Chapter 1

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Modern biochemical research is based on the premise that the life can ultimately be explained as coordinated series of various chemical reactions that carry out life processes. Amino acids, nucleosides and nucleotides are the important biochemicals in life processes, as these constitute a part of proteins, nucleic acids and other essential biomolecules. Also the metals like iron, zinc, cobalt, magnesium etc have been recognized as an essential micronutrients, which provide structure and activity basis to several metallobiomolecular systems. Investigation of conformational properties of such biomolecules, interactions of their chemical groups with metal ions and their interaction in aqueous solution play an important role in understanding the biochemical processes occurring in the living systems. The study of such molecular interactions containing biomolecules has been of intense activity in the recent past and there are still more areas of scientific research to be explored completely.

Until recently, heredity has always seemed the most mysterious of life’s characteristics. The current realization that the structure of DNA already allows us to understand practically all its fundamental features at the molecular level is thus most significant. It is seen that the laws of chemistry are not only sufficient for understanding protein structure, but also that they are consistent with all known heredity phenomenon. Complete certainty now exists essentially among all biochemists that the other characteristics of the living organisms will be completely understood in terms of the coordinative interactions of small and large molecules.

The study of solute-solvent interactions have been of intense activity in the recent past in all branches of chemistry and in other parallel disciplines as well, since these interactions are the driving force for the essential biochemical reactions. Various experimental methods have been employed to explore the information from the study of such interactions. Experimental data on thermodynamic, acoustic and transport properties of solutions are of great importance to get insight into such intermolecular forces. For many years the experimental data and reliable methods of estimating the physical and thermodynamic
properties were not available, except few measurements of viscosity, surface tension, sound velocity and refractive index. Till date, extensive work has been done on physical and thermodynamic properties and still vast progress is going on in many laboratories\(^{(1-6)}\).

Accurate knowledge of thermodynamic of solutions has relevance in understanding the molecular interactions between the components of the solution i.e. solute and solvent in developing new theoretical models. Although many tabulated values of the above properties are generally available for the pure solvent, literature data relative to various binary solutions are scarce. Thermodynamic methods are important because changes in properties caused by variations of temperature, composition and pressure can be studied without any reference to assumptions, model or hypothesis the problem becomes more interesting when the interactions between like and unlike molecules in solution are investigated by these techniques. The theoretical and experimental studies of thermodynamic and ultrasonic properties have been used as qualitative and quantitative guide to predict the extent of complex formation in binary solution\(^{(7-22)}\). Changes in entropy, enthalpy, Gibb's free energy, viscosity, compressibility, heat capacity, volume, velocity of sound etc. occurs when the interaction between the various components in solution takes place. The changes may be considered to be the sum of several contributions such as (1) combinatorial (2) energetic (3) free volume (4) steric hindrance and (5) molecular orientation. In polar component, other additional considerations due to dipole-induced dipole interactions and dipole-dipole interaction also play an important role.

During recent years several workers\(^{(23-26)}\) have successfully used ultrasonic velocity and it's related thermodynamic properties to study the intermolecular interactions in binary systems. The measurement of sound velocity under various conditions allows the computation of thermodynamic functions with accuracy higher than direct measurements. Sound velocity depends on the density of medium. Greater the density higher is the sound velocity. The number of workers\(^{(27-31)}\) have applied various empirical, semi-empirical, and statistical theories to evaluate ultrasonic velocity.

Most of the physical, thermodynamic and acoustic properties of the solutions have been theoretically derived from those of the components, by assuming that the dissimilar

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molecules are non-interacting. This case can exist in mixtures where both the components are non-polar. In the binary mixture where one component is polar and the other is nonpolar, interactions have been observed. Even if the interaction between the polar and non-polar molecules is weak, there will be considerable change in the molecular environment. In such case the physical, thermodynamic and acoustic properties are likely to be affected by the intermolecular hydrogen bonding, dipole-dipole and dipole-induced dipole interactions between the unlike molecules due to the variation in the relative concentration of the components \(^{32-35}\).

