ABSTRACT

The research of inclusion complexation and solvation effect in aqueous and liquid systems by different physicochemical, thermodynamic and spectroscopic methods engage the alter in properties of one matter in the presence of another. 'Chemistry of Solution' mostly deals with the physicochemical approaches to estimate the extent of solvation in different solution media. These approaches include the studies of density, viscosity, refractive index and conductivity, surface tension, etc of different electrolytic and non electrolytic substances. Measurement of Thermodynamic parameters such as the change of Free Energy (ΔG), Enthalpy (ΔH) and Entropy (ΔS) afford the idea about the achievability of inclusion and solvation of a variety of compounds.

In liquid solution studies on diversified interactions of molecules are very valuable to obtain information on the geometrical effects as well as intermolecular interaction occurring in the liquid systems. Exact knowledge of thermodynamic properties of solution mixtures has great consequence in theoretical and applied region of research.

The accumulation of a solute or ion modifies both the solute and solvent structure to some extent. The interaction between solute-solute, solute-solvent and solvent-solvent molecules results ion–solvation of the solute molecules. The extent of ion-solvation is depended upon the interactions happening between solute-solute, solute-solvent and solvent-solvent molecules. Different non-covalent interactions, such as, hydrogen bonding, ion dipole, dipole-dipole, hydrophobic-hydrophobic, hydrophobic-hydrophilic interactions are also mixed up in this system. This explains the efficacy of solution chemistry to clarify the precise nature of interactions through different physicochemical, thermodynamic and spectroscopic techniques.

The physicochemical natures of solute and electrolyte depend entirely on ion-ion and ion-solvent interactions. Ion-ion interactions are usually stronger than ion-solvent interactions. Dilute solution of solutes is theoretically familiar but ion association or ion solvation still remains a complex procedure.

The inclusion and solvation phenomena of ionic liquid, drug and biologically-active molecules in aqueous and non-aqueous system can be confirmed by the spectroscopic method, The accurate part of the molecules which are related to the inclusion and solvation process can satisfactorily expressed by UV-Visible, FT-IR , NMR , 2D-ROESY NMR, P-XRD, EMI-MS, HR-MS, and MALDI-MS studies.

Thus from wide investigations in aqueous and non-aqueous binary solvents along with ternary systems, it is now growing interest of researcher because of the majority of the electrolytes and biologically lively molecules are appreciably customized by solvent systems.

In this effort ionic liquids 1-butyl-4-methylpyridinium hexafluorophosphate ([BMPy]PF_6) and 1,3-dimethylimidazoliummethyl sulphate are measured respectively. They have good transport and surface properties. Its intrinsic physicochemical properties make it "designer solvents" or "green solvent", such as the favorable solubility of organic and inorganic compounds, negligible vapour pressures, low melting points, high thermal stability, solvated many organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical stability. In adding up, along with these outstanding properties, ionic liquids are used as heat transfer materials for processing biomass and electrically transport liquids as electrochemical tool in electrochemistry.

On the other hand, Thiamine Hydrochloride (Vitamin B1), Allopurinol (ALP), Theophylline (THP), Uric Acid (UA), and Nortriptyline Hydrochloride (NTPH) are the bio-active molecules and have dormant applications in Biochemic Body . In order to achieve the potential health profit of bioactive molecular information regarding the knowledge of their solubility, absorption, metabolic activity and biological effects are necessary. Pharmacological action is frequently measured to explain advantageous effects of bio-molecules. This translates towards recommending a diet rich in a different vegetables, fruits, whole grains, legumes, oils, and nuts. Many essential functions are synchronized by transient release of biochemically active body at a definite time and site in the body under bio-chemical conditions. In the drug delivery research work, they

have been markedly used as curative agents to a patient in a palatine or staggered release contour more than the last two decades.

The interactions of host molecules in aqueous and non-aqueous media with the hollow space based molecules, e.g., α-Cyclodextrins, β-Cyclodextrins, HP-β-Cyclodextrins 15-Crown-5 ether furnishes the new insight into the molecular inclusion or complexation through non-covalent interactions.

Supramolecular Host-Guest Chemistry provide a extensive idea about the construction of Inclusion Complex(IC) between the host and the guest molecules. Thus, most of these interactions have been exhibited by host-guest interactions. Amongst the host molecules, Cyclodextrins and Crowns Ethers seems to be the most promising to form inclusion complexes, specially with a variety of guest molecules with appropriate polarity and dimensions. In Host-Guest Chemistry, an inclusion compound is a typical complex in which one chemical compound (the "Host") forms a cavity in which a second molecule "Guest" compound is placed.

The study of these solutes and solvents are, therefore, essentially significant because of their extensive utilization in many industries ranging from pharmaceutical to cosmetic products.

SUMMARY OF THE WORK DONE

CHAPTER I

This chapter contains the objectives, scope and applications of the research work. This mainly comprises the selection of solute and solvent molecules used and applications in diverse fields, technique of work done and abstract of the work allied with this thesis.

CHAPTER II

This chapter includes the general preface of the thesis and the review of the previous work. The brief conversation on ion-ion/solute-solute,ion-solvent/ solute-solvent and solvent–solvent interactions have been offered here. Different theoretically models for weak interactions are also well measured, stressing the significance of the work related with this thesis.

CHAPTER III

This component of the thesis explains the experimental sections consisting of the source, purity, structure and application of the solute and solvents. A variety of experimental techniques are included for measurement of volumetric, transport and spectroscopic principle.

