CHAPTER I

NECESSITY OF THE RESEARCH WORK

1.1 OBJECT, SCOPE AND APPLICATION OF THE RESEARCH WORK

Diet supplies sufficient nutrients to meet metabolic requirements and contributes for the development of human health. Therefore each compound which has beneficial effect to the human health should be identified. The term 'bioactive' originated from the two Greek words "bios" and "activus". "Bios" means life and "activus" means full of energy or involvement to any activity. So the bioactive compounds have some kinds of activity on living tissue. A material may be defined bioactive if it interacts with any cell tissue of human body. Any non-nutrient ingredient of plants or edible mushrooms which has health promoting or harmful properties when ingested is called bioactive plant food compounds. Bioactive plant foods are of intense interest among the scientists at present due to their well accepted beneficial characteristics especially against cancers, diabetes, cardiovascular diseases etc. Bioactive compound are basically extra nutritional constituents which is present in very small amount in foods and has effect on living cells. The beneficial properties of bioactive compounds are termed on the basis of pharmacological activities of these compounds. The diet rich in bioactive compounds are vegetables, variety of fruits, legumes, oils, whole grains and nuts. Many physiological functions are controlled by pulsed release of bioactive compounds. Rice bran is as an exceptional source of bioactive components, but very small quantity is consumed by humans. Different approaches like acid, alkali, thermal and chemical treatments have been established to improve the level of bioactive components in food materials. The phenolic compounds perform as antioxidant and some studies showed positive effects of it on thrombosis and tumorogenesis. Similarly, resveratrol which is found in nuts and red wine inhibits carcinogenesis. Lycopene found in tomatoes and some fruits are considered to defend against prostate and other cancers and inhibit the growth of tumor cell. Mannitol is used medically to reduce highly raised intracranial pressure also for oliguria renal failure. Glucose flows in the blood and provides energy to every cell of the living body. Glucose is known as ubiquitous fuel in biology. Caffeine, an alkaloid acts as a stimulant on nervous system and occasionally used as natural insecticide. Similarly some anti-carcinogenic bioactive compounds are Organosulfur compounds found in garlic and onions, isothiocyanates found in cruciferous vegetables, monoterpenes found in citrus fruits and

cherries etc. Nicotinamide which is also known as niacinamide, is used as medication to prevent pellagra and high blood cholesterol levels. Nicotinic acid which is known as niacin in combination with nicotinamide is used to prevent pellagra, skin flushing and acne. Similarly the amino acid, flavonoids, fatty acids, anthocyanins, phytosterols, glucosinolates, prebiotics, polyphenols, flavonoids, carotenoids, caffeine, carnitine, choline, coenzyme, creatine, dithiolthiones, phytoestrogens, polysaccharides, taurine etc. have favourable health effects.

The minerals also perform significant activities in our body. Minerals in very small quantities are essential to do important life functions. They're usually present in foods in the form of salts and take key role in the formation of body substances like hormones, enzymes etc. Human body needs "trace elements" also in minute quantities.

Bulk properties of solution like viscosities, densities, excess molar enthalpies, refractive indices, isentropic compressibility can be measured easily and very accurately in laboratory. These properties give some information understanding the molecular/ ionic arrangement of the solution and also help to evaluate some thermodynamic parameters of the solution. Acoustic properties are also of immense interest to understand molecular/ ionic interactions in solute-solvent systems. The intermolecular interactions at microscopic and macroscopic level can be studied from physicochemical properties of mixed components system. The excess thermodynamic property is related to the difference between the actual property and the property if the system behaves ideally. Excess properties are also significant parameters to examine the nature and extend of solute-solvent interactions in the solution. These excess thermodynamic properties are helpful for development of new theoretical models.

Light does not propagate at the same velocity in different solutions. The refractive index, n_D, may be termed as the ratio of velocity of light in the vacuum to the velocity of light in the concerned medium and it is always more than one. The refractive index value for gases is close to one. The refractive index can be obtained by refractometer at certain temperature using the sodium D line. Many thermo-physical parameters like critical constants, transport properties and heat capacity may be calculated from refractive index of any solution.

Rheology is branch of physics and physical chemistry which deals with the deformation and flow of matters and "soft solid". It has wide range of application in human biology, geophysics, creams, science engineering, ointments, pastes, physiology, and

pharmaceutics [1-3]. The science of rheology may also be used in case of industrially important substances having complex flow characteristics like cement, paint, polymeric materials and chocolate to maintain the quality of the products [4-9].

The investigation of viscous synergy and antagonism is important for the multicomponent industrial products to retain the desired physical properties. The study of synergy and antagonism help us to find the mutual enhancement of the physicochemical, pharmaceutical biological activity of any product. The study of viscous property of any pharmaceuticals, foodstuffs, cosmetics is necessary for getting the idea whether its viscosity is suitable for the long term use or not and also its expiry information 10-12].