In the present investigation the interaction studies of biomolecules is of special interest. The biomolecules, which play vital role in various metabolic activities are the amino acids, proteins, nucleotides, nucleosides, purines/pyrimidine bases, enzymes etc. Amino acids are the chemical building blocks from which proteins are constructed. Proteins can have wide variety of biochemical properties. There are approximately twenty-nine commonly known amino acids that account for the hundreds of different types of proteins present in all the living things. Hence from the study of amino acids, the nature of more complex proteins can be properly understood. Thermodynamic and ultrasonic studies of such compounds can yield the data such as apparent molar volume, specific acoustic impedance, relative association, adiabatic compressibility, apparent molar compressibility, intermolecular free length and viscosity which have been extensively studied. The electrical conductance of such systems is also reported. These properties can provide the useful information about in intermolecular interactions in solution and have been used to draw the important conclusions pertaining to protein unfolding\(^ {36}\), the extent of hydrophobic interactions of non-polar side chains\(^ {37}\) and differential affinities\(^ {38}\) of amino acid side chain for water molecules. The conformational properties of nucleotides, nucleosides and nucleic acid bases and the interaction between their chemical groups with water molecules provide the important clue to understand the thermodynamic of many biological processes involving such species.

The wide spread use of the ultrasound in the field of structural chemistry is well known. Ultrasonic studies are carried out at different amplitudes viz. one dealing with high amplitude vibrations and other with low amplitude vibrations. The present work has been
carried out with the application of low amplitude ultrasonic waves. The most valuable parameters used to solve the various physico-chemical and structural problems associated with the solutions are the viscosity density, velocity and refractive index. Thus the measurement of above parameters is very much useful in the study of molecular interactions in solution of organic compounds.

The transition metals\(^{39}\) play vital role in many biological processes. Isomerization, redox reaction, oxygen activation, electron transfer and respiratory system or photosynthesis can not be envisioned without metalloproteins. The synthesis and functional study of bioinorganic model compounds for metalloenzyme can lead to interesting "bioanalogous" systems with practical application in catalysis. Hence the role of metals in biological systems cannot be ignored. The metals like zinc, copper, iron, cobalt, nickel etc are also called as micronutrient which is involved in structural and regulatory cellular functions. These metals interact with other biomolecules during the various metabolic activities. Therefore the interaction studies of biomolecules in the presence of such metal ions can provide the further insight and application in the field of research. Therefore we have tried to look into the interactions of such biomolecules like amino acids and nucleosides through ultrasonic and volumetric studies.

1.1 Ultrasonic Studies:

The term ultrasound defines sound waves of frequency above the threshold of human hearing, 20 kHz. Ultrasound may be propagated in variety of modes through different materials and offer wide range of both medical and industrial applications. The use of ultrasound is one of the well-recognized approaches for the study of molecular interactions in fluids. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. The acoustical methods of calculations of such parameters seem to be interesting because of the relative simplicity and precision of sound velocity measurements. These methods are based on the assumptions that the macroscopic velocity of sound results from two processes; the propagation of sound waves inside the molecules, the velocity of which is assumed to be infinite and through the
free space between them. During recent years, several workers\(^{40-42}\) have reported ultrasonic velocity, non-linearity parameters and other related parameters in a number of pure solvents and solutions. It is possible to obtain certain information about physical attributes of solutions such as internal pressure, intermolecular spacing etc. from values of non-linearity parameters. The non-linearity parameter plays a significant role in non-linear acoustic and it's determination is of increasing interest in a number of areas from underwater acoustic to medicine.

It is the well known fact that in solutions of electrolytes, the water molecules bound to an electrolyte ions are compressed due to strong electrostatic force between them Passinski\(^{43}\), Wada\(^{44}\), Yasunga and Sasaki\(^{45}\) evaluate the degree of hydration of ions from adiabatic compressibility. Apparent molar isentropic compressibility was first calculated for aqueous solutions of amino acids by Gucker et al\(^{46}\). Shilo et al\(^{47}\) has introduced a general theory taking into account the compressibility of the bound water and solute particle to calculate the amount of bound water of non-electrolyte and of high polymer in solution from ultrasonic measurements. They obtained the following relation containing effect of hydration.

\[
K = \beta_0/\beta_w \cdot 1/p_0 - [v_0/\beta_0/\beta_w - v_2/\beta_2/\beta_w] c \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1.1.1)
\]

where \(v_0 = v_0/v\) and \(v_2 = v_2/v\)

'\(v_0\)' is the volume of solvent attached to the solute, '\(v_2\)' is the volume of compressed solvent and '\(v\)' is the volume of solution. The second term in the above equation is due to hydration.

