

CHAPTER: I

NECESSITY OF THE RESEARCH WORK

1.1 SCOPE , OBJECTIVE AND APPLICATIONS OF THE RESEARCH WORK

Ionic Liquids (ILs) have recently emerged as “green” and environment friendly solvents for their use in the industrial manufacture of chemicals. In the past decade, ionic liquid have been increasingly used for diverse application such as organic synthesis, catalysis, electrochemical devices and solvent extraction of a variety of compounds. Ionic liquids are composed of cations and anions having low melting point ($<373\text{K}$).^[1,1] While the cations may be organic or inorganic, the anions are inorganic.

The interest in ionic liquids was initiated because of their advantageous physicochemical properties such as negligible vapour pressure, high thermal and electrochemical stability, high solvating power, etc. The choice of the cation and the anion constituting an ionic liquid has a profound effect on the physicochemical properties such as density, viscosity, conductivity and polarity. Ionic liquids offer a great flexibility in their properties since the possible combinations of cations and anions are quite high. This variety opens wide opportunities in the tailoring of ILs suitable for practical applications. The understanding of the behavior of ILs and their properties is crucial for any

practical application. But the available chemical and physical data are unfortunately inadequate in comparison to the amount of already commercially available ILs. Moreover, the existing data are often inconsistent. In this work we focused on the reliable determination of physicochemical, transport and spectral properties of ILs in solvent systems using different independent methods.

Recent years ionic liquids have been using as a new generation of solvents to replace the traditional organic solvents. They are presented as novel solvents for the replacement of organic solvents and the formation of smart liquids. The investigation also proposed nano- and atom-scale structuring of ionic liquids, a feature that appears to totally underpin their unique behavioural characteristics and facilitate accurate predictions of trends.

Understanding the properties of the RTILs is required for choosing a suitable liquid for each of their industrial applications. Moreover, complete data sets of RTIL properties are used for validating and improving molecular interaction and property prediction methods,^[1,2] which later will be applied to process interaction and process development and design.

Solvent organisation is one of the most fundamental properties of any liquid as it determines more complex processes such as solvation and reaction dynamics. It is believed that unique ordering in ionic liquids results from a balance between anion-cation, cation-cation and most importantly, ion-pair formation. The final parameter has been found to be critical to the '*ionicity*' or transport properties of the liquids and these atom-atom interactions mediate the dissociation of the ions and thus the ability to form solvation shells associated with the '*ionic liquid effect*'. To probe ionic liquid behaviour, the effect

of cation changes were examined experimentally and compared to that of model systems drawn for conventional molecular solvents.

Both the physical and chemical properties of a solution (liquid) is a result of the strength of their intermolecular forces and the forces between molecules arises from the same source: differing charges on adjacent molecules that lead to electrostatic attractions and governed by coulombs law. The molecules are acquired partial charges through the *intermolecular forces*, e.g., dipole-dipole forces, dipole-induced dipole forces, hydrogen bonding, Van der Waal forces and electrostatic interaction etc. *Intermolecular forces* in a solution control their thermodynamic properties and the understanding of the solvation thermodynamics is essential to the characterization and interpretation of any process performed in the liquid systems. These thermodynamic properties are quantities which are either an attribute of an entire system or are functions of position which is continuous and does not vary rapidly over microscopic distances, except in cases where there are abrupt changes at boundaries between phases of the system. Therefore, the studies on the thermodynamic along with the transport and spectral properties of solutions would provide a clear idea about the nature of the forces, interacting manner existing between the constituents of solution.

Hence, the real understanding of the large assortment of molecular interfaces is a difficult task. The aspect embraces a wide range of topics but we have embarked on a series of investigations based on the volumetric, viscometric, interferometric, refractometric, conductometric, potentiometric and spectroscopic behaviour to explore the chemical nature of the ILs in various solvent systems or of some electrolytes/ non-electrolytes interfaces in aqueous-IL solvent media.

Therefore, the main objective of the present research work is to explore and to understand the molecular as well as ionic level of interfaces of ILs prevailing in solvent systems by studying their thermodynamic properties based on various physicochemical approach.

