ABSTRACT

Thermo-physical and bulk properties of solutions are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover, knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research.

The branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance is termed as solution chemistry. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent.

The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed in terms of many thermodynamic parameters, by excess properties in case of liquid-liquid mixtures and apparent molar properties in case of solid-liquid mixtures. These thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species. However, the exact structure of the solvent molecule is not known with certainty. The addition of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The assessment of ion-pairing in these systems is important because of its effect on the ionic mobility and hence on the ionic conductivity of the ions in solution. These phenomenon thus paves the path for research in solution chemistry to elucidate the nature of interaction through experimental studies involving
densitometry, viscometry, interferometry, refractometry and other suitable methods and to interpret the experimental data collected.

Caffeine, nicotinamide, resorsinol, glycine, catechol, oxalic acid, tetrabutyl ammonium iodide, tetra pentyl ammonium iodide, tetra hexyl ammonium iodide, tetra heptyl ammonium iodide, N-Cetyl-N,N,N-trimethyl ammonium bromide, D-Glucose, D-Mannitol, D-Sucrose, thorium nitrate, sodium molibdate, phosphomolibdic acid, lithim nitrate, potassium nitrate, sodium nitrate, silver sulphate which are considered as solutes, have been chosen in this research work.

Nitrobenzene, carbon tetrachloride, 2-Methoxy ethanol, along with water also considered as solvents.

These solutes and solvents have wide application in chemical fields and various industries like pharmaceuticals, cosmetics, battery technology, agricultural products etc.

In this research work more emphasis have been given to Bio active compounds (“plant bioactives” or “bioactive compounds”) they are mainly inherent non-nutrient constituents of food plants and edible mushrooms with anticipated health promoting and toxic effects when ingested. Bioactive compounds derived from plant foods, are of growing interest to the scientific community and food industry because of their putative health-promoting properties. Increasing evidences report beneficial effects of bioactive compounds, particularly against cancers, cardiovascular diseases and diabetes. They may also serve as adjusting factors in human body due to their physiological activity. Most bioactive compounds of natural origin are secondary metabolites, i.e., species-specific chemical agents. Information about food sources, concentrations and intakes of bioactive compounds, as well knowledge of their absorption, metabolism and biological effects, is needed in order to evaluate their potential health benefits. Pharmacological activity is usually taken to describe beneficial effects of bioactive compounds. There is sufficient evidence to recommend consuming food sources rich in bioactive compounds. From a practical perspective, this translates to
recommending a diet rich in a variety of fruits, vegetables, whole grains, legumes, oils, and nuts. In the body under physiological conditions, many vital functions are regulated by pulsed or transient release of bioactive substances at a specific time and site. Thus, to mimic the function of living systems, it is important to develop new drug delivery devices to achieve pulsed delivery of a certain amount of a bioactive compound at predetermined time intervals. The ability to deliver bioactive compounds and/or therapeutic agents to a patient in a palatine or staggered release profile has been a major goal in drug delivery research over the last two decades. Rice bran has been recognized as an excellence source of bioactive compounds, but only a small amount is consumed by humans. The limitation of using rice bran in a food industry is its rough texture and low concentration of bioactive compounds, when incorporated into food products. Various methods have been developed to enhance the level of bioactive components in food materials, including thermal, alkali, acid and chemical treatments. Many bioactive compounds have been discovered. These compounds vary widely in chemical structure and function and are grouped accordingly. Phenolic compounds, including their subcategory, flavonoids, are present in all plants and have been studied extensively in cereals, legumes, nuts, olive oil, vegetables, fruits, tea, and red wine. Many phenolic compounds have antioxidant properties, and some studies have demonstrated favorable effects on thrombosis and tumorogenesis and promotion. One of many phenolics in olives and olive oil is a potent antioxidant. Resveratrol, found in nuts and red wine, has antioxidant, antithrombotic, and anti-inflammatory properties, and inhibits carcinogenesis. Lycopene, a potent antioxidant carotenoid in tomatoes and other fruits, is thought to protect against prostate and other cancers, and inhibits tumor cell growth in animals. 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. Mannitol is used clinically to reduce acutely raised intracranial pressure until more definitive treatment can be applied, e.g., after head
trauma. It is also used to treat patients with oliguric renal failure. Glucose circulates in the blood, providing energy to organs, glands, muscles, indeed to every cell. Glucose is used in oxidation. More complex sugars have to be changed to glucose first before they can be broken down to release energy in respiration. Glucose is a ubiquitous fuel in biology. Caffeine is an alkaloid of methylxanthine family, its main pharmacological properties are a stimulant action on the central nervous system. It also acts as a natural pesticide since it paralyses and kills some of the insects. Organosulfur compounds in garlic and onions, isothiocyanates in cruciferous vegetables, and monoterpenes in citrus fruits, cherries, and herbs have anticarcinogenic actions in experimental models, as well as cardioprotective effects. Sodium Molybdate 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. Phosphomolybdic acid is widely used to stain connective tissues by dyes. It has been found polyvalent phosphomolybdic acid appears to form a bridge between the basic group of the substrate and the basic group of the dye. Oxalic acid and oxalates are useful as reducing agents for photography, bleaching, and rust removal. They are widely used as a purifying agent in pharmaceutical industry, precipitating agent in rare-earth metal processing, bleaching agent in textile and wood industry, rust-remover for metal treatment, grinding agent, waste water treatment. It is used as acid rinse in laundries and removing scale from automobile radiators. Nicotinamide is commonly known as vitamin B. It plays a very important role to maintain the normal function of the digestive systems and cholesterol levels in the human body. The combination of nicotinic acid and nicotinamide is clinically referred to as niacin. Glycine serves as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Glycine is an intermediate in the synthesis of a variety of chemical products. In summary numerous bioactive compounds appear to have beneficial health effects.
Much scientific research needs to be conducted before we can begin to make science-based dietary recommendations.