The further thermodynamic studies of apparent quantities have been carried out by Harned and Owen\(^{48}\), Desaoyers-Philip\(^{49}\) and Blandmer\(^{50}\). Deshpande et al\(^{51}\) have studied the ultrasonic velocity and related properties in binary solution of aniline. The adiabatic compressibility of pure water and aqueous solutions have been calculated by Endo\(^{52}\) and the compressibility data were correlated to the structure of water. Baumgartner and Atkinson\(^{53}\) have reported the sound velocities in 1,3 dioxane-water system. The sound velocities for number of binary systems has been reported by Shyder and Shyder\(^{54}\). Kaulgud and Patil\(^{55}\) have studied the ultrasound velocities of some amines in aqueous solutions at 298.15K and the
data were used to calculate the partial molar compressibility. Partial molar compressibility of carbohydrates in water has been determined by Holland and Holmik\(^{(56)}\). Millero et al\(^{(57)}\) have calculated the adiabatic compressibility of nearly fifteen different amino acids in water.

Cabani et al\(^{(58)}\) have studied the adiabatic and isothermal apparent molar compressibility of cyclic and open chain secondary alcohols and ethers. Adiabatic compressibility of aqueous transition metal chlorides at 298.15 has been determined by Surdo and Millero\(^{(59)}\). The molecular interactions containing the biomolecules like nucleoside and nucleotides, with respect to dependence on their chemical structure have also been studied\(^{(60)}\). The pH dependant solute-solvent interactions\(^{(61)}\) and of base stacking\(^{(62)}\) have been carried out by Hemmes and others. Ultrasonic studies of urea-THF-water and urea-DMSO-water system have been carried out by Thakare et al\(^{(63)}\) and corresponding molecular interactions have been discussed. Physical properties of some amino acids have been studied by Jahagirdar et al\(^{(64)}\) and Bala et al\(^{(65)}\) by measuring the ultrasonic velocities of the solutions.

Ogawa et al\(^{(66)}\) have calculated the apparent molar compressibility of some amino acids in aqueous alkali chloride solution. Temperature and concentration dependence of ultrasonic velocity and allied parameters of monochloro acetic acid in aqueous ethanol has been studied by Nikam and Hasan\(^{(67)}\). Rao et al\(^{(68)}\) have measured ultrasonic velocity in binary liquid mixture containing 2-butonyl ethanol. The ultrasonic velocity of aqueous and non-aqueous solutions of tetracycline hydrochloride and chlorotetracycline at 298.15K. and 308.15K have been reported by Pandey et al\(^{(69)}\).

Iqbal and Verrall\(^{(70)}\) have carried out the apparent molar compressibility studies of aqueous solutions of drug compounds. Chalikian et al\(^{(71)}\) have studied the adiabatic compressibility of series of a homologous series of amino carboxylic acids and they interpreted the resulting data in terms of the hydration of the aliphatic component and charged atomic groups. Patil and Mehta\(^{(72)}\) reported excess molar compressibility of mixing of aqueous mixed salt solutions at 298.15K. Chalikian et al\(^{(73)}\) have carried out the ultrasonic study of proton transfer reactions in aqueous solutions of amino-acids. Kukuchi et al\(^{(74)}\) have measured the densities and sound velocities in aqueous and dilute solutions of amino acids at different
temperature. They have also studied the features of temperature dependence of partial molar quantities. Compressibility measurements of various tetra alkyl ammonium halides in DMSO + Water mixture have been made by Das et al. Singh et al have calculated the ultrasonic velocity for tetra-alkyl ammonium and copper salts in acetonitril and benzonitril and limiting apparent molar compressibility were splitted into limiting ionic compressibility.

Since the ultrasonic study reveals clear reflection of the intermolecular interactions in terms of various parameters, in recent past many related articles are found in the literature.  

