# ***ABSTRACT***

The study of surface behaviour, inclusion complexation and solvation consequence in aqueous system by physicochemical, thermodynamic, advanced microscopic and spectroscopic methods involve the change in properties of one substance solely or in the presence of another compound. 'Solution Chemistry' mainly deals with the physicochemical approaches to estimate the extent of solvation in liquid media. This approach includes the studies of density, viscosity, refractive index conductance and surface tension, etc of electrolytes and non electrolytes. Thermodynamic approach by measuring the free energies, enthalpies and entropies gives the idea about the feasibility of micellar aggregation, inclusion and solvation of various compounds.

Studies on interactions of molecules in solution are very useful to acquire information regarding the geometrical effects as well as intermolecular interaction taking place in the liquid systems. Accurate knowledge of thermodynamic properties of solution mixtures has great importance in theoretical and applied area of research.

The addition 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 taking place between solute-solute, solute-solvent and solvent-solvent molecules. Various non-covalent interactions, such as hydrogen (H)-bonding, ion dipole, dipole-dipole, hydrophobic-hydrophobic and hydrophobic-hydrophilic interactions are also involved in this system. This explains the effectiveness of solution chemistry to elucidate the exact nature of interactions through different physicochemical, thermodynamic and spectroscopic techniques.

The chemical nature of solute or electrolyte depends totally on ion-ion and ion-solvent interactions. Ion-ion interactions are generally stronger than ion-solvent

interactions. Dilute solution of solutes is hypothetically well known but ion association or ion solvation still remains a complex procedure.

The spectroscopic contribution confirms the inclusion, aggregation and solvation phenomena of some electrolyte and bio-active molecules in aqueous media. The exact part of the molecules which are associated with the inclusion, aggregation and solvation process can nicely expressed by UV-visible, FT-IR, fluorescence and FT-NMR studies.

Thus from extensive investigations in aqueous system, it is now growing interest of researcher because of the majority of the electrolytes and bio-active solutes are significantly modified by solvent systems.

In this research work, surfactant, ionic liquids, ionic liquid based surfactants e.g. sodium dodecyl(lauryl) sulfate, 1-butyl-3-methylimidazolium chloride, 1-butyl-1-methylpyrrolidinium tetrafluoroborate, 1-butyl-4-methylpyridinium chloride, 1-butyl-4-methylpyridinium lauryl sulfate (Synthesized), 1-dodecyl-4-methylpyridinium iodide (Synthesized) are investigated. They have good transport and surface properties. Long chain ionic liquid behaves also as surface active compounds due to the presence of long hydrophobic chain. Their intrinsic physicochemical properties make them “designer solvents” or “green solvent”, such as the favourable 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 addition, along with these exceptional properties, ionic liquids are used as heat transfer materials for processing biomass and electrically transport liquids as electrochemical tool in electrochemistry. Due to the presence of surface activity they can be used as benign surfactant. Head group modified (by ionic liquid) surfactant more efficient than the precursor surfactant.

On the other hand, alkaloids (e.g. trigonelline hydrochloride), amino acids (e.g. L-Cysteine), citric acid monohydrate are the organic bio molecules and have potential applications in living systems. In order to obtain the potential health benefits of bio molecules information regarding the knowledge of their solubility,

absorption, metabolism and biological effects, interaction of surfactant or disease containing substance (e.g. uric acid) is essential. Pharmacological activity is often considered to describe beneficial effects of bio molecules. This translates towards recommending a diet rich in a variety of vegetables, fruits (especially citrus fruits), whole grains, legumes, oils etc. Many vital functions are regulated by pulsed or transient release of bio-active substance at a specific time and site in the body under physiological conditions. In drug delivery research, they have been notably used as therapeutic agents to a patient in a palatine or staggered release profile over the last two decades. Sustainable release of anti diabetic agent for diabetic patients is also important aspect of modern research.

Incorporation of solutes molecules in aqueous media with the cavity based molecules, e.g., α-cyclodextrins, β-Cyclodextrins or highly water soluble hydroxypropyl β-cyclodextrin provides the new insight into the molecular recognition (e.g. inclusion or complexation) through non-covalent interactions.