Viscosity may be applied understanding the molecular interactions playing between solute and solvent or ion and solvent in a solution. We can measure the partial molar volumes and viscosity B -coefficient of various solutes in a solution at different temperatures. Some physicochemical and thermodynamical parameters derived from viscosity may be applied understanding extend of molecular interactions quantitatively. The extend of ion-solvent or solute-solvent interactions helps the chemists for choosing suitable solvents which may enhance (i) the rates of reactions, (ii) the solubility of compounds in leaching operations or (iii) reverse the direction of any equilibrium reactions.

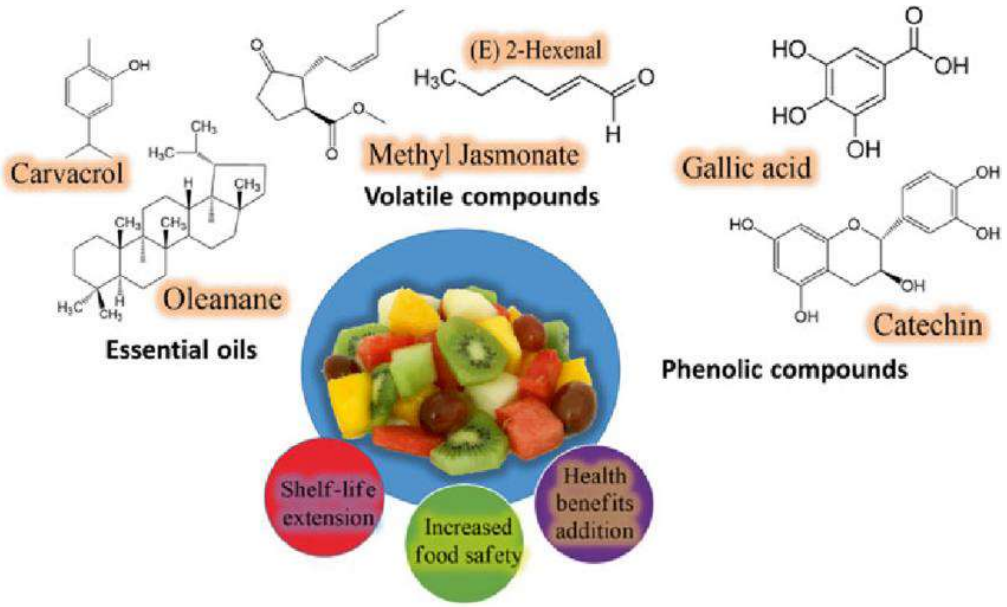
The significance uses of the chemistry of electrolytes in mixed solvents are now well accepted. A lot of studies of reaction in non-aqueous and mixed solvents have been carried out by many scientists [13-22]. In spite of enormous research in this field, the various types of interaction of electrolytes and non-electrolytes in diverse solvent or mixed solvents are yet to be understood properly. However, studies on solution properties provide some valuable information to understand the variation in ionic structure, ionic mobility and thermodynamic properties of different electrolytes and non-electrolytes in their aqueous or non- aqueous solutions [23]. Now a day, interest in the behavior of electrolytes or solutes in non-aqueous and mixed solvents to investigate solute-solute and solute-solvent interactions under various conditions is increasing severely. The difference in solvating power and possibilities of chemical or electrochemical reactions of non-aqueous solvents or mixed solvents unlikely than aqueous solvents have opened views for physical chemists and exploration in this field has removed the boundaries among inorganic, physical, organic, analytical and electrochemistry 24]. High-energy batteries, double-layer capacitors or super capacitors, and electroplating are some field where non-aqueous electrolyte solutions had carried the remarkable successes and opened the eyes of scientists to carry out more and more

researches. Some others devices or areas where non-aqueous electrolyte solutions are widely applicable are electro-chromic displays, photo-electrochemical cells, smart windows, etching, electro-machining, polishing, electro-synthesis etc. [25-27]

Exploration on of transport and acoustic properties of electrolytes along with their physicochemical and thermodynamic parameters provides significant information about molecular interactions in aqueous and non-aqueous solutions [28, 29]. The ion solvation is an another physicochemical property which has wide range of applicability in different fields like organic and inorganic synthesis, determination of reaction mechanisms, extraction of any compounds from mixtures, non-aqueous batteries etc.[30]

Thus from the above mentioned reasons, it is apparent that the solutes in aqueous, non-aqueous and mixed solvents are considerably influenced by the solvents and the structure of the solvents are greatly modified. Information about ion-solvent interactions of non-aqueous solutions is very essential in numerous real-world problems such as energy, heat, mass transport and fluid flow.

Real understanding about molecular interactions in solute-solvent systems is a huge difficult task. The works in this field embraces numerous issues but we confined our investigations on volumetric, conductometric, viscometric, refractometric, interferometric behaviors in understanding chemical nature and the structure of solutes and solvents and their mutual interactions in solution.