1.2 Volumetric Studies

The volume properties of solutes in solution have proved to be a very useful tool in elucidating the structural interactions (solute – solute and solute-solvent ) occurring in solution. For example, the partial molar volumes of solutes at infinite dilution can be used to study the solute - solvent and solvent-solvent interactions while concentration dependence of apparent and partial molar volumes of the solutes can be used to study the solute-solute interactions. The partial molar volumes of solutes can also be used to calculate the effect of pressure of ionic equilibria for the processes of engineering and oceanographic importance. Volume properties of electrolytic solutions have been of scientific interest since long. Measurements of molar volume are now made with either dilatometer, or by accurate density measurements. It is well known that the sign and magnitude of molar volume gives a good estimate of the strength of unlike molecules in the binary solution. Higher positive values for molar volumes are taken as indicative of weak interactions whereas, large negative values of molar volumes are usually found when these interactions are strong and intermolecular association complexes are believed to be present. Isentropic compressibility(K_s) also, proves to be one of the most reproducible to the molar properties. Several workers have pointed out that the thermodynamic parameters are sensitively dependent not only on the difference in intermolecular forces, but also on the difference in the size of molecules. It is obvious that the study of compressibility and molar volumes gives important information on intermolecular forces determining the properties of solutions.
The very first observation on volumetric measurement was made by Archimedes. But actual volumetric measurements particularly in solutions was probably made by Watson(91) in 1770, who made accurate measurement on volume changes on addition of electrolytes in water. These volumetric measurements were acting as a major turning points for the further development in that field. The theory of dissociation of electrolytes is presented by Arrhenius(92) in 1887. In 1923 Debye and Hückel(93) presented famous theory of interionic interactions. Watson observed that when salt is added to fixed volume of water, it results in decrease in volume. Watson’s observations definitely raised some questions about the prevailing theory of porosity of water. Dalton(94), in 1840, made some volume measurements, which supported the porosity theory of water. Dalton suggested that the volume of water did not change on addition of salt except when the dissolved salt contained water. However Holkar (95) found that the volume change on addition of salt to water could be positive or negative depending upon the nature of salt, temperature and concentration. Keeping in view the approach by Holkar, Playfair and Joule(96) were able to establish a relationship between the volume of salt in solution and in crystal. Their conclusion was different than those of Dalton and Holkar. Marigand(97) finally cleared up this confusion by showing that Playfair and Joule’s work was incorrect and that Holkar work was correct. In 1872, Faure and Valson(98) assumed that volume change on addition of a salt to water as a result of two opposing forces i.e. contraction in volume due to absorption of water on the dissolved salt and expansion in volume due to salt dissolution.

The increase in apparent molar volume ($\phi_v$) of electrolytes with concentration is given by Nicol(99) on the basis of theory of attraction. Traulic(100) have studied the $\phi_v$ for different solutes in solution. Drude-Nernst(101) electrostriction theory can explain about the $\phi_v$ and still support many theories of ion-solvent interaction. Kohlrausch and Hallwachs(102), experimentally proved that $\phi_v$ was proportional to $(\rho/\rho_0 - 1)/c$. This follows from the definition of apparent molar volume as,

$$\phi_v = [10^3(\rho/\rho_0 - 1)/c] + M/\rho_0 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
$M$ is the molar mass of solute. $\rho$ & $\rho_0$ are the densities of solution and pure solvent respectively. Gimelli\(^{103}\) have studied the effect of dissolved electrolytes on the properties of water.

The linear relationship between apparent molar properties and the concentration is given by Masson. In case of $\Phi_v$, the Masson’s equation is given by

$$\Phi_v = \Phi_v^0 + S_v \cdot c^{1/2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
M is molar mass of solute

c is molar concentration of solute

The \( \phi_v \) values are plotted against \( c^{1/2} \) and the best curve is fitted to them. By rearranging above equation,

\[
\frac{1000 (\rho_0 - \rho)}{c} \cdot \phi_v = \phi_v - M \quad \text{..........................(1.2.6)}
\]

Substituting \( F = \frac{1000 (\rho_0 - \rho)}{c} \), equation (1.2.6) becomes

\[
F = \rho_0 \phi_v - M \quad \text{.......................... (1.2.7)}
\]

Differentiating above equation (1.2.7) with respect to \( c^{1/2} \)

\[
\frac{\delta F}{\delta c^{1/2}} = \rho_0 \frac{\delta \phi_v}{\delta c^{1/2}} \quad \text{.......................... (1.2.8)}
\]

Since

\[
\phi_v = \frac{(F + M)}{\rho_0}
\]

\[
\frac{\delta \phi_v}{\delta c^{1/2}} = \frac{1}{\rho_0} \cdot \frac{\delta F}{\delta c^{1/2}}
\]

To obtain the final values of the coefficient, it requires the \( F \) value plot as well as the extra calculations for \( \rho_0 \) & \( M \) terms. For the verification of the this method, he used the density data of CaCl\(_2\) at 298 K from international critical tables to calculate \( F \) and \( \phi \). The plot of \( \phi \) values obtained from \( F \) plot, reflects the almost identical results. It was pointed out by Gucker that the method of calculating \( \phi \) from \( F \) plot was not limited to special case in which each is the linear function of \( c^{1/2} \). If \( F \) is any function of \( c^{1/2} \), then corresponding equation for \( \phi \) can be easily calculated. Thus,

\[
\phi = \phi^0 + \frac{1}{\rho_0} \cdot F (c^{1/2}) \quad \text{..........................(1.2.9)}
\]
\[ F = (F^0 + M') \rho_0 + 1/ \rho_0 \cdot F (c^{1/2}) \] .................(1.2.10)

