CHAPTER: I

NECESSITY OF THE RESEARCH WORK

I.1. OBJECT, SCOPE AND APPLIANCES OF THE RESEARCH WORK

Ionic solid may be defined as a customary salt in solid state having symmetric cation and anion. Ionic solids are mainly made up by the chemical combination of ***metallic*** and ***non-metallic*** elements. "Salt"- a broad chemical expression refers to ionic compounds (ionic solids) created when a reaction between acid and base occurs. In case of ionic solid or salt, due to having strong forces between the particles, they are hard, brittle crystal and having high melting temperature. Since in solid state of ionic solids no free moving particles are present, they do not conduct electricity in solid state. Only in molten state or in solution having free moving particles ionic solids conduct electricity. Ionic salts are generally hard but brittle and having high melting and boiling temperatures. The unique properties of ionic solids signify strong forces between the particles and it takes a lot of energy to move them all relative to each other. In case of ionic solid the three dimensional lattice is held together strongly by electrostatic forces of attraction between positive and negative ions. This electrostatic force is called ionic bonding. At present, salt extends to be of leading monetary corollary, with thousands of uses in accumulation to senescing and conserving food. Sodium chloride (NaCl) occurs in nature as the mineral halide, generally known as rock salt, in great subversive deposits on each continent. Salts have so many uses such as Salt became an essential element of commercial dealings and was often used as money or trade. Ionic solids used as phase transfer catalyst, surface-active agents etc. In industrial usages ionic solids act as active ingredient for conditioners, antistatic agent, detergent sanitizers, softener for textiles and paper products etc. Due to low cost and low toxicity [1] of but_4NI in recent times it has appeared as a promising substitute as

a catalyst for functionalization of C–H bonds [2]. In medicinal field it uses as antimicrobials, algaecide, slimicidal agents, disinfection agents and sanitizers etc.

Ionic Liquids (ILs), a new assemblage of resources existing as a salt in the liquid state attract very much attention in scientific and engineering investigate. ILs are the generic term for a class of materials, consisting entirely of ions and being liquid below 100°C. It is habitually defined as salts with low melting point, typically below 373K. [3] The straightforward combinatory investigation designates vis-à-vis 10^{18} ILs can perhaps be manufactured. These assortments unwrap broad occasions in the couture of ILs apposite for convenient appliances. The considerate of the performance of ILs and their properties is essential for any practical relevance.

Ionic liquids have achieved global awareness as green solvents in the preceding decade. These studies investigate the essential science and engineering of using ionic liquids as a novel cohort of solvents to reinstate the customary organic solvents. They are accessible as novel solvents for the alternative of organic solvents and the configuration of elegant liquids. The exploration also anticipated nano- and atom-scale structuring of ionic liquids, a characteristic that emerges to entirely buttress their unique behavioural features and assist exact prophecies of inclinations. Due to having various properties such as easy separation, very low vapor pressure, non-flammable substance, high thermally stable, high mechanically stable, electrochemically stable, low toxicity, non-volatility etc. properties ionic liquids have growing interest as ***green solvent***. Ionic liquids are widely used as environmental-friendly reaction systems. An ionic liquid is mainly typified by a range of minimum specific conductivity in the $mScm^{-1}$, jointly with a molar conductivity [4,5] perhaps beyond 0.1 $Scm^2 mol^{-1}$. In accumulation, the liquid ought to merely restrain ions with minor numbers of ion pairs or parent molecules. Ionic liquids are apt to have low dielectric constants, which signify they are not ionizing solvents [6,7]. With the extent of major issues we may assign ionicity [8] of an ionic liquid in terms of its conductivity values. From the above tête-à-tête one basic question may arise and thus in respond to the aperture issue, “What is an ionic liquid?” I desire the respond, “It be an appearance of liquid salt restraining ions and ion pairs in its current affirm.”[9]

If at room temperature ionic liquids become liquid, we christen them as room temperature ionic liquids (RTILs). Information of the properties of the RTILs is essential for selecting an appropriate liquid for apiece of their trade employments.

The phrase '*solution*' is mainly employed in meticulous case of an assortment between diverse components, explicitly, when a little quantity of solid, liquid or gaseous substances disband to a firm limit in a liquid or solid substance (it may be pure, or a mixture itself), solvent.

An ionic solid is a conformist salt present in solid state having symmetric cation and anion. On the other hand an ionic liquid (IL) is a salt in the liquid state or phase having symmetric anion and asymmetric cation. Ionic Liquids (ILs) is the broad expression pro a set of resources, exclusively consisting ions and become liquid below 100°C. (Figure 1) Ils are a novel invention of chemicals having a great potential to contribute in the greenness of chemical procedures and developing new appliances such as in pharmaceutical industry. Green chemistry acts an extremely imperative function in the sustainable improvement, looking for reducing and averts effluence at its resource; reduce the vulnerability and exploit the effectiveness of the chemical procedures.