On the other hand minerals are naturally-occurring elements needed by the body and its vital activities. Each mineral, with its own specific task, even in the small and often minute quantities necessary, is indispensable for important life functions; they are needed for the formation of hormones, enzymes and other body substances. They're generally found in foods in the form of chemical compounds called salts and in water in the form of ion soluble. Animals need more than salt for proper health and nutrition. Animals need trace mineral supplements. They are needed in very small amounts, or traces, in the diet, and hence their name, "trace minerals. Mineral salts do not usually contain the element carbon and are therefore inorganic (organic compounds always contain carbon). Plant roots absorb individual mineral ions from soil water. Some of the ions travel by diffusion into the root; others are absorbed by active transport. The minerals required in the greatest amounts are those containing the element nitrogen, for example nitrate ions (or 'nitrates'), which are a key component of inorganic fertilizer. A plant uses nitrates in the production of proteins such as enzymes, so they are important for plant growth. They are often in short supply in the soil, which is why inorganic fertilizers are required. Plants also require magnesium in order to make chlorophyll, the green chemical that absorbs the energy of sunlight for photosynthesis.

Sodium nitrate is used as an ingredient in fertilizers, pyrotechnics, as an ingredient in smoke bombs, as a food preservative, and as a solid rocket propellant, as well as in glass and pottery enamels. Potassium nitrate is a strong oxidizer which burns and explodes with organics. It is used in the manufacture of gunpowder. It is also used in explosives, fireworks, matches, and fertilizers, and as a preservative in foods especially meats. It is sometimes used in medicine as a diuretic. Lithium nitrate is used as an electrolyte for high temperature batteries. It is also used for long life batteries as required, for example, by artificial pacemakers. The solid is used as a phosphor for neutron detection. Quaternary ammonium compounds
compounds are used as, Surface-active agents, Solvents, Intermediates, Active Ingredient for Conditioners, Antistatic Agent, Detergent Sanitisers, Softner for textiles and paper products, Phase Transfer Catalyst, Antimicrobials, Disinfection Agents And Sanitizers, Slimicidal Agents, Algaecide, Emulsifying Agents, Pigment Dispersers.