He further tried to develop an equation for calculating partial molar properties from apparent molar properties and after some drastic mathematical calculations, he arrived at the following simple equation connecting above two thermodynamic properties.

\[ V_2 = \phi_v + c^{1/2} \left( \frac{1000 - c \cdot \phi_v}{2000 + c^{1/2} \cdot \phi_v / \delta c^{1/2}} \right) \delta \phi_v / \delta c^{1/2} \] .................(1.2.11)

In order to verify Redlich and Rosenfeld equation, Wirth et al.\(^{106}\) determined partial molar volumes \((\phi_v^0)\) for number of electrolytes in aqueous solution, and they observed that \(V_2\) for KCl and KBr depend only on the total volume ionic strength, but the question was raised against the same dependency for non-electrolyte. Redlich\(^{107}\) showed that the density of electrolyte solution can be determined from the equation.

\[ \rho = \frac{\rho_0 + (M - \rho_0 \cdot \phi_v^0) / 1000}{1000} [S, \rho_0 / 1000] c^{1/2} - [b, \rho_0 / 1000] c^2 \] .................(1.2.12)

Where \(b\) is the empirical constant.

Lamprea and Ferreira\(^{108}\) deduced the equation for the calculation of observed \(\phi_v\) for the aqueous solution of non-electrolytes for which the dependence of apparent molar volume on concentration is non-linear.

\[ \phi_v^{obs} = (1 - \alpha) \phi_v (B_{H2O}) + \alpha \phi_v (B_{H^+ OH^-}) \] ................. (1.2.13)

where '\(\alpha\)' is the degree of hydrolysis.

In order to calculate partial molar volume \((\phi_v^0)\), Kaulgud et al.\(^{109}\) introduced a few modifications in the above equation.
\[ \Phi_v^0 = (1-\alpha) c_v - (B_{H_2O}) + (1-\alpha)^2 \chi c^2 \] ..........................(1.2.14)

Both the equations are tested by Lampreia and Ferreira and found that equation (1.2.14) gives better fit than the equation (1.2.13).

The model of solution is another conceptual approach applied for the interpretation of partial molar volume. According to that theory

\[ V = V_m + \Delta V_h \] ..............................(1.2.15)

Where \( \Delta V_h \) is effect of hydration on volume

and \( \Delta V_h = n_h (V_h - V_0) \) hence eqn. (1.2.15) becomes,

\[ V = V_m + n_h (V_h - V_0) \] ..............................(1.2.16)

Where \( n_h \) is the hydration number \( V_0 \) and \( V_h \) are the partial molar volumes of water in the bulk state and in hydration shell of solution respectively.

In the recent past extensive volumetric studies has been carried out on electrolytes and mixture of electrolytes\(^{119-115}\). Volumetric measurements of the systems containing mixed salts and binary mixture of electrolytes, containing common ion as well as non-electrolytes have been done\(^{116-120}\).

The study of partial molar volume of complexes is found to be an effective tool to investigate the effect of size and charge of ionic solute on solute-solvent interactions. Kats et al\(^{111}\) have studied the apparent molar volume of some drug compounds in aqueous and non-aqueous solutions. Also the volumetric studies of the systems containing biomolecules and the fruitful results of such investigations have fascinated the attention of many workers.
1.3 Viscometric Studies:

Viscosity is one of the most important physical properties of the liquid and it implies resistance to flow. The significance of viscosity may be further elucidated by considering flow of liquid through narrow capillary. Physical properties of liquid and binary liquid mixture have been the subject of interest in research laboratories. Viscosity of liquid provides a useful basis for understanding the nature of liquid state and has been widely used to study physicochemical behavior and molecular interactions in varieties of liquid solutions. The study of viscous behavior of liquid is important in understanding the mechanism of transport process. The numerous efforts have been made to study the viscosity of pure solvents and solutions in engineering, biomedical and physical aspects. In addition viscosity data for solution have often been regarded as a probe to be used to gain valuable information regarding the nature of interaction forces operating within and between the molecules and existence of complex.

The viscosity of liquid mixtures has attracted much attention in the literature Poiseuille has a great contribution in the research on viscosity. He found that some salt increase the viscosity of water whereas the other decrease the viscosity. The very first viscosity study report on BaCl$_2$ as an electrolyte, was put forward by Sprung. Further Arrhenius observed that at low concentrations the change in viscosity is proportional to the concentration but at moderate concentrations viscosity increases comparatively fast. He proposed a new formula for the relationship between viscosity and concentration

$$\eta = Ae^{-c} \quad \text{(1.3.1)}$$

Where $\eta$ is relative viscosity & $A$ is constant for given solute and temperature $c$ is the molar concentration.