Supramolecular host-guest chemistry gives a broad idea about the formation of inclusion complex between the host and the guest molecules. Thus, most of this interaction has been performed by host-guest interaction. Among the host molecules, cyclodextrins and its derivative seems to be the most promising to form inclusion complexes, especially with various guest molecules with suitable polarity, resulting solubility and dimensions. In host-guest chemistry, an inclusion complex is a complex in which one chemical compound (the "host") forms a cavity in which molecules of a second "guest" compound are suitably positioned.

Therefore, the study of these solutes and solvents and their surface behaviour, solution thermodynamics and supramolecular recognition etc. are necessarily significance because of their wide range of applications in many industries ranging from pharmaceutical to cosmetic as well cleaning products.

**PHYSICO-CHEMICAL PARAMETERS AND THEIR SIGNIFICANCE**

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent/ion-solvent and solute-solute/ion-ion interactions in solution. The sign and magnitude of partial molar volume ($\phi_V^0$) also provides information about the nature

and magnitude of ion-solvent interaction while the experimental slope ($S_v^*$) provides information about ion-ion interactions. Viscosity B-coefficient obtained from the viscosity values indicates the extent of ion-solvent interaction in a solution. From experimental speed of sound values, limiting apparent molar adiabatic compressibility ($\phi°_K$) and the experimental slope ($S_k^*$) can be estimated. These parameters also give an idea about the ion-solvent and ion-ion interaction in the solution.

The transport properties in most cases are studied using the conductance data, especially conductance at infinite dilution. Limiting molar conductance ($\Lambda_0$) gives an idea about the ion-solvent interaction in the solution. The CMC values obtained from different techniques provides information about the aggregation concentration. The aggregation number obtained theoretically as well as from experiment is the average number of molecules present in a micelle once critical micelle concentration (CMC) has been reached.

## Summary of the works emphasize in the dissertation

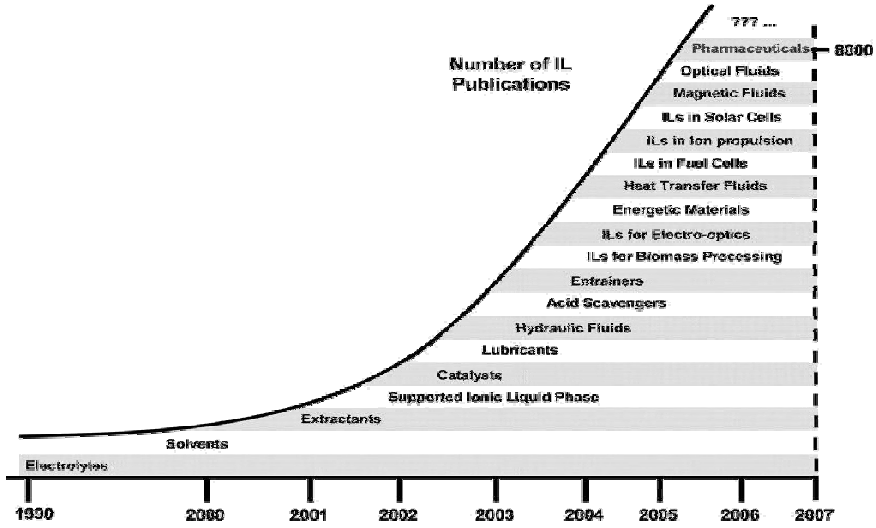
**CHAPTER I**

This chapter deals with the **principle, scope and applications** of the research work. This mainly comprises the selection of solute and solvent molecules used and applications in a variety of fields, method of work done and summary of the work associated with this thesis.

**CHAPTER II**

This chapter states the **general introduction** of the thesis and the review of the previous work. The brief discussion on solute-solute, solute-solvent and solvent–solvent interactions have been presented here.

Various theoretically models for weak interactions are well considered, stressing the importance of the work connected with this thesis.