The exploration of molecular interaction in fluids by physicochemical approaches has attracted attention, as thermodynamic parameters are convenient for interpreting intermolecular interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents. The different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for chemists and interest in the organic solvents transcends the traditional boundaries of physical, inorganic, organic, analytical and electrochemistry.^[1,3]

I.1.1 Importance of Physicochemical Parameters

The studied *physicochemical, thermodynamic, transport, optical, acoustic, and tensiometric properties* are of great importance in characterizing the properties and structural aspects of solutions. The nature of intermolecular interactions can be exposed from the interpretation of the derived properties by physicochemical approach.

Density of solvent mixtures and related volumetric properties like apparent molar volume are of also immense significance in measured the properties and feature of solutions. The facts therefore encourage us to extent the study of binary or ternary solvent systems with some industrially important solvents: polar, weakly polar and non polar solvents as well as with some solutes/electrolytes. The sign and magnitude of partial molar

volume (ϕ_v^0), a thermodynamic quantity, provides information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_v^*) provides information about ion-ion interactions.^[1.4] Furthermore, the derivative parameters derived from experimental density, viscosity and speeds of sound data and subsequent interpretation of the nature and strength of intermolecular interaction help in testing and development of various theories of solution. Thus the properties provide important information about the nature and strength of intermolecular forces operating among mixed components also.

Precious information concerning the nature and strength of forces of electrolytes/non-electrolytes effective in solutions can be obtained 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.^[1.5, 1.6]

The study of interactions like dissociation or association from ultrasonic speed measurements and from the calculation of isentropic compressibility has achieved a great deal. 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.

The refractive index is also important optical physical property of liquids and liquid mixtures influence the solution of different problems in chemical engineering in order to develop industrial processes. Knowledge of refractive index of multicomponent systems

provides decisive information regarding the molecular interactions occurring in the solutions,^[1.7-1.9] that is essential for many physicochemical calculations counting the correlation of refractive index with density.^[1.10-1.12]

The study of thermodynamic behaviours like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. 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. Physicochemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the industrial separation processes. However, the studies on properties of aqueous solutions have provided sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties.^[1.13]

The outcome and application of the chemistry of electrolytes (ionic liquids)/non-electrolytes (amino acids) in non-aqueous and mixed solvents have been abridged by Meck,^[1.14] Popovych^[1.15] Franks^[1.16] Bates^[1.17, 1.18] Parker^[1.19, 1.20] Criss and Salomon^[1.21] Marcus^[1.22] and others^[1.23-1.25]. The ion-ion or solute-solute and ion-solvent or solute-solvent interactions have been subject of ample attention and have been explicitly represented in *Faraday Trans. of the Chemical Society*.^[1.26] Elementary research on non-aqueous electrolyte solution has catalysed their wide technical application in many fields. They are really challenging with other ionic conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents,

additives and electrolytes with widely varying properties. High energy primary and secondary batteries, wet double-layer capacitors and super capacitors, electro-deposition and electroplating are some devices and processes for which the use of non-aqueous electrolytes solutions has brought the biggest success. [1.27-1.29] Other fields where the non-aqueous electrolyte solutions are used broadly include electrochromic displays and smart windows, photoelectrochemical cells, electro machining, etching, polishing and electrosynthesis. In spite of the wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of molecular interactions and their influence on the structural and dynamic properties of non-aqueous electrolyte solution.

Drug transport across biological cells and membranes is dependent on physicochemical properties of drugs. But direct study of the physicochemical properties in physiological media is difficult to realize. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as parameters are convenient for interpreting intermolecular interactions in solution. Also the study of thermodynamic properties of drug in a suitable medium can be correlated to its therapeutic effects. [1.30, 1.31]

I. 2 CHOICE AND IMPORTANCE OF SOLUTES AND SOLVENTS USED

A short description of the electrolytes (ionic liquids), non-electrolytes (amino acids), solutes (electrolyte other than ionic liquid) and solvents has been used throughout the research work is given below. The detailed description has been given in **Chapter III**.