The reason for decrease in viscosity by dissolved salts was given by Sutherland. The next prominent investigator on this subject was Gruneisen who made careful and critical study of experimental techniques with the Ostwald type of viscometer and made
precise measurements on aqueous solutions of sixteen salts and sucrose over a wide range of concentration.

It was expected that the viscosity concentration curve should be straight at dilute end but Gruneisen observed that the viscosity concentration curve exhibit negative curvature and this may invalid the Arrhenius equation. From the viscometric data obtained by viscometric studies, the plot of \((\eta - 1)/c\) versus \(c\), it was noted that that at low concentrations, the values of \((\eta - 1)/c\) decreases rapidly with increase in concentration, pass through minimum and then slowly increases. He proposed the equation

\[ \eta = 1 + Aic + B (1 - i) c + C c^2 \]  \hspace{1cm} (1.3.2)

Where \(A, B, \text{and} C\) are constant for only given salt and temperature. ‘A’ represent the effect of friction between ions (solute) and solvent, ‘B’ that of unionized molecules of solute and solvent and ‘C’ that of ions and molecules of solutes on each other, ‘i’ is the degree of dissociation.

The viscosity studies of even more dilute solutions than those studied by Gruneisen, were carried out by Appleby\(^{(135)}\) and he observed that at very low concentrations, negative curvature becomes more pronounced. He also showed that the negative curvature becomes greater as the temperature decreased. He tried to explain the effect on the viscosity, on the basis of following concept (1) Decrease in the viscosity was due to the depolymerization of water (solvent) and (2) an increase in viscosity is due to the presence of ions of solute and unionized solute molecules.

Since the viscosity depends on the size of ions and molecules that ultimately correlated to the extent of hydration of solute species; the decrease in viscosity is explained on the basis that the depolymerization of water (solvent) dominates the extent of hydration of solute species which tends to increase the friction and hence the viscosity. Whereas the increase in the viscosity is supported by the conditions in solution that diminishes the depolymerization, Appleby had tried to derive an equation for the measurement of viscosity, but he was unable to interpret the exact function which can connect the related variables for association factor of
solvent, dissociation of solute and the hydration number of solute species. Further Einstein\(^{(136)}\) had studied the systems containing dilute suspensions and derived an equation

\[
\frac{\eta}{\eta_0} = 1 + 2.5 \phi \quad \cdots \quad (1.3.3)
\]

Where \(\phi\) is the volume fraction occupied by the particles.

since \(\phi = c V_h\)

Where \(V_h\) is the molar volume of solute including hydrated solute and \(c\) is the molar concentration. Hence eqn (1.3.3) becomes

\[
\frac{\eta}{\eta_0} = 1 + 2.5 c V_h \quad \cdots \quad (1.3.4)
\]

Since this relation by Einstein was restricted to very dilute solutions the solute-solvent interactions was neglected. The theoretical equation of Einstein had been modified by Vand\(^{(137)}\)

\[
\ln \eta_r = 2.5 \phi / (1 - Q \phi) \quad \cdots \quad (1.3.5)
\]

Thomas\(^{(138)}\) also modified Einstein equation to represent the viscosity of both electrolytes and non-electrolytes at higher concentration

\[
\eta_r = 1 + 2.5 \phi + 10.05 \phi^2 \quad \cdots \quad (1.3.6)
\]

Where \(\eta_r\) is relative viscosity, \(\phi\) is volume fraction and \(Q\) is an interaction parameter dealing with mutual interactions between solutes and with their Brownian motion.

John and Dole\(^{(139)}\) tried to fit the data of electrolytes by taking into consideration the parameter fluidity i.e. reciprocal of viscosity. They found that fluidity also was not a linear function of concentration. Since fluidity is the reciprocal of viscosity, the fluidity-concentration curve had a positive curvature at dilute conditions. But no point of inflection and double curvature was found when the others workers studied the same parameters by taking different salts, it was observed that fluidity is proportional to concentration. According to
Jones and Dole, the curvature found in the dilute end of fluidity concentration curve, is due to some special effect. The interionic attraction theory of electrolytes supports to this effect. According to that theory the ions tend to build and maintain a space lattice structure in the solution and any influence disturbing this space lattice arrangement, whether by heat motion of the solvent molecules, the electrostatic force of charged electrodes in the solution, or any relative motion of the liquid will be opposed by the inter-ionic forces. These forces are only responsible for stiffening the solution and hence increase in viscosity. Debye-Hückel have studies the effect of such interionic forces which opposes the motion of ions in an electric field. They showed that these forces were proportional to the square root of concentration in very dilute solutions. This fact initiates Jones and Dole to try to introduce a term proportional to square root of the concentration into the equation of fluidity.

