

# CHAPTER - I

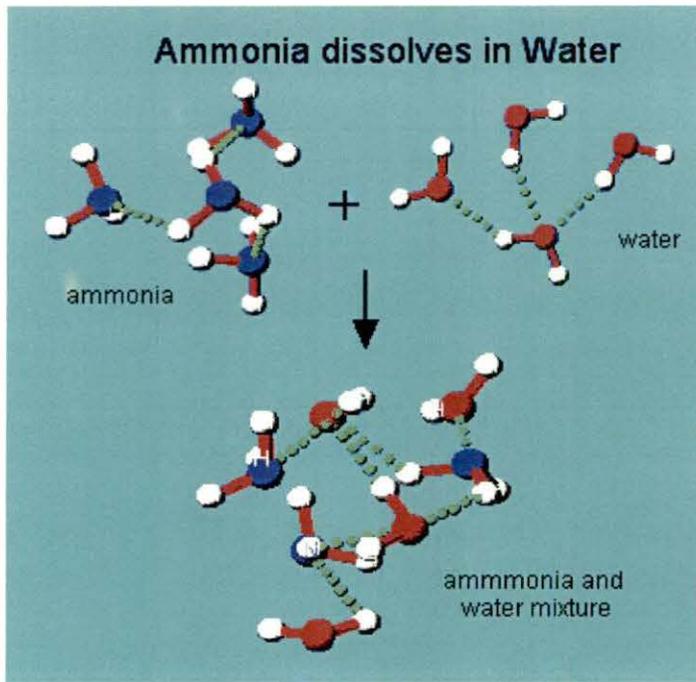
## **1.1 Scope and Objective of the Research**

The object of this introductory chapter is to call attention to the significance of solvents and the study made on various interaction prevailing in liquid systems. The bearing of solution on natural processes was early recognized. It was clearly seen that without solution there would be no chemistry. This was summarized by the alchemists in the terse generalization, "Corpora non agunt nisi soluta," or in the equally concise, "Menstrua non agunt nisifluida." These generalizations are a little too broad in the light of what was known about solutions at the time when they were written.

A "solution" in the days of the alchemists was primarily a solution of a solid in a liquid. Even if solution was not limited by them to those systems which result when liquids are brought in contact with solids, this type of solutions was given such a prominence, that it was generally in mind when the term "solution" was used. The present use of the term "solution" is not only much broader than that adopted by the alchemists, but is far broader than that employed even forty years ago<sup>1</sup>.

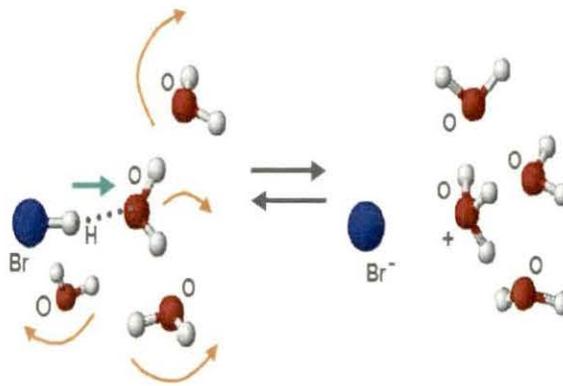
We know matter in three states of aggregation — solid, liquid, and gaseous. Matter in every one of these three states can be dissolved in matter of the same state of aggregation as itself and in both of the other states. Thus, we have solutions of gases in gases, or mixtures of gases which do not act chemically upon one another. The characteristic here is unlimited solubility, the properties of the mixture being the sum of the properties of the constituent gases.

Solutions of gases, liquids, and solids in liquids are the best and longest known types of solutions. Gases dissolve in liquids to only a limited extent, the amount, in keeping with Henry's law, increasing with the pressure to which the gas is subjected.



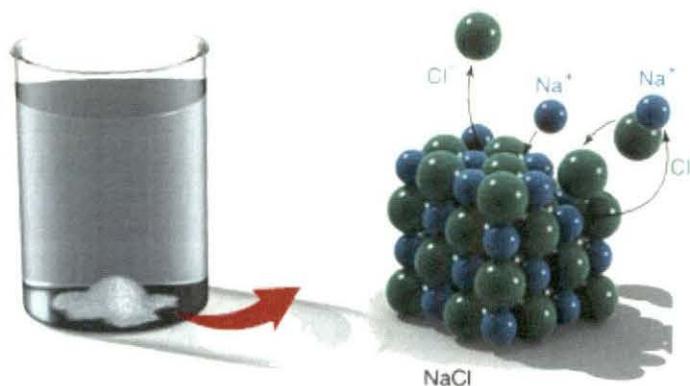
### Dissolution of gas in liquid

Liquids dissolve in liquids, many of them to an unlimited extent. Liquids which, at ordinary temperatures, have only limited solubility in other liquids, often become infinitely soluble at more elevated temperatures.



