MOLECULAR INTERACTIONS OF CYCLIC ALANYLALANINE AND GLYCINE BETAINE IN AQUEOUS METAL CHLORIDE SOLUTIONS

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION

By the Ph.D. Research Scholar

I hereby *declare* that the Research Thesis entitled **'Molecular interactions of cyclic alanylalanine and glycine betaine in aqueous metal chloride solutions'** which is being submitted to the **National Institute of Technology Karnataka Surathkal,** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Chemistry** *is a bonafide report of the research work carried out by me***.** The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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CERTIFICATE

This is to *certify* that the Research Thesis entitled **'Molecular interactions of cyclic alanylalanine and glycine betaine in aqueous metal chloride solutions'** submitted by **Karanth Vijayganapati Ramesh** (Register Number**: 100505CY10F01)** as the record of the research work carried out by him, is accepted as the Research Thesis submission in partial fulfilment of the requirements for the award of degree of **Doctor of Philosophy.**

Prof. D. Krishna Bhat
Research Guide

Chairman - DRPC

This thesis is dedicated to all those persons who have given me knowledge, support and experience to shape my life

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ABSTRACT

The research thesis entitled '**Molecular interactions of cyclic alanylalanine and glycine betaine in aqueous metal chloride solutions**' deals with the volumetric, compressibility and refractometric studies of two important biomolecules namely cyclic alanylalanine and glycine betaine in water as well as in aqueous solutions of NaCl, KCl, $CaCl_2$, $MgCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ under varied conditions of concentration and temperature. The derived thermodynamic parameters have been computed from the experimental density, speed of sound and refractive index measurements. Hydrophobic hydration was observed in cyclic alanylalanine-metal chloride solutions through the results of volumetric and compressibility studies. While in glycine betaine-metal salts systems, a characteristic zwitterionic behaviour of glycine betaine molecule was elucidated. Effect of the size of the metal ions on the partial molar quantities in solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ in biomolecules was investigated and the same has been attributed to the relative sizes of metal ions in solutions. However, transition metal-biomolecules systems, influence of metal to water bond distance in aqueous solutions on the solution behaviour has been observed. Hepler's coefficients calculated for glycine betaine-transition metal salt solutions with varying concentrations reveal that glycine betaine behaves as a structure maker in these systems. However, in concentrated salt solutions it has been found that glycine betaine behaves as a structure breaker. The volumetric and compressibility studies have also been checked by the refractometric observations. The results of the present work may be used to elucidate the thermodynamic parameters of protein molecules under various environments.

Keywords: Molecular Interactions, Cyclic Alanylalanine, Glycine Betaine, Metal Salts, Molar Refraction.

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NOMENCLATURE

Density	ρ
Ultrasonic velocity	c
Refractive index	n_D
Isentropic compressibility	κ_S
Apparent molar volume	ϕ_v
Apparent molar compression	ϕ_k
Partial molar volume	ϕ_v^0
Partial molar isentropic compression	$\phi_k{}^0$
Transfer partial molar volume	$\Delta_{tr}\phi_v^0$
Transfer partial molar isentropic compression	$\Delta_{tr}\phi_k^0$
Intermolecular free length	L_f
Specific acoustic impedance	Z
Relative association	R_A
Molecular Weight of the Solute	M
Molar Concentration of the solute	m

CHAPTER 1

INTRODUCTION

Chapter 1 gives a general introduction to the topic of proteins, electrolytes, solvents, volumetric, refractometric and compressibility properties along with an overview of the state of art in the field. This chapter also outlines the scope and objectives of the present work.

1.1. SOLUTIONS

Chemistry in life very often involves the use of solutions. Solutions are often the medium for most of the bio-chemical processes. Thus it is imperative to study the solution behaviour from the theoretical and practical point of view to have an insight of liquid theory. Studies on density, viscosity, specific heat capacity, ultrasonic speed and refractive index of various solutions are of intense use in characterising the structures and properties of solution constituents. Since various types of interactions exist among the entities of the solutions, understanding such solute-solute, solute-solvent and solvent-solvent interactions forms the basis of a new branch of chemistry; the solution chemistry. Knowledge of these interactions finds application in a wide strata of fields ranging from biology to physics to chemical engineering. In recent years, crescent advents in technology have necessitated the development of efficient separation, concentration, purification process of many important chemicals such as biomolecules. Thus it is essential for a solution chemist to have the basic idea of some of the physico-chemical properties of the above mentioned important class of molecules (Ninni and Merelles 2001).

1.2. PROTEINS

Two major classes of macromolecules which predominantly rule the chemistry of life are: nucleic acids and proteins. Nucleic acids carry the genetic information from generation to generation and are considered to be the blueprint for a particular living organism. The blueprint is essentially a set of instructions for making proteins and it is on the activities of those proteins that life processes depend.

Proteins are the key molecules in the processes of life and it is now known that virtually all the activities which sustain living organisms are carried out by proteins. The major structural components of animal and human tissues comprise of these macromolecules.

They are constructed on a simple pattern, but that pattern allows for an almost endless diversity of structure and function. They are also very large molecules. For these reasons, the study of proteins has provided a very considerable challenge for a chemist who wishes to determine their structures and to find out how they work (Doonan 2002).

Since proteins are extremely complex chemical entities, analysis of their structures and the ways in which they carry out their particular functions are essentially problems in chemistry. It is no surprise then that, for more than a century, chemists have been involved in purifying proteins, analysing their structures and investigating their modes of action. Protein generally acquires the stable conformation from a fine balance among various non-covalent forces like ionic and dipolar interactions, hydrogen bonding and hydrophobic forces (Privalov 1979).

Protein folding is a phenomenon occurring in nature which essentially a result of combination of intramolecular forces, dipole interactions, pure ionic interactions, hydrogen bonds, van der Waals forces and hydrophobic interactions**.** In protein molecules, most of the charged groups are at the surface of the folded protein. The interaction of these charged species with the salts present in their environment may produce solvation and neutralization by counter ions of the salts. Consequently, if proteins fail to fold into the intended shape, usually produce inactive proteins with different properties including toxic prions. Many diseases such as Alzheimer's, cystic fibrosis and Parkinson's disease are caused by the improper folding of the proteins (Bruce et al. 2010).

By denaturation one means that class of reactions which leads to changes in structure of the macromolecule with no change in molecular weight (Rice et al. 1958). During the denaturation process, the disruption and possible destruction of both the secondary and tertiary structures take place. Since denaturation reactions are not strong enough to break the peptide bonds, the primary structure (sequence of amino acids) remains the same after a denaturation process.

Human body contains considerable portions of proteins besides water. Thus it is imperative to study the interactions of proteins with their surrounding environment to understand the role of biological molecules in the living organisms. These interactions are mainly those between the protein molecules and ions present in biological fluids. Salts comprise 3.9% of our body weight and are very important for

the maintenance of homeostasis (i.e. well balanced organism). Due to the complexities of protein in terms of conformations and structures, molecules like amino acids, peptides (or linked amino acids) and their analogues have been quite useful as model for understanding the thermodynamic behaviour of proteins in solutions. Amino acids are the building blocks of proteins and the proteins are the correct combination of amino acids. They possess two characteristic functional groups, namely amino group $-NH_2$ and carboxylic group -COOH. In aqueous solutions, these molecules behave as zwitterions and the electrostatic field of zwitterions has a tendency to alter structure of the solution as it affects or influences the structural arrangement of molecules of the solvent. Hence this in turn has pronounced effect on compressibility of the system. Thus compressibility and related parameters provide significant information regarding the state of affairs taking place in the solution on the background of ion-solvent interactions (Kaur 2012).

The amino acids and their derivatives have various side groups which differ in size, shape, charge, hydrogen bonding capacity, chemical reactivity and hydrophobicity, etc. Hence the study of these model compounds has mainly two advantages: (i) The relative ease of the microscopic interpretation of experimental data, (ii) the fact that model studies readily allow one to systematically alter the structure so that the contribution of a chosen atomic group can be addressed (Kaur 2012).

1.3. ESSENTIAL ELEMENTS TO LIFE

Chemical elements essential to life can be categorized into four major classes:

(1) Bulk elements (H/H^+, C, N, O_2^-, P, S/S^{2-});

(2) Macro minerals and ions Na/Na^+, K/K^+, Mg/Mg^{2+}, Ca/Ca^{2+}, Cl^-, PO_4^{3-}, SO_4^{2-};

(3) Trace elements Fe/Fe(II)/Fe(III)/Fe(IV), Zn/Zn(II), Cu/Cu(I)/Cu(II)/Cu(III); and

(4) Ultra-trace elements, comprised of non-metals (F/F^-, I/I^-, Se/Se^{2-}, Si/Si(IV), As, B and metals Mn/Mn(II)/Mn(III)/Mn(IV), Mo/Mo(IV)/Mo(V)/Mo(VI), Co/Co(II)/Co(III), Cr/Cr(III)/Cr(VI),

V/V(III)/V(IV)/V(V), Ni(I)/Ni(II) /Ni(III), Cd/Cd^{2+}, Sn/Sn(II) /Sn(IV), Pb/Pb^{2+}, Li/Li^{+}.

If no charge is shown, the element predominately bonds covalently with its partners in biological compounds, although elements such as carbon (C), sulphur (S), phosphorus (P), arsenic (As), boron (B), selenium (Se) have positive formal oxidation states in ions containing oxygen atoms; that is, S = +6 in the SO_4^{2-} ion or P = +5 in the PO_4^{3-} ion. The identities of these essential elements are based on historical work done by Klaus Schwarz in the 1970s.

Other essential elements may be present in various biological species. Criteria for essentiality have been defined by:

(1) A physiological deficiency appears when the element is removed from the diet;

(2) The deficiency is relieved by the addition of that element to the diet; and

(3) A specific biological function is associated with the element (Roat-Malone 2002).

1.4. METAL SALTS IN BIOLOGLY

Biological functions of many proteins are carried in presence or in participation of metal ions. Also, at least one-third of all proteins which are encoded in the human genome appear to contain metal ions which perform a wide range of specific functions (Lu and Valentine 1997).

The importance of metals in biology, the environment and medicine has become increasingly evident over the last three decades. Na and K (together with H and Cl), which bind weakly to organic ligands, are ideally suited in generating ionic gradients across membranes and for the maintenance of osmotic balance. In contrast, Mg(II) and Ca(II) with intermediate-binding strengths to organic ligands, can play important structural roles, and as a messenger signalling key changes in cellular metabolism, are also important in muscle activation, in the activation of many proteases, both intra- and extracellular, and as a major component of a range of bio minerals, including bone.

The four transition metals manganese, cobalt, nickel, and zinc are of undisputed importance in the living world. Cobalt is used in a number of enzymes, some of which catalyse complex isomerization reactions. Like cobalt, nickel appears to be much more extensively utilized by anaerobic bacteria, in reactions involving chemicals such as CH_4, CO and H_2, the metabolism of which was important before the appearance of

dioxygen. In higher organisms, notably plants, the only nickel-containing enzyme is urease. Zinc not only plays a structural role but can also fulfils a very important function as a Lewis acid. It is also involved in a characteristic motif, termed zinc finger, in a number of eukaryotic DNA-binding proteins (that regulate the transcription of DNA into RNA), first described by Aaron Klug (Crichton 2008).

1.5. ELECTROLYTE SOLUTIONS

An electrolyte solution is the one which can conduct electricity. Electrolyte solutions (i.e. metal salt solutions) have significant roles in different branches of science and engineering such as environment, chemistry and biology and hence thermodynamic and transport properties of electrolyte solutions are of extreme importance. These thermodynamic properties are generally used to explain solute-solvent and solute-solute interactions in the solution phase.

An ideal electrolyte solution can be defined as an infinitely dilute solution where the concentration of the solute tends to zero. But due to interactions between solute-solute, solute-solvent and solvent-solvent particles in electrolyte solutions (Wright 2007), these systems by nature are always non-ideal, and represented an early challenge to theoreticians interested in describing their thermodynamic properties. The solute components such as cations, and anions, which carry opposite charges, interact very differently with one another. In the vicinity of each ion, certain shrinkage of the solvent is likely to occur as a result of the attraction between the ionic charge and the polar molecules of the solvent. This is called electrostriction and leads to a local increase in the density of the solvent around each ion since more molecules will be packed around the ion than would be present in that volume where the ion is not present. It follows that a complete description of an electrolyte solution at the molecular level requires the consideration of ion–dipole, ion–ion, and dipole–dipole interactions. In addition to these simple electrostatic interactions, one must also consider the role of hydrogen bonding in protic solvents like water.

In very dilute electrolyte solutions, the important consideration is ion–dipole interactions. One expects these interactions to be different for cations and anions. This follows from the fact that the solvent molecule is not a simple dipole in the electrostatic sense but instead it has a chemical structure which is different at each end of the

molecular dipole. Each ion interacts locally with four to six solvent molecules in its immediate surroundings. In case of water, the concentration of water molecules in the pure liquid is 55.5 M; it follows that the number of water molecules experiencing direct interaction with ions in dilute solutions represents a small fraction of the total number.

With the increase in electrolyte concentration, ion–ion interactions become more important in determining the thermodynamic properties of the solution. The electrostatic field of an ion is long ranged, decreasing with the reciprocal of the distance from the charge centre of the ion. As a result a given ion has an ionic atmosphere in which the concentration of oppositely charged ions in its vicinity is slightly greater on the average than that of ions of the same charge. The properties of the ionic atmosphere depend on temperature, that is, on the randomizing effects of thermal motion. Thus, the composition of the ionic atmosphere fluctuates with time, and the relative difference between the local concentration of cations and anions in the vicinity of a given ion varies with both temperature and distance. As the electrolyte concentration increases, both the average distance between ions and the thickness of the ionic atmosphere decrease (Fawcett 2004).

1.6. SALTING IN AND SALTING OUT

It has been found that salt solutions have large impact on the structure and properties of protein molecules. The solubility, denaturation, dissociation into sub-units and the activity of enzymes have been studied extensively in the past. Franz Hofmeister (1888) established that the effectiveness of salts for protein precipitation generally follows a specific order, regardless of the protein being investigated. Since then, the so-called Hofmeister series of salt effects has been taken into account in physical properties of aqueous salt solutions (Frumkin 1924). The same series equally applied for the effects of salts on a various macromolecular processes (Long and McDevit 1952, Nandi and Robinson 1972 and Ray and Nemethy 1971). Hofmeister series was obeyed by enzyme activity, protein stability, protein-protein interactions, and protein crystallisation, optical rotation of sugars and amino acids as well as bacterial growth.

'Salting in' is an increase in protein solubility upon the addition of a salt. This effect occurs when ions bind to proteins and increase their net charge. On the other hand, 'Salting out' is a result of interfacial effects of strongly hydrated anions near the surface

of proteins. According to this concept, various workers distinguished the salts as structure maker or structure breakers.

The effectiveness of various salts towards the destabilizing tendency of proteins is known as Hofmeister series. The ability of salt out of protein of various cations and anions follow the order:

Cations: $NH_4^+ > K^+ > Na^+ > Mg^{2+} > Ca^{2+} > Gdn^+$

Anions: $CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > HPO_4^- >$ acetate > citrate > tartrate > $F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$

The species to the left of Cl^- are referred to as kosmotropes, while those to its right are called chaotropes. These terms originally referred to an ion's ability to alter the hydrogen bonding network of water (Collins and Washabaugh 1985). The kosmotropes, which were believed to be 'water structure makers', are strongly hydrated and have stabilizing and salting-out effects on proteins and macromolecules. On the other hand, chaotropes ('water structure breakers') are known to destabilize folded proteins and give rise to salting-in behaviour. Left to Cl^-, the, protein stability as well as surface tension increases and protein solubility as well as denaturation decreases. The reverse effect is observed with the anions right to Cl^- (Zhang and Cremer 2006). Thus for the present study, chlorides of several metal ions have been considered to investigate the effect of cations on physical properties of biomolecules in aqueous solutions.

1.7. NATURE OF THE SOLVENT

Solvent is the most abundant species in solution and it can exist in various possible forms such as free ions, undissociated molecules in equilibrium with free ions and ion pairs in equilibrium with free ions. Hence it is of vital importance to know the structure of the pure liquid solvent before one studies the solution parameters. This is because introduction of a solute molecule into a solvent alters or disrupts the solvent's molecular structure and behaviour. In liquids, molecules exhibit relatively long-range attractive forces among themselves which give rise to the cohesive forces. These forces arise because the electronic distribution in the molecule or atom making up the liquid is not uniform either on a time-averaged basis or with respect to its instantaneous value. Non uniformity in the time-averaged electronic distribution in a molecule is a well-

known phenomenon, and is discussed in terms of the experimentally measured dipole moment, and higher-order moments such as the quadrupole and octapole moments. The major attractive component of intermolecular forces is due to dipole-dipole interactions, of which there are three principal contributions, namely, that due to permanent dipole interactions, that due to induced dipole-permanent dipole interactions, and the dispersion contribution arising from interactions between the instantaneous dipole moments. These are collectively called van der Waals forces and give rise to an attractive potential between two molecules which is inversely proportional to the distance between them to the sixth power (Fawcett 2004).

Water is the matrix of life and plays a crucial role in biological processes, particularly in its co-operative interactions with proteins (Maheshwary et al. 2001). It is well known for its hydrogen bonding and the existence of this hydrogen bond has a major influence on the structure of both liquid water and its solid phase, ice (Mirsky and Pauling 1936). A partial structure exists in water as a result of H-bonding between water molecules. The charge distribution in H-bond is the most stable form and is believed to be the linear H-bond, though this does not preclude the possibility that bent H-bonds could exist within the overall structure of water (Padova 1963). When solvation occurs, it is important to note that solvation shells are not typically comprised of solvent species permanently bonded to an ion, but rather represent solvent molecules that are able to position themselves around an ion in a coordinated fashion over a statistically meaningful amount of time and the solvent molecules directly outlying the stable ion solvation structures that contribute to the soft volume quantity. One of the main functions of the solvent is simply to reduce the forces of interaction between ions and thereby, reduce the electrostatic potential energy of this interaction. Physically, this corresponds to allowing the ions to exist as ions. If the molecule is polar, alignment of the permanent dipoles is the major effect, but polarizability effects must not be ignored; if the molecule is non-polar, the only effect comes from induced dipoles and this can be of crucial importance. Both these effects are of great importance for ion-solvent interactions in solution. This in turn implies that, there must be consequent modification of solute-solute interactions in particular and also, of solvent-solvent interactions though these are of relatively less importance. Nonetheless, it is still possible to talk about the effect of the field on the solvent. The ions in solution can

align the permanent dipoles of the solvent and can also induce dipoles in the solvent (Landis 1985).

Furthermore, the possibility of alignment of the dipoles of the solvent molecules by the ions leads to the following conclusion. For the solution, the simplest model to be envisaged is one where three possible situations can be thought of. There can be situations where the energy of the interaction between two ions of opposite charge becomes so high that the ions cease to be independent of each other and move around as a single unit which survives throughout several collisions before being able to separate. Such a unit is called 'ion pair'. Chemical studies have shown that the solvent is made up of molecules with a certain microscopic structure, so it is perfectly reasonable to expect that the microscopic structure may be of vital importance when the solvent plays its role as a solvent in electrolyte solutions.