1.2.1 Electrolytes

The most noteworthy ionic liquids have been used as electrolytes during the research work are

- (a) 1-Butyl-2,3dimethylimidazoliumtetrafluoroborate
- (b) 1-Butyl-pyridinium bromide
- (c) Tetrabutylphosphonium methanesulfonate
- (d) 1-Methyl-3-octyl imidazolium chloride
- (e) N-Butyl-4-methylpyridinium chloride

1.2.2 Non-Electrolytes

- a. Amino acids, viz. glycine, L-alanine, L-valine
- b. β -cyclodextrin

1.2.4 Solvents

The industrially important solvents have been used in the work are

The universal solvent water has been used throughout the work and the non-aqueous solvent e.g., Methyl cellosolve, Tetrahydrofuran, 1,4 Dioxane, Nitromethane, N,N-dimethylacetamide, Formamide, Methanol, Acetonitrile, and aqueous solution of 1-butylpyridinium bromide([BPy]Br) and Beta-Cyclodextrin.

The study of electrolytes (ionic liquids), non-eleetrolytes (amino acids) and solvents is of great importance because of their wide use as solvents, solutes and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

I. 3 METHODS OF INVESTIGATION

Existence of free ions, solvated ions, ion-pairs and triple-ions of the electrolytes/non-electrolytes in aqueous and non-aqueous media depends upon the concentrations of the solution, size of ions, and *intermolecular forces*, e.g., electronegativity of the atom, dipole-dipole forces, dipole-induced dipole forces, H-bonding, Van der Waal forces, columbic forces and electrostriction, +I, -I effect, side chain effect etc. Hence, the study of assorted interfaces and equilibrium of ions in diverse concentration regions are of immense importance to the technologist, theoretician, industrialist, researchers as most of the chemical processes take place in these systems.

Interestingly the different experimental techniques have been employed to find out a better understanding the occurrence of solvation and different interactions prevailing in solution. Therefore, we have employed the five significant physicochemical methods, viz., conductometry, volumetry, viscometry, ultrasonic interferometry, and refractometry to explore the solvation phenomena.

Apparent molar volumes obtained from density measurements, are usually expedient parameters for interpreting ion-solvent/solute-solvent and ion-ion/solute-solute interactions in solution. Ionic apparent molar volume for the individual ions has been obtained with the help of "*reference electrolyte*" method. The compressibility, a second derivative to Gibbs energy, is also a sensitive indicator of molecular interactions, which provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in viscosity of solutions by the addition of electrolyte is attributed to inter-ionic and ion-solvent effects. The viscosity *B*-coefficients are also separated into ionic

components by the '*reference electrolyte*' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. has been given.

The transport properties in most cases 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 calculated from the same method "*reference electrolyte*" using tetrabutylammonium tetraphenylborate. The ionic conductances are also play the crucial role to the interpretation of the ionic level of interaction, association or ion-solvent interactions of ions as well as molecules.

The surface tension experiments were done by platinum ring detachment method using a Tensiometer (K9, KRÜSS; Germany) at the experimental temperature. The accuracy of the measurement was within $\pm 0.1 \text{ mN}\cdot\text{m}^{-1}$. Temperature of the system has been maintained by circulating auto-thermostated water through a double-wall glass vessel containing the solution.

The spectroscopic study has been established by the investigation of FTIR spectroscopy. The study has been taking into account to qualitative interpreting the molecular as well as ionic association of the electrolytes in the solutions.

The total internal energy of a molecule in a first approximation can be resolved into the sum of rotational, vibrational and electronic energy levels. Infrared spectroscopy is the study of interactions between matter and electromagnetic fields in the IR region. In this spectral region, the EM waves mainly couple with the molecular vibrations. In other words, a molecule can be excited to a higher vibrational state by absorbing IR radiation. The

probability of a particular IR frequency being absorbed depends on the actual interaction between this frequency and the molecule. In general, a frequency will be strongly absorbed if its photon energy coincides with the vibrational energy levels of the molecule. IR spectroscopy is therefore a very powerful technique which provides fingerprint information on the chemical composition of the sample. FTIR spectrometer is found in most analytical laboratories.

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule.

