluid structure is mentioned. The phenomenon of thermal relaxation and structural relaxation are discussed. The earlier theories on ultrasonic absorption are reviewed. The different optical methods of observing wave propagation are outlined. Pulse Echo Overlap Technique (PEO) is described in detail. Using PEO, ultrasonic velocity of monoalcohols determined at various temperatures are reported. The application of Eyring's hole theory to ultrasonic absorption is outlined and in the light of it, the hole volume ($v$) and the molecular binding energy ($U_0$) are obtained at different temperatures. The role of free volume and internal pressure in the
thermodynamics of associated alcohols is discussed. A correlation between internal pressure and ultrasonic absorption is attempted. The results are encouraging. Using ultrasonic velocity data at different temperatures, fluctuation parameters are computed and the results are discussed.

CHAPTER - 4

The dependence of the equilibrium properties of liquids on the force between the molecules is outlined. The reduction of entropy due to hydrogen bonding is also outlined. The Pseudo-Grunelsen parameter ($\Gamma$) is a characteristic constant of a liquid which could be used to study the liquid structures like clustering phenomenon and quasi-structural behaviour. $\Gamma$ is given in terms of internal pressure. The Pseudo-Grunelsen parameter for liquids ($\Gamma'$) is discussed and its temperature dependence is outlined. A review of earlier work is presented. The relation between $\Gamma$, thermal expansion coefficient ($\alpha$) and the specific heat capacity is discussed. The microscopic Gruneisen parameter for liquids is given in terms of $\alpha$, isothermal compressibility ($\beta_T$) and molar volume($V$). That part of the specific heat capacity($C_{v,1}$) which characterises the inter molecular normal modes of vibrations is obtained. From the values obtained from the measured ultrasonic velocities good correlation between absorption
measurements and velocity measurements were obtained. The results are discussed.

CHAPTER - 5

A brief introduction to hydrogen bonding is given. The different band shaping mechanisms of the IR bands of the complexes are discussed. The role of dipolar coupling in the broadening mechanism of the H-bonded systems is discussed. The H-bonding of monoalcohols with cyclohexanone and m-bromo aniline in carbon tetrachloride is investigated from the study of IR absorption spectra in O-H regions. The formation constants $K_{11}$ and $K_{12}$ for 1:1 and 1:2 complexes are reported. The relative abundances of these complexes are reported. The results are discussed in relation to various mechanisms involved in H-bonding.

CHAPTER - 6

The theoretical studies on Hydrogen-bonding is outlined. The charge redistribution phenomenon is related to the changes in molecular properties like dipole moment and IR intensity. Using dielectric measurements, the dipole moment of the complexes are evaluated and reported. The dielectric polarization studies are reported for the systems,

1) 1-propanol + cyclohexanone/triethylamine (TEA) in benzene.
2) 1-pentanol + cyclohexanone/TEA in benzene.
3) 2-pentanol + TEA in benzene.
4) 1-octanol + cyclohexanone in benzene.

The measured values of dielectric constants, refractive indices and densities are reported. The possible structures of 1:1 complexes were explored and $\Delta \mu$, the dipolar increment is evaluated for the most stable configuration predicted by hybridization theories. The results are interpreted on the basis of existing theories of H-bonding.

CHAPTER - 7

The oriented monolayer is a corner stone of modern colloidal chemistry and interface science. It has importance in such industrial and domestic situations as the manufacture of detergents, dyes and photographic film and in biology. Fatty alcohols are known to form molecular thin films over water subphase and exhibit interesting surface properties. In the course of our studies on monoalcohols we have investigated the spreading properties of fatty alcohols on a subphase and the characteristics of the Langmuir-Blodgett films.

Molecular orientations in multilayers of long chain amphiphilic alcohols are meagre. We report here our studies
on the formation and stability of L.B. films of 1-tetra decanol and 1-hexa decanol with reference to the influence of physical conditions like temperature, surface pressure and pH of the subphase.

The pressure-area (π-A) isotherm and hysteresis of the spread films were studied using KSV 5000 L.B. film balance and deposition system. Highly purified water was used as subphase. 1-tetra decanol and 1-hexa decanol supplied by Aldrich, USA was used. Monolayers were spread from chloroform solutions of 2mg/mL on a teflon trough of size 150mmx450mm. The spreading was fast, but the evaporation losses were large compared to fatty acids.

It was observed that a change in pH from 4 to 7 had no influence on the π-A isotherm. The temperature was varied from 20°C to 30°C and it was found that the spread films maintained at a surface pressure of 20N/m at a temperature of 20°C are stable for periods longer than 120 minutes. The collapse pressure of 1-tetra decanol and 1-hexa decanol are observed to be 38.4 mN/m and 33.5 mN/m respectively at 25°C. The mean molecular areas of these fatty alcohols changes from 28Å² to 19Å² and 39Å² to 28Å². In both the alcohols, the hysteresis run indicates that the second sweep more or less retrace the first sweep and the energy loss is minimum. Hence after the first cycle, the films are closely packed like a solid.
The films were transferred to a thoroughly cleaned glass substrate. The optimum dipping speed was found to be 5mm/min and the delay after the first withdrawal was 30 minutes. The transfer ratio was almost equal to unity during withdrawals of the substrate forming y-type films. The monolayers transferred on the glass substrate were studied by Multiple Internal Reflection spectroscopy using Perkin Elmer FIIR spectrograph. The $-\text{CH}_2$ stretching bands at $2851\text{cm}^{-1}$ and $-\text{CH}_2$ scissoring band at $1465\text{cm}^{-1}$ confirm that multilayer L.B. films are successfully transferred to the substrate.