Under some conditions it is likely to happen for a solvent molecule to have simultaneous participation in solvating two or more ions in close proximity. It is now realized that molecular details of ion-solvent interactions and consequent modifications to ion-ion and solvent-solvent interactions make a significant contribution to the behaviour of electrolyte solutions. The presence of ionic fields and the volume occupied by solvated ions can have a constraining influence on the movement and orientation of solvent molecules within an electrolyte. In simple terms, a solvent molecules freedom to move and rotate diminishes in the presence of ions and this constraint becomes worse at higher salt concentrations (Gering 1989).The degree of ion solvation in the bulk electrolyte will proceed to reach an optimal or full value dependent on the prevailing conditions of charge densities of the ions, solvent properties, the relative concentrations between solvent and ions, degree of ion association, temperature, etc. The ions are as fully solvated as their environment allows them to be.

According to a three region model, around the ion is a region of bound or strongly affected water molecules forming layers or shells which are highly orientated by the ion–dipole interactions between the ion and the polar water molecules. The arrangement of these bound or strongly affected water molecules is considerably distorted from that of the pure solvent. Next to this region and separating it from the unmodified solvent, is an intervening region of water molecules whose structural arrangement gradually changes from the highly orientated water to that of unmodified

water. This is a region of 'misfit' between bound and unbound water, and is expected to be highly disordered because of this misfit.

A comparison can be made between the degree of ordering in the pure solvent and the degree of ordering in the electrolyte solution in terms of:

(a) The highly ordered region around the ion;

(b) The disordered intervening region of misfit;

(c) The order of the unmodified solvent.

Whether an ion will cause an overall increase in order in the solution compared with the pure solvent depends critically on the balance between the order/disorder introduced by (a) and (b).

If on balance region (a) is dominant, there will be an overall increase in order in the solution relative to the pure solvent, the degree of 'structure' will be enhanced and the ion is termed a 'structure maker'.

If, on the other hand, on balance region (b) is dominant, there will be an overall decrease in order in the solution relative to the pure solvent, the degree of 'structure' will be decreased and the ion is termed a 'structure breaker'. The structure which is being discussed, i.e. in the strongly orientated and the misfit regions, is not the structure of ordinary water.

When a solute is added to a solvent, e.g. an electrolyte to water, it might be expected that the final volume of the solution would be greater than the volume of the solvent used. However, this is not always the case, and large negative changes in volume are often found experimentally. These are found by measuring the density of solutions as a function of concentration of the electrolyte. Analogous interpretations to the entropy data can be given for changes in volume on solution of an electrolyte, though the effects are less definite than with the entropies. If the decrease in volume is greater than expected, then the ion is a structure-maker – constriction of the solvent in the bound shell more than outweighs the effect of the 'misfit' region. If the decrease in volume is less than expected, then the ion is a structure-breaker – the constriction of the loosely bound water molecules in the bound region is not sufficiently great to outweigh the effects of the 'misfit' region (Wright 2007).

In addition to these effects, hydrophobic interactions may also come into picture. These interactions are prevalent in different phenomena such as structure

stabilization of proteins, binding of enzymes to substrates, and folding of proteins and are noncovalent in nature. This kind of interaction appears when non-polar compounds are put into water, and it is an entropy-driven process. Hydrophobic interactions cause the linear polypeptide to fold into a compact structure and are believed to be of dominating importance for protein structure, aggregation and function.

There are reports on the importance of hydrophobic interactions in protein folding (Kauzmann 1959, Privalov and Gill 1988, Privalov and Kechinashvili 1974 and Privalov 1979) which have been discussed in terms of various models for water structures.

1.8. BASIC VOLUMETRIC PARAMETERS

1.8.1. Density

Density (ρ) of a material is defined as its mass per unit volume. In a qualitative manner it can be defined as the measure of the relative "heaviness" of an object with a constant volume. In general, increasing the pressure will always increase the density of a material and the reverse effect can be seen with the temperature. Density is also affected by the atomic mass of an element or a compound. Since different substances have different densities, density measurements are often used as means of identifying substances. In solution chemistry, conversion of mass concentrations to volumetric concentrations, for making buoyancy corrections while weighing samples, for converting mean molal activity coefficients to mean molar values, for calculation of partial molal volumes, to investigate electrolytic and nonelectrolytic behaviour of molecules in different solvents and excess thermodynamic properties of binary liquid mixtures, etc., the density measurements have been utilized (Cabeza et al. 2003).

1.8.2. Ultrasound Velocity

Ultrasound velocity (c) can be used to determine some of the thermodynamic parameters of the propagation medium, such as isentropic or isothermal compressibility, internal pressure of the propagation medium, relative association, solvation number, specific acoustic impedance, intermolecular free length etc. (Islam and Waris 2004 and Pandey et al. 2007) These data can be processed to obtain a quantitative estimation of the ultrasound effects in various domains such as industry,

medicine, research, etc. (Marin et al. 2008). It is the speed in which sound propagates in a certain medium. It depends largely on material density & elasticity. Speed of sound is a constant for a given material at a given temperature. The ultrasound propagation velocity also depends on the nature and aggregation state of the propagation medium. In the condensed media, the ultrasound velocity depends on their viscosity and density, offering information about the nature of the interactions between the component particles. It is the most important and universally accepted technique to study the physico-chemical properties of the liquids, liquid mixtures and electrolytic and polymeric solutions. Speed of sound measurement also finds application in the study of dynamics of systems (Rao and Verrall 1987, Kawaizumi et al. 1977, Millero and Lepple 1972), physical nature of the aggregates occurring in the solutions and structural changes of solutes and solvents in solutions.

1.8.3 Refractive Index

In optics the refractive index or index of refraction (n_D) of a substance or medium is a measure of the speed of light in that medium. It is expressed as a ratio of the speed of light in vacuum to that in the medium of concern. This physical property occurs because there is a change in the velocity of light going from one medium into another. It has been a quick, convenient, and accurate way to estimate densities of liquid mixtures (Bauer and Fajans 1945, Zamvil et al. 1978 and Fucaloro 2002). The packing effect and solute-solvent interactions of the solute among the solvent molecules can be understood by the knowledge of refractive index measurements (Fontao and Iglesias 2002). Even one can calculate the molecular composition of hydrogen-bonded complexes by refractive index measurements (Pineiro et al. 2002). These measurements have been carried out to study the miscibility of organic solvents in water, control of adulteration of liquids and in applications of evanescent wave techniques in biochemistry. Also they have been considered as a tool to verify the results obtained from volumetric studies (Chen et al. 2013, Khoshkbarchi et al. 2004 and Li et al. 2007).

1.9. DERIVED VOLUMETRIC AND ACOUSTIC PARAMETERS

1.9.1. Molar Volume

The volumetric properties of a substance such as the partial molar volumes are the key parameters which provide sensitive information of solute-solvent interactions in solutions. Apparent molar volume (ϕ_v) is a useful thermodynamic parameter which indicates how the molar volume of a solution or a mixture varies with changes in the molar composition of the mixture at constant temperature and pressure. A comparison of the volume of the system with those of its components can assess gross changes in the volume of the system, because it is an additive property. However, the temperature-dependence of partial molar volume may still be more useful in characterizing the structural hydration effects of the solute (Banipal and Kapoor 1999). The apparent molar volume further details about the hydration shell model which enables us to distinguish a contribution from each hydration shell. However, it appears that volumetric properties of a solute such as apparent molar volume still remain as a powerful tool for probing the hydrational state of the solute in the solution.

1.9.2. Isentropic Compressibility

The speed of sound measurement allows one to compute the isentropic compressibility (κ_S) of any substance in the solution. These are related with the structural effects and packing phenomena (Rao and Verrall 1986). The isentropic compressibility is an essential physical characteristic reflecting hydration property, inter-residual interaction and dynamic processes occurring in solutions. In aqueous solution, the isentropic compressibility of peptides or proteins consists of three components: (i) intrinsic, from the residue-residue interaction in the globule interior, (ii) relaxational, from the structural transformations accompanied by volume changes and (iii) hydrational, from surface atomic group-water interaction. To derive the contribution from all kinds of interactions occurring in the solution, a systematic investigation of the partial compressions of molecules of different structure and complexity, from small to large ones, in diluted aqueous solutions is necessary. In particular, the hydrational part is the most important one and should be quantitatively investigated. The isentropic compressibility increases in presence of relaxation terms and decreases with increase in hydration. Isentropic compressibility can yield

characteristic information about intermolecular interaction for peptides and proteins (Rao and Verrall 1986). Also, it is a second pressure derivative of the Gibbs free energy and can be precisely obtained from the measurement of density and ultrasonic velocity in solutions by the well-known Newton-Laplace equation (Strutt and Baron 1986).

1.9.3. Apparent Molar Isentropic Compression

The apparent molar compression (ϕ_k) is a useful parameter to have an insight on the pressure effect on various equilibria and interactions. The apparent molar isentropic compression contains contribution arising from the intrinsic compression of the solute and from the interactions between solute and solvent (Gekko and Noguchi 1979). The intramolecular fluctuation has a more essential effect on apparent molar compression than on the apparent molar volume (Imai 2007). The changes in compression reveal the electrostriction contributions which dominate in the size dependence of the apparent molar compression. Similar to the apparent molar volume, apparent molar compression also helps us to distinguish a contribution from each hydration shell from the hydration shell model (Yuan et al. 2006). Since the extent of protein hydration changes during the course of protein unfolding from the native state, through compact intermediate states or partially unfolded state to the fully unfolded state, compression measurements provide useful means to characterize protein transitions (Chalikian et al. 1993, Chalikian et al.1996 and Kharakoz 1997). However, isothermal compressibility, a thermodynamic parameter, is a sensitive measure of solute-solvent interactions and can be used to monitor solute hydration in aqueous solutions (Hoiland 1986, Mathieson and Conway 1974). Direct evaluation of isothermal compressibility values is impossible (Hoiland 1986) though the precise measurements of speed of sound and density have been used to calculate the isentropic compressibility than isothermal compressibility. However, it is possible to convert isentropic compressibility into isothermal compressibility from the knowledge of coefficient of thermal expansion and heat capacity (Millero et al. 1974 and Hedwig 2010).

1.9.4. Partial Molar Quantities

These are used to describe the change in properties of a multicomponent system such as apparent molar volume or apparent molar isentropic compression, when one component is added at constant temperature, pressure, and amounts of all other components (Fawcett 2004).

1.9.5. Transfer Thermodynamic Properties

They provide qualitative and quantitative information regarding the co-solvent-solute interactions without take into account the effects of solute-solute interactions. A thermodynamic transfer function may be defined as the change in an apparent molar thermodynamic property obtained at infinite dilution when one mole of a solute is transferred from one solvent system to another solvent system (Hakin 2003).

1.9.6. Intermolecular Free Length

The intermolecular free length (L_f) is concerned mainly with the solvent-solute interactions and solute-solute interactions (Pandey et al. 2003). Through intermolecular free length it is possible to understand the nature of molecular interactions, internal structure and the aggregation behaviour of the species present in a system. This also helps in predicting the intermolecular interactions between unlike molecules of the mixture. Furthermore, is possible to know whether the interactions are strong or weak which arise due to charge transfer, dipole-dipole, dipole-induced dipole and hydrogen bonding.

1.9.7. Specific Acoustic Impedance

Specific acoustic impedance (Z) is associated with the acoustic pressure to specific flow, or flow per unit area, or flow velocity. The nature of acoustic impedance play vital role in assessing the compactness due to molecular rearrangement (Baskaran and Kubendran 2007). The variations in specific acoustic impedance suggest the type of interactions and bonding. The changes in the values of specific acoustic impedance can be explained on the basis of hydrophobic interaction between solute and solvent molecules which increases the intermolecular distance, making relatively wider gaps between the molecules and vice-versa, becoming the main cause of impedance in the propagation of ultrasound waves (Mehrotra and Upadhyaya 1988).

1.9.8. Relative Association

Relative association (R_A) is the associations in the newly deployed metal salts relative to the associations of the substrate dipeptides. It is also possible to predict the making or breaking of the solvent aggregates. Also, these variations indicate the like and unlike interactions between the solute and solvent molecules. Knowledge about solvation is vital to the understanding of the behaviour of electrolyte solutions and has proved to be of crucial importance in determining the behaviour of biological systems. The solvation can decrease more rapidly as the solvent to salt ratio decreases to reach a limiting value, say near the salt solubility limit. The trends in solvation number over concentration and temperature somewhat mirror the trends of solvated ion sizes. Also the solvation numbers are not limited to integral values. Thus, when speaking of solvation numbers/shells reflect the average probability of finding solvent species coordinated around an ion at any point of time (Santosh et al. 2009, 2010 and 2011).

1.10. UNCERTAINTY IN MEASUREMENTS

Uncertainty associated with the experimental measurement of parameters; density, ultrasonic speed and refractive index have been evaluated based on "Evaluation of measurement data – Guide to the expression of uncertainty in measurement" JCGM 100:2008.

1.11. A BRIEF OVERVIEW OF THE STATE OF ART IN THE FIELD

1.11.1. Solution Behaviour of Amino Acids in Aqueous Solutions

The study of volumetric properties of solutions dates back to 19th century. During this period scientists were curious over the effect of mixing of different liquids on the volume and temperature of the mixture (Guthrie 1884). A classical paper by Peel et al. (1928) indeed discussed the volume change on mixing of 28 liquid systems. Growing advances in biotechnology have greatly expanded the production and study of a wide variety of biomolecules in chemical, pharmaceutical and food industries. Investigations of the nature of the interactions of these molecules attracted various scientists round the globe. A vast volume of literature can be found on the studies of molecular interaction in aqueous and mixed environment. Among them, the pioneering work by Cohn et al. (1934) was the first of its kind in this particular field. Since then,

the investigations have been intensified drastically with the advent in measuring techniques and availability of more sophisticated instruments. It has been established that several low molecular weight model compounds such as amino acids, peptides and their derivatives have been considered because of the complexities of proteins and infeasibility of direct thermodynamic studies. Moreover, small derivatives of amino acids have been used recently as protein model compounds in the thermodynamic studies of proteins. Since these molecules contain more complex structure and more component of protein than amino acids, it is beneficial utilize the thermodynamic data of these molecules to correlate the same to the whole protein structure. Direct experimental investigation of the ideal reference state of proteins has been criticized on the grounds that some residual structure could remain in the system. To overcome such criticisms many researchers have turned to the use of additivity models to predict the thermodynamic properties of proteins in the denatured state. This approach utilizes thermodynamic data derived from small organic compounds, known as protein model compounds, which mimic some specific aspects of protein structure, can be checked to estimate properties of structurally complicated molecules in solutions.

The molecular interactions are generally weak and hence spectroscopic probe has major difficulties in monitoring these interactions (Jayabalakrishnan 2009). Hence, studies on density, viscosity, speed of sound, heat capacity, conductance and refractive index are of great use in characterizing the nature of solute-solvent reactions in solutions.

Studies of compressibility of aqueous solutions of proteins have started a long time ago (Passynskii 1946 and Jacobson 1952). Ellerton et al. in 1964 measured the isopiestic vapour pressure, densities and relative viscosities of several amino acids in aqueous solutions. The precise density measurements at higher pressure have been utilised by Yayanos (1972) to find the temperature effect on apparent molar volumes. Millero et al. (1978) determined the apparent molar volumes and adiabatic compressibilities of fifteen amino acids in water from accurate density and sound velocity measurements. Shahidi and Farrell (1978) reported the partial molar volumes of betaines of α,ω-amino carboxylic acids at 298.15 K. They observed electrostriction in aqueous solutions which resulted in an apparent decrease in the overall volume of the water by solute-solvent interactions associated with the independent hydration of

the charged end groups. From 1990's the research in solution behaviour of aqueous and mixed aqueous solutions gained momentum. Hedwig and Hoiland (1991)[a,b] studied the partial molar isentropic pressure coefficients at infinite dilution for aqueous diglycine, triglycine and tetraglycine solutions. Pioneering works by Kharakoz (1991) as well as Chalikian et al. (1993) suggested that the data obtained from the volumetric studies of amino acids are useful in the analysis of hydration contribution to amino acid volume as well as the relationship between the temperature dependences of partial molar volumes and structure of amino acids. Hakin et al. (2001) studied the relative densities and heat capacity ratios for the cyclic dipeptides cyclo-glycylserine, cyclo-alanylglycine, cyclo-alanylserine and cyclo-serylserine in water over the temperature range 288.15 to 328.15 K. The partial molar properties at infinite dilution have been used to calculate the thermodynamic parameters for the amino acid side chains of alanine and serine.

Even though many authors investigated molar volumes of amino acids and the related compounds during the course of last three decades (Ramasami 2002, Bhat and Ahluwalia 1985, 1987, Hedwig 1993, Hedwig and Hoiland 1991[a], Hedwig and Hoiland 1991[b], Reading and Hedwig 1990, Liu et al. 2006 and Romero and Munar 1998), only few could study the compressibility of amino acids in aqueous solutions (Cabani et al. 1981, Chalikian et al. 1993, Kharakoz 1991 and Chalikian et al. 1996).

1.11.2. Solution Behaviour of Amino Acids in Aqueous Metal Salt Solutions

It is evident that the all biological fluids are not pure water and additives in the environment of proteins have a significant impact on its stability and functions (Zhao 2006).Since salt solutions are prone to affect the structure, conformation and properties of proteins, researchers concentrated on the study of effect of ions on the solution behaviour of amino acids (Lippard and Berg 1994, Kumar et al. 2011 Ramasami and Kakkar 2006, Sadeghi and Goodarzi 2008 and Badarayani and Kumar 2006).

Preferential interactions of bovin serum and lysozymes with CH_3COONa, NaC1, Na_2SO_4, KSCN, $MgCl_2$, $CaCl_2$ and $MgCl_2$ were studied by Timasheff and Arakawa in 1982. They observed unfavourable free-energy change due to the hydration of proteins in the salt solution and co-related it to the large surface tension increment

of the salts. Partial molar volumes of several amino acids and peptides in water and aqueous NaCl solutions at 298.15 K have been reported by Bhat and Ahluwalia in 1985. They showed that the volumes of transfer for amino acids, peptides and peptide groups are positive and correlated them to the dominant interactions of sodium chloride ions with the charged centres of the amino acids and peptides.

Zhao et al. (1995) determined the excess enthalpies of ethanol + water + $ZnCl_2$ and discussed the interactions among water, ethanol and $ZnCl_2$ in terms of solute-solvent and solvent-solvent forces. Banipal and Sehgal (1995) reported that electrolytes induce dissociation in the dipeptide hydration shells thereby increasing partial molar volume. Khoshkbarchi and Vera (1997) determined the activity coefficient using electrochemical cell and co-related the volumetric results. Vera et al. (1998) studied the effect of electrolytes using a new calculation model which had only two adjustable parameters.

An appreciable growth in solution chemistry of amino acid derivatives-metal salt solutions has been evident from last two decades. Wherein researchers focused on the study of volumetric and viscometric behaviour of amino acids or their derivatives in appropriate solvent system. There are several reports on the ultrasonic studies of some derivatives of sulphonamide in dimethylformamide by Baluja and Oza (2001) and that of aqueous KCl solutions by Kumar (2003). In 2002, Yan et al. studied volumetric behaviour in a system of α-amino acids in aqueous sodium acetate solutions at varying temperatures. Same group (2003) reported viscosity and density behaviour of α-amino acids in aqueous calcium chloride solutions.

