

CHAPTER: I

NECESSITY OF THE RESEARCH WORK

I. 1 SCOPE, OBJECTIVE AND APPLICATIONS OF THE RESEARCH WORK

Thermophysical studies are of great importance, providing a wide range of services and products by modifying the inner properties of raw materials. Despite the great benefits obtained from these practices, a comprehensive understanding of the properties of raw materials is essential to the success of process design.

Ionic Liquids (ILs) are a new class of materials, which has attracted a lot attention in scientific and industrial research recently. Due to their combination of chemical and physical properties they significantly differ from common molecular liquids. It is often defined as salts with low melting point, usually below 373K.^[1,1] The simple combinatory analysis indicates that about 10^{18} ILs can be possibly synthesized. 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 scarce 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 thermodynamic properties of ILs using different independent methods.

Ionic liquids have gained worldwide attention as green solvents in the last decade. This study explored the fundamental science and engineering of using ionic liquids 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.

Knowledge of the properties of the RTILs is required for choosing a suitable liquid for each of their envisaged industrial applications. Additionally, 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.

The idiom '*solution*' is mostly used for the particular case of a mixture between different components, i.e., when a small amount of substance, solute (solid, liquid or gas) dissolves to a certain limit in a liquid or solid substance (pure, or a mixture itself), solvent. A solution may be considered, *prima facie*, as a large assembly of molecules held together by non-covalent interactions. An investigation of such interactions in physical systems of increasing complexity should start with dimmers, continue through larger clusters, and end with solutions. In general, solutions are more complex than assemblies of weakly interacting molecules and in particular, the study of reactivity in the presence of a solvent can't be diminished to that of non-covalent interactions.

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

thermophysical/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 thermophysical/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 thermophysical along with the transport properties of solutions would provide a clear idea about the nature of the forces, interacting manner existing between the constituents of solution.

It is thus, apparent that the real understanding of the molecular interactions 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 and spectroscopic behavior to study the chemical nature of the structure of electrolytes/nonelectrolytes and solvents and their mutual and specific interactions in solution systems.

1.1.1 Objective

Considering these conflicting results, the following questions arise:

1. What is the reasonable inkling between experimental results and theory and the spread of the experimental results?
2. Are the observations in the experimental and theoretical results depends on the alkyl chain length of ionic liquids, functional groups, shape, size and structure of cation and anion, a consequence of the ionic interactions?
3. What makes the dependence and advantage of ionic liquids, different in comparison with the molecular liquids?
4. How can be act amino acids in the molecular interaction with aqueous/non-aqueous solvents?
5. How they can apply in academic, research area, industry and other sustainable chemistry, biochemistry and engineering?

We attempted to answer of these questions using a combination of precise experimental measurements and derived thermophysical/thermodynamic properties to examine the molecular interactions occurring in the solutions system.

The main objective of the present research work is to explore and to understand the molecular as well as ionic level of interactions prevailing in solutions by studying their thermophysical properties of ionic liquids and amino acids in some liquid systems. To avoid unnecessary effort in synthesis of ionic liquids taken from the huge pool of possible ion combinations, several approaches were tried for the prediction of physical properties.

The study of molecular interaction in fluids by thermophysical, thermodynamic methods has attracted attention, as thermophysical 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]

1.1.2 Importance of Thermophysical Parameters

The studied *thermophysical, thermodynamic, transport, optical, acoustic and spectroscopic 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 through the thermophysical study.

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 thermophysical calculations counting the correlation of refractive index with density.^[1.10-1.12]

The study of thermophysical 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. Thermophysical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the industrial separation processes. The importance 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 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] Mercus^[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 thermophysical properties of drugs. But direct study of the thermophysical 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) Tetrabutylphosphonium tetrafluoroborate,
- (b) tetrabutylphosphonium methanesulfonate
- (c) 1-ethyl-3-methylimidazolium nitrate
- (d) 1-ethyl-3-methylimidazolium methanesulfonate
- (e) 1-ethyl-3-methylimidazolium tosylate
- (f) 1-ethyl-3-methylimidazolium bromide etc.

1.2.2 Non-Electrolytes

- a. Amino acids, viz. glycine, L-alanine, L-valine, and L-leucine
- b. *N*-cetyl-*N,N,N*-trimethyl ammonium bromide or cetrimonium bromide
- c. Citric acid monohydrate
- d. β -cyclodextrin
- e. Folic Acid etc.

1.2.3 Electrolytes other than ionic liquids

- Alkyl halide viz. lithium chloride, lithium bromide, and lithium iodide,
- Tetrabutylammonium hexafluorophosphate,
- Tetrabutylammonium tetraphenylborate, etc.

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., acetonitrile, tetrahydrofuran, 1,3-dioxolane, methanol,

nitromethane, formamide, methylamine, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulphoxide, formic acid, etc.

The study of electrolytes (ionic liquids), non-electrolytes (amino acids), solutes (electrolyte other than ionic liquid) 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, coulombic forces and electrostriction, +I, -I effect, side chain effect etc. Hence, the study of assorted interactions 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 thermophysical methods, namely, conductometry, densitometry, 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 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.

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 thermophysical 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

thermophysical/thermodynamic, transport, acoustic, optical and spectroscopic properties.

