CHAPTER–I

1.1. Object and Application of the Research Work

A material is considered bioactive if it has interaction with or effect on any cell tissue in the human body. Bioactive plant food compounds ("plant bioactives" or "bioactive compounds") can be defined as 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. Bioactive compound are mainly extra nutritional constituents that typically occur in small quantities in foods so they are intensively studied to evaluate biological 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 pulsatile 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
excellent 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 methyloxanthine 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 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, acid rinse in laundries and removing scale from automobile radiators. Nicotinamide, commonly known as vitamin B, 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. Alanine is used as a source of energy for muscle tissue, the brain, and central nervous system, in strengthening the immune system by producing antibodies. It has been used as a source for the production of glucose in order to stabilise blood sugar levels over lengthy periods. 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 for its vital activities. Each mineral, with its own specific task, even 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 solubles. 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. Potassium nitrate prill type is mainly used to produce kinescope, optics glass, high grade craft glassware. 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.

Measurements of the bulk properties, such as viscosities and densities of liquids, measurements of excess molar enthalpies, measurements of refractive indices and measurements of isentropic compressibilities provide insight into the molecular arrangement in liquids and help one to understand the thermodynamic properties of liquid mixtures.

Proper understanding of these properties is very imperative in many practical problems regarding energy transport, heat transport, mass transport, and fluid flow. Acoustic properties have been the subject of extensive research activity to study the intermolecular interactions in ion-solvent systems. Besides finding applications in the engineering branch, the study is important from practical and theoretical points of view in understanding liquid theory. The non-aqueous systems
have been of immense importance to the technologist and theoretician as many chemical processes occur in these systems.

The physico-chemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts in recent years have been directed at an understanding of such properties at microscopic and macroscopic levels. In order to gain insight into the mechanism of such interactions thermodynamic, transport, acoustic and optical studies on binary and ternary solvent systems are highly useful. Young \(^1\) made the first systematic attempt in these directions by collecting a number of data on the thermodynamic and mechanical properties of liquid mixtures.

Excess thermodynamic properties are important parameters for understanding molecular interactions in the solution phase. 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.

The refractive index, \(n_D\), is defined as the ratio of velocity of light in the vacuum to the velocity of light in the medium and, therefore, for a fluid it is greater than unity. The refractive index is a thermodynamic property and is a state function, which for a pure fluid depends on temperature and pressure. For gases, the refractive index is very close to unity, but for liquids, it is greater than 1. The refractive index or refractivity \((n_D)\) can be easily measured by the sodium D line of a simple refractometer at a temperature of interest. The refractive index, is easily measurable, and used to estimate the thermo-physical properties of solvent/solution mixtures. Properties such as critical constants, heat capacity, and transport properties are related to the refractive index.
The rheological and molecular behaviour of a formulation can influence aspects such as, patient acceptability, since it has been well demonstrated that viscosity and density both influence the absorption rate of such products in the body. Rheology is the branch of Science that studies material deformation and flow, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied to the analysis of the viscous behaviour of many pharmaceutical products, and to establish their stability and even bioavailability.

Considering the rheological perspective, the study of viscous synergy and antagonism is important, since many products are formulated with more than one component in order to yield the desired physical structure and properties. Synergy and antagonism give the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components of a given mixture.

The study of the viscous behaviour of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction.

In solution chemistry, the way for proper understanding of the different phenomena regarding the molecular interactions forms the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents. Estimates of ion-solvent interactions can be known thermodynamically and also from the measurement of partial molar volumes, viscosity \( B \)-coefficient and limiting ionic conductivity studies. Estimates of single-ion values enable us to refine our model of ion solvent interactions. Acceptable values of ion-solvent interactions would enable the chemists to choose solvents that will enhance (i) the rates of chemical reactions, (ii) the solubility of minerals in leaching operations or (iii) reverse the direction of equilibrium reactions. The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are now well recognized.
The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck, Franks, Popovych, Bates, Parker, Criss and Salomon, Marcus and others. In spite of vast collections of data on the different electrolyte and non-electrolyte solutions in water, the structure of water and the different types of interactions that water undergoes with electrolytes are yet to be properly understood.

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.

In recent years, there has been increasing interest in the behaviour of electrolytes or solutes in non-aqueous and mixed solvents with a view to investigate 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 opened vistas for physical chemists and interest in the organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry.

Fundamental research on non-aqueous electrolyte solutions has catalyzed their wide technical applications 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, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions had brought the biggest successes. Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photoelectrochemical cells, electromachining, 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 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 acoustic studies, give very valuable information about molecular interactions in
solutions. The influence of these solute-solvent interactions is sufficiently large
to cause dramatic changes in chemical reactions involving ions. The changes in ionic
solvation have important applications in diverse areas such as organic and inorganic
synthesis, studies of reaction mechanisms, non-aqueous battery technology and
extraction.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents,
it has become evident that the majority of the solutes are significantly influenced by
the solvents. Conversely, the nature of strongly structured solvents like water is
substantially modified by the presence of solutes. Knowledge of ion-solvent
interactions in non-aqueous solutions is very important in many practical problems
concerning energy transport, heat transport, mass transport and fluid flow. Besides
finding applications in engineering branch, the study is important from practical and
theoretical point of view in understanding liquid theories. The non-aqueous systems
have been of immense importance to the technologist and theoretician as many
chemical processes occur in these systems.