Rohankar and Aswar (2002) measured the apparent molar volume and apparent molar compressions of glycine in aqueous vanadyl sulphate solutions at different temperatures and explained the results on the basis of electrostriction. The mixing effect of simple dipeptide such as glycylglycine in presence of aqueous electrolytes has been studied by Badarayani and Kumar (2004) where, the measured apparent molar properties of both dipeptide and electrolyte were attributed to the interactions present along cation, anion, the head groups of peptide, and the peptide bond.

Ramasami and Kakkar (2006) studied partial molar volumes and isentropic compressions at infinite dilution of amino carboxylic acids and glycylglycine in water

and aqueous solutions of sodium sulphate at different temperature. Intermolecular interactions in leucine, asparagine and glycylglycine-aqueous electrolyte systems were evaluated by Riyazuddeen and Bansal in 2006. The effect of manganese acetate on the volumetric and transport behaviour of some amino acids in aqueous solutions at 25°C has been reported by Banipal et al. (2006). Same authors (2008) studied the interactions between amino acids with $ZnCl_2$ solutions from which the structure-breaking property of $ZnCl_2$ was discussed.Venkatesu et al. (2007) even considered cyclic dipeptides along with other dipeptides in investigating volumetric properties of these peptides in aqueous and in aqueous electrolyte solutions. They studied the solution behaviour of biomolecules in aqueous potassium chloride, potassium bromide and potassium acetate solutions at T = 298.15 K under atmospheric pressure.

Contribution of zwitterionic side groups to partial molar volumes and free energy of activation of viscous flow was indicated through a paper published by Ali et al. in 2007. Isentropic compressibility studies were performed by Riyazuddeen and Khan (2008, 2009) where they studied of L-alanine, L-proline, L-valine, and L-leucine in aqueous KCl/KNO_3 solutions at different temperatures. The limiting partial molar volumes at infinite dilution and the infinite dilution partial molar expansibilities of glucose in aqueous urea solutions at various temperatures were studied by Samanta and Saharay (2010).

A better understanding of the hydration effects in biological systems was obtained by the results of the experiment carried-out by Pal and Chauhan (2011) and Nain and Pal (2013). Chauhan and Kumar (2014) studied the effect of sugars on the volumetric properties of amino acids. They demonstrated that the hydrophilic-ionic interaction between the solute and solvent is greater than other types of interactions. In addition to these, there are still more reports on volumetric studies of amino acids and peptides in presence of some other metal ions which play an important role in vital functions of living organisms (Pal and Kumar 2004, Santosh et al. 2009, 2010 and 2011 and Riyazuddeen and Afrin 2012).

Savaroglu and Ildaser (2014) determined the speed of sound and densities of different concentrations of L-tyrosine + L-glutamic acid + water ternary solutions, L-tyrosine + water and L-glutamic acid + water binary solutions at 298.15 K, 308.15 K

and 318.15 K. They discussed the results of their study in view of hydrophobic-hydrophobic and hydrophilic–hydrophobic group interactions as well as, structure-making and structure-breaking effects in L-tyrosine + L-glutamic acid + water.

Volumetric properties of some amino acids in aqueous D-manitol were reported by Wang et al. in 2014 where they concluded that the hydrophobicity of the zwitterionic head was stronger than the side group of amino acids. Volumetric study of N-acetyl glycine in aqueous sucrose solutions has been considered by Sharma et al. (2014) which suggested predominance of hydrophilic–hydrophilic interactions at lower temperatures while hydrophilic–hydrophobic interactions at higher temperatures for all the solutions. Makarov et al. (2014) measured solution thermodynamics of glycine betaine at different temperatures and pressures. They found the breaking of water structure because of electrostriction of glycine betaine which weakened with temperature and pressure rising. Several other workers reported the solution behaviour of amino acids and related compounds in aqueous metal salt solutions (Pinho et al. 2014 and Riyazuddeen and Gazal 2013). A study on molecular interactions of some amino acids and peptides in the combined presence of surfactants and glycine betaine by Kishore and Misra (2012) indicated that glycine betaine primarily exhibits polar interactions with the zwitterionic centres of the amino acids and peptide bonds of the peptides but might enhance the overall solvent structure in the presence of amino acids with bulkier alkyl groups.

Recently, the research on molecular interaction has been directed towards ionic liquids which have got more importance due to their potential applications (Shekaari and Jebali 2010, Tong et al. 2012 and Venkatesu et al. 2013).

Therefore, in order to understand the interactions of biomolecules with aqueous metal salts under diverse conditions, it is essential to study the volumetric and compression data which may reveal good volume of information on solution behaviour.

1.12. SCOPE AND OBJECTIVES OF THE PRESENT WORK

One of the obstacles preventing the direct thermodynamic investigation of proteins is its complex structure. Also, the lower solubility of most of the proteins in water makes it difficult to study the structural features. Due to the complexity of

proteins, the nature of these biomolecules can only be studied by using simple molecules like amino acids, di-, tri-peptides and their derivatives. The origin of protein stability in aqueous solutions is traced to the solute (protein amino acid side chain)-solvent (mostly water) interactions. These interactions are influenced by several structural and steric factors of the solute molecules. Further, the nature of the solvent media; that is, whether it is pure water or contains electrolytic or non-electrolytic additives also has its effect. Through the measurements of various thermo-physical quantities based on volumetric, speed of sound and transport properties, effects due to solute-solvent interactions between the hydrophilic-ionic groups, hydrophilic-hydrophilic groups, and hydrophilic-hydrophobic groups of the additives and protein model compounds in the aqueous solutions have been monitored.

In probing the structures of proteins in aqueous solution using the model compound approach it has become apparent that there are significant differences between various sets of thermodynamic parameters for amino acid side-chains. Therefore, in order to understand the behaviour of amino acids or dipeptides in aqueous metal salt solutions, it is crucial to study their thermodynamic and volumetric data.

1.12.1. Protein Model Compounds

1.12.1.1. Cyclic dipeptides: Cyclic dipeptides or 2, 5- diketopiperazines are the cyclic derivatives of peptides found in nature (Prasad 1995). They impart a metallic bitter taste in various foods and beverages (Chen et al. 2004). These compounds possess many of the structural characteristics one looks for in model compounds. For example, charged end groups, which influence partial molar properties of protein side chains, are not present. In addition, they have been found to possess many of the interactions required to quantitatively characterize the interactions of the solid like core of globular proteins. One such cyclic dipeptide is cyclic alanylalanine or alanine anhydride or 3, 6-dimethyl-2,5-piperazinedione.

Cyclic peptides are polypeptide chains in which the amino and carboxyl termini are themselves linked together with a peptide bond that forms a circular chain. A number of cyclic peptides have been discovered in nature and they can range anywhere from just a few amino acids in length, to hundreds. Cyclic dipeptides are relatively rigid compounds than that of their acyclic analogues and are formed by the cyclization of

simple amino acids. The ease of cyclisation depends on the amino acids present and their configuration though the processes by which cyclic peptides are formed in cells are not yet fully understood. The simplest cyclodipeptides, 2,5-diketopiperazines, are derived from a dipeptide ester. The simplest method of making cyclic peptides involves preparing a reactive ester of an *N*-protected linear peptide, deprotecting the α-amino group, adding tertiary base and allowing cyclisation to occur in dilute solution to favour cyclisation over intermolecular condensation.

One interesting property of cyclic peptides, however, is that they tend to be extremely resistant to the process of digestion, enabling them to survive intact in the human digestive tract. Drug delivery has been a persistent challenge in the pharmaceutical arts, particularly when a drug is unstable and/or poorly absorbed at the locus in the body to which it is administered. Cyclic dipeptides such as 2, 5-diketopiperazines have been shown to be useful in drug delivery, particularly those bearing acidic R groups (U.S. Pat. Nos. 5,352,461 entitled "Self Assembling Diketopiperazine Drug Delivery System;" 5,503,852 entitled "Method for Making Self-Assembling Diketopiperazine Drug Delivery System"; 6,071,497 entitled "Micro particles For Lung Delivery Comprising Diketopiperazine" and 6,331,318 entitled "Carbon-Substituted Diketopiperazine Delivery System"). Diketopiperazines can be formed into particles that incorporate a drug or particles onto which a drug can be adsorbed. The combination of a drug and a diketopiperazine can thus impart improved drug stability. These particles can also be administered by various routes such as inhalation of powders, intravenous administration of suspension and oral delivery as tablets or capsules. Diketopiperazines may also facilitate absorption of an associated drug. This trait makes cyclic peptides attractive to designers of protein-based drugs that may be used as scaffolds which, in theory, could be engineered to incorporate any arbitrary protein domain of medicinal value, in order to allow those components to be delivered orally. This is especially important for delivery of other proteins that would be destroyed without such implementation (Craik 2006). One of the study showed that 3,6-dimethylpiperazine-2,5-dione (cyclic alanylalanine) holds promise as indicators of decomposed fingerprint residues and, therefore, may serve as good candidate substrates for developing reagent for fingerprint residue at high temperatures (Richmond et al. 2007).

The biological importance of cyclic dipeptides has been attested by numerous examples (antibiotics such as Gramicidin S and immunosuppressant agents such as cyclosporin). Many attempts to restrict conformational freedom of amino-acid and peptide analogues synthesized for pharmaceutical studies have been described in reports of drug research, one such approach being the synthesis of cyclic analogues of biologically active short peptides. For example, the importance of the cell-adhesion sequence RGDS (i.e., —Arg—Gly—Asp—Ser—) has stimulated research in which cyclic peptides enclosing it in such a manner as to constrain its conformation have been synthesized for biological testing. Many such compounds have been identified which possess biological activity including antiviral, antibiotic and antitumor properties, and show promise as environmentally friendly marine anti fouling agents. Due to their simplicity, unique spatial conformations and limited conformational freedom, cyclic peptides are widely used as model molecules for larger peptides in chemistry, biochemistry, pharmaceutical chemistry, and life sciences (Martins and Carvalho 2007 and Rhee 2002).

1.12.1.2. Glycine betaine: The trimethylglycine, an N-trimethylated amino acid, whose IUPAC name is *N,N,N*- trimethylammonioacetate, was the first betaine discovered by Science. Originally, it was simply called betaine. Since that many other betaines have been discovered, the more specific name 'glycine betaine' is distinctive of the trimethylglycine. Other synonyms of glycine betaine include Oxyneurine and (Carboxymethyl) trimethylammonium. Beets, broccoli, grains, shellfish and spinach contain an appreciable amount of glycine betaine. Betaine supplements are manufactured as a by-product of sugar beet processing, consumed by the body builders to build muscles.

As an osmolyte, glycine betaine protects the cells, proteins and enzymes under environmental stress and also finds applications in various other fields including pharmaceutical and agro-industrial (Schwab et al. 2002, Xiuling et al. 2009 and Pirjo 2004). It is found in all the three taxonomic kingdoms; bacterial, plant as well as the animal. However, it is particularly found in organisms that are exposed to extremely saline conditions (Papageorgiou and Murata 1995). Further, it functions as

osmoprotector, osmoregulator and transmethylating agent in biological systems (Cayley et al. 1992, Waditee et al. 2003 and Mak 1990).

Glycine betaine is an analogue of amino acid-'glycine' and has also been considered by many researchers as a model compound for the thermodynamic study of protein molecules (Bhattacharya and Sengupta 1985, Pitkanen et al. 2010 and Shen et al. 2011). Furthermore, Krakowiak et al. (2013) considered volumetric and acoustic study of aqueous solutions of glycine betaine along with trimethylamine-N-oxide, glycine, sarcosine and N,N-dimethylglycine and predicted structure breaking property of glycine betaine.

1.12.2. Significance of Cyclic Dipeptides and Glycine Betaine

The cyclic dipeptides and betaines have been of considerable interest to those concerned with the constitution of proteins. Substituted diketopiperazines have shown to be present among the products of protein hydrolysis and much experimental evidence has suggested that these compounds might play a major role in the elucidation of the structure of protein molecules.

Proteins often have charged groups at the surface which believed to have an immobilizing or electrostricitive effect on the surrounding solvent. The electrostatic field of the protein or peptide orients or orders the dipole moments of the surrounding solvent molecules (i.e. water in aqueous solutions). It is important to understand the role of water in the fundamental processes of molecular stability and structural integrity. These, at the atomic length scale would necessarily be described by the hydration of biological molecules as well as the bulk water structure present around biomolecules. Also, salt-induced electrostatic forces are known to play a vital role in modifying the amino acid structure by affecting the properties like solubility, denaturation and activity of enzymes. Due to the complex structure of protein, a variety of different interactions with salts may occur and it is difficult to resolve the various interactions participating in them (McLain et al. 2008). Thus it is easy to study those interactions in simple model compounds such as cyclic dipeptides or glycine betaine and correlate them to the protein structure.

This work is focused on the molecular interactions in biomolecules (namely cyclic alanylalanine and glycine betaine)-metal salt (chloride) aqueous solutions. In

other words, it is concentrated on the study of basic properties of solutions such as density, speed of sound and refractive index at different temperatures and laboratory pressure. The experimentally determined volume of data is utilised to investigate various molecular interactions operating in such solutions. The following objectives are laid down in preview of the present study:

i. In order to understand the interaction of biologically important molecules with the solvent environment it has been planned to determine thermodynamic, volumetric, acoustic and refractometric properties of a series of cyclic alanylalanine-metal chloride as well as glycine betaine-metal chloride aqueous solutions under the varied conditions of concentration and temperature.
ii. To calculate partial molar quantities of cyclic alanylalanine and glycine betaine from aqueous to aqueous metal chloride solutions.
iii. To identify and estimate the kind of molecular interactions present in the studied systems on the grounds of the experimental and computed parameters.

1.13. PRESENT WORK

The present thesis consists of seven chapters. **Chapter 1** introduces the topic "solution chemistry" which deals with volumetric, acoustical and refractometric properties of aqueous solutions of cyclic alanylalanine or glycine betaine in several metal chlorides. It also presents background information, literature review, problem definition, scope and objectives of the present research work.

Chapter 2 presents a brief description of the materials and experimental methods used in this study. It provides details about the source, purity and CAS number of the chemicals along with the characterization methods followed. The instruments used, uncertainties estimated in various measurements, laboratory pressure, temperatures and details of other experimental conditions are provided in this chapter. The concentration range chosen for the present work and the reason behind the choice are given at the end.

Chapter 3 outlines a detailed study of density, speed of sound and refractive index of cyclic alanylalanine in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at different temperatures. The values of isentropic compressibility, apparent molar volume, apparent molar isentropic compression, molar refraction, transfer molar

quantities, specific acoustic impedance, intermolecular free length and relative association are also been provided. The derived parameters have been co-related to various molecular interactions taking place in the above systems.

Chapter 4 deals with the volumetric, optical and compression study of cyclic alanylalanine in some transition metal chloride aqueous solutions. A representative study on variation of metal chloride concentration in aqueous cyclic alanylalanine has also been carried out to understand the behaviour of such systems. The results have been utilised to have an insight of nature of all the systems under the experimental conditions.

Chapter 5 describes the molecular interaction of glycine betaine in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at various temperatures. This also provides details on the study of compression and molar volumes of glycine betaine-NaCl aqueous systems at increasing concentration of electrolyte.

Chapter 6 comprises of the study of solution parameters of glycine betaine in aqueous transition metal chloride solutions such as $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$. The effect of concentration of metal chlorides on the volumetric properties of glycine betaine has been elucidated by considering solvents of different concentrations (i.e. 0.1 to 0.5 $mol \cdot kg^{-1}$). The study on glycine betaine-$ZnCl_2$ has been carried out only at 0.1 $mol \cdot kg^{-1}$ due to precipitation constraints. The general trend in the compression values suggested and molar volumes of all the solutions are discussed in detail. Hepler's coefficient $(\partial^2 \phi_v^0 / \partial T^2)$ for each of the systems are also included in this chapter.

The summary and conclusions of the present study are presented in **Chapter 7**. This chapter also includes scope for further research in the current field. The conclusions drawn out of the above chapters suggest that cyclic alanylalanine and glycine betaine can be used as a model compound for the thermodynamic elucidation of protein molecules. The same study can be extended to other cyclic di-, tri- or polypeptides and betaines in aqueous as well as mixed-aqueous solvents to understand the behaviour of those compounds in such solutions.

CHAPTER 2

EXPERIMENTAL

Chapter 2 provides information about the materials used in the research work and the experimental techniques employed.

2.1. MATERIALS

Details of the chemicals used in the present study are presented in Table 2.1. Cyclic alanylalanine and glycine betaine of 0.99 mass purity were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., India.

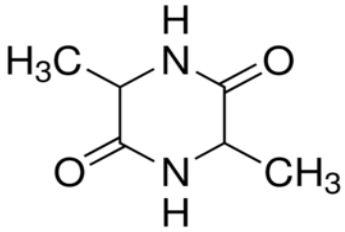

Figure 2.1a. Cyclic alanylalanine

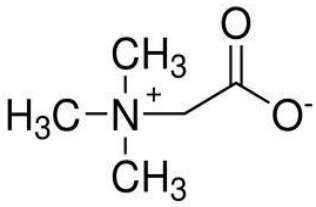

Figure 2.1b. Glycine betaine

These commercial chemicals were analysed and used without further purification. All the samples were kept in a vacuum desiccator over anhydrous P_2O_5 at room temperature prior to use. Deionized, doubly distilled water with a specific conductance less than $1.6 \cdot 10^{-6}$ $\Omega^{-1}.cm^{-1}$ was used to prepare all the solutions. The solutions were prepared on a weight basis by using a Mettler balance having a precision of ±0.01 mg. The estimated uncertainties in molality and mole fraction were found to be $\pm 1 \cdot 10^{-4}$ mol·kg^{-1} and $<\pm 1 \cdot 10^{-4}$ respectively. To prevent formation of air bubbles, all solutions were preheated in sealed Eppendorf tubes to 5 K above the measurement temperature before filling the densimetric and interferometer cells.

2.2. METHODS

2.2.1. Speed of Sound Measurements

Speed of sound in the solutions was measured by variable path fixed frequency interferometer manufactured by Mittal Enterprises, New Delhi (Model-F-05). The instrument utilises a simple principle to measure ultrasonic velocity of liquids with a high degree of accuracy. It consists of a high frequency generator and a measuring cell,

the frequency of which is fixed at 2 MHz. The measurement of sound velocity is based on the accurate determination of wavelength of sound waves in the medium. The quartz crystal fixed at the bottom of the cell produces sound waves of 2 MHz frequency. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. The space between the crystal and metallic plate is filled with solutions of concern. When the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium and this acoustic resonance gives rise to an electrical reaction on the generator, which excites the quartz crystal and the anode current of the generator, becomes maximum. Anode current varies by increasing or decreasing the distance exactly one half of the wavelength or its multiple. The maximum or minimum current corresponds to antinode or nodes of the standing waves. From this the velocity of sound in the solution can be calculated.The instrument was calibrated by measuring the speed of sound in AR grade benzene and carbon tetrachloride. The maximum estimated error in ultrasonic velocity measurements was estimated to be ±0.2 $m \cdot s^{-1}$. The temperature of the measuring cell was controlled by circulating water around it from a thermostatically controlled water bath supplied by Raaga Industries, Chennai.