\[ \phi = 1 + A \ c^{1/2} + B \ c \]  
(1.3.7)

\[ \phi - 1 = A \ c^{1/2} + B \ c \]

(1.3.8)

The above equation (1.3.8) was verified by plotting \((\phi - 1) / c^{1/2}\) for different salts, which give excellent fit for dilute solutions but failed for higher concentrations. Since the stiffening effect of ionic space lattice is absent in case of non-electrolytes, there should not be any negative curvature in curve of viscosity and concentration.

Gruneisen carried out viscosity measurement of the systems containing sucrose below 0.01M and he deduced the equation as

\[ \eta_r = 1 + A \ c + B \ c^2 \]  
(1.3.9)

From the above equation (1.3.8) it was clear that there is no influence, which is proportional to \(c^{1/2}\).

Suryanarayana and Venkatesan\(^{140}\) studied the viscometric data for various electrolyte solutions at higher concentration and derive an equation and verified that equation by studying
the viscosities for number of electrolytes. Though this equation can explain the experimental results in better way, the deviation from these equations is common.

Moulik\(^{(141)}\) had tried to overcome these deviations and introduced another equation for the systems at higher concentration

\[
\left( \frac{\eta}{\eta_0} \right)^2 = M + K'c^2 \quad \ldots \ldots \ldots \ldots \ldots \quad (1.3.10)
\]

Where M and K' are constants

Though the various equation related to viscosity were introduced by number of workers. Jones-Dole equation has its own importance because it can provide better insight of solute-solvent as well as solute-solute interactions.

\[
\eta_r = 1 + A c^{1/2} + B c
\]

Where A-coefficient corresponds to ion-ion electrostatic interaction and B-coefficient corresponds to ion-solvent and solvent-solvent interactions. A-coefficient can be calculated from Falkenhagen Vernon equation\(^{(142)}\) whereas B-coefficient is a measure of solvation effect, ionic influence on solvent structure and hydrodynamic effects related to ionic influence on solvent structure and hydrodynamic effects related to ionic size and shape. Wadi and Goyal\(^{(143)}\) have determined the viscosity B-coefficient of amino acid in aqueous potassium thiocyanate solutions in the temperature range of 15 to 35°C. Bhattacharya et al\(^{(144)}\) have reported viscosity B-coefficient of some drug molecules. Gopal and Rastogi\(^{(145)}\) have studied N-methyl propionamide solutions assuming that \(B_{\text{EH}N^+} = B_i\) at all temperatures. Criss and Mastroianni\(^{(146)}\) resolved the B-coefficient for methanol electrolyte solution at 298.15K into ionic component assuming that \(B_{K^+}\) and \(B_{C_i}\) are equal. But it is not possible to select any two ions having equal limiting equivalent conductance, therefore any method of resolution based on the assumption that \(B^+ = B^-\) suffer the disadvantage. Also if we consider the equal motilities of respective ions at infinite dilutions but at moderate concentration the equality does not exist, hence the assumption \(B^+ = B^-\) does not valid.
In view to develop the method of resolution of B-Coefficient, Krumgalz\(^{(147)}\) suggested the phenomenon of unsolvation of tetra alkyl ammonium ion in organic solvent. He assumed that the B values are proportional to their ionic dimensions. In subsequent communication Krumgalz\(^{(148)}\) has shown that

\[ B_{\text{tot}} = B_{\text{inst}} + B_{\text{orient}} + B_{\text{str}} + B_{\text{refr}} \]  

(1.3.11)

Where \( B_{\text{tot}} \) is the positive increment arising from the shape and size of solvated ion and this is closely related to Einstein effect. \( B_{\text{orient}} \) is a positive increment related to destruction of solvent structure in the region of the ionic cosphere \( B_{\text{refr}} \) the positive increment due to the effect of reinforcement of the water structure by large tetra alkyl ammonium ions due to hydrophobic hydration.

Since for the large ions like tetra alkyl ammonium ions, in organic solutions, the \( B_{\text{orient}} \) and \( B_{\text{refr}} \) have negligible contribution, therefore equation (1.3.10) implies

\[ B_{\text{R4N+}} = B_{\text{inst}} + B_{\text{str}} \]  

(1.3.12)

\( B_{\text{inst}} \) in above equation was calculated by using Einstein’s equation and \( B_{\text{str}} \) is proportional to the ionic concentration.