### Solution of binary liquids

Solids dissolve in liquids to a limited extent, the amount for any solid being a function of the temperature. Solutions of gases and liquids in solids are well known. Carbon dioxide dissolves in charcoal, hydrogen in many metals, etc., and a large number of liquids dissolve in many solid substances.



### **Solubility of solid in liquid**

One of the newest and most interesting types of solutions is that of solid in solid. Solid solutions came into prominence about twenty-five years ago, when it was shown, as we shall see, that mixtures of certain solids exhibit all of the properties of solutions of liquids or solids in liquids. For example Yellow gold is a solid solution of solutes (silver and copper) in a solvent (gold).



### **Solid solution**

To date, most chemical reactions have been carried out in molecular solvents. For two millennia, most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Recently, however, a new class of solvent has emerged—ionic liquids. These solvents are often fluid at room temperature, and consist entirely of ionic species. They have many fascinating properties which make them of fundamental interest to all chemists, since both the thermodynamics and kinetics of reactions carried out in ionic liquids are different to those in conventional molecular solvents, then the chemistry is different and unpredictable at our current state of knowledge. However, in addition to the scope for exciting new discoveries with

which they tease us, ionic liquid shave no measurable vapor pressure, and hence can emit no volatile organic compounds (VOCs). They have attracted, quite justifiably, enormous attention as media for green synthesis and this review attempts to capture, in a few pages, the scope and promise of the work published to date. As they are made up of at least two components which can be varied (the anion and cation), the solvents can be designed with a particular end use in mind, or to possess a particular set of properties. Hence, the term “designer solvents” has come into common use<sup>2</sup>. At first, the prospect of carrying out chemical reactions in ionic liquids may seem daunting to a chemist who has not worked with them before, but it turns out that carrying reactions out in ionic liquids can be exceptionally easy. The field of ionic liquids has been reviewed by several authors, including Welton<sup>3</sup>, Holbrey<sup>4</sup>, and Seddon<sup>5</sup>. The first room-temperature ionic liquid [EtNH<sub>3</sub>][NO<sub>3</sub>] (m.pt. 12 °C) was discovered in 1914<sup>6</sup>, but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum(III) chloride and *N*-alkylpyridinium<sup>7</sup> or 1,3-dialkylimidazolium chloride<sup>8</sup>. In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point. Ionic liquids come in two main categories, namely simple salts (made of a single anion and cation) and binary ionic liquids (salts where equilibrium is involved). For example, [EtNH<sub>3</sub>][NO<sub>3</sub>] is a simple salt whereas mixtures of aluminum (III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species.

In recent years there has been an upsurge in the study of physico-chemical properties of various solvent-solvent and solute-solvent systems in interpreting the intermolecular interactions among mixed components. The determination of density, viscosity, sound speed and refractive index is a valuable tool to develop new theoretical models and learn about the liquid state because of the close connection between liquid structure and macroscopic properties. Ultrasonic methods and refractive index measurements finds extensive applications owing to their ability of characterizing the physicochemical behavior of systems. Young<sup>9</sup> made the first systematic attempt

in these directions by collecting a number of data on the thermodynamic and mechanical properties of industrially important liquid mixtures.

Molecular interactions in solution phases can be better understood by studying various excess thermodynamic properties. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus, these properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Also, physico-chemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the process industries and in the design of industrial separation processes. Information of these excess thermodynamic functions can also be used for the development of empirical correlations and improvement of new theoretical models.

Rheology is the branch of science <sup>10</sup> that studies material deformation and flow, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied in the analysis of the viscous behavior of many pharmaceutical products, and to establish their stability and even bio-availability. Considering the rheological behavior, thermodynamic investigation is very important, since many products are formulated with more than one component in order to yield the desired physical structure and properties. Synergy and antagonism gives the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components for a given mixture. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system <sup>11</sup> is said to lack interaction. The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the product.