Figure 2.2. Ultrasonic interferometer

2.2.2. Density Measurements

Densities of the dilute cyclic alanylalanine-metal salt solutions were measured using a single stem pycnometer (Pyrex glass) of bulb capacity of $10 \cdot 10^{-3}$ dm^3.The stem

had graduated marks and a well fitted Teflon cap. The marks on the stem were calibrated using doubly distilled water. Sufficient care has been taken to avoid the air bubble entrapment in the pycnometer. The reproducibility of density measurements was found to be $\pm 3 \cdot 10^{-2}$ kg·m^{-3}. However, the densities of glycine betaine-metal salt systems were measured by a Mettler Toledo Densito 30PX digital densitometer having an uncertainty of $\pm 2 \times 10^{-4}$ g·cm^{-3}. The determination of density involves the time-lapse measurement for a certain number of oscillations of vibrating U-shaped sample tube in which the sample is filled. A hollow glass oscillator is electronically excited in an undamped fashion. The natural frequency of the tube gets disturbed only when it is filled with test sample. The difference in frequencies is correlated to the density of the sample being investigated. The instrument was calibrated using double-distilled-deionized water and dry air. The sample and reference resonator cells were maintained at constant temperature using a Raaga thermostat having an accuracy of ±0.01 K, and all measurements were carried out using a previously described differential techniques (Sarvazyan 1982).

2.2.3. Refractive Index Measurements

Refractive indices were measured using an automatic digital refractometer RX-7000α, Atago Co. Ltd., Japan, with an uncertainty of ±0.00011. Refractometry is based on the principle that as the density of a substance increases, its refractive index rises proportionately. The refractometer was calibrated using double-distilled water and its temperature was controlled by an internal peltier unit.

Figure 2.3. Digital refractometer

To study the interactions in cyclic alanylalanine-metal salt solutions, the concentration of metal salt was kept constant at 0.10 mol·kg^{-1} and that of cyclic alanylalanine was varied from 0 to 1.50 mol·kg^{-1}. To have an insight of variation of solution properties of metal chloride-cyclic alanylalanine aqueous systems, study of $CoCl_2$-cyclic alanylalanine system has been considered. In glycine betaine-metal salt systems, the concentration of betaine was varied from 0 to 3.00 mol·kg^{-1} while the concentration of metal salt was kept constant at 0.30 mol·kg^{-1}. However in glycine betaine-$ZnCl_2$ system, the concentration of $ZnCl_2$ was restricted to 0.10 mol·kg^{-1} due to the formation of turbidity at higher metal salt concentrations. Furthermore, in glycine betaine-transition metals systems, concentration of metal salt was varied from 0.1 to 0.3mol·kg^{-1}. The physical parameters of the glycine betaine-metal salt systems were measured at seven temperatures T = (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 313.15) K while for the system: cyclic alanylalanine-metal salts, the temperatures 288.15 K and 318.15 K have been omitted due to solubility and precipitation constraints. Each parameter measurement was repeated thrice and the average of all the three measurements has been reported as the final value.

Table 2.1. Sample Information Table.

Chemical Name	CAS Number	Source	Mass Fraction Purity	Purification Method	Method of Analysis
Cyclic Alanylalanine (mixture of DL and meso)	5625-46-7	Sigma-Aldrich	0.990	None	HPLC[a]
Glycine Betaine	107-43-7	Sigma-Aldrich	0.990	None	HPLC[a]
Sodium Chloride	7647-14-5	Sigma-Aldrich	0.995	None	-
Calcium Chloride	10043-52-4	Alfa-Aesar	0.970	None	-
Potassium Chloride	7447-40-7	Alfa-Aesar	0.990	Drying at 523 K for 3 h	-
Magnesium Chloride	7786-30-3	Sigma-Aldrich	0.980	Drying at 523 K for 3 h	-
Manganese Chloride Tetrahydrate	13446-34-9	Sigma-Aldrich	0.990	None	-
Cobalt Chloride	7646-79-9	Sigma-Aldrich	0.980	None	-
Nickel Chloride	7718-54-9	Sigma-Aldrich	0.980	Recrystallization	-
Zinc Chloride	7646-85-7	Alfa-Aesar	0.990	None	-

[a] High pressure liquid chromatography.

CHAPTER 3

ACOUSTIC AND VOLUMETRIC STUDY OF CYCLIC ALANYLALANINE - SODIUM CHLORIDE, POTASSIUM CHLORIDE, CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES

Chapter 3 outlines a detailed study of density, speed of sound and refractive index of the systems: cyclic alanylalanine in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at different temperatures. The values of apparent molar volume, isentropic compressibility, apparent molar isentropic compression, intermolecular free length, specific acoustic impedance, relative association, molar refraction and transfer molar quantities have been computed from the experimental data and discussed in terms of various molecular interactions present in the systems.

3.1. DENSITY, SPEED OF SOUND AND REFRACTIVE INDEX STUDIES

Owing to the biological importance of metal ions such as, Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-, the volumetric, acoustic and refractometric study of cyclic alanylalanine in aqueous metal salt solutions can reveal some of the structural interactions taking place in such systems. Since hydration also plays a major role in determining the structural properties, the role of metal ions on the variation of these properties needs systematic explorations. In the present chapter, densities, ultrasonic velocities and refractive indices of cyclic alanylalanine in water and in aqueous NaCl, KCl, $CaCl_2$ as well as $MgCl_2$ solutions have been reported over a wide range of composition and temperature T = (293.15 to 313.15) K. The derived parameters calculated from these experimental values have been discussed in terms of various interactions taking place in the above systems.

The experimental densities ρ, ultrasonic velocities c, refractive indices, n_D and isentropic compressibilities, κ_S of cyclic alanylalanine in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at temperatures T = (293.15, 298.15, 303.15, 308.15, and 313.15) K are given as a function of cyclic alanylalanine concentration in Table 3.1. The variation of density, speed of sound and refractive index for the system: cyclic alanylalanine in water are plotted as Figures 3.1, 3.2 and 3.3, respectively as representative figures. A close scrutiny of the figures indicates that the densities of the solutions show regular linear trend with respect to solute concentration and temperature.

Table 3.1. Density, ρ, Speed of Sound, c, Refractive Index, n_D and Isentropic Compressibility, κ_S for the Systems : Cyclic Alanylalanine in Water and in Aqueous metal salt Solutions at T = 293.15 K to 313.15 K.

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
Cyclic alanylalanine in water				
T/K = 293.15				
0.0000	0.99821	1482.38	1.33300	4.559
0.0110	0.99855	1483.51	1.33348	4.550
0.0261	0.99902	1485.05	1.33411	4.539
0.0352	0.99931	1485.96	1.33467	4.532
0.0750	1.00058	1489.90	1.33618	4.502
0.0965	1.00129	1491.93	1.33703	4.487
0.1264	1.00227	1494.70	1.33832	4.466
0.1502	1.00306	1496.82	1.33934	4.450
T/K = 298.15				
0.0000	0.99705	1496.67	1.33252	4.477
0.0110	0.99738	1497.82	1.33295	4.469
0.0261	0.99783	1499.39	1.33352	4.458
0.0352	0.99810	1500.33	1.33412	4.451
0.0750	0.99929	1504.37	1.33545	4.422
0.0965	0.99993	1506.52	1.33626	4.406
0.1264	1.00083	1509.45	1.33746	4.385
0.1502	1.00154	1511.74	1.33843	4.369
T/K = 303.15				
0.0000	0.99568	1509.46	1.33194	4.408
0.0110	0.99600	1510.60	1.33232	4.400
0.0261	0.99645	1512.14	1.33284	4.389
0.0352	0.99672	1513.07	1.33341	4.382
0.0750	0.99791	1517.02	1.33471	4.354
0.0965	0.99856	1519.12	1.33551	4.340
0.1264	0.99945	1522.01	1.33665	4.319
0.1502	1.00017	1524.23	1.33756	4.304

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 308.15		
0.0000	0.99406	1519.44	1.33131	4.357
0.0110	0.99438	1520.59	1.33172	4.349
0.0261	0.99482	1522.15	1.33222	4.339
0.0352	0.99509	1523.07	1.33276	4.332
0.0750	0.99627	1527.07	1.33397	4.304
0.0965	0.99692	1529.17	1.33473	4.290
0.1264	0.99783	1532.01	1.33582	4.270
0.1502	0.99856	1534.22	1.33667	4.255
		T/K = 313.15		
0.0000	0.99222	1528.88	1.33059	4.312
0.0110	0.99253	1530.04	1.33097	4.304
0.0261	0.99296	1531.62	1.33155	4.293
0.0352	0.99322	1532.55	1.33202	4.287
0.0750	0.99436	1536.57	1.33323	4.259
0.0965	0.99499	1538.66	1.33394	4.245
0.1264	0.99585	1541.53	1.33500	4.226
0.1502	0.99655	1543.77	1.33579	4.211
Cyclic alanylalanine in 0.0783 mol·kg^{-1} NaCl solution				
		T/K = 293.15		
0.0000	1.00219	1493.38	1.33415	4.474
0.0050	1.00234	1493.84	1.33436	4.471
0.0100	1.00249	1494.31	1.33463	4.467
0.0250	1.00295	1495.71	1.33501	4.457
0.0350	1.00326	1496.65	1.33534	4.450
0.0530	1.00384	1498.35	1.33577	4.437
0.0750	1.00456	1500.46	1.33668	4.422
0.1000	1.00542	1502.88	1.33734	4.404
0.1250	1.00632	1505.30	1.33829	4.385
0.1500	1.00723	1507.80	1.33949	4.367

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 298.15		
0.0000	1.00021	1505.98	1.33397	4.408
0.0050	1.00036	1506.44	1.33415	4.405
0.0100	1.00050	1506.93	1.33439	4.401
0.0250	1.00094	1508.35	1.33485	4.391
0.0350	1.00124	1509.30	1.33510	4.384
0.0530	1.00178	1511.04	1.33555	4.372
0.0750	1.00247	1513.20	1.33641	4.356
0.1000	1.00327	1515.70	1.33696	4.339
0.1250	1.00408	1518.22	1.33790	4.321
0.1500	1.00492	1520.78	1.33909	4.302
		T/K = 303.15		
0.0000	0.99822	1517.89	1.33377	4.348
0.0050	0.99836	1518.36	1.33406	4.345
0.0100	0.99850	1518.83	1.33429	4.341
0.0250	0.99893	1520.24	1.33469	4.332
0.0350	0.99923	1521.18	1.33488	4.325
0.0530	0.99976	1522.90	1.33532	4.313
0.0750	1.00044	1525.00	1.33620	4.298
0.1000	1.00123	1527.48	1.33675	4.281
0.1250	1.00206	1529.98	1.33772	4.263
0.1500	1.00291	1532.44	1.33888	4.246
		T/K = 308.15		
0.0000	0.99629	1528.20	1.33355	4.298
0.0050	0.99643	1528.67	1.33385	4.295
0.0100	0.99657	1529.14	1.33403	4.291
0.0250	0.99700	1530.55	1.33452	4.282
0.0350	0.99729	1531.51	1.33471	4.275
0.0530	0.99781	1533.25	1.33509	4.263
0.0750	0.99848	1535.39	1.33593	4.248
0.1000	0.99925	1537.88	1.33646	4.231
0.1250	1.00003	1540.42	1.33735	4.214
0.1500	1.00084	1543.00	1.33857	4.197

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 313.15		
0.0000	0.99423	1535.04	1.33334	4.268
0.0050	0.99437	1535.51	1.33370	4.265
0.0100	0.99451	1535.99	1.33390	4.262
0.0250	0.99494	1537.40	1.33436	4.252
0.0350	0.99523	1538.35	1.33461	4.246
0.0530	0.99575	1540.08	1.33484	4.234
0.0750	0.99642	1542.20	1.33570	4.220
0.1000	0.99720	1545.64	1.33627	4.203
0.1250	0.99796	1547.14	1.33718	4.186
0.1500	0.99878	1549.64	1.33835	4.169
		Cyclic alanylalanine in 0.0826 mol·kg^{-1} KCl solution		
		T/K = 293.15		
0.0000	1.00182	1491.27	1.33439	4.488
0.0050	1.00197	1491.72	1.33460	4.485
0.0110	1.00215	1492.27	1.33477	4.481
0.0250	1.00259	1493.54	1.33526	4.471
0.0351	1.00291	1494.46	1.33558	4.464
0.0500	1.00339	1495.82	1.33601	4.454
0.0747	1.00422	1498.09	1.33692	4.437
0.1000	1.00511	1500.34	1.33758	4.420
0.1248	1.00602	1502.59	1.33853	4.403
0.1550	1.00718	1505.34	1.33973	4.382
		T/K = 298.15		
0.0000	1.00094	1503.87	1.33411	4.417
0.0050	1.00108	1504.33	1.33439	4.414
0.0110	1.00126	1504.87	1.33463	4.410
0.0250	1.00169	1506.14	1.33506	4.401
0.0351	1.00200	1507.08	1.33534	4.394
0.0500	1.00247	1508.44	1.33579	4.384
0.0747	1.00330	1510.68	1.33665	4.367
0.1000	1.00416	1512.96	1.33722	4.351
0.1248	1.00506	1515.18	1.33814	4.334
0.1550	1.00621	1518.04	1.33933	4.313

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 303.15		
0.0000	1.00030	1515.80	1.33401	4.351
0.0050	1.00044	1516.26	1.33428	4.348
0.0110	1.00062	1516.81	1.33448	4.344
0.0250	1.00104	1518.10	1.33491	4.335
0.0351	1.00135	1519.03	1.33512	4.328
0.0500	1.00181	1520.41	1.33556	4.318
0.0747	1.00261	1522.71	1.33644	4.302
0.1000	1.00347	1525.06	1.33704	4.285
0.1248	1.00434	1527.40	1.33796	4.268
0.1550	1.00545	1530.25	1.33910	4.247
		T/K = 308.15		
0.0000	0.99944	1526.09	1.33379	4.296
0.0050	0.99958	1526.55	1.33408	4.293
0.0110	0.99975	1527.12	1.33427	4.289
0.0250	1.00016	1528.42	1.33466	4.280
0.0351	1.00046	1529.37	1.33490	4.273
0.0500	1.00092	1530.76	1.33533	4.264
0.0747	1.00168	1533.12	1.33616	4.247
0.1000	1.00252	1535.53	1.33670	4.230
0.1248	1.00337	1537.90	1.33759	4.214
0.1550	1.00445	1540.85	1.33879	4.193
		T/K = 313.15		
0.0000	0.99872	1532.96	1.33358	4.261
0.0050	0.99886	1533.42	1.33388	4.258
0.0110	0.99903	1533.99	1.33407	4.254
0.0250	0.99943	1535.30	1.33448	4.245
0.0351	0.99972	1536.26	1.33470	4.238
0.0500	1.00017	1537.66	1.33518	4.229
0.0747	1.00093	1540.02	1.33600	4.213
0.1000	1.00174	1542.49	1.33651	4.196
0.1248	1.00257	1544.90	1.33738	4.179
0.1550	1.00362	1547.86	1.33859	4.159

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$K_S \cdot 10^{10}$/(m^2·N^{-1})
Cyclic alanylalanine in 0.0977 mol·kg^{-1} $CaCl_2$ solution				
		T/K = 293.15		
0.0000	1.00721	1497.46	1.33449	4.428
0.0048	1.00735	1497.92	1.33470	4.424
0.0108	1.00753	1498.49	1.33499	4.420
0.0248	1.00795	1499.84	1.33537	4.410
0.0350	1.00826	1500.84	1.33570	4.403
0.0511	1.00876	1502.40	1.33613	4.392
0.0758	1.00954	1504.82	1.33704	4.374
0.0994	1.01031	1507.12	1.33769	4.358
0.1252	1.01117	1509.66	1.33854	4.339
0.1532	1.01214	1512.43	1.33954	4.319
		T/K = 298.15		
0.0000	1.00592	1507.03	1.33432	4.377
0.0048	1.00605	1507.50	1.33450	4.374
0.0108	1.00622	1508.09	1.33474	4.370
0.0248	1.00662	1509.47	1.33513	4.360
0.0350	1.00692	1510.48	1.33538	4.353
0.0511	1.00739	1512.10	1.33583	4.342
0.0758	1.00813	1514.59	1.33669	4.324
0.0994	1.00886	1517.00	1.33730	4.307
0.1252	1.00967	1519.66	1.33814	4.289
0.1532	1.01058	1522.52	1.33914	4.269
		T/K = 303.15		
0.0000	1.00458	1519.02	1.33408	4.314
0.0048	1.00471	1519.49	1.33437	4.311
0.0108	1.00488	1520.08	1.33460	4.307
0.0248	1.00528	1521.46	1.33509	4.297
0.0350	1.00558	1522.47	1.33528	4.290
0.0511	1.00605	1524.07	1.33572	4.279
0.0758	1.00679	1526.54	1.33660	4.262
0.0994	1.00752	1528.94	1.33715	4.246
0.1252	1.00833	1531.56	1.33796	4.228
0.1532	1.00924	1534.38	1.33895	4.209

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 308.15		
0.0000	1.00300	1528.91	1.33392	4.265
0.0048	1.00312	1529.39	1.33422	4.262
0.0108	1.00327	1530.00	1.33437	4.258
0.0248	1.00363	1531.43	1.33486	4.248
0.0350	1.00390	1532.47	1.33502	4.242
0.0511	1.00433	1534.14	1.33540	4.231
0.0758	1.00502	1536.73	1.33624	4.213
0.0994	1.00570	1539.26	1.33677	4.197
0.1252	1.00646	1542.08	1.33756	4.178
0.1532	1.00731	1545.18	1.33851	4.158
		T/K = 313.15		
0.0000	1.00168	1536.74	1.33368	4.227
0.0048	1.00179	1537.22	1.33404	4.224
0.0108	1.00193	1537.83	1.33421	4.220
0.0248	1.00227	1539.26	1.33467	4.211
0.0350	1.00252	1540.31	1.33492	4.204
0.0511	1.00292	1542.00	1.33518	4.193
0.0758	1.00357	1544.54	1.33578	4.177
0.0994	1.00421	1547.02	1.33640	4.161
0.1252	1.00493	1549.80	1.33726	4.143
0.1532	1.00575	1552.86	1.33823	4.123
Cyclic alanylalanine in 0.1428 mol·kg^{-1} $MgCl_2$ solution				
		T/K = 293.15		
0.0000	1.01379	1490.12	1.33700	4.442
0.0055	1.01394	1490.67	1.33712	4.438
0.0107	1.01409	1491.18	1.33724	4.435
0.0248	1.01449	1492.60	1.33760	4.425
0.0358	1.01481	1493.72	1.33784	4.416
0.0507	1.01527	1495.24	1.33826	4.406
0.0751	1.01604	1497.78	1.33880	4.387
0.0995	1.01686	1500.34	1.33938	4.369
0.1264	1.01780	1503.25	1.34004	4.348
0.1518	1.01875	1506.00	1.34065	4.328

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 298.15		
0.0000	1.01281	1501.69	1.33666	4.378
0.0055	1.01294	1502.27	1.33675	4.374
0.0107	1.01307	1502.82	1.33686	4.371
0.0248	1.01342	1504.31	1.33719	4.360
0.0358	1.01371	1505.47	1.33742	4.353
0.0507	1.01411	1507.06	1.33782	4.342
0.0751	1.01478	1509.69	1.33832	4.324
0.0995	1.01549	1512.34	1.33886	4.306
0.1264	1.01630	1515.30	1.33948	4.285
0.1518	1.01710	1518.13	1.34005	4.266
		T/K = 303.15		
0.0000	1.01168	1514.49	1.33621	4.309
0.0055	1.01180	1515.09	1.33639	4.306
0.0107	1.01192	1515.65	1.33652	4.302
0.0248	1.01225	1517.19	1.33678	4.292
0.0358	1.01252	1518.40	1.33707	4.284
0.0507	1.01290	1520.01	1.33737	4.273
0.0751	1.01355	1522.70	1.33778	4.255
0.0995	1.01425	1525.42	1.33826	4.237
0.1264	1.01506	1528.44	1.33885	4.217
0.1518	1.01589	1531.32	1.33933	4.198
		T/K = 308.15		
0.0000	1.01002	1526.30	1.33570	4.250
0.0055	1.01012	1526.91	1.33588	4.246
0.0107	1.01023	1527.47	1.33599	4.243
0.0248	1.01051	1529.05	1.33623	4.233
0.0358	1.01075	1530.28	1.33644	4.225
0.0507	1.01107	1532.00	1.33666	4.214
0.0751	1.01163	1534.78	1.33710	4.196
0.0995	1.01221	1537.72	1.33755	4.178
0.1264	1.01289	1540.98	1.33805	4.158
0.1518	1.01357	1544.00	1.33851	4.139

Table 3.1. (*continued***)**

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D	$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})
		T/K = 313.15		
0.0000	1.00779	1534.14	1.33525	4.216
0.0055	1.00789	1534.74	1.33545	4.212
0.0107	1.00799	1535.31	1.33555	4.209
0.0248	1.00827	1536.86	1.33576	4.199
0.0358	1.00849	1538.10	1.33593	4.191
0.0507	1.00881	1539.80	1.33618	4.181
0.0751	1.00935	1542.65	1.33657	4.163
0.0995	1.00992	1545.58	1.33696	4.145
0.1264	1.01061	1548.90	1.33741	4.124
0.1518	1.01128	1551.96	1.33781	4.106

[a] m is the molality of cyclic alanylalanine in aqueous solutions.
Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.025 kg·m^{-3}; for speed of sound u(u) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.05 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

It is also observed that the speed of sound values of cyclic alanylalanine in water as well as aqueous electrolyte solutions increase with solute concentration which may be attributed to the overall increase of cohesion due to solute-solute, solute-solvent and solvent-solvent interactions (Baluja and Shah 2004, Oswal et al. 2004 and Rao and Suryanarayana 1975). The refractive index also shows an increase in the values with an increase in concentration. However, it can be noted that such changes are due to the electronic perturbation of the individual molecules during mixing and therefore depends very much on the nature of the mixing molecules.