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is a research technique that exploits the magnetic properties of certain atomic nuclei. It determines the physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the structure, dynamics,

reaction state, and chemical environment of molecules. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule. NMR spectra are unique, well-resolved, analytically tractable and often highly predictable for small molecules. Thus, in organic chemistry practice, NMR analysis is used to confirm the identity of a substance. Different functional groups are obviously distinguishable, and identical functional groups with differing neighbouring substituents still give distinguishable signals. The chemical shift provides information about the structure of the molecule. The shape and area of peaks are indicators of chemical structure too.

I. 4 SUMMARY OF THE WORKS EMPHASIZE IN THE DISSERTATION

CHAPTER-I

This chapter contains the *objective, utility and applications of the research work*, the important electrolytes/solutes and solvents used and methods of investigation. This also occupies the summary of the works done allied with the dissertation.

CHAPTER-II

The chapter encloses *the general introduction* of the thesis and forms the strong background of the work embodied in the thesis. A brief review of noteworthy works in the field of molecular as well as ionic interaction has been given. The discussion includes ion-solvent/solute-solvent, ion-ion/solute-solute and solvent-solvent interactions in binary, ternary mixed solvent systems and of electrolytes in pure and non-aqueous solvent

systems at various temperatures in terms of various derived parameters, estimated from the experimentally observed physicochemical properties *viz.*, *density, viscosity, ultrasonic speed, refractive index and conductance*. Several semi-empirical models to estimate dynamic viscosity of binary liquid mixtures have been discussed. Ionic association and its dependence on ion-size parameters as well as relation between solution viscosity and limiting conductance of an ion has been discussed using Stokes' law and Walden rule. Crucial assessment of different methods on the relative merits and demerits on the basis of various assumption employed from time to time of acquiring the single ion values (viscosity *B*-coefficient and limiting equivalent conductance) and their implications have been discussed. The molecular interactions are interpreted based on various derived parameters.

CHAPTER-III

The chapter comprises *the experimental section* which principally involves the basic information's, structure, source, purification and uses of the ionic liquids, electrolytes/non-electrolytes or solutes, and solvents have been used throughout the entire research work. It is also restrains the details of the instruments, procedure, working principle and equations that are employed to understand the physicochemical/thermodynamic, transport, acoustic, optical, potentiometric and spectroscopic properties.

CHAPTER-IV

The chapter deals precise measurements on electrolytic conductivities, densities, viscosities, and FT-IR studies of 1-butyl-2,3 dimethylimidazolium tetrafluoroborate

([bmmim][BF₄]) in Tetrahydrofuran, Dimethyl acetamide and Methyl Cellosolve at different temperatures. The limiting molar conductivities, association constants, and the distance of closest approach of the ion have been evaluated using the Fuoss conductance equation (1978). The molar conductivities observed were explained by the formation of ion-pairs and triple ion formation. Ion-solvent interactions have been interpreted in terms of apparent molar volumes and viscosity *B*-coefficients which are obtained from the results supplemented with densities and viscosities, respectively. The limiting apparent molar volumes, experimental slopes derived from the Masson equation and viscosity *A* and *B* coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions respectively. However, the deviation of the conductometric curves (Λ vs \sqrt{c}) from linearity in tetrahydrofuran indicated triple-ion formation and therefore corresponding conductance data have been analyzed by the Fuoss-Kraus theory of triple-ion. The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate as the "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_P \approx K_A$ and K_T). The FT-IR spectra for the solvents as well as the solute in solvent have also been studied. The results have been discussed in terms of ion-dipole interactions, hydrogen bonds formation, structural aspect, and configurational theory.

CHAPTER-V

This chapter presents a study of the experimental data evaluated from surface tension and conductance, the formation of inclusion complexes of β -Cyclodextrin with an Ionic

Liquid, viz. N-butyl-4-methylpyridinium chloride ([C₄mpy]Cl) in aqueous media. The limiting apparent molar volume, viscosity *B*-coefficient and limiting molar refraction have been studied to derive the appropriate parameters for the formation of inclusion complexes prevailing in the investigated solvent systems.