The importance and uses of the chemistry of electrolytes in non-aqueous and reactions in non-aqueous and mixed solvents have been summarized by Meck <sup>12</sup>, Popovych <sup>13</sup>, Franks<sup>14</sup>, Bates <sup>15, 16</sup>, Parker <sup>17, 18</sup>, Criss and Salomon <sup>19</sup>, Mercus <sup>20</sup> and others <sup>21-23</sup>. The solute-solute and solute – solvent interactions has been subject of wide interest as apparent from recent Faraday Trans. of the Chemical society <sup>24</sup>.

Although a great deal of work and collection of data on various electrolytic and non-electrolytic solution in water have been made, the structure of water and the various types of interactions that water undergoes with electrolytes are yet to be understood properly. However, a great deal of information has been obtained on the thermodynamic properties of different electrolytes and non-electrolytes in aqueous solution. Also, the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties in aqueous solutions have been well studied.

Understanding of solute-solvent interactions in solution chemistry, forms the basis of explaining quantitatively the influence of solvent, the extent of interaction of ions in solvents and thus paves the way for real understanding of the different phenomena associated with solution chemistry. Estimate of solute- solvent interactions can be obtained thermodynamically and also from the measurement of partial molar volumes, viscosity *B*-coefficient and conductivity studies.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute and solute-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for physical chemists and interests in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry <sup>25</sup>.

Research on non-aqueous electrolyte solutions has manifested their wide applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion 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 electrolyte solutions has brought the biggest success <sup>26, 27</sup>. Other fields where non-aqueous solutions are broadly used include

electro-chromic displays and smart windows, photo-electrochemical cells, electro-machining, etching, polishing and electro-synthesis. In spite of 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 ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions <sup>28</sup>. The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction <sup>29,30</sup>.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents like water is substantially modified by the presence of solutes <sup>31</sup>.

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 and conductometric behavior to study the chemical nature of the structure of solutes and solvents and their mutual and specific interactions in solution.

### **1.2 Importance and Scope of Physico-Chemical Parameters**

The nature of intermolecular interactions among the mixed components can be revealed from the interpretation of excess properties through the rheological and thermodynamic study of physico-chemical properties. The interactions between molecules can be established from a study of characteristic departure from ideal behavior of some physical properties such as density, volume, viscosity, isoentropic compressibility, refractive index <sup>32,33</sup> etc.

Density of solvent mixtures and related volumetric properties like excess molar volume and apparent molar volume are of great importance in characterizing the properties and structural aspects of solutions. The sign and magnitude of excess molar volume imparts estimate of strength of unlike interactions in the binary and ternary solvent systems. The negative values of excess molar volume ( $V^E$ ) suggest specific interactions<sup>34, 35</sup> between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces between them. The negative  $V^E$  values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. Similarly, the sign and magnitude of apparent 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<sup>36</sup>.

Valuable information about the nature and strength of forces operating within and between the unlike molecules can be obtained from viscosity data. Recently the employment 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<sup>37, 38</sup>. The study of physico-chemical behaviors 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.

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 <sup>39-41</sup>. Prediction of refractive index of multicomponent liquid mixtures is essential for many physicochemical calculations, which include correlation of refractive index with density <sup>42-44</sup>.

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 <sup>45, 46</sup>.

These facts therefore prompted us to undertake the study of binary or ternary solvent systems with some polar, weakly polar and non-polar solvents as well as with some solutes. Furthermore, the excess properties derived from experimental density, viscosity, speeds of sound data, refractive index and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

### **1.3 Choice and Importance of Solvents and Solute Used**

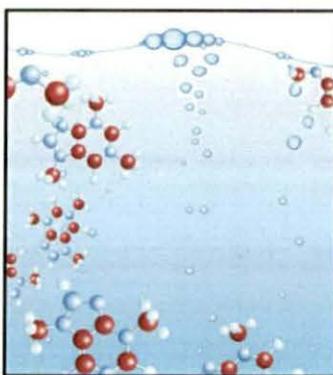
Alcohols, viz., isopropyl alcohol, 2-butanol, methyl alcohol, amyl alcohol, isoamyl alcohol, ethane 1, 2-diol; alkoxyethanols, viz., 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol; benzene and its derivatives, viz., anisole, chlorobenzene, nitrobenzene, toluene, acetophenone; 1,3 dioxolane, diethylether, tetrahydrofuran, carbontetrachloride, dichloromethane, methyl salicylate along with water were chosen as solvents for the research purpose.