3.2. VOLUMETRIC AND ACOUSTIC PARAMETERS

Volumetric properties such as apparent molar volume, ϕ_v and acoustic parameters such as isentropic compressibility, κ_S, apparent molar compression, ϕ_k, intermolecular free length, L_f, specific acoustic impedance, Z and relative association, R_A for all the systems have been computed using the following equations,

$$\phi_v = \frac{(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M_2}{\rho} \tag{3.1}$$

$$\kappa_S = \frac{1}{\rho u^2} \tag{3.2}$$

$$\phi_k = \left[\frac{(\kappa_S - \kappa_0)}{m\rho_0}\right] + \kappa_S\phi_v \tag{3.3}$$

$$L_f = k\kappa_S^{(1/2)} \tag{3.4}$$

$$Z = \rho c \tag{3.5}$$

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{c_0}{c}\right)^{(1/3)} \tag{3.6}$$

where m is the molality of the solution, M_2 is the molar mass of the solute, ρ and ρ_0 are the densities of the solution and solvent, respectively, c and c_0 are the speed of sound in solution and solvent, respectively, k is the Jacobson constant (Jacobson 1952), which is different for different temperatures, κ_S and κ_0 are the isentropic compressibilities of solvent and solute, respectively. All the above parameters for each of the cases are presented in Table 3.2.

The variations in apparent molar volumes and apparent molar isentropic compressibilities were least square fitted using the equations,

$$\phi_v = \phi_v^0 + S_v m \tag{3.7}$$

$$\phi_k = \phi_k^0 + S_k m \tag{3.8}$$

where ϕ_v^0 and ϕ_k^0 are the partial molar volume and partial molar isentropic compression of the solute, respectively. m is the molality of cyclic alanylalanine, S_v and S_k are the experimental slopes.

Water is believed to be an equilibrium mixture of two structures; an ice like structure and a close packed structure (Arakawa and Sasaki 1969, Lepple and Millero 1971 and Hall 1948). The increase in ultrasonic velocity causes a decrease in intermolecular free

length and vice versa (Kirkwood 1939). The M^{n+} and Cl^- ions furnished by electrolytes (where M = Na/K/Ca/Mg) electrostatically interact with polar groups present in the resonance structure of cyclic alanylalanine molecule.

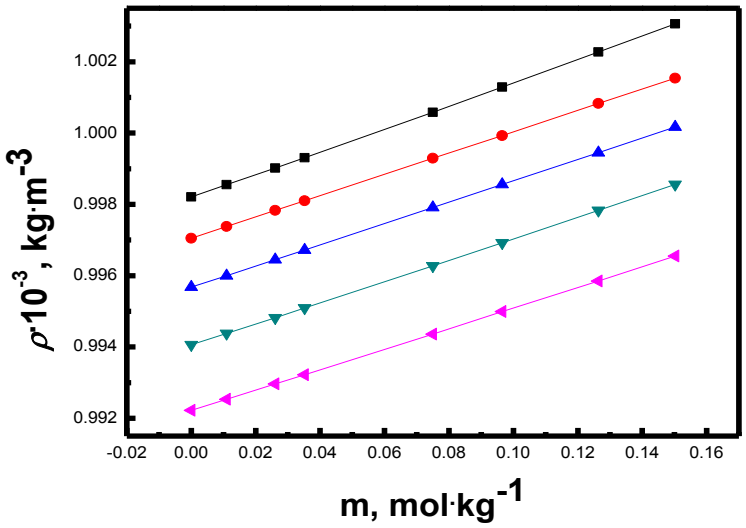

Figure 3.1. Plot of variation of density, ρ versus molal concentration, m, of cyclic alanylalanine in water at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◄, T = 313.15 K.

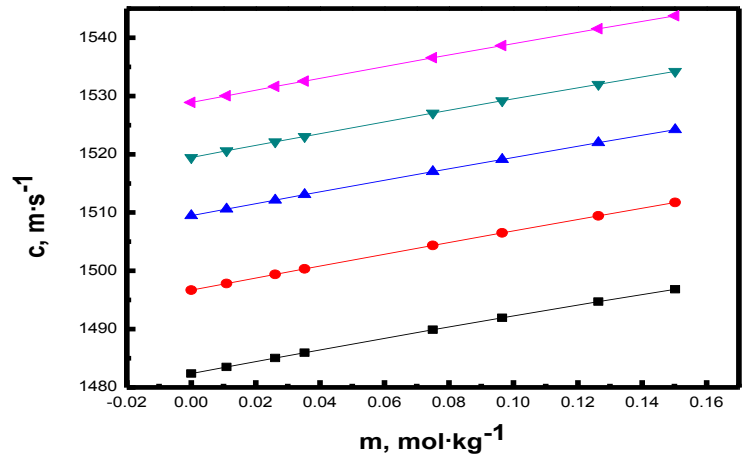

Figure 3.2. Plot of variation of speed of sound, c versus molal concentration, m, of cyclic alanylalanine in water at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◄, T = 313.15 K.

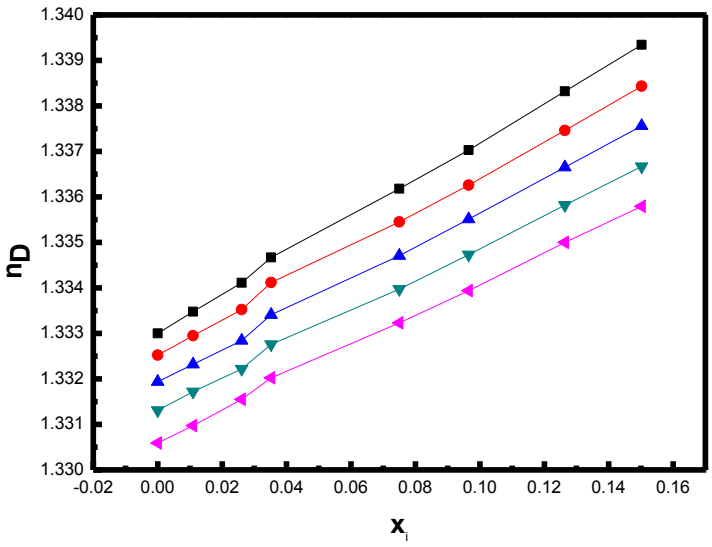

Figure 3.3. Plot of variation of refractive index, n_D of the system: cyclic alanylalanine in water versus mole fraction x_i, of cyclic alanylalanine at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◄, T = 313.15.

In addition, electrostatic forces reinforce the water dipoles to strongly align to the cations/anions as well as the polar groups of cyclic alanylalanine molecules.The addition of cyclic alanylalanine may also occupy the cavities of water clusters which may lead to the formation of denser structure of the aqueous electrolyte solution. Increasing the molar concentration of the solute and temperature initiates the thermal rupture of the ice-like structure of water, which in turn enhances cohesion in the solutions. From the Table 3.1, it is evident that the isentropic compressibilities of the individual solutions decrease with respect to cyclic alanylalanine concentration. This decreasing trend of κ_S values may be attributed to a corresponding increase in cohesive forces in (Cyclic alanylalanine + aqueous metal salt) solutions at all temperatures of study. Compressibility of liquid water is a combination of two factors given by, $\kappa_S = \kappa_\infty + \kappa_{relax} / (1+\omega^2\tau^2)$, where κ_∞ is an instantaneous part and κ_{relax} is a relaxational part of compressibility (Hall 1948).

Table 3.2. Apparent molar volume, ϕ_v, Apparent molar compression, ϕ_k, Intermolecular free length, L_f, specific acoustic impedance, Z and relative association, R_A of the systems: Cyclic Alanylalanine in water and in aqueous metal salt solutions at T = 293.15 K to 313.15 K.

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$ /(m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
Cyclic alanylalanine in water					
		T/K = 293.15			
0.0110	111.08	-26.92	0.4348	1481.36	1.0001
0.0261	111.06	-26.64	0.4342	1483.59	1.0002
0.0352	110.84	-26.46	0.4339	1484.93	1.0003
0.0750	110.40	-25.91	0.4324	1490.76	1.0007
0.0965	110.01	-25.42	0.4317	1493.85	1.0009
0.1264	109.71	-24.73	0.4307	1498.09	1.0013
0.1502	109.46	-24.11	0.4299	1501.40	1.0016
		T/K = 298.15			
0.0110	112.37	-25.93	0.4348	1493.90	1.0001
0.0261	112.43	-25.65	0.4343	1496.14	1.0002
0.0352	112.46	-25.47	0.4339	1497.48	1.0002
0.0750	112.28	-24.77	0.4325	1503.30	1.0005
0.0965	112.23	-24.43	0.4318	1506.41	1.0007
0.1264	112.07	-23.95	0.4307	1510.70	1.0010
0.1502	112.01	-23.51	0.4299	1514.07	1.0012
		T/K = 303.15			
0.0110	113.40	-23.74	0.4354	1504.56	1.0001
0.0261	112.93	-23.57	0.4348	1506.77	1.0002
0.0352	112.86	-23.55	0.4345	1508.11	1.0002
0.0750	112.53	-22.74	0.4331	1513.85	1.0006
0.0965	112.35	-22.47	0.4324	1516.93	1.0008
0.1264	112.27	-22.03	0.4314	1521.17	1.0010
0.1502	112.12	-21.57	0.4306	1524.49	1.0013
		T/K = 308.15			
0.0110	113.86	-23.40	0.4368	1512.04	1.0001
0.0261	113.59	-23.19	0.4362	1514.27	1.0002
0.0352	113.38	-22.95	0.4359	1515.59	1.0002
0.0750	112.99	-22.44	0.4345	1521.37	1.0005
0.0965	112.73	-22.11	0.4338	1524.46	1.0007
0.1264	112.43	-21.54	0.4328	1528.69	1.0010
0.1502	112.21	-21.11	0.4320	1532.01	1.0013

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
		T/K = 313.15			
0.0110	114.61	-22.87	0.4384	1518.61	1.0001
0.0261	114.39	-22.77	0.4378	1520.84	1.0001
0.0352	114.30	-22.43	0.4375	1522.16	1.0002
0.0750	114.05	-21.62	0.4361	1527.90	1.0005
0.0965	113.80	-21.13	0.4354	1530.95	1.0007
0.1264	113.69	-20.48	0.4344	1535.13	1.0009
0.1502	113.50	-20.08	0.4336	1538.44	1.0011
Cyclic alanylalanine in 0.0783 mol·kg^{-1} NaCl solution					
		T/K = 293.15			
0.0050	111.96	-18.28	0.4309	1497.34	1.0000
0.0100	111.95	-18.89	0.4308	1498.03	1.0001
0.0250	111.50	-19.39	0.4303	1500.12	1.0002
0.0350	111.29	-19.70	0.4299	1501.53	1.0003
0.0530	110.67	-20.43	0.4293	1504.10	1.0005
0.0750	110.13	-21.26	0.4286	1507.30	1.0008
0.1000	109.34	-22.28	0.4277	1511.03	1.0011
0.1250	108.51	-23.18	0.4268	1514.81	1.0015
0.1500	107.85	-24.16	0.4259	1518.70	1.0018
		T/K = 298.15			
0.0050	112.13	-17.64	0.4317	1506.98	1.0000
0.0100	113.11	-18.53	0.4315	1507.68	1.0001
0.0250	112.86	-18.61	0.4310	1509.77	1.0002
0.0350	112.60	-18.87	0.4307	1511.17	1.0003
0.0530	112.34	-19.43	0.4301	1513.73	1.0005
0.0750	111.76	-20.38	0.4293	1516.94	1.0007
0.1000	111.20	-21.37	0.4284	1520.66	1.0009
0.1250	110.75	-22.14	0.4275	1524.41	1.0012
0.1500	110.22	-22.99	0.4266	1528.26	1.0014

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
		T/K = 303.15			
0.0050	114.30	-16.47	0.4326	1515.87	1.0000
0.0100	114.28	-16.48	0.4325	1516.55	1.0001
0.0250	113.83	-16.86	0.4320	1518.61	1.0002
0.0350	113.34	-17.28	0.4316	1520.01	1.0003
0.0530	113.08	-17.79	0.4310	1522.53	1.0004
0.0750	112.46	-18.46	0.4303	1525.67	1.0007
0.1000	111.87	-19.57	0.4294	1529.36	1.0009
0.1250	111.16	-20.61	0.4286	1533.13	1.0012
0.1500	110.52	-21.28	0.4277	1536.90	1.0015
		T/K = 308.15			
0.0050	114.46	-16.00	0.4340	1523.21	1.0000
0.0100	114.45	-16.01	0.4339	1523.90	1.0001
0.0250	114.00	-16.39	0.4334	1525.96	1.0002
0.0350	113.79	-16.88	0.4330	1527.36	1.0003
0.0530	113.62	-17.41	0.4324	1529.89	1.0004
0.0750	113.02	-18.23	0.4317	1533.06	1.0006
0.1000	112.53	-19.14	0.4308	1536.73	1.0009
0.1250	112.13	-19.99	0.4299	1540.47	1.0011
0.1500	111.62	-20.89	0.4290	1544.30	1.0013
		T/K = 313.15			
0.0050	114.64	-15.74	0.4364	1526.87	1.0000
0.0100	114.63	-16.31	0.4362	1527.56	1.0001
0.0250	114.17	-16.35	0.4357	1529.62	1.0002
0.0350	113.97	-16.61	0.4354	1531.01	1.0003
0.0530	113.80	-17.03	0.4348	1533.53	1.0004
0.0750	113.20	-17.73	0.4341	1536.68	1.0006
0.1000	112.60	-18.50	0.4332	1540.32	1.0009
0.1250	112.38	-19.11	0.4323	1543.98	1.0011
0.1500	111.79	-19.86	0.4315	1547.75	1.0014

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
Cyclic alanylalanine in 0.0826 mol·kg^{-1} KCl solution					
		T/K = 293.15			
0.0050	111.99	-17.23	0.4316	1494.66	1.0000
0.0110	111.97	-17.79	0.4314	1495.48	1.0001
0.0250	111.13	-18.47	0.4310	1497.41	1.0003
0.0351	110.84	-18.76	0.4306	1498.81	1.0004
0.0500	110.44	-19.17	0.4301	1500.89	1.0006
0.0747	109.63	-20.05	0.4293	1504.41	1.0009
0.1000	108.76	-20.42	0.4285	1508.01	1.0013
0.1248	107.92	-21.14	0.4276	1511.64	1.0017
0.1550	106.87	-22.05	0.4266	1516.15	1.0022
		T/K = 298.15			
0.0050	114.06	-15.96	0.4321	1505.95	0.9964
0.0110	112.95	-16.29	0.4319	1506.77	0.9964
0.0250	112.00	-17.06	0.4315	1508.69	0.9966
0.0351	111.77	-17.64	0.4311	1510.09	0.9967
0.0500	111.31	-17.99	0.4307	1512.17	0.9968
0.0747	110.23	-18.77	0.4298	1515.67	0.9972
0.1000	109.53	-19.20	0.4290	1519.25	0.9975
0.1248	108.63	-19.80	0.4282	1522.85	0.9979
0.1550	107.52	-21.17	0.4271	1527.47	0.9984
		T/K = 303.15			
0.0050	114.12	-15.33	0.4328	1516.93	0.9931
0.0110	113.01	-16.18	0.4326	1517.75	0.9932
0.0250	112.45	-16.76	0.4321	1519.68	0.9933
0.0351	112.10	-17.07	0.4318	1521.08	0.9934
0.0500	111.77	-17.44	0.4313	1523.16	0.9936
0.0747	110.96	-18.29	0.4305	1526.68	0.9939
0.1000	110.09	-19.07	0.4296	1530.35	0.9942
0.1248	109.32	-19.89	0.4288	1534.03	0.9945
0.1550	108.35	-20.83	0.4278	1538.59	0.9950

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
		T/K = 308.15			
0.0050	114.19	-14.82	0.4339	1525.91	0.9900
0.0110	113.99	-15.91	0.4337	1526.74	0.9901
0.0250	113.33	-16.22	0.4333	1528.66	0.9902
0.0351	113.03	-16.60	0.4329	1530.07	0.9903
0.0500	112.44	-17.07	0.4324	1532.17	0.9904
0.0747	111.97	-17.85	0.4316	1535.70	0.9907
0.1000	111.06	-18.75	0.4308	1539.40	0.9910
0.1248	110.28	-19.51	0.4299	1543.08	0.9913
0.1550	109.33	-20.60	0.4289	1547.71	0.9918
		T/K = 313.15			
0.0050	114.25	-14.49	0.4360	1531.67	0.9878
0.0110	114.05	-15.57	0.4358	1532.50	0.9879
0.0250	113.79	-15.76	0.4354	1534.42	0.9880
0.0351	113.67	-16.09	0.4350	1535.83	0.9881
0.0500	113.10	-16.55	0.4345	1537.92	0.9882
0.0747	112.43	-17.38	0.4337	1541.45	0.9885
0.1000	111.73	-18.38	0.4328	1545.17	0.9887
0.1248	110.99	-19.18	0.4320	1548.87	0.9890
0.1550	110.11	-20.13	0.4309	1553.46	0.9894