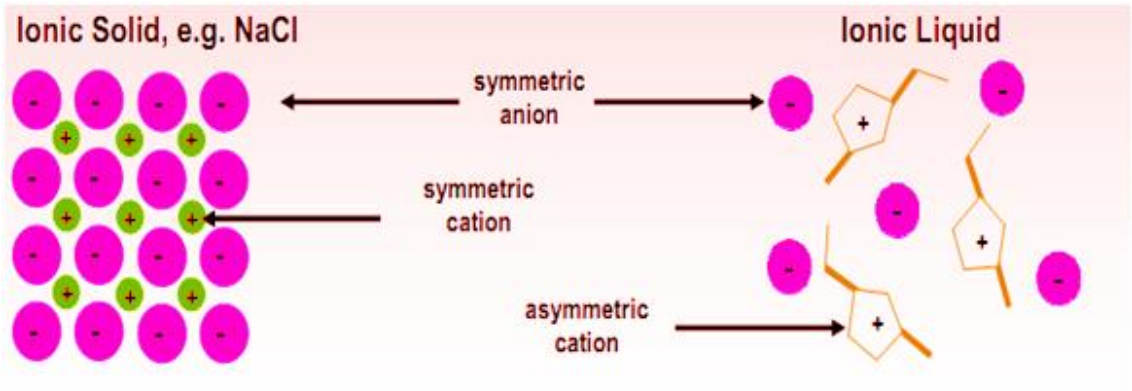

Figure 1: Basic structural differences between ionic solid and ionic liquid

HOST-GUEST INCLUSION CHEMISTRY

The greatest improvement of supramolecular chemistry was occurred from 1987 after the achievement of the Nobel Prize of Lehn, Cram, and Pedersen on explanation of their

important innovations about the host–guest systems. Host-guest chemistry majorly describes complexes that are composed of two or more molecules which are held together in unique structural relationships by non covalent interactions. Yet as its innovation, the notion of supramolecular chemistry has concerned plenty of interest from chemists, biologists, and material scientists, where they exploit the noncovalent interactions, together with hydrogen-bonding communication, π–π stacking interface, electrostatic interface, van der Waals force and hydrophobic/hydrophilic attraction [6-10]. Throughout the previous decades, substantial efforts have been remunerated to expand copious supramolecular systems and to inspect their appliances in catalysis, electronic devices, functional materials, nanomedicine, sensors and so on [7–10]. In virtue of the reversibility and adaptableness of host–guest communication, (Figure 2) supramolecular systems have been developed into diverse morphologies with diverse purposes to execute precise necessities in biomedical relevances.

Figure 2: Schematic Representation of Host-Guest Inclusion Complex Formation

In an emblematic host–guest inclusion complex, a host molecule affords a cavity to encapsulate a guest molecule through noncovalent communications. Due to having a variety of noncovalent interfaces in host-guest complexation, host–guest interaction

based on macrocyclic molecules is an extremely imperative incident that has been widely explored. Two or more chemical moieties can be incorporated together during such host–guest inclusion, in a facile and reversible manner which provids immense potential for the edifice of new-fangled supramolecular structures.

Major uses of host-guest chemistry are as follwes

Pharmaceutical industry: Treatment of inflammation or throat infection (with iodine), coronary dilatation (with nitroglycerin), anti-ulcerate (with benexate), vectors for vitamins or hormones, decrease of side-effects and amplify in efficiency of anti-cancer drugs.

Cosmetics & Hygiene: Long-lasting perfume release deodoriser (with peppermint oil, i.e.), to remove dryness wrinkles (with seaweed compounds, vitamin A & E), anti-cellulitis compound, shampoo industry, teeth cleaning, anti-plaque compound, antibacterial in refrigerators.

Food industry: Emulsion stabiliser, taste-masking, long-lasting flavouring, removal of cholesterol from milk, butter, eggs etc.

Paint industry: Increase in compatibility of paint ingredients, enhance in stability of the paint, increase in the range of colours and in the quality of dyes.

Environmental protection: Reduction in oxidiser requirements in paper production, environmentally friendly oil-spill clean-up, treatment of tree-wounds (with auxin), mobilisation of toxins without leaving toxic residues behind (innovative technique), removal or detoxification of dissipate stuff, specially aromatic toxins, employ in agriculture for increasing the steadiness and the competence of herbicides, insecticides, repellents.