Menthol, sodium molybdate, sodium tungstate, catechol, phosphomolybdic acid, lithium acetate, sodium acetate, potassium acetate, tetraalkylammonium iodides, viz., tetrabutylammonium iodide, tetrapentylammonium iodide, tetrahexylammonium iodide, tetraheptylammonium iodide were considered as solutes.

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.

## Uses of some industrially important solvents which I have chosen during my course of research are as follows:

**Water**, water is the most widely used solvent in the chemical and pharmaceutical industry, since it is the most physiological and best tolerated excipient. Water is a superb solvent, generally taken as the universal solvent, due to the marked polarity of the water molecule and its tendency to form hydrogen bonds with other molecules. Life on earth totally depends on water. Not only a high percentage of living things, both plants and animals are found in water, all life on earth is thought to have arisen from water and the bodies of all living organisms are composed largely of water. About 70 to 90 percent of all organic matter is water. The chemical reactions in all plants and animals that support life take place in a water medium. Water not only provides the medium to make these life sustaining reactions possible, but water itself is often an important reactant or product of these reactions. In short, the chemistry of life is water chemistry.



**Water as a solvent**

**2-Methoxyethanol** or methyl cellosolve, is an organic compound that is used mainly as a solvent. It is used as a solvent for many different purposes such as varnishes, dyes, and resins. It is also used as an additive in airplane deicing solutions and in the semiconductor laminate circuit board manufacturing industries.

**2-Ethoxyethanol** also known by the trademark **Cellosolve** or **ethyl cellosolve**, is a solvent used widely in commercial and industrial applications. 2-

ethoxyethanol has the useful property of being able to dissolve chemically diverse compounds. It dissolves oils, resins, grease, waxes, nitrocellulose, and lacquers. This is an ideal property as a multi-purpose cleaner and therefore 2-ethoxyethanol is used in products such as varnish removers, degreasing solutions and as an additive in brake fluid. They are formulated for dyeing textiles and leathers and for insecticides and herbicides.

**2-Butoxyethanol** is a solvent in paints and surface coatings, as well as cleaning products and inks. Other products that contain 2-butoxyethanol include acrylic resin formulations, asphalt release agents, firefighting foam, leather protectors, oil spill dispersants, bowling pin and lane degreaser, and photographic strip solutions. Other products containing 2-butoxyethanol as a primary ingredient include some whiteboard cleaners, liquid soaps, cosmetics, dry cleaning solutions, lacquers, varnishes, herbicides, and latex paints.

**Isoamyl Alcohol** is a colorless liquid with pungent taste and disagreeable aroma. It is soluble in alcohol and ether but slightly soluble in water. It is used as a chemical intermediate and solvent, and in pharmaceutical products and medicines. Isoamyl alcohol is good solvent and diluent for printing inks, lacquers, gum, inhibitors and hydraulic fluids. Paraffin wax dissolves in the hot isoamyl alcohol. Various polar plastics and high molecular weight esters also employ isoamyl alcohol based solvent systems.

**1-Pentanol** is an alcohol with five carbon atoms and the molecular formula  $C_5H_{12}O$ . 1-Pentanol is a colorless liquid with an unpleasant aroma. There are 7 other structural isomers of pentanol (see amyl alcohol). The ester formed from butanoic acid and 1-pentanol, pentyl butyrate, smells like apricot. The ester formed from acetic acid and 1-pentanol, amyl acetate (pentyl acetate), smells like banana.

**Diethyl ether** also known simply as ether, is the organic compound with the formula  $(C_2H_5)_2O$ . It is a colorless and highly flammable liquid with a low boiling point and a characteristic odor. It is the most common member of a class of chemical compounds known generically as ethers. It is particularly important

as a solvent in the production of cellulose plastics such as cellulose acetate<sup>47</sup>. Diethyl ether has a high cetane number of 85 - 96 and is used as a starting fluid for diesel and gasoline engines, because of its high volatility and low autoignition temperature. For the same reason it is also used as a component of the fuel mixture for carbureted compression ignition model engines.