CHAPTER-VI

Quantitative and qualitative analysis of molecular interactions prevailing in the ionic liquid tetrabutylphosphonium methanesulfonate [Bu₄PCH₃SO₃] in aqueous (H₂O) and non-aqueous solvents, i.e., acetonitrile (CH₃CN), methanol (CH₃OH), nitromethane (CH₃NO₂), and formamide (HCONH₂) probed by precise measurements of electrical conductance (*Λ*) and FTIR spectroscopy respectively at 298.15K and atmospheric pressure have been studied in this chapter. The conductance data have been analyzed by the Fuoss conductance equation (1978) in terms of the limiting molar conductance (*Λ*₀), the association constant (*K*_A), and the association diameter (*R*) for ion-pair formation. The limiting ionic conductance (*λ*₀[±]) of the ions (Bu₄P⁺ and CH₃SO₃⁻) have been estimated from the appropriate division of limiting molar conductance of tetrabutylammonium tetraphenylborate [Bu₄NBPh₄] as "reference electrolyte" method along with a numerical evaluation of ion-pair formation constant. The molecular as well as ionic association have been discussed in terms of ion-dipole interactions, H-bonding formation, structural aspect, and configurational theory. The FTIR spectroscopic studies of the variational intensity of characteristic functional group of the solvents have been undertaken and the solvation phenomenon is evident by the shifting of the band intensity in presence of the ionic liquid.

CHAPTER-VII

In this chapter Solute-Solvent interactions prevailing in α -amino acids (glycine, L-alanine, L-valine) and aqueous solution of 1-butylpyridinium bromide ([BPy]Br) have been reported by physicochemical properties. The apparent molar volume (ϕ_V), viscosity B-coefficient, molal refraction (R_M) and adiabatic compressibility (ϕ_K) of glycine, L-alanine, and L-valine have been studied in 0.001, 0.003, 0.005 mol dm⁻³ aqueous 1-butylpyridinium bromide([BPy]Br) solutions at 298.15 K from the values of densities (ρ), viscosities(η), refractive index (n_D) and speed of sound (u) respectively. The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed using the Jones-Dole equation, and the derived parameters A and B have also been interpreted in terms of solute-solvent and solute-solute interactions, respectively in the mixed solutions. Molal refractions (R_M) have been calculated using the Lorentz-Lorenz equation and discussed. The role of the solvent (aqueous ionic liquid solution) and the contribution of solute-solute and solute-solvent interactions to the solution complexes have also been analyzed through the derived properties.

CHAPTER-VIII

This chapter explore the inclusion behaviour of a guest ionic liquid (IL) 1-methyl-3-octylimidazolium chloride into the host cavity of β -cyclodextrin in aqueous solution has been studied on modern research gaining far reaching effect. Surface tension and Conductivity measurements results showed that 1:1 hosts-guest inclusion complexes are

formed and favourable with the above system. The formation and nature of the inclusion complexes have been also characterized using job method by ultraviolet spectroscopy. The inclusion phenomenon has been confirmed by proton NMR study, association constants and thermodynamic parameters have been evaluated for the formed inclusion complexes by ultraviolet spectroscopy.

CHAPTER-IX

The chapter embraces the analysis of electrolytic conductivities, densities, viscosities, refractive index and FT-IR studies of 1-butyl-pyridinium bromide ([bupy]Br) in 1,4 Dioxane, Tetrahydrofuran, and Acetonitrile at different temperatures. The molar conductivities observed were explained with the manifestation of the formation of ion-pairs and triple ion formation. The limiting ionic conductances have been estimated from the appropriate division of limiting molar conductance of tetrabutylammonium tetraphenylborate as "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_P \approx K_A$ and K_T). Ion-solvent interactions have been interpreted in terms of apparent molar volumes, viscosity B -coefficients and molar refraction which are obtained from the results supplemented with densities, viscosities and refractive index respectively. The FT-IR spectra of the solvents as well as solutions have also been studied. The results have been discussed in terms of ion-dipole interactions, structural aspect and configurational theory.

CHAPTER-X

This chapter contains the concluding remarks of the works related or detailed described in the thesis (dissertation).