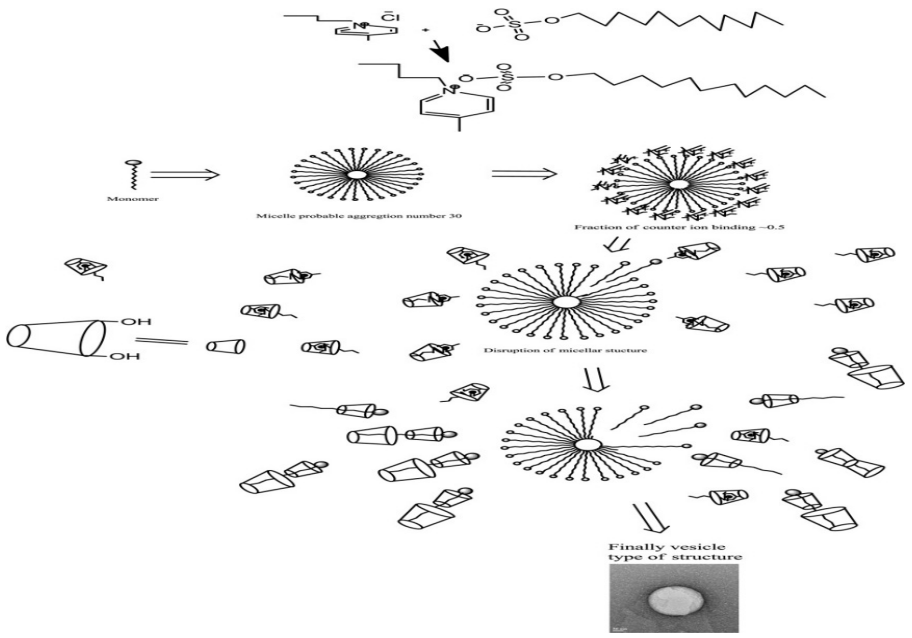



**CHAPTER III**

This part of the thesis explains **the experimental sections** consisting of the source, purity, structure and application of the solute and solvents. Various experimental techniques are incorporated for measurement of volumetric, transport, microscopic and spectroscopic purpose.

**CHAPTER IV**

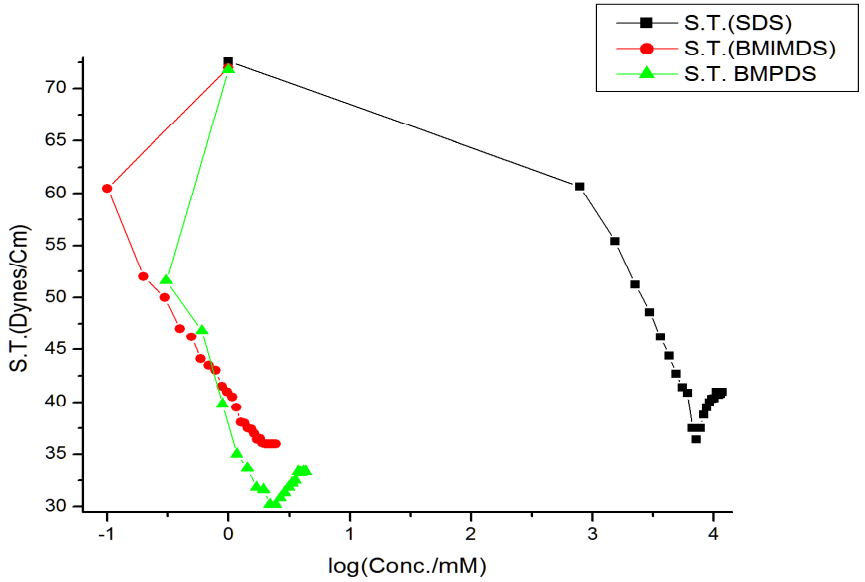
1-Butyl-4-methylpyridinium lauryl sulfate was synthesized and a number of spectroscopic techniques were used for the characterization. The surface active property was explored in different ways. The Host Guest inclusion complex formation with the synthesized compound inside the β-Cyclodextrin was studied qualitatively as well as quantitatively with physicochemical, spectroscopic and advanced microscopic techniques. The Job plot from the UV–vis spectroscopy indicates the formation of both 1:1 and 2:1 inclusion. The inclusion complex was given the determining morphology with further evidence of 2:1 inclusion in HRTEM supported by DLS. Lastly, the 2D-NOESY was provided a conclusive mechanism for the inclusion phenomenon.