**Methyl salicylate** though its source plants are not true mints, is used as a mint in some kinds of chewing gum and candy, as an alternative to the more common peppermint and spearmint oils. It can also be found as a flavoring of root beer. Methyl salicylate is used as a rubefacient in deep heating liniments (such as Bengay ointment), and in small amounts as a flavoring agent at no more than 0.04%. It is also used to provide fragrance to various products and as an odor-masking agent for some organophosphate pesticides.

**Isopropyl alcohol** is a solvent in pharmaceutical and paint industries. Like acetone, it dissolves a wide range of non-polar compounds. It is also relatively non-toxic and evaporates quickly. Thus it is used widely as a solvent and as a cleaning fluid, especially for dissolving lipophilic contaminants such as oil. Examples include cleaning electronic devices such as contact pins (like those on ROM cartridges), magnetic tape and disk heads (such as those in audio and video tape recorders and floppy disk drives), the lenses of lasers in optical disc drives (e.g. CD, DVD) and removing thermal paste from IC packages (such as CPUs.) Isopropyl alcohol solutions of 90-99% are optimal for preserving specimens, although concentrations as low as 70% can be used in emergencies.

**2-Butanol** is used as a direct solvent and as an intermediate in the manufacture of other organic chemicals (2-butanone). It is used as Solvent for paints, coatings, varnishes, resins, gums, camphor, vegetable oils, dyes, fats, waxes, resins, shellac, rubbers, and alkaloids, alkyd resins, lacquers, enamels, paint removers, and adhesives .it is widely used in Manufacture of industrial cleanners, perfumes, dyes, wetting agents.

**Dichloromethane** due to its volatility and ability to dissolve a wide range of organic compounds makes it a useful solvent for many chemical processes.

Concerns about its health effects have led to a search for alternatives in many of these applications<sup>48</sup>. It is widely used as a paint stripper and a degreaser. In the food industry, it has been used to decaffeinate coffee and tea as well as to prepare extracts of hops and other flavorings. Its volatility has led to its use as an aerosol spray propellant and as a blowing agent for polyurethane foams. Dichloromethane chemically welds certain plastics, for example, it is used to seal the casing of electric meters. Often sold as a main component of plastic welding adhesives it is also used extensively in the model-making industry for joining plastic components together — it is commonly referred to as "Di-clo."



**Ethanol, turpentine, and ethyl acetate are useful solvents for matter that does not dissolve in water.**

**1,3-Dioxolane** is used as a Reaction solvent for pharmaceutical manufacturing. It finds application as Lithium battery electrolyte solvent component, as Replacement for many chlorinated solvents, Co-monomer for manufacture of polyacetals and other polymers, Stabilizer for halogenated organic solvents, Copolymerization agent with trioxane and formaldehyde for manufacturing polyacetal resins .It is also used as Paint stripper and Glue stabilizer.

**Acetophenone** is commercially significant as it is used in production of resins by treatment with formaldehyde and base. The resulting polymers are conventionally described with the formula  $[(C_6H_5C(O)CH)_x(CH_2)_x]_n$ , resulting from aldol condensation. These materials are components of coatings and inks.

Modified acetophenone-formaldehyde resins are produced by the hydrogenation of the aforementioned ketone-containing resins. The resulting polyol can be further crosslinked with diisocyanates<sup>49</sup>. These modified resins are again found in coatings, inks, as well as adhesives. It is a raw material for the synthesis of some pharmaceuticals<sup>50,51</sup>. Acetophenone is used to create fragrances that resemble almond, cherry, honeysuckle, jasmine, and strawberry. It is used in chewing gum. Being prochiral, acetophenone is also a popular test substrate for asymmetric transfer hydrogenation experiments. Acetophenone is also commonly used as a flavouring agent in many cherry flavoured sweets and drinks, as it costs far less and proves as satisfying to consumers this way.

**Ethylene glycol**, approximately 60% of ethylene glycol is consumed for antifreeze, and the remainder is mainly used as a precursor to polymers. Because this material is cheaply available, it finds many niche applications<sup>52</sup>. ethylene glycol to act as an intermediate in a wide range of reactions. Especially significant is resin formation, including the condensation with dimethyl terephthalate or terephthalic acid resulting in a polyester resin. It is used for Water-based formulations (adhesives, latex paints, asphalt emulsions), Rubber Manufacture as Rubber Softener. The major use of ethylene glycol is as a medium for convective heat transfer in, for example, automobiles and liquid cooled computers.