The study of these solvents and solutes, in general, are of interest because of their wide use in many industries with interests ranging from pharmaceutical to cosmetic products.

Summary of the Works Done

CHAPTER I

This chapter contains the object and applications of the research work, the solvents and solutes used and methods of investigations. This also involves the summary of the works done associated with the thesis.

CHAPTER-II

This chapter contains the general introduction of the thesis and forms the background of the present work. A brief review of notable works in the field of ion-solvent interaction has been given. The discussion includes solute-solvent, solute-solute and solvent-solvent interactions of mixed solvent systems and of electrolytes in pure, aqueous, non-aqueous solvent systems at various temperatures in terms of various derived parameters of conductance, density, viscosity, ultrasonic speed, and refractive index. Critical evaluations of different methods on the relative merits and demerits on the basis of various assumptions employed from time to time of obtaining the single ion values and their implications have been made. The molecular interactions are interpreted based on various equations.

CHAPTER-III
This chapter contains the experimental section which mainly involves the structure, source, purification and application of the solvents and solutes used and the details of the experimental methods employed for measurement of the thermodynamic, transport, acoustic and optical properties.

CHAPTER-IV

This chapter quantifies the Precise measurements on electrical conductances of tetraalkylammonium iodides, $R_4NI$ ($R$ = 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 ($K_d$) 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 ($\lambda_0$) have been calculated by the reference electrolyte method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_p \approx K_d$ and $K_T$); the results have been discussed in terms of solvent properties, configurational theory and molecular scale model.

CHAPTER-V

In this chapter, Partial molar volumes ($\phi_f^0$) and viscosity $B$-coefficients for nicotinamide in (0.00, 0.05, 0.10, 0.15, and 0.20) mol.dm$^{-3}$ aqueous resorcinol solutions have been determined from solution density and viscosity measurements at (298.15, 308.15, and 318.15) K as a function of the concentration of nicotinamide (NA). Here the relation $\phi_f^0 = a_0 + a_1T + a_2T^2$, has been used to describe the
temperature dependence of the partial molar volume ($\phi^0_v$). These results and the results obtained in pure water were used to calculate the standard volumes of transfer ($\Delta\phi^0_v$) and viscosity $B$-coefficients of transfer for nicotinamide from water to aqueous resorcinol solutions to study various interactions in the ternary solutions. The partial molar volume ($\phi^0_v$) and experimental slopes obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data have been analyzed using the Jones-Dole equation, and the derived parameters $B$ and $A$ have also been interpreted in terms of solute-solvent and solute-solute interactions, respectively in the ternary solutions. The structure making or breaking ability of nicotinamide has been discussed in terms of the sign of $(\delta^2\phi^0_v / \delta T^2)_v$. The activation parameters of viscous flow for the ternary solutions studied were also calculated and explained by the application of transition state theory.

CHAPTER-VI

Proteins are complex molecules and their behavior in solutions is governed by a combination of many specific interactions. One approach that reduces the degree of complexity and requires less complex measurement techniques is to study the interactions in systems containing smaller biomolecules, such as amino acids and peptides. Some studies have revealed that the presence of an electrolyte drastically affects the behaviors of amino acids in solutions and this fact can be used for their separation and purification. Therefore, in this chapter an attempt has been made to unravel the various interactions prevailing in a amino acid, Glycine in aqueous silver sulphate solutions by volumetric, viscometric study at 298.15, 308.15, 318.15 K.

CHAPTER-VII
In this chapter Apparent molar volume ($\phi_r$) and viscosity $B$-coefficients were measured for phosphomolybdic acid in aqueous solution of 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 $(\delta^2 \phi_r^0 / \delta T^2)_\rho$. The activation parameters of viscous flow were determined and discussed by application of transition state theory.