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 behaviours 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 study of physico-chemical properties involves the interpretation
of the excess properties as a mean of unravelling the nature of intermolecular
interactions among the mixed components. The interactions between molecules can
be established from a study of characteristic departure from ideal behaviour of
some physical properties such as density, volume, viscosity, speeds of sound, refractive index etc. Density of solvent mixtures and related volumetric properties like excess molar volume are essential for theoretical as well as practical aspects. The sign and magnitude of excess molar volume imparts estimate of strength of unlike interactions in the solvent mixtures. The negative values of excess molar volume ($V_E$) suggest specific interactions 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 volumes. The negative ($V_E$) values may also be due to the difference in the dielectric constants of the components of the liquid mixtures.

Understanding of fluid’s viscosity is required in most engineering calculations where fluid flow, mass transport and heat transport are important factors. Viscosity data provides valuable information about the nature and strength of forces operating within and between the unlike molecules. 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 electrolyte solvent mixtures involving both hydrogen bonding and non hydrogen bonding solvents. 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.

Deviations in refractive index and molar refractivity also provide valuable information about molecular interactions prevailing in solution. Positive and
negative values of $\Delta n_D$ or $\Delta R$ have immense significance to understand the molecular interactions.

The study of bio-molecules plays a key role in the elucidation of thermodynamic properties of bio-chemical processes in living cells. The process of drug transport, protein binding, anaesthesia, etc. are few examples where drug and bio-macromolecules appear to interact in an important and vitally significant way. Drug transport across biological cells and membranes is dependent on physico-chemical 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 theraptic effects.38, 39

These facts therefore prompted us to undertake the study of different binary or ternary systems. Furthermore, the excess properties derived from experimental density, viscosity, speeds of sound and refractive index data and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

1.3. **Solutes and Solvents Used**

During the course of research work the study was made on 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 molybdate, phosphomolybdic acid, lithium nitrate, potassium nitrate, sodium nitrate and silver sulphate as solutes and water, 2-Methoxy ethanol, nitrobenzene, carbon tetrachloride as solvents.
1.4. **Methods of Investigations**

The phenomenon of ion-ion, ion-solvent, synergy, antagonism, solvent-solvent interactions is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed four important methods, namely, Densitometry, Viscometry, Ultrasonic Interferometry and Conductometry to probe the problem of solvation phenomena.

Viscosity and density have been used to interpret the synergic and antagonic behavior in the solvent mixtures. The values of synergic and antagonic interaction indexes determines the nature of the molecular package.

Thermodynamic properties, like apparent molar volumes, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution.

The change in solvent viscosity by the addition of electrolyte solutions is attributed to interionic and non-solvent effects. The $B$-coefficients give a satisfactory interpretation of ion-solvent interactions such as the effects of solvation and structure-breaking or structure-making capacity of the solutes.

The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and provides useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions. Various acoustical parameters have been derived in carrying out the investigation.

The excess properties such as excess molar volume, viscosity deviations, excess isentropic compressibility, excess molar refractivity along with the correlating equations explains molecular interactions more effectively.

To investigate thermodynamic properties refractive index, molar refractivity and deviation in both have been calculated.

The transport properties are studied using the conductance data, specially the conductance at infinite dilution. Conductance data obtained as a function of concentration are 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 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 conductance 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 ($K_a$) 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 (Λ versus √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 (λ0±) have been calculated by the reference electrolyte method along with a numerical evaluation of ion-pair and triple–ion formation constants (Kp ≈ KA and KT); the results have been discussed in terms of solvent properties, configurational theory and molecular scale model.

CHAPTER V

In this chapter, Partial molar volumes (φV0) 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 φV0 = a0 + a1T + a2T², has been used to describe the temperature dependence of the partial molar volume (φV0). These results and the results obtained in pure water were used to calculate the standard volumes of transfer (ΔφV0) 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 (φV0) 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 (δ²φV0/δT²)ₚ. 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 ($V_\phi$) 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 318.15)K 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 $(\delta^2\phi^0 / \delta T^2)$. 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 ($\phi_\nu$) and viscosity $B$-coefficients were calculated at (303.15, 313.15 and 323.15)K 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 ($\phi^0_\nu$) 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 have been discussed in terms of sign of $(\delta^2 \phi^0_\nu / \delta T^2)$. 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 ($\phi^0_\nu$) 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 ($\phi^0_\nu$) and viscosity $B$-coefficients for some carbohydrates (D-Glucose, D-Mannitol and D-Sucrose) in 0.05%, 0.10%, 0.15%, aqueous cetrimmonium bromide (N-Cetyl-N,N,N-trimethyl ammonium bromide) ($\text{C}_{19}\text{H}_{42}\text{BrN}$) 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 ($\phi^0_\nu$) and experimental slopes ($S^\nu_\phi$) 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 $(\delta^2\phi_v^0 / \delta T^2)_p$ 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.
References

Object and Application of the Research Work