**Carbon tetrachloride** was formerly used for metal degreasing and as a dry-cleaning fluid, fabricspotting fluid, fire-extinguisher fluid, grain fumigant and reaction medium (DeShon, 1979). Carbon tetrachloride is used as a solvent for the recovery of tin in tin-plating waste and in the manufacture of semiconductors. It is used in petrol additives, refrigerants, metal degreasing, and as a catalyst in the production of polymers. Carbon tetrachloride is also used as a chemical intermediate in the production of fluorocarbons and some pesticides (HSDB, 1995). It finds application in Pharmaceuticals and Rubber industries.

**Nitrobenzene**, one of the major uses for nitrobenzene is for the production of aniline, which is a chemical intermediate used during the manufacture of polyurethane. Nitrobenzene is also used industrially in the

manufacture of some pharmaceuticals, dyes and rubbers, as a constituent in some polishes and paint solvents and as a solvent in the refining of petroleum.

More specialized applications include the use of nitrobenzene as a precursor to rubber chemicals, pesticides, dyes, explosives, and pharmaceuticals. Nitrobenzene is also used in shoe and floor polishes, leather dressings, paint solvents, and other materials to mask unpleasant odors. Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps. A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol.

### **Uses of some solutes which I have chosen during my course of research are as follows:**

**Sodium molybdate**,  $\text{Na}_2\text{MoO}_4$ , is useful as a source of molybdenum.<sup>53</sup> It is often found as the dihydrate,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . The agriculture industry uses one million pounds per year as a fertilizer. In particular, its use has been suggested for treatment of whiptail in broccoli and cauliflower in molybdenum-deficient soils<sup>54,55</sup>. However, care must be taken because at a level of 0.3 ppm sodium molybdate can cause copper deficiencies in animals, particularly cattle. It is used in industry for corrosion inhibition, as it is a non-oxidizing anodic inhibitor. The addition of sodium molybdate significantly reduces the nitrite requirement of fluids inhibited with nitrite-amine, and improves the corrosion protection of carboxylate salt fluids<sup>56</sup>.

**Sodium tungstate**,  $\text{Na}_2\text{WO}_4$ , a tungstate of sodium, is useful as a source of tungsten. It is prepared from tungsten ores used to manufacture tungsten by reducing it. It is often found as the dihydrate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ . This salt is soluble in water and is a moderately strong oxidizing agent, but finds no common use in the chemistry laboratory. Like the molybdate, the deep-coloured complex tungstate (VI, V) is formed on reducing the compound with a very mild reducing agent, such as complex organic compounds. It is also thought to be a possible inhibitor of protein-tyrosine phosphatase (PTPase). It is also sometimes used as a fireproofing agent.

**Catechol** is used mainly as a precursor to pesticides, flavors and fragrances. It is also consumed in the production of pesticides, the remainder being used as a precursor to fine chemicals such as perfumes and pharmaceuticals.

**Phosphomolybdic acid**, also known as dodeca molybdophosphoric acid or PMA is a component of Masson's trichrome stain. It is a yellow-green compound, freely soluble in water and polar organic solvents such as ethanol. It is used as a reagent in thin layer chromatography for staining phenolics, hydrocarbon waxes, alkaloids and steroids. It is also used as stabilizer for hydrogen peroxide.

**Oxalic acid** finds its application in cleaning or bleaching, especially for the removal of rust, e.g. Bar Keepers Friend is an example of a household cleaner containing oxalic acid. About 25% of produced oxalic acid is used as a mordant in dyeing processes. It is used in bleaches, especially for pulpwood.<sup>57</sup> Used as purifying agent in pharmaceutical industry. Crystals of oxalic acid rubbed onto wooden beams and floors removes unsightly stains caused by age, exterior exposure or rust easily. It is not only wood that oxalic acid works wonders on. It can also be used to treat, polish and repair other materials such as stone, marble and stainless steel.

**Menthol** is an organic compound made synthetically or obtained from peppermint or other mint oils. It is a waxy, crystalline substance, clear or white in color, which is solid at room temperature and melts slightly above. In non-prescription products for short-term relief of minor sore throat and minor mouth or throat irritation. It also find use as an additive in certain cigarette brands, for flavor, to reduce the throat and sinus irritation caused by smoking. In certain medications used to treat sunburns, as it provides a cooling sensation (then often associated with aloe).