CHAPTER IV

This Chapter includes the inclusion complex of antidepressant drug molecule with crown ether 15-C-5 was prepared and characterised successfully. The inclusion complexes with Crown ether in the aqueous medium and in solid state were studied by different physicochemical methodologies. Formation of inclusion complex was confirmed by 1H NMR, FT-IR studies. Surface tension and conductance, was studied in the aqueous system, the 1:1 stoichiometric ratio of inclusion complex was obtained. The UV-VIS study supported the formation as well as stoichiometry of inclusion complex. Association Constant and Thermodynamic Parameters were calculated which strongly supported the elevated stability and feasibility of formation of the host guest inclusion complex.

CHAPTER V

This Chapter consists of the significance of release from gout pain in Biochemic body caused by limitation of precipitation of uric acid by allopurinol has been measured through physicochemical study. Here, we have carried out the density (ρ), viscosity (η) and UV-Vis measurements of allopurinol in w_1= 0.00001, 0.00002 and 0.00003 mass fraction of aqueous uric acid binary mixtures at T= 298.15K, 303.15K, 308.15K, 313.15K. These measurements have been performed to ternary mixture (allopurinol +uric acid+ water) to develop some important parameters, namely, limiting apparent molar volume (φ_V^0), viscosity B-coefficients from extended Masson equation and Jones-Dole equation respectively. The refractive index (n_D) has been calculated on the same ternary mixtures at T=298.15K. Lorentz-Lorenz eq^n has used to estimate molar refractive index (R_M) and limiting molar index (R_M^0). Nature of interaction is determined

from UV-Visible spectroscopy. These parameters have been interpreted in terms of interactions of solute-solute and solute- solvent.

CHAPTER VI

This Chapter incorporates the steady host–guest inclusion complexes have been produced with medicinally important guest molecule Theophylline (THP) within aqueous α-Cyclodextrin (∝-CYD) and β-Cyclodextrin (β-CYD). α-and HP-β-Cyclodextrins (HP-β-CYD) have been established with favourable structural features for inclusion with theophylline which include diversified applications in modern science such as controlled delivery in the field of pharmaceuticals, food processing, pesticides, foodstuffs etc. Theophylline is one of the most widely accepted drugs for the treatment of asthma and chronic obstructive pulmonary disease (COPD) worldwide, even if it has been used clinically for many years. With both α and HP-β- Cyclodextrins it is found that 1:1 hosts-guest inclusion complexes are formed with the guest molecule theophylline. The construction and quality of the inclusion complexes have been characterized by using conductivity measurement, surface tension study, and Job's method. The inclusion phenomenon has been confirmed by FTIR spectroscopy, proton NMR study. Association constants and thermodynamic parameters have been evaluated for the created inclusion complexes by ultraviolet spectroscopy.

CHAPTER VII

This Chapter comprise solution behaviour prevailing in 1, 3-dimethyl imidazolium methyl sulfate (IL) and some diverse industrially important alkoxy - alcohols or cellosolves have been investigated by electrolytic conductivity, density (ρ), viscosity (η) and FT-IR spectroscopic investigation. The derived parameters such as the limiting molar conductivities (Λ_0), association constants (K_A), the distance of closest approach (R), etc. of the ions supplemented with conductance, density and viscosity have been evaluated using the Fuoss conductance equation (1978). The quantitative values of molecular interactions from thermodynamic parameters have been discussed in terms of some non-covalent interactions. Functional groups of the pure solvents and structural

characteristics of ionic liquid in different solvents have been discussed and taken into contemplation for spectroscopic study.

CHAPTER VIII

This Chapter covers examination of molecular interaction widespread in [ALP] and in aqueous solutions of α- , β-, HP-β-CD cyclodextrin have been probed by thermo physical properties. UV studies establish formation of inclusion complexes with 1:1 stoichiometry. Coverage of interaction (solute–solvent interaction) is articulated in terms of complexes, have also been analyzed via stability constant-NMR, Steady state Fluorescence, FT-IR, ESI-MS, XRD, SEM, and Cytotoxicity, Hydrophobic effect, Hydrogen-bonds, structural effects creation of inclusion complexes.

CHAPTER IX

This Chapter contains the preparation and characterisation of water soluble inclusion complex incorporating water insoluble ionic liquids 1-butyl-4-methylpyridinium hexafluorophosphate ([BMPy]PF_6), ∝-CD and β-CD. To investigate the formation and feasibility of ICs by various physico-chemical methods including the spectroscopic methods have been used. The inclusion complexes of pyridinium typed hydrophobic ionic liquids (IL) were prepared. The ICs are water soluble and characterised effectively. The inclusion complexes of sparingly soluble IL prepared with ∝- and β-cyclodextrin in the mixed solvent medium and in solid state were studied by different physicochemical methodologies. Comparison of the chemical shift of the pure CDs, guest and complexes formed in 1H NMR spectra, appearance of the crossed peaks in 2D-ROESY NMR spectra and shift of the positions of the band in FT-IR spectra established the formation of inclusion complexes. Surface tension and conductance studies in the mixed solvent system supported the 1:1 stoichiometric ratio of the inclusion complex.

CHAPTER X

This chapter includes the concluding remarks on the research works associated with the thesis.

"Ultimately, when you at any biological question it becomes a chemical problem." – Venkatraman Ramkrishan, received Nobel Prize for Chemistry of Life