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
Cyclic alanylalanine in 0.0977 mol·kg^{-1} $CaCl_2$ solution					
		T/K = 293.15			
0.0048	112.38	-19.23	0.4287	1508.93	1.0000
0.0108	111.90	-19.37	0.4285	1509.77	1.0001
0.0248	111.65	-19.92	0.4280	1511.76	1.0002
0.0350	111.45	-20.43	0.4277	1513.24	1.0003
0.0511	111.07	-20.80	0.4271	1515.56	1.0004
0.0758	110.59	-21.42	0.4263	1519.18	1.0007
0.0994	110.06	-21.90	0.4254	1522.66	1.0009
0.1252	109.53	-22.47	0.4245	1526.52	1.0012
0.1532	108.89	-23.13	0.4236	1530.79	1.0016
		T/K = 298.15			
0.0048	114.06	-15.96	0.4321	1505.95	0.9964
0.0108	112.95	-16.29	0.4319	1506.77	0.9964
0.0248	112.00	-17.06	0.4315	1508.69	0.9966
0.0350	111.77	-17.64	0.4311	1510.09	0.9967
0.0511	111.31	-17.99	0.4307	1512.17	0.9968
0.0758	110.23	-18.77	0.4298	1515.67	0.9972
0.0994	109.53	-19.20	0.4290	1519.25	0.9975
0.1252	108.63	-19.80	0.4282	1522.85	0.9979
0.1532	107.52	-21.17	0.4271	1527.47	0.9984
		T/K = 303.15			
0.0048	114.66	-17.47	0.4309	1526.65	1.0000
0.0108	113.95	-18.20	0.4307	1527.50	1.0001
0.0248	113.46	-18.73	0.4303	1529.49	1.0002
0.0350	113.09	-19.16	0.4299	1530.97	1.0002
0.0511	112.84	-19.48	0.4294	1533.29	1.0004
0.0758	112.37	-20.05	0.4285	1536.91	1.0006
0.0994	111.88	-20.78	0.4277	1540.44	1.0008
0.1252	111.42	-21.33	0.4268	1544.32	1.0010
0.1532	110.86	-21.82	0.4258	1548.56	1.0013

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
		T/K = 308.15			
0.0048	116.87	-16.37	0.4324	1534.16	1.0000
0.0108	116.85	-16.90	0.4322	1535.00	1.0000
0.0248	116.41	-17.63	0.4317	1536.99	1.0001
0.0350	116.07	-17.98	0.4313	1538.45	1.0001
0.0511	115.71	-18.61	0.4308	1540.78	1.0002
0.0758	115.01	-19.61	0.4299	1544.44	1.0003
0.0994	114.43	-20.61	0.4290	1548.03	1.0004
0.1252	113.87	-21.62	0.4281	1552.04	1.0006
0.1532	113.28	-22.62	0.4271	1556.48	1.0008
		T/K = 313.15			
0.0048	114.25	-14.49	0.4360	1531.67	0.9878
0.0108	114.05	-15.57	0.4358	1532.50	0.9879
0.0248	113.79	-15.76	0.4354	1534.42	0.9880
0.0350	113.67	-16.09	0.4350	1535.83	0.9881
0.0511	113.10	-16.55	0.4345	1537.92	0.9882
0.0758	112.43	-17.38	0.4337	1541.45	0.9885
0.0994	111.73	-18.38	0.4328	1545.17	0.9887
0.1252	110.99	-19.18	0.4320	1548.87	0.9890
0.1532	110.11	-20.13	0.4309	1553.46	0.9894
Cyclic alanylalanine in 0.1428 mol·kg^{-1} $MgCl_2$ solution					
		T/K = 293.15			
0.0055	113.67	-20.10	0.4294	1511.45	1.0000
0.0107	112.91	-20.23	0.4292	1512.19	1.0001
0.0248	112.69	-20.96	0.4287	1514.23	1.0001
0.0358	112.39	-21.53	0.4283	1515.84	1.0002
0.0507	111.66	-22.41	0.4278	1518.07	1.0003
0.0751	110.83	-23.69	0.4269	1521.80	1.0005
0.0995	109.87	-24.91	0.4260	1525.64	1.0007
0.1264	108.93	-26.35	0.4250	1530.01	1.0010
0.1518	107.91	-27.61	0.4240	1534.24	1.0013

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
		T/K = 298.15			
0.0055	117.30	-19.45	0.4302	1521.71	1.0000
0.0107	116.64	-20.11	0.4300	1522.46	1.0000
0.0248	116.31	-20.40	0.4295	1524.50	1.0000
0.0358	115.75	-20.85	0.4291	1526.11	1.0001
0.0507	115.22	-21.49	0.4286	1528.32	1.0001
0.0751	114.57	-22.37	0.4277	1532.00	1.0002
0.0995	113.80	-23.28	0.4268	1535.77	1.0003
0.1264	113.06	-24.25	0.4258	1540.00	1.0004
0.1518	112.34	-25.18	0.4248	1544.09	1.0006
		T/K = 303.15			
0.0055	119.19	-19.19	0.4307	1532.97	1.0000
0.0107	118.58	-19.33	0.4305	1533.72	1.0000
0.0248	118.00	-20.08	0.4300	1535.78	1.0000
0.0358	117.50	-20.69	0.4296	1537.41	1.0000
0.0507	116.87	-21.02	0.4290	1539.62	1.0000
0.0751	115.98	-22.00	0.4282	1543.33	1.0000
0.0995	114.99	-23.10	0.4272	1547.16	1.0001
0.1264	114.01	-24.17	0.4262	1551.46	1.0003
0.1518	112.95	-25.30	0.4253	1555.65	1.0005
		T/K = 308.15			
0.0055	122.91	-16.49	0.4316	1542.36	1.0000
0.0107	121.49	-16.84	0.4314	1543.10	1.0000
0.0248	121.32	-17.82	0.4309	1545.12	0.9999
0.0358	120.67	-18.52	0.4305	1546.73	0.9999
0.0507	120.32	-19.49	0.4299	1548.96	0.9998
0.0751	119.54	-20.40	0.4290	1552.63	0.9997
0.0995	118.92	-21.91	0.4281	1556.50	0.9997
0.1264	118.16	-23.25	0.4270	1560.84	0.9996
0.1518	117.41	-24.09	0.4261	1564.95	0.9997

Table 3.2. (*continued*)

m^a/ (mol·kg^{-1})	$\phi_v \cdot 10^6$/ (m^3·mol^{-1})	$\phi_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	L_f/ (Å)	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A
		T/K = 313.15			
0.0055	123.15	-15.13	0.4337	1546.85	1.0000
0.0107	122.63	-15.70	0.4335	1547.58	0.9999
0.0248	121.95	-16.45	0.4330	1549.57	0.9999
0.0358	121.72	-17.14	0.4326	1551.16	0.9998
0.0507	121.13	-18.19	0.4321	1553.37	0.9998
0.0751	120.42	-19.67	0.4311	1557.07	0.9997
0.0995	119.73	-21.12	0.4302	1560.91	0.9996
0.1264	118.76	-22.85	0.4291	1565.33	0.9996
0.1518	118.02	-23.77	0.4282	1569.47	0.9996

[a] *m* is the molality of cyclic alanylalanine in aqueous solutions.

τ is the relaxational time which corresponds to κ_{relax} of the order of 10^{-11} s and ω is the angular frequency. The relation $\omega\tau < 1$ is assumed to be valid in the present study and hence, the isentropic compressibility obtained is equal to $(\kappa_\infty + \kappa_{relax})$. κ_∞ Increases with the rise in temperature which can be attributed to thermal expansion while κ_{relax} decreases due to thermal rupture of the ice-like structure of water. Thus, the decrease in isentropic compressibility values with an increase in temperature may be attributed to the corresponding decrease in κ_{relax}, which is dominant over the corresponding increase in κ_∞ (Gazal 2012). With the increase in temperature, the electrostricted water molecules are also released into the bulk, making the medium more compressible.

The decrease in intermolecular free length is due to the solvent-solute and dipole-dipole interaction in the system (Masson 1929, Rao and Verrall 1987 and Regmi 2007). This also indicates that the molecules are nearer in the system. Specific acoustic impedance is a quantity depending on the molecular packing of the system. The specific acoustic impedance is the product of density and speed of sound of solvent or solution. The calculated values of *Z* have been found to increase with an increase in molal concentration of cyclic alanylalanine in solutions as well as with increase in temperature. Such trends of variation of *Z* may be ascribed to an overall reduction in

repulsive forces with an increase in cyclic alanylalanine concentration and temperature. The effect molal concentration of solute on *Z* in the system 'cyclic alanylalanine in water' can be seen from the Figures 3.4. Same kind of linear behaviour has been obtained in almost all the systems under investigations (Figures. 3.5 to 3.8). The increase in *Z* also suggests the presence of a strong interaction through hydrogen bonding (Rao and Verrall 1987 and Regmi 2007). Eucken's theory (Regmi 2007) states that there is a decrease in the number of aggregates of solvent molecules as the concentration and temperature increase. Consequently, with the rise in temperature, water begins to behave like an unassociated liquid and the addition of a salt to a solvent enhances the process of breaking of aggregates of solvent molecules.

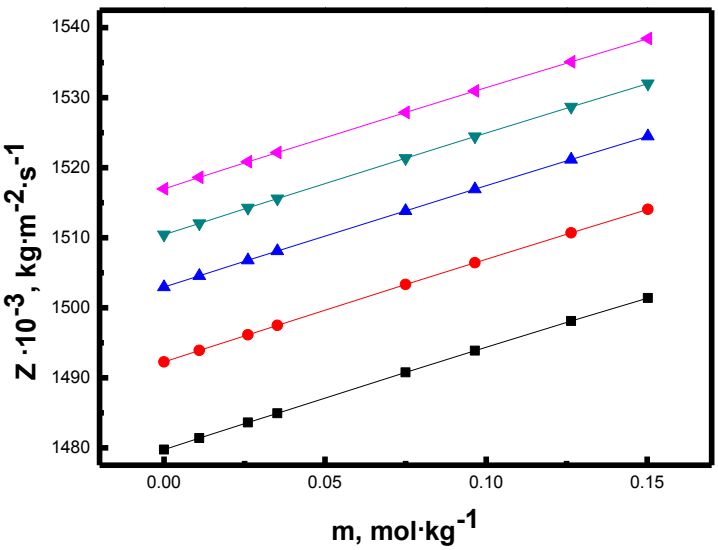

Figure 3.4. Plot of variation of specific acoustic impedance, *Z* of the system: cyclic alanylalanine in water versus molal concentration *m*, of cyclic alanylalanine at various temperatures. ■, *T* = 293.15 K; ●, *T* = 298.15 K; ▲, *T* = 303.15 K; ▼, *T* = 308.15 K; ◄, *T* = 313.15 K.

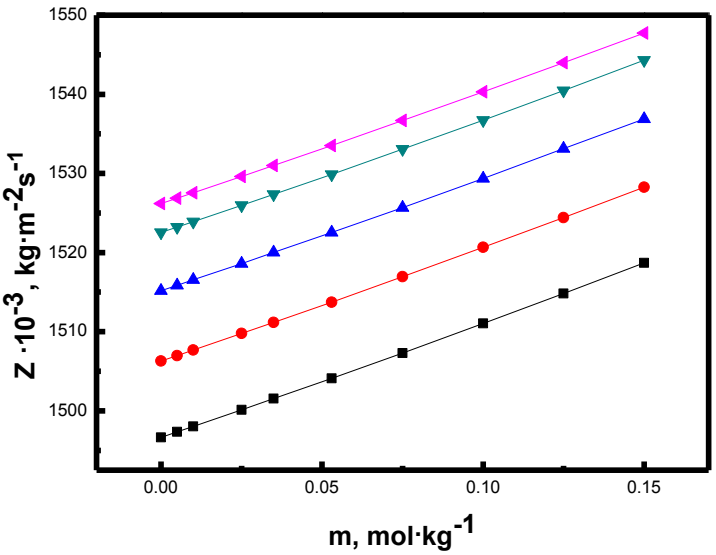

Figure 3.5. Plot of variation of specific acoustic impedance, *Z* of the system: cyclic alanylalanine in aqueous NaCl solution versus molal concentration *m*, of cyclic alanylalanine at various temperatures. ■, $T = 293.15$ K; ●, $T = 298.15$ K; ▲, $T = 303.15$ K; ▼, $T = 308.15$ K; ◄, $T = 313.15$ K.

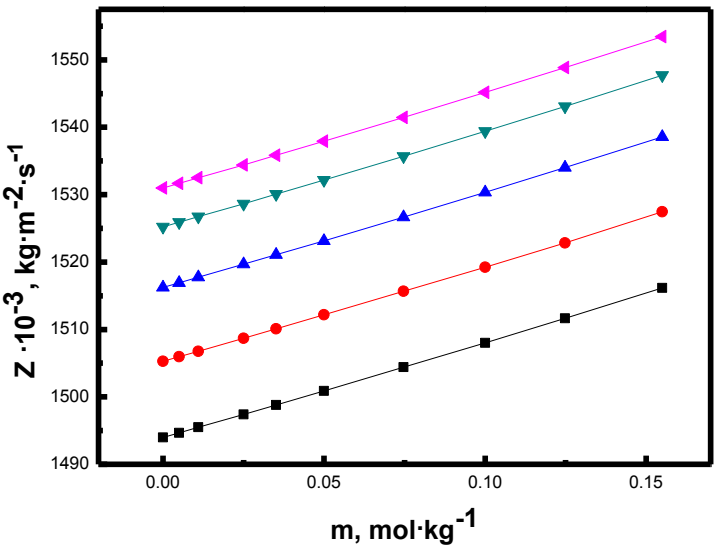

Figure 3.6. Plot of variation of specific acoustic impedance, *Z* of the system: cyclic alanylalanine in aqueous KCl solution versus molal concentration *m*, of cyclic alanylalanine at various temperatures. ■, $T = 293.15$ K; ●, $T = 298.15$ K; ▲, $T = 303.15$ K; ▼, $T = 308.15$ K; ◄, $T = 313.15$ K.

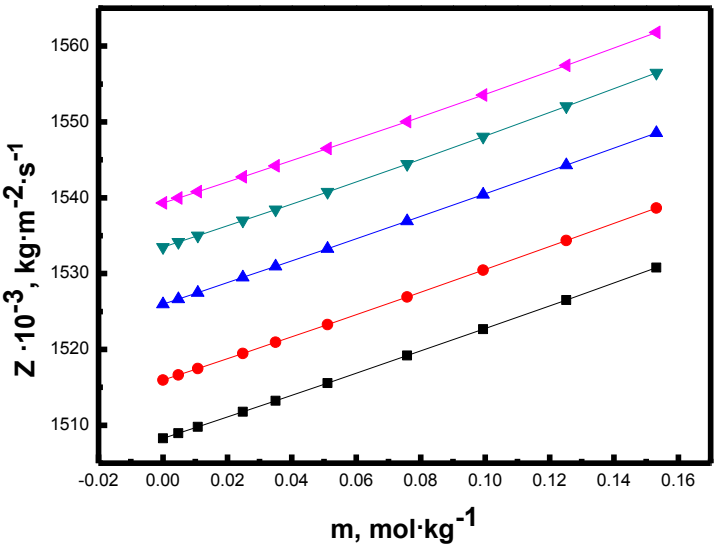

Figure 3.7. Plot of variation of specific acoustic impedance, *Z* of the system: cyclic alanylalanine in aqueous $CaCl_2$ solution versus molal concentration *m*, of cyclic alanylalanine at various temperatures. ■, $T = 293.15$ K; ●, $T = 298.15$ K; ▲, $T = 303.15$ K; ▼, $T = 308.15$ K; ◄, $T = 313.15$ K.

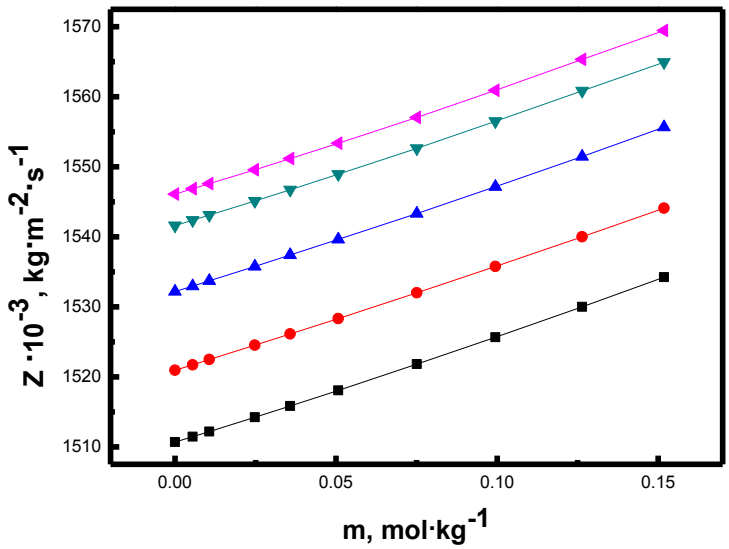

Figure 3.8. Plot of variation of specific acoustic impedance, *Z* of the system: cyclic alanylalanine in aqueous $MgCl_2$ solution versus molal concentration *m*, of cyclic alanylalanine at various temperatures. ■, $T = 293.15$ K; ●, $T = 298.15$ K; ▲, $T = 303.15$ K; ▼, $T = 308.15$ K; ◄, $T = 313.15$ K.

Similar kind of trend has been observed in R_A values which slightly increase with the molal concentration of cyclic alanylalanine in aqueous electrolyte solutions. This indicates a regular trend in the breaking up of the solvent aggregates (Rao and Verrall 1987). As the temperature of solution rises, the aggregates of solvent molecules break up themselves, resulting in increased solvent molecules. Another observation in R_A values is that they are either one or close to one. This indicates that the systems under investigation possess weak interactions (Gazal 2012). However, the variation in R_A values with an increase in temperature is insignificant over the temperature range of 298.15–323.15 K. Consequently, the variation in temperature over the said range does not seem to affect the nature of interactions operative in solutions significantly. Such kind of behaviour was observed in L-leucine/L-isoleucine/L-glutamine/L-alanine/glycylglycine in 0.512 $mol \cdot kg^{-1}$ aqueous K_2SO_4/KNO_3 solutions (Gazal 2012).

The decrease in apparent molar volume with an increase in concentration for a solution of cyclic alanylalanine in aqueous metal salt indicates predominance of a structure breaking interaction with water (Sinha and Roy 2006 and Wahab et al. 2006). The decrease in the apparent molar compression indicates strong interaction with the solvent which gives a less compressible environment for the solute (Yan et al. 2003 and Riyazuddeen and Bansal 2006). This may also be produced by electrostriction and structure breaking. The interpretation of this effect can be accounted from Kirkwood model (Rao and Suryanarayana 1975). The electrostricted water has a less open structure as compared to bulk water and is therefore less compressible. Upon addition of electrolyte, bulk water becomes electrostricted water and this accounts for the apparent molar compressions of cyclic alanylalanine in water varying with the corresponding ones in mixed solvents.