**Potassium acetate** can be used as a deicer instead of chloride salts such as calcium chloride or magnesium chloride. It offers the advantage of being less aggressive on soils and much less corrosive, and for this reason is preferred for

airport runways. It is, however, more expensive. Potassium acetate is also the extinguishing agent used in class K fire extinguishers because of its ability to cool and form a crust over burning oils. In medicine, potassium acetate is used as part of replacement protocols in the treatment of diabetic ketoacidosis because of its ability to break down into bicarbonate and help neutralize the acidotic state.

**Lithium acetate** is used in the laboratory as buffer for gel electrophoresis of DNA and RNA. It has a lower electrical conductivity and can be run at higher speeds than can gels made from TAE buffer (5-30V/cm as compared to 5-10V/cm). At a given voltage, the heat generation and thus the gel temperature is much lower than with TAE buffers, therefore the voltage can be increased to speed up electrophoresis so that a gel run takes only a fraction of the usual time. Downstream applications, such as isolation of DNA from a gel slice or Southern blot analysis, work as expected when using lithium acetate gels.

**Sodium acetate** is used in the textile industry to neutralize sulfuric acid waste streams, and as a photoresist while using aniline dyes. It is also a pickling agent in chrome tanning, and it helps to retard vulcanization of chloroprene in synthetic rubber production.

## 1.4 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 solvent systems. 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, viscometric, conductometric, ultrasonic interferometer and refractometric to probe the problem of solvation phenomena.

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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 interionic and ion-solvent effects. The *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.

## **1.5 Summary of the Works Done**

### **Chapter I**

This chapter contains the object and applications of the research work, the reasons for choosing the main solvents and solutes and methods of investigation. This also includes a summary of the works associated with the thesis.

### **Chapter II**

This chapter contains the general introduction of the thesis and forms a background of the works embodied in the thesis. A brief review of notable works on the behavior of viscous synergy and antagonism, ion-ion, ion-solvent and solvent-solvent interaction has been made. Also an attempt has been made to define these interactions. Various derived parameters dependent on density, viscosity, ultrasonic speed of sound, refractive indices and conductance along with their importance in solution chemistry has been discussed. 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. Critical evaluations of different methods employed frequently for obtaining the single ion values (viscosity  $B$ -coefficient and limiting equivalent conductance) and their implications have been discussed.

### **Chapter III**

This chapter contains the experimental section mainly involving the source and purification of the solvents and solutes used and the details of the experimental methods employed for measurement of the thermodynamic, transport, refractive indices and acoustic properties.

### **Chapter IV**

In this chapter Densities and viscosities were measured for the binary mixtures of iso-amyl alcohol with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol over the entire range of composition at 303.15, 313.15 and 323.15K and ultrasonic speeds and refractive indices at 303.15K. From the experimental values of density, viscosity, ultrasonic speed and refractive index the values of excess molar volume ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ), deviations in isentropic compressibility ( $\Delta K_S$ ) and excess molar refraction ( $\Delta R$ ) have been calculated. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

### **Chapter V**

This chapter presents a study of the excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), deviation in isentropic compressibility ( $\Delta K_S$ ) and excess molar refraction ( $\Delta R$ ) have been investigated from the experimentally measured densities, viscosities, sound speeds and refractive indices for three binary mixtures of 1,3 dioxolane (1) and diethylether (2), diethylether (2) and n-n-amyl alcohol (3) and 1,3 dioxolane (1) and n-amylalcohol (3) and their corresponding

ternary mixtures at 298.15 K. The calculated quantities are further fitted to the Redlich-Kister equation to estimate the binary fitting parameters and standard deviations from the regression lines. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

## Chapter VI

This chapter presents a study of molar conductance of some alkali metal acetates, viz., lithium acetate, sodium acetate and potassium acetate has been studied in aqueous 2-butanol solutions with an alcohol mass fraction ( $w_2$ ) of 0.70, 0.80 and 0.90 at 298.15, 303.15 and 308.15 K. The conductance data were analyzed with the Fuoss conductance-concentration equation to evaluate the limiting molar conductances ( $\Lambda_0$ ), association constants ( $K_{A,c}$ ) and cosphere diameter ( $R$ ) for ion-pair formation. Gibbs energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) for ion-association reaction were derived from the temperature dependence of  $K_{A,c}$ . The activation energy of the ionic movement ( $\Delta H^\ddagger$ ) was also derived from the temperature dependence of  $\Lambda_0$ . Based on the composition dependence of Walden products ( $\Lambda_0\eta_0$ ) and different thermodynamic properties, the influence of the mixed solvent composition on ion-association and solvation behaviour of ions were discussed in terms of ion-solvent, ion-ion interactions and the structural changes in the mixed solvent media.