The explorations on supramolecular chemistry provide a wide range idea regarding the formation of 'inclusion complex' between any host and the guest molecule. The molecule fits inside the cavity of a host molecule through non-bonding interaction. Cyclodextrins, cucurbitrils, crown ethers, calixarenes, porphyrins are some well-known host molecules. Inclusion complex is a compound in which a guest molecule becomes encapsulated inside the cavity of certain dimension and polarity of a host molecule. The Ionic liquids having a long chain hydrophobic non-polar group may be regarded as a guest molecule for the formation of inclusion complexes with cyclodextrins [31].

The controlled release of any drug molecule from the inclusion complex of it into the biological system depends on physicochemical aspects of both the drug and host compound [32, 33]. But direct investigation of various physicochemical properties of any drug molecule in biological fluid media is very difficult to achieve. One of the competent methods is to study the molecular interactions by physicochemical and thermodynamical parameter of the drug molecule in our appropriate laboratory system as a model experiment and correlate it in our biological fluid system.

Objectives of the research work

- The primary object of this research work is to examine the molecular interactions of some biologically active molecules in diverse solvent systems and gather the details information about the nature and extend of various interactions.
- To investigate the interactions of bioactive molecules in physiological fluid media by physicochemical and spectroscopic techniques.
- To investigate of the transport property, ion solvation and solubility of some electrolytes in aqueous, non- aqueous mixed solvent systems.
- To investigate the interactions of some industrially important chemicals in diverse solvent system.
- To explore the molecular interactions by physicochemical and thermodynamical parameter of the drug molecule in our appropriate laboratory system as a model experiment and correlate it in our biological fluid system.
- To probe the various kinds of hydrophobic- hydrophobic and hydrophilic- hydrophilic interactions playing between host and guest molecule in case of inclusion complexes.

- Exploration of interaction of bioactive compounds with ionic liquids by physicochemical investigations.

1.2. Tools of Investigation

The various experimental methodologies employed to investigate the different kinds of interactions in solvation and inclusion phenomena are viscometric, densitometric, refractometric, conductometric and spectroscopic techniques.

1.3. Methods of Investigation

To get a better understanding into the phenomena of various interactions in solvation and inclusion complexation different experimental methodologies in solution and in solid phase have been employed. Therefore, various important methods that have been used are densitometric, viscometric, conductometric, tensiometric, refractometric and spectroscopic techniques to probe the solvation and inclusion phenomena. The spectroscopic studies can explain the different types of interactions specifically. The spectroscopic techniques such as UV-Vis, FT-IR, 1HNMR and 2D ROSEY NMR etc. have used to study various molecular interactions.

Physicochemical parameter like limiting apparent molar volume (ϕ_V^0) and experimental slopes (S_V*) obtained from the Masson equation are very helpful to examine the solute-solvent and solute-solute or ion-solvent and ion-ion interactions in solution chemistry. The limiting apparent molar volume (ϕ_V^0) signifies the existence of solute-solvent or ion-solvent interactions however, the experimental slope (S_V*) indicates the existence of solute-solute or ion-ion interactions. Similarly from the viscosity measurements we can evaluate viscosity-A and B-coefficient. The viscosity B-coefficient provides the idea about the nature and extend of solute-solvent or ion-solvent interactions while viscosity-A coefficient provide the valuable information about the of solute-solute or ion-ion interactions.

The transport properties of any electrolyte in aqueous, non- aqueous solvent can be examined from conductance measurements. Tensiometric study may be used to determine the CMC of any ionic liquid having long alkyl part and also to probe the formation and stoichiometry of host-guest inclusion complexes.

The molar refraction, R_M of a solution determined from the Lorentz–Lorenz equation provides the information about the solute-solvent or ion-solvent interactions as well as compactness of the solution.

FTIR spectroscopy is a well-established method to probe the various non-bonded interactions playing between host and guest molecules in case of inclusion complexes. The presence of numerous groups in a compound may be preciously detected by FTIR spectroscopy. The shifting of characteristic frequency of any group of an inclusion complex from its pure host or guest compound provides the important clue about the presence of non-bonded interactions.

UV–visible spectroscopy termed as absorption spectroscopy is very helpful to study the stoichiometry of inclusion complex and also to evaluate the association constant (K_a) of host-guest system. A molecule may undergo electronic transitions (π-electrons or non-bonding electrons) upon absorption of light in the UV- visible regions. From the UV–visible spectra we can easily draw the Jobs plot to confirm the stoichiometry of inclusion complex and from the Benesi-Hildebrand equation we can calculate the association constants (K_a) precisely. Nuclear Magnetic Resonance spectroscopy is sophisticated tool to investigate the inclusion phenomena. Proton NMR and 2D-ROSEY NMR spectroscopy help finding the mechanism of inclusion complex formation more specifically.