Chemical and biochemical appliances: Reaction catalyst in glue, apply in chromatography (separation of stereoisomers), enhance in speed of diagnostic test reaction.

In my present research study ionic solids and ionic liquids are taken as guest molecules and the major host molecules such as CDs and CBs are taken owing to their extensive appliances in the biomedical field.

Objective

The significance and exploits of chemical electrolytes (ionic solids and ionic liquids) in non-aqueous pure and mixed solvents have been abridged by very legendary scientists [11-23]. In recent times solute-solute/ion-ion and solute-solvent/ion-solvent communications have been focus of extensive attention.

The main aim of my present research work is to discuss and explain various interactions of some electrolytes especially ionic solids and ionic liquids in different industrially important solvent media through various physicochemical techniques. Elementary exploration on non-aqueous electrolyte solutions has catalysed their broad procedural appliance in a lot of grounds. Due to their elevated suppleness based on the variety of various solvents, additives and electrolytes with extensively varying properties, non-aqueous electrolyte solutions are essentially challenging with other ionic conductors. Prevalent achievement of non-aqueous electrolytic solutions are high energy primary and secondary batteries, photoelectrochemical cells, electro machining, etching, polishing, electrosynthesis, wet double layer capacitors, electro-deposition and electroplating.

Drug transport across biological cells and membranes is dependent on thermophysical properties of drugs. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as parameters are expedient for interpreting intermolecular interactions in solution. Also the study of thermodynamic properties of drug in a apposite medium can be correlated to its therapeutic effects [24,25].

Host-guest inclusion complexation studies majorly covered in biomedical relevances, chiefly addressing drug delivery, photodynamic cancer therapy, gene delivery as well as bioimaging.

The major aims of the research work are:

- To explore the physicochemical properties of ionic solids and ionic liquids in pure and mixed solvent systems.
- To comprehend the character and potency of diverse communications, their influence on structural and dynamic properties of ionic solids and ionic liquids in pure and mixed solvent systems.

- To study the transport properties of ionic solids and ionic liquids along with thermodynamic and acoustic ones to characterize molecular interactions in solutions.
- To survey the host-guest inclusion complex formation of some guest molecules (ionic solids and ionic liquids) with diverse host molecules.

Importance of Thermodynamic Parameters

The considered *thermophysical, thermodynamic, transport, optical, acoustic and spectroscopic properties* are of immense significance in illustrating the properties and structural features of solutions. The nature of intermolecular communications can be exposed from the interpretation of the derived properties through the thermophysical study.

Volumetric properties like apparent molar volume calculated from density measurement are of also enormous consequence in considered the properties and characteristic of solutions. The facts therefore hearten us to extent the study of binary or ternary solvent systems with several industrially imperative solvents (polar, weakly polar and non polar) and some solutes/electrolytes. The sign and magnitude of thermodynamic quantity such as partial molar volume (ϕ_V^0), affords information concerning the nature and extent of ion-solvent interaction whilst the experimental slope (S_v^*) affords information regarding ion-ion interactions.[xx] Furthermore, the derived parameters obtaind from experimental density, viscosity and speeds of sound data and succeeding elucidation of the nature and strength of intermolecular interface assist in testing and improvement of various theories of solution. Thus the properties present imperative information regarding the nature and potency of intermolecular forces effective amongst assorted components also.

Precious information concerning the nature and strength of forces of electrolyres/non-eletrolytes viz. viscosity *B*-coefficient, useful in solutions can be attained from viscosity data. Recently the use of computer simulation of molecular dynamics has led to major development in the direction of a unbeaten molecular theory of transport properties in fluids and a proper understanding of molecular motions and

interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents has been established.[26,27]

The mode of communications akin to dissociation or association has accomplished an immense agreement which obtained from ultrasonic speed measurements and from the calculation of isentropic compressibility. It can also be used for the test of various solvent theories, statistical models and are fairly responsive for alteration in ionic concentration in addition to useful in illuminating the solute-solvent interactions.

Molar refraction obtained (R_M^0) from refractive index study using Lorenz-Lorentz relation is also an significant optical physical property of liquids and liquid mixtures persuade the solution of diverse problems in chemical engineering to facilitate the development of industrial processes. Knowledge of refractive index of multicomponent systems affords significant information vis-à-vis the molecular interactions happening in the solutions, [28-30] that is crucial for a lot of thermophysical calculations including the correlation of refractive index with density [31-33].