## Chapter VII

This chapter quantifies the Precise measurements on electrical conductances of tetraalkylammonium iodides,  $R_4NI$  ( $R = \text{butyl to heptyl}$ ) in different mass% (20-80) of carbon tetrachloride + nitrobenzene at 298.15 K have been performed. Limiting molar conductances ( $\Lambda_0$ ), association constants ( $K_A$ ) and co-sphere diameter ( $R$ ) for ion-pair formation in the mixed solvent mixtures have been evaluated using the Lee-Wheaton conductivity equation. However, the deviation of the conductometric curves ( $\Lambda$  versus  $\sqrt{c}$ ) from linearity for the electrolytes in

80 mass% of carbon tetrachloride + nitrobenzene indicated triple ion formation and therefore corresponding conductance data have been analyzed by the Fuoss-Kraus theory of triple ions. Limiting ionic molar conductances ( $\lambda_0^\pm$ ) have been calculated by 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, configurational theory and molecular scale model.

## Chapter VIII

This chapter presents a study of the excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), deviation in isentropic compressibility ( $\Delta K_s$ ), excess molar refraction ( $\Delta R$ ) and excess Gibbs free energy of activation ( $\Delta G^E$ ) of viscous flow have been investigated from the experimentally measured densities, viscosities, sound speeds and refractive indices for three binary mixtures of acetophenone + amyl alcohol, acetophenone + dichloromethane and amyl alcohol + dichloromethane and their corresponding ternary mixtures at 298.15K over the entire composition range. The calculated quantities are further fitted to the Redlich-Kister equation to estimate the binary fitting parameters and root mean square deviations from the regression lines. These excess properties have been used to discuss the presence of significant interactions between the component molecules in the binary and ternary mixtures. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures and have been discussed in terms of molecular interactions and structural changes.

## CHAPTER IX

This chapter presents a study of the excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), deviation in isentropic compressibility ( $\Delta K_s$ ), excess molar refraction ( $\Delta R$ ) and excess Gibbs free energy of activation ( $\Delta G^E$ ) of viscous flow have been investigated from the experimentally measured densities, viscosities, sound speeds and refractive indices for three binary mixtures of isoamyl alcohol with with 2-methoxy ethanol (2-M.E), 2-ethoxy ethanol (2-E.E) and 2-butoxy ethanol (2-B.E) over the entire range of composition at 303.15, 313.15, and

323.15K. The calculated quantities are further fitted to the Redlich-Kister equation to estimate the binary fitting parameters and root mean square deviations from the regression lines. These excess properties have been used to discuss the presence of significant interactions between the component molecules in the binary mixtures. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures and have been discussed in terms of molecular interactions and structural changes.

## CHAPTER X

In this chapter Apparent molar volume ( $\phi_v$ ) and viscosity  $B$ -coefficients were estimated for sodium molybdate and sodium tungstate in aqueous binary mixture of ethane-1, 2-diol from measured solution density ( $\rho$ ) and viscosity ( $\eta$ ) at 298.15, 308.15 and 318.15K at various electrolyte concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data has been analyzed using Jones –Dole equation and the derived parameters,  $B$  and  $A$ , have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of sign of  $(\delta\phi_E^0/\delta T)_p$ .

## Chapter XI

In this chapter an attempt has been made to reveal the nature of various types of interactions prevailing in solution of phosphomolybdic acid in aqueous catechol from solution density ( $\rho$ ) and viscosity ( $\eta$ ) at 298.15, 308.15 and 318.15K at various solute concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data have been analyzed using Jones–Dole equation and the derived parameters,  $B$  and  $A$ , have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure-making or breaking capacity of the solute under investigation has been discussed in terms

of sign of  $(\delta\phi_E^0/\delta T)_P$ . The activation parameters of viscous flow were determined and discussed by application of transition state theory.

## **Chapter X11**

The thesis ends with some concluding remarks in this chapter.

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