CHAPTER-VIII

This chapter presents a study of densities, viscosities and sound speeds have been determined for sodium molybdate in various mole-fractions of aqueous oxalic acid solutions. From the experimental data, apparent molar volume ($\phi_r$) and viscosity $B$-coefficients were calculated at 303.15, 313.15 and 323.15K using Masson equation and Jones – Dole equation respectively. Adiabatic compressibility of different solutions has been determined from measurement of ultrasonic speeds of sound at 303.15K. Partial molar volumes ($\phi_r^0$) and viscosity $B$-coefficients ($\Delta B$) of transfer from water to aqueous oxalic acid mixtures have been calculated and discussed. The structure-making or breaking capacity of the solute under investigation has been discussed in terms of sign of $(\delta^2 \phi_r^0 / \delta T^2)_\rho$. The activation parameters of viscous flow were determined and discussed by application of transition state theory.
CHAPTER-IX

This chapter presents a study of Apparent molar volumes ($\phi_v^0$) and viscosity $B$-coefficients for mineral salts in aqueous binary mixture of 2-methoxy ethanol have been estimated from solution density and viscosity measurements at 298.15 K and at various electrolyte concentrations as a function of the concentration of mineral salts. Experimental density data were analyzed using the Masson equation and the derived parameters interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data have been analyzed using the Jones-Dole equation, and the derived parameters $B$ and $A$ have also been interpreted in terms of solute-solvent and solute-solute interactions.

CHAPTER-X

In this chapter, Apparent molar volumes ($\phi_v$) and viscosity $B$-coefficients for some carbohydrates (D-Glucose, D-Mannitol and D-Sucrose) in 0.05%, 0.10%, 0.15%, aqueous cetrimimonium bromide (N-Cetyl-N,N,N-trimethyl ammonium bromide) (C$_{19}$H$_{42}$BrN) solutions have been determined from solution density ($\rho$) and viscosity ($\eta$) measurements at 298.15, 308.15, and 318.15 K as a function of the concentration of carbohydrates. The standard partial molar volume ($\phi_v^0$) 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-solvent and solute-solute interactions, respectively in the mixed solutions. The relation, $\phi_v^0 = a_0 + a_1T + a_2T^2$, has been used to describe the temperature dependence of the standard partial molar volume ($\phi_v^0$). The structure making or breaking ability of carbohydrates has been discussed in terms of sign of $(\delta^2\phi_v^0 / \delta T^2)_\rho$ as well as $dB/dT$. The activation
parameters of viscous flow were also determined and were discussed by the application of transition state theory.

CHAPTER-XI

This chapter contains Apparent molar volumes ($\phi_V$) and viscosity $B$-coefficients for the alkaloid caffeine in (0.00, 0.03, 0.05 and 0.07) mol·dm$^{-3}$ aqueous thorium nitrate, Th(NO$_3$)$_4$ solutions have been determined from solution density and viscosity measurements at temperatures in the range (298.15 to 318.15) K as function of concentration of caffeine. In the investigated temperature range, the relation: $\phi_V^0 = a_0 + a_1T + a_2T^2$, have been used to describe the temperature dependence of the standard partial molar volumes ($\phi_V^0$). These results have, in conjunction with the results obtained in pure water, been used to deduce the standard volumes of transfer ($\Delta\phi_V^0$) and viscosity $B$-coefficients of transfer for caffeine from water to aqueous Th(NO$_3$)$_4$ solutions for rationalizing various interactions in the ternary solutions. The structure making or breaking ability of caffeine has been discussed in terms of the sign of $(\delta^2\phi_V^0 / \delta T^2)_P$. An increase in the transfer volume of caffeine with increasing Th(NO$_3$)$_4$ molarity has been explained by Friedman-Krishnan co-sphere model. The activation parameters of viscous flow for the ternary solutions were also determined to discuss in terms of transition state theory.

CHAPTER-XII

This chapter contains the concluding remarks on the works related to the thesis.