The study of thermophysical behaviours like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has achieved much significance. The acoustic measurements can also be used for the test of various solvent theories and statistical models and are quite sensitive to changes in ionic concentrations as well as useful in elucidating the solute-solvent interactions. Thermophysical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the industrial separation processes. The significance and use of the chemistry of electrolytes in non-aqueous and mixed solvents are well-recognised. However, the studies on properties of aqueous solutions have afforded adequate information on the thermodynamic properties of diverse electrolytes and non-electrolytes, the effects of variation in ionic structure, ionic mobility and common ions along with a multitude of other properties [34].

I. 2. ASSORTMENT OF SOLUTES AND SOLVENTS USED

Solvents: Industrially momentous solvents such as acetonitrile, diethyl carbonate, o-toluidine, o-xylene and 2-nitrotoluene, formamide, 2-methoxyethanol or methyl

cellosolve, N,N-dimethylformamide, N,N-dimethylacetamide, 1,3-dioxolane, tetrahydrofuran and widespread solvent water, have been preferred as main solvent in this research work.

Electrolytes: Ionic solids such as Lithium iodide, lithium perchlorate, lithium hexafluoroarsenate, tetrabutyl ammonium iodide, tetraheptyl ammonium iodide and ionic liquids such as 1-butyl-1-methylpyrrolidium bromide, n-dodecyln, n-dimethyl-3-ammonio-1-propanesulfonate, 1-butyl-3-methylimidazolium chloride, 1-butyl-1-methylpyrrolidinium chloride, 1-butyl-2,3 dimethylimidazolium, tetrafluoroborate, 1-butyl-4-methylpyridinium hexafluorophosphate etc. are used as electrolytes.

Non-Electrolytes: The used non-electrolytes are α-cyclodextrin, β-cyclodextrin, D(-)fructose, D(+)galactose, cucurbit[6]uril etc.

I. 3. METHODS OF EXPLORATION

The subsistence of free ions, solvated ions, ion-pairs and triple-ions of electrolytes/non-electrolytes in aqueous and non-aqueous media depends upon the concentrations of the solution, size of ions, and intermolecular forces, such as, electronegativity of the atom, dipole-dipole forces, dipole-induced dipole forces, H-bonding, Van der Waal forces, columbic forces and electrostriction, Inductive effect, side chain effect etc. Therefore, the study of various communications and equilibrium of ions in miscellaneous concentration provinces are of enormous consequence to the technologist, theoretician, industrialist, researchers due to the occurrence of most of the chemical processes in these systems.

Fascinatingly the diverse experimental procedures have been engaged to find out a superior perceptive the occurrence of solvation and diverse communications established in solution. Hence, we have engaged the five considerable thermophysical methods, viz., conductometry, densitometry, viscometry, ultrasonic interferometry, and refractometry to investigate the solvation phenomena.

In most cases the transport properties are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function

of concentration can be used to study the ion-association with the help of appropriate equations. The limiting ionic conductance of the each ion has been anticipated from the "*reference electrolyte*" method using tetrabutylammonium tetraphenylborate. The ionic conductances are also play the vital function to the elucidation of the ionic level of interface, association or ion-solvent interactions of ions as well as molecules. From conductometric study equivalent Conductance and Ion-Association Constant can be determined with the help of Fuoss conductance equation and Fuoss- Kraus conductance equation for Triple-Ion formation respectively. From density measurement with the help of Masson equation apparent molar volumes can be obtained, which are usually convenient parameters for interpreting ion-solvent/solute-solvent interfaces while, the experimental slopes afford ion-ion/solute-solute interactions in solution respectively. With the help of "*reference electrolyte*" method, ionic apparent molar volume for the individual ions has been acquired. From viscosity measurement with the help of Jones-Dole equation viscosity *B*- and *A*- co-efficients have been determined which imply ion-solvent and ion-ion interaction respectively. Moreover, the viscosity B-coefficient is alienated into ionic components by the *'reference electrolyte'* method. From the temperature dependence of ionic values, a satisfactory elucidation of ion-solvent interactions such as the possessions of solvation, structure-breaking or structure-making, polarization, etc. has been prearranged. From refractometric measurements with the help of Lorentz-Lorenz relation molar refraction has been determined which implies the compactness of the solute in solution system. (Limiting apparent molar adiabatic compressibility) which implies solute-solvent interaction and (Experimental slope) which implies solute-solute interaction can be determined from experimental speed of sound measurements. Surface Tension measurement has also done to interpret correctly the host-guest phenomena.

The spectroscopic study has been ascertained by the exploration of FTIR, NMR spectroscopy. The study has been taking into explanation to qualitative interpreting the molecular as well as ionic association of the electrolytes in the solutions.