**CHAPTER V**

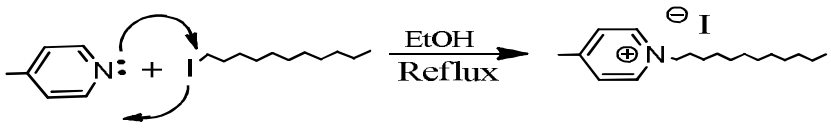
Halogen-free BMIMDS and BMPDS derived from inexpensive chemicals were synthesized using ion exchange, a method easier than that of the previous literature. Precursors for synthesis were BMIMCl and $BMPBF_4$ (Ionic liquids) with Sodium dodecyl (lauryl) sulfate as the common precursor. Characterization was done by FT-IR as well with more sensitive FT-NMR.

Physicochemical studies viz. surface tension, conductivity, DLS, zeta potential, Fluorimetry, polarisation optical microscope etc were performed. CMC values of both synthesized surfactants were quite lesser compare to our well know anionic surfactant as well as the common precursor sodium dodecyl sulfate. Aggregation number of both product was also determined with static fluorescence quenching technique as CPC as quencher. Higher value of zeta potential of BMIMDS compare to BMPDS at comparable concentration established role of counter ion in monomer as well as micellar stability. Equivalent size profiles from DLS for both derived surfactants indicate the existence of micellar aggregation even far beyond CMC.

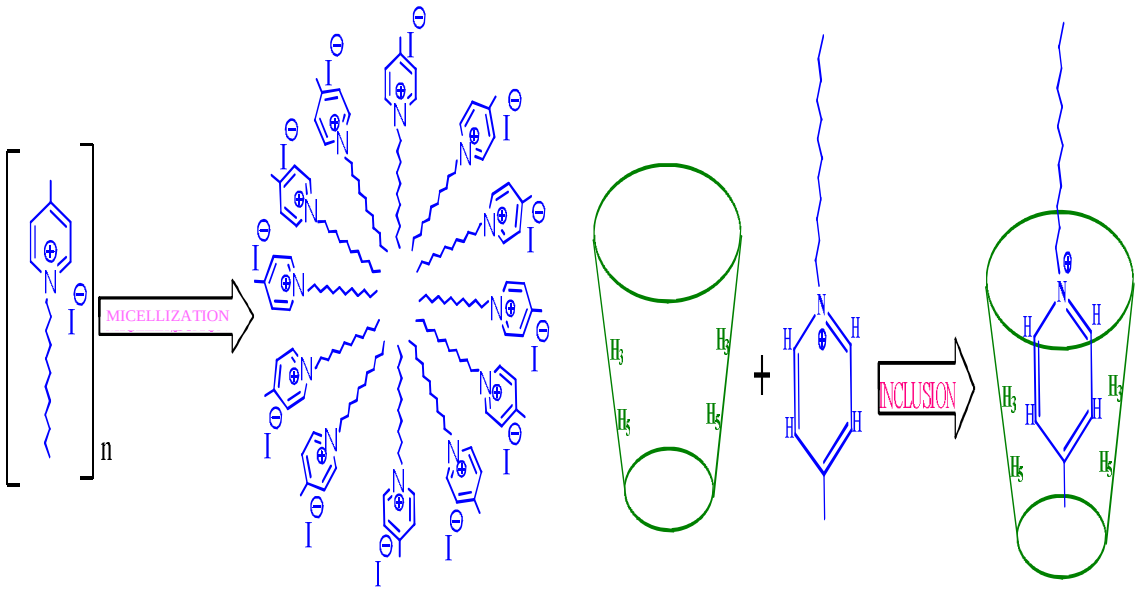



**CHAPTER VI**

1-Dodecyl-4-methylpyridinium iodide was prepared, purified and characterised. The surface activity, size and stability were judged by surface tension, SEM and DLS techniques. The Host guest inclusion complex formation of the synthesized guest with the β-Cyclodextrin and its hydroxypropyl derivative was explored with physicochemical, spectroscopic and scanning electron microscopic techniques. Conductance and surface tension experiment also provide subsistence of 1:1 inclusion. The Job plot from the UV-vis spectroscopy indicates the formation of 1:1 inclusion. Binding constants for the inclusion of DMPI with both β-CyD & HP-β-CyD was determined with UV-vis and fluorimetric techniques. Anti bacterial properties of DMPI and its both inclusion complexes were analyzed and compared.

