

## CHAPTER I

### NECESSITY OF THE RESEARCH WORK

#### 1.1. OBJECTIVE, SCOPE AND APPLICATION OF THE RESEARCH WORK

The term 'solution' is mostly used for the special case of a mixture between dissimilar components, i.e. when a small amount of substance, called solute (solid, liquid or gas), dissolves to a certain limit in a liquid or solid substance (pure, or a mixture itself) called the 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 dimers, 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 cannot be reduced to that of non-covalent interactions.

The properties, both physical and chemical, 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. Partial charges acquired by molecules results in dipole-dipole forces, dipole-induced dipole forces, hydrogen bonding, etc and are collectively termed as intermolecular forces. 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 carried out in the liquid phase. 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 properties of a solution would give a clear idea about the nature of the forces existing within the constituents of a solution.

Hence, the main objective of the present research work is to investigate and to understand the interactions prevailing in solutions by studying their thermodynamic and transport properties.

The study of molecular interaction in fluids by thermodynamic methods 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 inorganic, physical, organic, analytical and electrochemistry [1].

The facts therefore encourage us to extend 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 thermodynamic and transport properties are of great importance in characterizing the properties and structural aspects of solutions. The sign and magnitude of partial molar volume ( $\phi_v^0$ ), 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 [2]. Furthermore, the excess properties 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. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus the properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Valuable information about the nature and strength of forces operating in solutions can be obtained from viscosity data. Recently the use of

computer simulation of molecular dynamics has led to significant improvement towards a successful 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 [3,4].

The refractive index is an important physical property of liquids and liquid mixtures, which affects the solution of different problems in chemical engineering in order to develop industrial processes. Knowledge of refractive index of multicomponent mixtures provides information regarding the interactions in these mixtures [5-7] which is essential for many physicochemical calculations, including the correlation of refractive index with density [8-10].

The study of physico-chemical behaviours like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. Excess isentropic compressibility, intermolecular free length etc. impart valuable information about the structure and molecular interactions in pure and mixed solvents. 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. Physico-chemical 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 [11].

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents have been summarized by Meck [12], Popovych [13], Franks [14], Bates [15,16], Parker [17,18], Criss and Salomon [19], Marcus [20] and others [21-23]. The solute-solute and solute-solvent interactions have

been subject of wide interest and have been explicitly presented in Faraday Trans. of the Chemical Society [24]. Fundamental research on non-aqueous electrolyte solution has catalysed their wide technical application in many fields. Non-aqueous electrolyte solutions are actually competing 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 have brought the biggest success [25-27]. 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 physico-chemical properties in physiological media such as blood, intracellular fluids is difficult to accomplish. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as thermodynamic parameters are convenient for interpreting intermolecular interactions in solution phase. Also the study of thermodynamic properties of drug in a suitable medium can be correlated to its therapeutic effects [28,29].

## **1.2. CHOICE OF SOLVENTS AND SOLUTES USED**

Industrially important solvents have been used for the research work. The solvents used are Nitromethane, 1, 3-Dioxolane, Nitrobenzene, Methanol, N,N-dimethylformamide, N,N-dimethylacetamide, Dimethylsulphoxide, Ethylene Glycol, n-Hexanol, o-Toluidine, Aniline and Acetonitrile.

Mostly electrolytes are used as solutes in the research work. The solutes used are Sodium Tetrphenylborate, Tetrabutylammonium Tetrphenylborate, Lithium Hexafluoroarsenate, Tetraalkylammonium Iodides, 1-Ethyl-3-methylimidazolium Bromide and Tetrabutylammonium Hexafluorophosphate.

The study of these solvents and solutes is of great importance because of their wide use as solvents, solutes and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

### **1.3. METHODS OF INVESTIGATION**

The existence of free ions, solvated ions, ion-pairs and triple-ions in aqueous and non-aqueous media depends upon the concentrations of the solution. Hence, the study of various interactions and equilibrium of ions in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occurs in these systems.

It is of interest to employ different experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed five important methods, namely, densitometry, viscometry, conductometry, ultrasonic interferometry and refractometry to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative to Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in viscosity by the addition of electrolyte solutions 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. may be 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.

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