CHAPTER-IV

The chapter deals precise measurements on electrical conductance (Λ) of solutions of an ionic liquid (IL) tetrabutylphosphonium tetrafluoroborate in acetonitrile (ACN), tetrahydrofuran (THF), 1,3-dioxolane (1,3-DO) and their binary mixtures have been reported at 298.15K. 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 Walden product is obtained and discussed. However, the deviation of the conductometric curves (Λ vs \sqrt{c}) from linearity for the electrolyte in THF and 1,3-DO and their binary mixtures indicated triple-ion formation and therefore corresponding conductance data have been analyzed by the Fuoss-Kraus theory of triple-ions. The limiting ionic conductances (λ_0^\pm) have been estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] 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 results have been discussed in terms of solvent properties and configurational theory. Ionic association in the limiting molar conductances, as well as the single-ion conductivity values have been determined for the electrolyte in the solvent media.

CHAPTER-V

The chapter embraces the analysis of molecular interactions quantitatively by precise measurement of conductance (Λ) and qualitatively by the FTIR spectroscopy, in the solution systems between some imidazolium based ionic liquids ([emim] NO_3 , [emim] CH_3SO_3 , [emim]Tos) and non-aqueous solvents (acetonitrile, methanol, nitromethane, methylamine solution) have been reported at 298.15K. Fuoss conductance equation (1978) and Fuoss-Kraus theory, for ion-pair and triple-ion formations respectively have been used for analysing the conductance data. Using the appropriate division of the limiting molar conductivity value of [Bu_4NBPh_4] as

"reference electrolyte", the limiting ionic conductances (λ_0^\pm) for individual ions have been calculated and reported. Dipole-dipole interaction, hydrogen bonding formation, structural aspect, and configurational theory are the driving forces, have been employed for discussion of the results. FTIR spectroscopic studies of variational intensity of characteristic bands of the studied solvents have been undertaken and the solvation phenomenon is manifested by the change of these band intensities in the presence of ionic liquids.

CHAPTER-VI

Apparent molar volumes (ϕ_V) and viscosity B -coefficients for citric acid in (0.001, 0.003, and 0.005) mol.dm⁻³ aqueous cetrimonium bromide (*N*-cetyl-*N,N,N*-trimethyl ammonium bromide, C₁₉H₄₂NBr) solutions, determined from solution density and viscosity measurements at $T = (298.15, 308.15, \text{ and } 318.15)$ K and $p = 0.1$ MPa as a function of the concentration of citric acid have been reported in this chapter. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution (ϕ_V°), using the Redlich-Meyer equation, and the obtained parameters have been interpreted in terms of solute-solvent interactions. 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-solute and solute-solvent interactions, respectively, in the mixed solutions. The structure-making or -breaking ability of the electrolyte has been discussed in terms of sign of dB/dT . The activation parameters of viscous flow for the ternary solutions studied have also been calculated and explained by the application of transition state theory.

CHAPTER-VII

In this chapter physicochemical properties such as density (ρ), viscosity (η), ultrasonic speed (u) of ionic liquid tetrabutylphosphonium tetrafluoroborate [Bu₄PBF₄] in acetonitrile (AN), tetrahydrofuran (THF), 1,3-dioxolane (1,3-DO) and their binaries, have been studied over the entire range of composition at 298.15 K. Apparent molar volumes (ϕ_V) and viscosity B -coefficients supplemented with the

data of densities and viscosities respectively, have been interpreted in terms of ion-solvent interactions. The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the Masson equation and viscosity A and B coefficients analyzed by the Jones-Dole equation have also been interpreted. The adiabatic compressibility (β) has been evaluated using the ultrasonic speed (u) values. Thereafter, limiting apparent molar adiabatic compressibilities (ϕ_K^0) have been evaluated and discussed for the same.

CHAPTER-VIII

Keeping in mind the uses of amino acids the apparent molar volume (ϕ_V), viscosity B -coefficient, adiabatic compressibility (ϕ_K) and molar refraction (R_M) of glycine, L-alanine, L-valine and L-leucine have been determined in methanoic acid at 298.15 K from density (ρ), viscosity (η), speed of sound (u) and refractive index (n_D) respectively. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution using Masson equation. The limiting apparent molar volume (ϕ_V^0) and 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-solute and solute-solvent interactions, respectively in the solutions. Molar refraction (R_M) have been calculated using the Lorentz-Lorenz equation. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these amino acids at infinite dilution were evaluated.

CHAPTER-IX

This chapter presents a study of the qualitative and quantitative analysis of molecular interaction prevailing in glycine, L-alanine, L-valine and aqueous solution of β -cyclodextrin (β -CD), have been probed by thermophysical properties. Density (ρ), viscosity (η), ultrasonic speed (u) measurements have been reported at different temperatures. The extent of interaction (solute-solvent interaction) is expressed in

terms of the limiting apparent molar volume (ϕ_V°), viscosity B -coefficient and limiting apparent molar adiabatic compressibility (ϕ_k°). The changes on the enthalpy (ΔH°) and entropy (ΔS°), of the encapsulation analysis give information about the driving forces governing the inclusion. The temperature dependence behaviour of partial molar quantities and group contributions to partial molar volumes has been determined for the amino acids. The trends in transfer volumes, $\Delta\phi_V^\circ$, have been interpreted in terms of solute-cosolute interactions on the basis of a cosphere overlap model. The role of the solvent (aqueous solution of β -CD), and the contribution of solute-solute and solute-solvent interactions to the solution complexes, have also been analyzed through the derived properties.

CHAPTER-X

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

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