The new method for resolving viscosity B-coefficient was proposed by Bhattacharya\(^{(149)}\). He assumed that ionic B values should be a monotonic function of crystal radii cubed and independent of the sign of the charge for aqueous and non aqueous systems. He found an exact co-relation of B-values obtained in different solvents, with ionic partial molar volumes, ionic radii temperature coefficients of equivalent conductance as well as with ionic partial molar entropy.

Viscosity of glycine and DL-alanine in DMF-water solution had been studied by Raman and Naide\(^{(150)}\). Jain et al\(^{(151)}\) have reported the viscosities of glycine and DL-alanine in dioxane water system. Prakash et al\(^{(152)}\) have reported the viscosities of binary liquid mixtures of non electrolyte in dioxane-water mixture. Kimura\(^{(153)}\) observed that viscosity always decreases with increase in temperature. Irving\(^{(154)}\) has verified several viscosity of binary
liquid mixture and correlated the data with volume changes upon mixing. Moulik and Bisal\(^{(155)}\) have studied the solute-solvent interactions in aqueous PEG solution. The viscometric studies of some bioapplicable systems involving ZnCl\(_2\), dextrose and methionine in water have been carried out by Mishra\(^{(156)}\). Many other workers\(^{(157-161)}\) have reported the viscosities of electrolyte, non-electrolytes and polymers in aqueous and non-aqueous solutions.

Recently Aswar\(^{(162)}\) have carried out interactions studies on lysine and mixture of lysine and adenosine in the presence of Mg\(^{2+}\) ions at different temperature. Thermodynamic properties of substituted acetophenones in THF-water and Dioxane-water co-solvents have been studied by Kulkarni et al\(^{(163)}\). Acoustic properties of substituted acetic acid in organic co-solvent mixtures have also been investigated\(^{(188)}\). The interaction studies of glycine, adenosine, uridine and alanine in aqueous solutions of nickel sulphate as well as vanadium sulphate at different temperatures, have been carried out by Rohankar\(^{(164)}\).

1.4 Objective of the present study

The biomolecules like amino acid, proteins, nucleosides, nucleotides, enzymes purines / pyrimidine bases etc play vital role in various metabolic activities. The metals like zinc, copper, iron, cobalt, nickel etc. are the micronutrients involved in structural and regulatory cellular functions and play equivalent role alongwith biomolecules in various biological processes. Amino acids and nucleosides have potential site to co-ordinate with metal ions. Hence the interaction studies of biomolecules in the presence of above metal ions also provide the further insight. The ultrasonic and thermodynamics studies of such interactions of biomolecules in the presence of metal ions are still scanty. Indeed, it should be of relevant important to investigate the thermodynamic and ultrasonic properties of biomolecules in the presence of metal ions.

The present thesis entitled “Ultrasonic and thermodynamic studies of interactions in binary systems containing biomolecules” is compiled in forthcoming six chapters.

Chapter 1

The chapter is an introductory part, gives a concise account of the subject. It is devoted for historic development of the subject and the objective of the present work has been
discussed. The importance and need of experimental studies of binary systems are emphasized. An effort has been made to include the up to date references.

Chapter 2

It deals with the detailed mathematical formulations used for the calculations of various thermodynamic and acoustic parameters such as apparent molar volume, specific acoustic impedance, relative association, adiabatic compressibility, apparent molar compressibility, intermolecular free length, viscosity and conductance. These parameters are obtained from ultrasonic, volumetric, viscometric and conductivity measurements. This chapter also includes the significant contribution by various scientists, which induce the new dimensions in the field of present subject.

Chapter 3

The chapter deals with experimental techniques, which have been used in the present investigation and the description of equipments used for measurements of the ultrasonic velocity, density, viscosity and electrical conductance.

Chapter 4

This chapter deals with thermodynamic study of Glycine, Tryptophan, Adenosine and Adenosine di-phosphate(ADP) in 0.05, 0.01 and 0.005 M aqueous solution of zinc chloride and cobalt chloride solutions at 303.15 K.

Various parameters corresponding to intermolecular interactions in solutions have been incorporated.

Chapter 5

In this chapter the system containing bimolecules are studied through internal pressure. It indicates the overall solute-solvent, solute-solute and solvent-solvent interactions in liquid system.

Chapter 6

Being a last chapter of the thesis it comprises the summary and conclusive remarks drawn on the present investigation and also the scope for further studies.
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