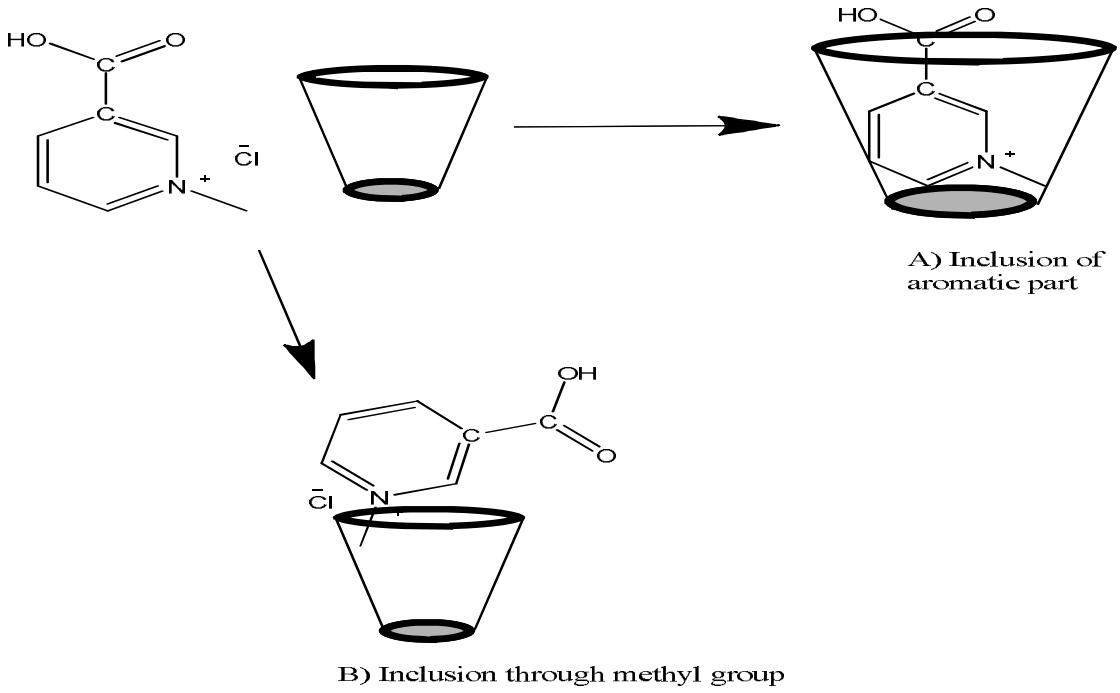



*Synthesis*



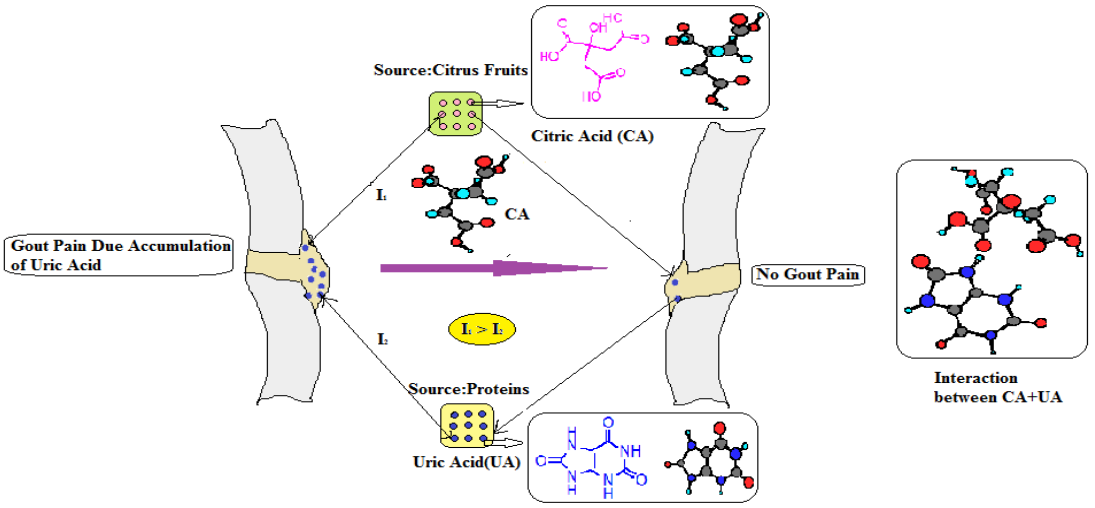

**CHAPTER VII**

Formation of the host-guest inclusion complex between Trigonelline hydrochloride (3-carboxy-1-methylpyridinium chloride), a hydrochloride salt of an anti-diabetic alkaloid and either α or β-Cyclodextrin (cyclomaltoheptaoses) was studied by several techniques including transmission electron microscopic (TEM) microscopy. A number of physicochemical and spectroscopic techniques, namely conductivity, surface tension, UV-Vis, FTIR, NMR and Mass spectroscopy were utilized for their characterization. Cyclodextrin-salt of alkaloid inclusion complex (IC) was found to exhibit a distinct change in the surface morphology, crystalline nature & size in the TEM. Its modified nature in inclusion complex was further explored by powder XRD, dynamic light scattering experiment. Role of the methyl group of Trigonelline hydrochloride in inclusion complex formation was well established by 2D-NOESY study. Anti diabetic property in the light of sustained release mechanism of the resultant complexes was also explored.



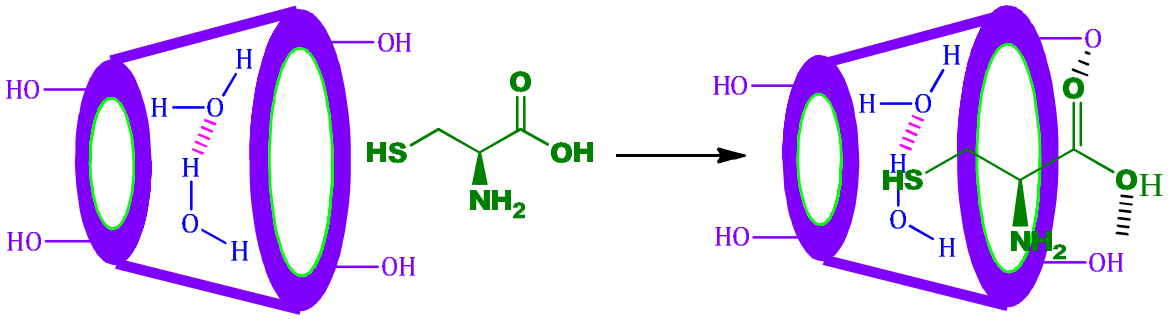

**CHAPTER VIII**

The effect of relief from gout pain due to the restriction of precipitation of uric acid (UA) by citric acid (CA) has been studied through physicochemical study. Here, we have carried out the density ($\rho$) and viscosity ($\eta$) measurements of CA in *w1*=0.00001, 0.00002, and 0.00003 mass fraction of aqueous UA binary mixtures at *T*=298.15K, 303.15K, 308.15K, and 313.15K and at pressure 1.013 bar. These measurements have been performed to ternary mixture (CA + UA + water) to derive some important parameters, namely, limiting apparent molar volume ($\varphi_V^0$), viscosity B-coefficients from extended Masson equation, and Jones–Dole equation, respectively. The refractive index (nD) was done on the same ternary mixtures at T=298.15K. Lorentz–Lorenz equation has used to evaluate molar refractive index (RM) and limiting molar index ($R_M^0$). These parameters have been interpreted in terms of interactions of solute itself and with solvent.




## CHAPTER IX

The host–guest interaction of an amino acid L-Cysteine as guest with α and β cyclodextrin have been investigated which have significant applications in the field of medicine such as controlled drug delivery. The $^{1}H$ NMR study confirms the formation of inclusion complex while surface tension and conductivity studies support the formation inclusion complex with 1:1 stoichiometry. The host-guest interaction has been explained on the basis of hydrogen bonding, Vanderwaal's force and exceptional structure of cyclodextrin.



## CHAPTER X

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