The partial molar volume, ϕ_v^0 and partial molar isentropic compression, $\phi_k^{\,0}$ values are given in Table 3.3 and Table 3.4 with the respective slopes. Dominance of hydrophobic hydration in cyclic alanylalanine-aqueous metal salt systems is evident by the trend of the slopes of the concentration dependence of the apparent molar volumes. The negative S_v considerably indicate the presence of hydrophobic hydration. Also, the more negative slopes suggest an enhancement of the effect which leads to the compression reduction.

Table 3.3. Least Squares Fit Parameters of the Equation $\phi_v = \phi_v^0 + S_v m$ for Cyclic Alanylalanine in Water and in Aqueous NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions at temperatures, T = (293.15 to 313.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
Cyclic alanylalanine in water			
293.15	111.28(±0.04)	-12.36(±0.47)	0.1
298.15	112.55(±0.02)	-3.67(±0.26)	0.1
303.15	113.06(±0.05)	-6.55(±0.52)	0.1
308.15	113.88(±0.04)	-11.49(±0.55)	0.1
313.15	114.61(±0.04)	-7.58(±0.45)	0.1
Cyclic alanylalanine in 0.0783 mol·kg^{-1} aqueous NaCl Solution			
293.15	112.22(±0.03)	-29.09(±0.57)	0.1
298.15	113.35(±0.03)	-20.98(±0.39)	0.1
303.15	114.44(±0.04)	-26.17(±0.57)	0.1
308.15	114.55(±0.04)	-19.71(±0.50)	0.1
313.15	114.73(±0.05)	-19.72(±0.69)	0.1
Cyclic alanylalanine in 0.0826 mol·kg^{-1} aqueous KCl solution			
293.15	112.14(±0.05)	-34.01(±0.72)	0.1
298.15	113.08(±0.09)	-36.10(±1.11)	0.2
303.15	113.30(±0.03)	-31.93(±0.42)	0.1
308.15	114.22(±0.06)	-31.71(±0.79)	0.1
313.15	114.69(±0.04)	-27.73(±0.60)	0.1

Table 3.3. (*continued*)

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
Cyclic alanylalanine in 0.0977 mol·kg^{-1} aqueous $CaCl_2$ Solution			
293.15	112.25(±0.05)	-22.05(±0.70)	0.4
298.15	113.85(±0.07)	-20.63(±0.70)	0.1
303.15	113.96(±0.07)	-20.65(±0.85)	0.1
308.15	116.99(±0.04)	-24.97(±0.55)	0.1
313.15	118.97(±0.07)	-26.77(±0.96)	0.1
Cyclic alanylalanine in 0.1428 mol·kg^{-1} aqueous $MgCl_2$ Solution			
293.15	113.73(±0.05)	-38.51(±0.68)	0.4
298.15	116.91(±0.06)	-30.63(±0.77)	0.1
303.15	118.94(±0.03)	-39.49(±0.36)	0.1
308.15	121.74(±0.03)	-28.56(±0.36)	0.1
313.15	122.84(±0.05)	-31.97(±0.63)	0.1

[a]σ is the standard deviation of the fit.

Hence the water molecules in the vicinity of non-polar groups such as –CH– and $–CH_3$ groups are less compressible than the bulk, but not quite as incompressible as electrostricted water. The temperature dependence of ϕ_k^0 values of cyclic alanylalanine-aqueous metal salt systems reveals the release of more number of water molecules from the secondary solvation layer of cyclic alanylalanine into the bulk thereby rendering the solutions more compressible at higher temperatures.

Table 3.4. Least Squares Fit Parameters of the Equation $\phi_k = \phi_k^0 + S_k m$ for Cyclic Alanylalanine water and in Aqueous NaCl, KCl, $CaCl_2$ and $MgCl_2$ Solutions at Temperatures T = (293.15 to 313.15) K.[a]

***T*/K**	$\phi_k^0 \cdot 10^{15}$/ **($Pa^{-1} \cdot m^3 \cdot mol^{-1}$)**	$S_k \cdot 10^{15}$/ **($Pa^{-1} \cdot m^3 \cdot mol^{-2} \cdot kg$)**	$\sigma \cdot 10^{15}$/ **($Pa^{-1} \cdot m^3 \cdot mol^{-1}$)**
	Cyclic alanylalanine in water		
293.15	-27.19(±0.08)	19.58(±0.94)	0.1
298.15	-26.09(±0.01)	17.18(±0.19)	0.1
303.15	-23.98(±0.07)	15.85(±0.56)	0.1
308.15	-23.59(±0.04)	16.16(±0.47)	0.1
313.15	-23.19(±0.05)	21.00(±0.60)	0.1
	Cyclic alanylalanine in 0.0783 mol·kg^{-1} aqueous NaCl solution		
293.15	-18.34(±0.06)	-39.00(±0.81)	0.3
298.15	-17.74(±0.11)	-35.17(±1.45)	0.2
303.15	-16.08(±0.04)	-34.66(±1.04)	0.1
308.15	-15.66(±0.13)	-34.60(±0.61)	0.2
313.15	-15.72(±0.07)	-27.25(±0.98)	0.1
	Cyclic alanylalanine in 0.0826 mol·kg^{-1} aqueous KCl solution		
293.15	-17.53(±0.13)	-39.00(±0.81)	0.1
298.15	-18.76(±0.16)	-31.77(±0.91)	0.1
303.15	-18.48(±0.09)	-34.66(±1.04)	0.1
308.15	-17.17(±0.05)	-34.60(±0.61)	0.1
313.15	-15.00(±0.07)	-33.05(±0.84)	0.1

Table 3.4. (*continued*)

T/K	$\phi_k^0 \cdot 10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-1}$)	$S_k \cdot 10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-2}\cdot kg$)	$\sigma \cdot 10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-1}$)
Cyclic alanylalanine in 0.0977 mol·kg^{-1} aqueous $CaCl_2$ Solution			
293.15	-19.29(±0.09)	-25.93(±1.17)	0.3
298.15	-18.76(±0.09)	-29.26(±1.16)	0.2
303.15	-17.90(±0.15)	-27.29(±1.92)	0.3
308.15	-16.45(±0.07)	-41.08(±0.94)	0.1
313.15	-14.68(±0.18)	-37.88(±2.27)	0.3
Cyclic alanylalanine in 0.1428 mol·kg^{-1} aqueous $MgCl_2$ Solution			
293.15	-19.72(±0.08)	-52.20(±0.40)	0.1
298.15	-19.50(±0.07)	-37.74(±0.89)	0.2
303.15	-18.99(±0.05)	-41.27(±0.70)	0.1
308.15	-16.48(±0.04)	-52.48(±1.74)	0.2
313.15	-15.01(±0.11)	-60.09(±1.40)	0.2

[a]σ is the standard deviation of the fit.

3.3. TRANSFER PARTIAL MOLAR VOLUMES AND COMPRESSIONS

The transfer molar properties at infinite dilution of cyclic alanylalanine from water to aqueous metal salt solutions have been calculated from:

$\Delta_{tr}Y = Y_\phi^0$ (in aqueous metal salt solutions) - Y_ϕ^0 (in pure water) (3.9)

Table 3.5 represent the trends in transfer properties of cyclic alanylalanine from aqueous to aqueous metal salt solutions. A close examination of the table reveals that the values of $\Delta_{tr}\phi_v^0$ and $\Delta_{tr}\phi_k^0$ are positive in aqueous NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions at all the temperatures.It is interesting to compare $\Delta_{tr}\phi_v^0$ and $\Delta_{tr}\phi_k^0$ values among various salt solutions to know which salt induces higher effect and what makes it to do so. The transfer molar volumes follow the order $MgCl_2$> $CaCl_2$> NaCl > KCl

which may beattributed to the sizes of these ions. Larger size of hydrated Mg^{2+} ions in aqueous solution than that of $Ca^{2+}/K^{+}/Na^{+}$ ions contributes towards the positive volume of transfer. On the other hand, $\Delta_{tr}\phi_v^0$ values in NaCl and KCl show a decreasing trend but for the $CaCl_2$ and $MgCl_2$ solutions, an increasing trend has been observed. This can be explained on the basis of ionic sizes of and charges in these ions. Being large and monovalent ions, Na^{+} and K^{+}, show lower transfer volumes which hydrate poorly in aqueous solution. But due to high charge and smaller size, Ca^{2+} and Mg^{2+}electrostrict more number of water molecules from the solvent network and hence contribute more positively towards $\Delta_{tr}\phi_v^0$. However insignificant results have been observed in $\Delta_{tr}\phi_k^0$ values.

3.4. MOLAR REFRACTIONS

The refractive indices, $n_{D,}$ of the systems; cyclic alanylalanine – water and in aqueous metal salt solutions were recorded as a function of the molar concentration of the solute. The values of n_D were found to increase with the solute concentration in all the cases.

Lorentz– Lorenz relation has been utilized to compute the molar refraction, R_D values of the systems: cyclic alanylalanine in water and in aqueous metal salt solutions,

$$R_D = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\left(\frac{\sum_{i=1}^{3} x_i M_i}{\rho}\right) \tag{3.10}$$

The obtained values have been fitted using the equation,

$$R_D = R_D^0 + Bx_i \tag{3.11}$$

where x_i is the mole fraction and M is the molecular mass of cyclic alanylalanine, respectively. The density of the solution is ρ and B is the experimental slope. Table 3.6 presents the tabulated values of R_D°. As per the table, molar refraction of the systems: cyclic alanylalanine – metal salts aqueous solutions increase with the temperature.

Table 3.5. Transfer Partial Molar Volumes, $\Delta_{tr}\phi_v^0$ and Transfer Partial Molar Isentropic Compressions, $\Delta_{tr}\phi_k^0$ of Cyclic Alanylalanine from Water to Aqueous NaCl, KCl, $CaCl_2$ and $MgCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.

***T*/K**	$\Delta_{tr}\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$\Delta_{tr}\phi_k^0 \cdot 10^{15}/(Pa^{-1} \cdot m^3 \cdot mol^{-1})$
Cyclic alanylalanine in 0.0783 mol·kg^{-1} aqueous NaCl solution		
293.15	0.94	9.45
298.15	0.80	9.15
303.15	1.38	7.90
308.15	0.67	7.93
313.15	0.12	7.47
Cyclic alanylalanine in 0.0826 mol·kg^{-1} aqueous KCl solution		
293.15	0.86	9.66
298.15	0.53	7.33
303.15	0.24	5.50
308.15	0.34	6.42
313.15	0.08	8.19
Cyclic alanylalanine in 0.0977 mol·kg^{-1} aqueous $CaCl_2$ solution		
293.15	0.97	7.9
298.15	1.30	7.33
303.15	0.90	6.08
308.15	3.11	7.14
313.15	4.36	8.51
Cyclic alanylalanine in 0.1428 mol·kg^{-1} aqueous $MgCl_2$ Solution		
293.15	2.45	7.47
298.15	4.36	6.59
303.15	5.88	4.99
308.15	7.86	7.11
313.15	8.23	8.18

Table 3.6. Values of Coefficients of the Equation $R_D = R_D^0 + Bx_i$ at T = (293.15 to 313.15) K.

***T*/K**	$R_D^{\circ}\cdot 10^6/(m^3\cdot mol^{-1})$	$B\cdot 10^6/(m^3\cdot mol^{-1})$	$\sigma\cdot 10^6/(m^3\cdot mol^{-1})$
Cyclic alanylalanine in water			
293.15	3.7134(±0.0011)	42.0625(±0.6948)	0.1
298.15	3.7125(±0.0009)	41.0301(±0.6264)	0.1
303.15	3.7116(±0.0009)	40.0934(±0.6526)	0.1
308.15	3.7117(±0.0011)	38.9965(±0.7530)	0.1
313.15	3.7115(±0.0011)	38.6696(±0.7491)	0.1
Cyclic alanylalanine in 0.0783 mol·kg^{-1} aqueous NaCl solution			
293.15	3.7160(±0.0016)	48.0272(±0.2191)	0.1
298.15	3.7222(±0.0006)	49.0495(±0.9249)	0.1
303.15	3.7281(±0.0007)	48.7197(±0.1161)	0.1
308.15	3.7332(±0.0007)	48.0936(±0.1161)	0.1
313.15	3.7395(±0.0008)	48.8366(±0.1239)	0.1
Cyclic alanylalanine in 0.0981 mol·kg^{-1} aqueous KCl solution			
293.15	3.7191(±0.0003)	17.3955(±0.2937)	0.1
298.15	3.7205(±0.0004)	16.5577(±0.4221)	0.1
303.15	3.7214(±0.0004)	16.2785(±0.3711)	0.1
308.15	3.7226(±0.0005)	15.7486(±0.4601)	0.1
313.15	3.7235(±0.0005)	15.5527(±0.4636)	0.1
Cyclic alanylalanine in 0.0977 mol·kg^{-1} aqueous $CaCl_2$ solution			
293.15	3.7310(±0.0004)	38.0929(±0.3708)	0.1
298.15	3.7331(±0.0004)	37.6456(±0.2643)	0.1
303.15	3.7369(±0.0004)	37.0255(±0.3243)	0.1
308.15	3.7410(±0.0004)	36.2917(±0.3158)	0.1
313.15	3.7442(±0.0006)	36.0211(±0.4831)	0.1

Table 3.6. (*continued*)

T/K	$R_D^{\circ}\cdot10^6/(m^3\cdot mol^{-1})$	$B\cdot10^6/(m^3\cdot mol^{-1})$	$\sigma\cdot10^6/(m^3\cdot mol^{-1})$
Cyclic alanylalanine in 0.0977 mol·kg^{-1} aqueous $MgCl_2$ solution			
293.15	3.7001(±0.0002)	11.2591(±0.1751)	0.1
298.15	3.7002(±0.0001)	29.1352(±0.0618)	0.1
303.15	3.7008(±0.0003)	28.4045(±0.1127)	0.1
308.15	3.7016(±0.0002)	28.2104(±0.0789)	0.1
313.15	3.7056(±0.0002)	27.7970(±0.0919)	0.1

In order to examine the intermolecular forces existing in pure solvents and solutions, dependence of R_D on composition and temperature can be taken into account. This is mainly because molar refraction depends on the composition of the solution and temperature (Marchetti et al. 1999). The molar refraction has the same units as the molar volume and could be understood, in fact, as a measure of the hard-core volume of a mole of liquid (Glasstone 1946). Thus, the dependence of R_D values with the amount of cyclic alanylalanine in aqueous metal salt solutions in the above systems confirms the argument of solute-solvent interaction as indicated by the volumetric studies. As R_D is directly proportional to the molecular polarizability, it can be noted that the overall polarizability of the cyclic alanylalanine increases with the solute concentration in aqueous metal salt solutions (Nikam et al. 2004).Since the measured molar refraction values of molecules in the present study are dependent on the temperature (Brocos et al. 2003), it can be predicted that the polarizability has a greater impact from orientation effects. Thus, the optical studies of cyclic alanylalanine in aqueous metal salt solutions in the systems indicate solute-co-solute interactions which are in par with the results deduced from volumetric studies.

CHAPTER 4

SOLUTION PROPERTIES OF CYCLIC ALANYLALANINE IN SOME TRANSITION METAL CHLORIDE AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES

Chapter 4 presents a detailed study on the interactions in cyclic alanylalanine-transition metal chlorides aqueous solutions. The transition metal chlorides employed are, $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$.

4.1. VOLUMETRIC PROPERTIES

The experimental densities, ρ, ultrasonic velocities, c and refractive indices, n_D of the mixture of cyclic alanylalanine (CAA) and aqueous MCl_2 (M = Mn, Co, Ni or Zn) solutions at temperatures T = (293.15, 298.15, 303.15, 308.15, and 313.15) K are given as a function of concentration in Tables 4.1 to 4.4.

The values of isentropic compressibility, κ_S of the systems have been calculated using the Equation 3.2 (Hedwig and Hoiland 1994). The isentropic compressibility values of cyclic alanylalanine in aqueous metal salt solutions at various temperatures have been plotted as Figures 4.1, 4.2, 4.3 and 4.4.

As can be seen by the figures, the isentropic compressibility values of cyclic alanylalanine-aqueous MCl_2 solutions decrease with an increase in the molal concentration of cyclic alanylalanine and decrease with increasing temperature. The isentropic compressibility is considered to be the sum of two contributions: $\kappa_{S\ (Solvent\ intrinsic)}$ and $\kappa_{S\ (Solute\ intrinsic)}$ (Rohman et. al. 2005).For a system forming the typical three-dimensional cage-like structure of water, the predominant interaction is water–water interaction. The introduction of cyclic alanylalanine molecule in to the solvent causes compression thus making less number of water molecules available for the next incoming cyclic alanylalanine molecule. Here, $\kappa_{S\ (Solvent\ intrinsic)}$ is the isentropic compressibility due to the compression of the three dimensional network structure of water and $\kappa_{S\ (Solute\ intrinsic)}$ is the isentropic compressibility due to the compression of of the hydration shell of the ions.Since the solution compressibility is lower than that of the solvent, the volumetric concentration of the solution increases with a decrease in compressibility of the solvent.

Table 4.1. Experimental Values of Density, ρ, Speed of Sound, *c*, and Refractive Index, n_D of the System: Cyclic Alanylalanine in 0.0899 mol·kg^{-1} Aqueous $MnCl_2$ Solutions at Temperatures, *T* = (293.15 to 313.15) K.

m^a/(mol·kg^{-1})	$\rho \cdot 10^{-3}$/(kg·m^{-3})	*c*/(m·s^{-1})	n_D
	***T*/K = 293.15**		
0.0000	1.00795	1500.92	1.33416
0.0097	1.00823	1501.95	1.33456
0.0254	1.00869	1503.56	1.33500
0.0349	1.00898	1504.51	1.33554
0.0758	1.01022	1508.46	1.33666
0.0991	1.01094	1510.60	1.33735
0.1254	1.01178	1512.85	1.33830
0.1516	1.01263	1515.02	1.33952
	***T*/K = 298.15**		
0.0000	1.00650	1505.19	1.33399
0.0097	1.00676	1506.22	1.33445
0.0254	1.00719	1507.85	1.33486
0.0349	1.00746	1508.81	1.33535
0.0758	1.00862	1512.80	1.33642
0.0991	1.00931	1514.94	1.33699
0.1254	1.01011	1517.24	1.33798
0.1516	1.01092	1519.40	1.33912
	***T*/K = 303.15**		
0.0000	1.00544	1511.64	1.33381
0.0097	1.00568	1512.66	1.33434
0.0254	1.00608	1514.28	1.33473
0.0349	1.00633	1515.23	1.33520
0.0758	1.00742	1519.25	1.33627
0.0991	1.00807	1521.44	1.33685
0.1254	1.00883	1523.76	1.33778
0.1516	1.00961	1526.10	1.33893

Table 4.1. (*continued*)

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
		***T*/K = 308.15**	
0.0000	1.00412	1515.88	1.33364
0.0097	1.00434	1516.91	1.33414
0.0254	1.00470	1518.55	1.33455
0.0349	1.00493	1519.51	1.33495
0.0758	1.00592	1523.62	1.33600
0.0991	1.00653	1525.83	1.33655
0.1254	1.00722	1528.30	1.33748
0.1516	1.00794	1530.66	1.33865
		***T*/K = 313.15**	
0.0000	1.00287	1521.54	1.33345
0.0097	1.00306	1522.60	1.33392
0.0254	1.00338	1524.29	1.33435
0.0349	1.00358	1525.28	1.33476
0.0758	1.00446	1529.53	1.33588
0.0991	1.00499	1531.84	1.33638
0.1254	1.00560	1534.42	1.33734
0.1516	1.00624	1536.90	1.33852

[a] m is the molality of cyclic alanylalanine in aqueous $MnCl_2$ solutions.

Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.025 kg·m^{-3}; for speed of sound u(u) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.05 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

Table 4.2. Experimental Values of Density, ρ, Speed of Sound, *c*, and Refractive Index, n_D of the System: Cyclic Alanylalanine in 0.1000 mol·kg^{-1} Aqueous $CoCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.

m^a/(mol·kg^{-1})	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
	T/K = 293.15		
0.0000	1.01400	1502.45	1.33727
0.0100	1.01429	1503.49	1.33739
0.0249	1.01474	1505.04	1.33751
0.0350	1.01504	1506.09	1.33787
0.0752	1.01630	1510.26	1.33811
0.0991	1.01708	1512.75	1.33853
0.1266	1.01800	1515.62	1.33907
0.1520	1.01889	1518.24	1.33965
	T/K = 298.15		
0.0000	1.01300	1512.03	1.33683
0.0100	1.01325	1513.11	1.33695
0.0249	1.01363	1514.72	1.33706
0.0350	1.01389	1515.81	1.33739
0.0752	1.01498	1520.15	1.33762
0.0991	1.01566	1522.73	1.33802
0.1266	1.01648	1525.71	1.33852
0.1520	1.01725	1528.45	1.33906
	T/K = 303.15		
0.0000	1.01184	1524.02	1.33612
0.0100	1.01207	1525.13	1.33623
0.0249	1.01244	1526.78	1.33635
0.0350	1.01270	1527.90	1.33668
0.0752	1.01375	1532.37	1.33691
0.0991	1.01440	1535.03	1.33731
0.1266	1.01519	1538.09	1.33782
0.1520	1.01592	1540.94	1.33837

Table 4.2. (*continued*)

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
		***T*/K = 308.15**	
0.0000	1.01016	1533.91	1.33558
0.0100	1.01036	1535.02	1.33568
0.0249	1.01068	1536.68	1.33578
0.0350	1.01090	1537.80	1.33608
0.0752	1.01180	1542.26	1.33628
0.0991	1.01235	1544.92	1.33664
0.1266	1.01300	1547.97	1.33709
0.1520	1.01362	1550.79	1.33758
		***T*/K = 313.15**	
0.0000	1.00789	1541.74	1.33500
0.0100	1.00810	1542.83	1.33510
0.0249	1.00839	1544.45	1.33520
0.0350	1.00859	1545.55	1.33552
0.0752	1.00945	1549.92	1.33572
0.0991	1.01002	1552.51	1.33605
0.1266	1.01071	1555.50	1.33648
0.1520	1.01138	1558.26	1.33693

[a] m is the molality of cyclic alanylalanine in aqueous $CoCl_2$ solutions.

Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.025 kg·m^{-3}; for speed of sound u(u) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.05 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

Table 4.3. Experimental Values of Density, ρ, Speed of Sound, c, and Refractive Index, n_D of the System: Cyclic Alanylalanine in 0.0981 mol·kg^{-1} Aqueous $NiCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.

m^a/(mol·kg^{-1})	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
	T/K = 293.15		
0.0000	1.01048	1491.58	1.33604
0.0112	1.01067	1492.83	1.33635
0.0246	1.01091	1494.28	1.33668
0.0353	1.01110	1495.44	1.33716
0.0735	1.01183	1499.44	1.33776
0.0987	1.01232	1502.02	1.33830
0.1261	1.01289	1504.72	1.33891
0.1511	1.01344	1507.10	1.33949
	T/K = 298.15		
0.0000	1.00886	1505.50	1.33549
0.0112	1.00901	1506.78	1.33580
0.0246	1.00920	1508.28	1.33618
0.0353	1.00937	1509.44	1.33663
0.0735	1.01000	1513.53	1.33719
0.0987	1.01044	1516.10	1.33776
0.1261	1.01094	1518.80	1.33836
0.1511	1.01141	1521.16	1.33893
	T/K = 303.15		
0.0000	1.00723	1517.96	1.33506
0.0112	1.00738	1519.20	1.33534
0.0246	1.00757	1520.65	1.33574
0.0353	1.00772	1521.79	1.33604
0.0735	1.00831	1525.77	1.33657
0.0987	1.00872	1528.30	1.33719
0.1261	1.00920	1530.92	1.33777
0.1511	1.00965	1533.20	1.33831

Table 4.3. (*continued*)

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
	***T*/K = 308.15**		
0.0000	1.00561	1528.65	1.33457
0.0112	1.00575	1529.89	1.33484
0.0246	1.00593	1531.34	1.33521
0.0353	1.00608	1532.47	1.33552
0.0735	1.00664	1536.42	1.33593
0.0987	1.00705	1538.88	1.33653
0.1261	1.00751	1541.48	1.33715
0.1511	1.00797	1543.78	1.33771
	***T*/K = 313.15**		
0.0000	1.00398	1537.70	1.33419
0.0112	1.00410	1538.95	1.33440
0.0246	1.00426	1540.40	1.33472
0.0353	1.00439	1541.55	1.33494
0.0735	1.00488	1545.52	1.33539
0.0987	1.00525	1548.00	1.33600
0.1261	1.00567	1550.62	1.33658
0.1511	1.00606	1552.90	1.33711

[a] m is the molality of cyclic alanylalanine in aqueous $NiCl_2$ solutions.

Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.025 kg·m^{-3}; for speed of sound u(u) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.05 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

Table 4.4. Experimental Values of Density, ρ, Speed of Sound, *c*, and Refractive Index, n_D of the System: Cyclic Alanylalanine in 0.0933 mol·kg^{-1} Aqueous $ZnCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.

m^a/(mol·kg^{-1})	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
	T/K = 293.15		
0.0000	1.00992	1495.53	1.33568
0.0115	1.01026	1496.71	1.33602
0.0253	1.01068	1498.08	1.33635
0.0353	1.01099	1499.04	1.33660
0.0762	1.01229	1502.66	1.33763
0.1022	1.01314	1504.74	1.33829
0.1260	1.01394	1506.53	1.33890
0.1502	1.01477	1508.19	1.33946
	T/K = 298.15		
0.0000	1.00848	1503.67	1.33521
0.0115	1.00879	1504.88	1.33560
0.0253	1.00917	1506.30	1.33585
0.0353	1.00945	1507.30	1.33604
0.0762	1.01064	1511.10	1.33706
0.1022	1.01144	1513.30	1.33765
0.1260	1.01217	1515.20	1.33824
0.1502	1.01293	1516.94	1.33878
	T/K = 303.15		
0.0000	1.00735	1516.61	1.33462
0.0115	1.00764	1517.81	1.33500
0.0253	1.00800	1519.20	1.33522
0.0353	1.00826	1520.20	1.33545
0.0762	1.00938	1524.06	1.33643
0.1022	1.01011	1526.38	1.33709
0.1260	1.01079	1528.40	1.33762
0.1502	1.01152	1530.36	1.33812

Table 4.4. (*continued*)

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$ /(kg·m^{-3})	c/(m·s^{-1})	n_D
	***T*/K = 308.15**		
0.0000	1.00609	1526.78	1.33390
0.0115	1.00637	1527.98	1.33428
0.0253	1.00671	1529.39	1.33453
0.0353	1.00697	1530.38	1.33473
0.0762	1.00806	1534.30	1.33564
0.1022	1.00877	1536.70	1.33631
0.1260	1.00946	1538.72	1.33679
0.1502	1.01018	1540.66	1.33725
	***T*/K = 313.15**		
0.0000	1.00484	1534.08	1.33311
0.0115	1.00510	1535.28	1.33349
0.0253	1.00542	1536.69	1.33371
0.0353	1.00566	1537.68	1.33393
0.0762	1.00666	1541.68	1.33488
0.1022	1.00733	1544.10	1.33552
0.1260	1.00795	1546.24	1.33600
0.1502	1.00863	1548.30	1.33651

[a] m is the molality of cyclic alanylalanine in aqueous $ZnCl_2$ solutions.

Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.025 kg·m^{-3}; for speed of sound u(u) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.05 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

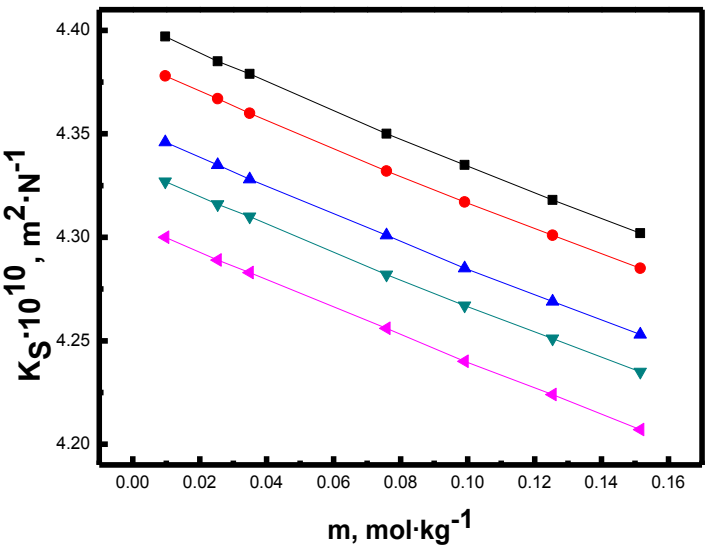

Figure 4.1. Isentropic compressibility, κ_S versus molal concentration, m of cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $MnCl_2$ solutions at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◀, T = 313.15 K.

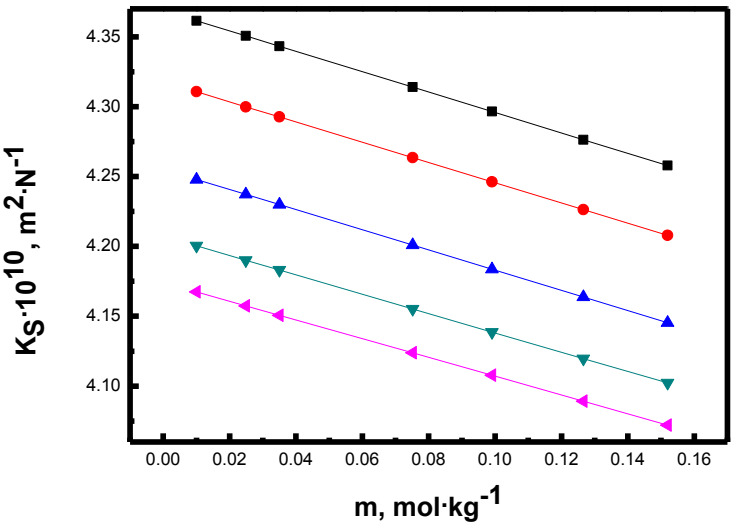

Figure 4.2. Isentropic compressibility, κ_S versus molal concentration, m of cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $CoCl_2$ solutions at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◀, T = 313.15 K.

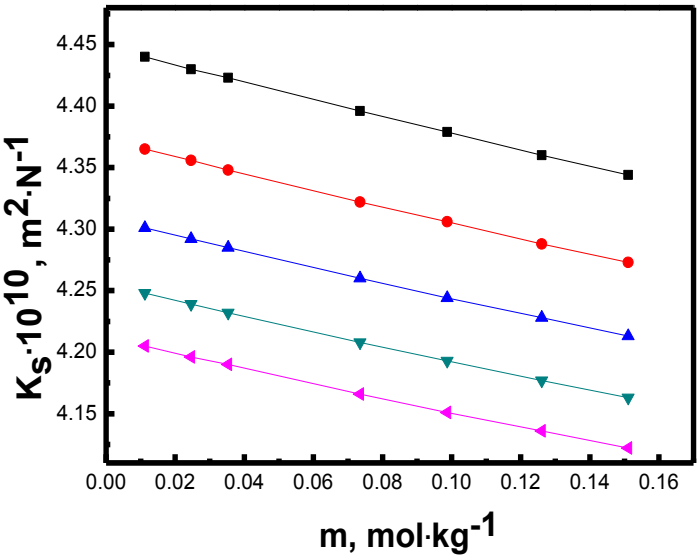

Figure 4.3. Isentropic compressibility, κ_S versus molal concentration, m of cyclic alanylalanine in 0.0981 $mol \cdot kg^{-1}$ aqueous $NiCl_2$ solutions at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◄, T = 313.15 K.

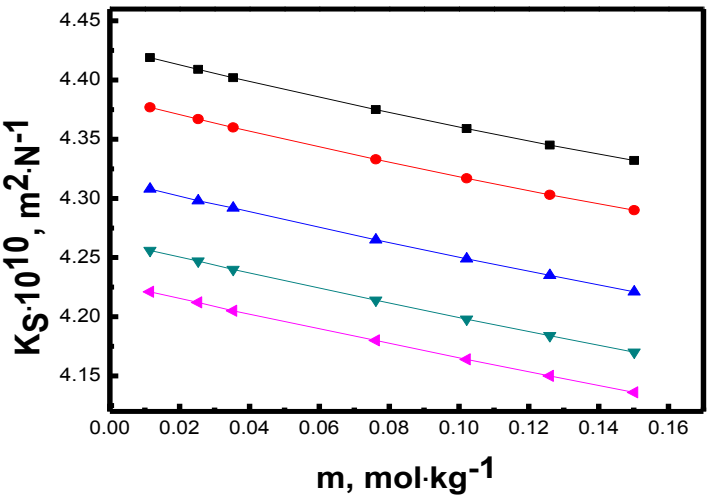

Figure 4.4. Isentropic compressibility, κ_S versus molal concentration, m of cyclic alanylalanine in 0.0933 $mol \cdot kg^{-1}$ aqueous $ZnCl_2$ solutions at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◄, T = 313.15 K.

The compressibility values follow the order $NiCl_2$>$ZnCl_2$>$CoCl_2$>$MnCl_2$ attributed to the fact that these ions hydrate differently in water. The Ni^{2+} to water,Zn^{2+} to water, Co^{2+} to water and Mn^{2+} to water bond distances due to cation hydration from the X-ray diffraction studies are 206.2 pm, 209.6 pm, 210.0 pm and 220.0 pm,

respectively (Bol et al. 1970 and Ohtaki and Radnai 1993). The Ni^{2+} to water bond distance is smaller than rest of the metal ions and therefore isentropic compressibilities of cyclic alanylalanine in $NiCl_2$ solvent are higher than in remaining metal chloride solutions.

The values of apparent molar volume, ϕ_v of cyclic alanylalanine have been calculated from the experimental data using the Equation 3.1 (Hedwig 1988),

Calculated values of the apparent molar volume of cyclic alanylalanine in aqueous MCl_2 solution are presented in Table 4.5. The values have been fitted by using least-squares method described by the Equation 3.7 (Hedwig 1988). The values of ϕ_v^0 and S_v along with their standard deviations are listed in Table 4.6.

The ϕ_v^0 value is considered to be unaffected by solute-solute interactions and deals only with the information concerning solute-solvent interactions. In the present study, the ϕ_v^0 values have been found to be positive for cyclic alanylalanine in aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at all composition and temperatures of the study while varying the cyclic alanylalanine concentration. This behaviour attributes to the presence of strong solute-solvent interaction in the systems considered. In addition, the ϕ_v^0 values of cyclic alanylalanine in aqueous MCl_2 solutions are higher than the corresponding values in an aqueous solution at all the temperatures. Thus, one can speculate the structure of cyclic alanylalanine in aqueous MCl_2 solutions by using the present trend. The diketopiperazines are expected to resonate among three structures (Corey 1938) as shown in Figure 4.5. Out of these structures, the zwitterionic structure has been found to be more predominant in aqueous metal chloride solutions.

Table 4.5. Apparent Molar Volume, ϕ_v of Cyclic Alanylalanine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, T = (293.15 to 313.15) K.[a]

m^b/(mol·kg^{-1})	T/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
			$\phi_v \cdot 10^6$/(m^3·mol^{-1})		
Cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $MnCl_2$ solution					
0.0097	112.60(±0.59)	114.75(±0.58)	116.89(±0.57)	119.06(±0.56)	122.25(±0.55)
0.0254	112.28(±0.22)	114.35(±0.22)	116.39(±0.22)	118.86(±0.22)	121.73(±0.21)
0.0349	111.88(±0.16)	113.98(±0.16)	116.06(±0.16)	118.46(±0.16)	121.44(±0.15)
0.0758	111.31(±0.08)	113.39(±0.07)	115.32(±0.07)	117.81(±0.07)	120.71(±0.07)
0.0991	111.01(±0.06)	112.94(±0.06)	114.84(±0.06)	117.18(±0.05)	120.23(±0.05)
0.1254	110.56(±0.05)	112.42(±0.05)	114.26(±0.05)	116.70(±0.04)	119.78(±0.04)
0.1516	110.14(±0.04)	111.97(±0.04)	113.71(±0.04)	116.14(±0.04)	119.25(±0.04)
Cyclic alanylalanine in 0.1000 mol·kg^{-1} aqueous $CoCl_2$ solution					
0.0100	111.96(±0.56)	115.94(±0.55)	117.61(±0.54)	121.11(±0.53)	120.35(±0.53)
0.0249	111.22(±0.23)	115.62(±0.22)	116.90(±0.22)	120.21(±0.21)	121.23(±0.21)
0.0350	111.18(±0.16)	115.45(±0.16)	116.40(±0.16)	119.92(±0.15)	121.27(±0.15)
0.0752	110.19(±0.08)	114.45(±0.07)	115.46(±0.07)	119.16(±0.07)	120.43(±0.07)
0.0991	109.63(±0.06)	113.88(±0.06)	114.97(±0.06)	118.81(±0.05)	119.63(±0.05)
0.1266	109.04(±0.05)	113.16(±0.04)	114.28(±0.04)	118.42(±0.04)	118.79(±0.04)
0.1520	108.39(±0.04)	112.62(±0.04)	113.82(±0.04)	118.02(±0.04)	118.14(±0.04)
Cyclic alanylalanine in 0.0981 mol·kg^{-1} aqueous $NiCl_2$ solution					
0.0112	111.62(±0.46)	115.29(±0.45)	115.45(±0.46)	116.50(±0.46)	118.44(±0.45)
0.0246	111.09(±0.21)	114.84(±0.21)	115.01(±0.21)	115.98(±0.21)	117.76(±0.21)
0.0353	110.99(±0.15)	114.21(±0.15)	114.93(±0.15)	115.66(±0.15)	117.51(±0.14)
0.0735	110.12(±0.07)	113.09(±0.07)	114.06(±0.07)	114.90(±0.07)	116.83(±0.07)
0.0987	109.80(±0.05)	112.56(±0.05)	113.62(±0.05)	114.29(±0.05)	116.17(±0.05)
0.1261	109.28(±0.04)	112.02(±0.04)	113.05(±0.04)	113.76(±0.04)	115.60(±0.04)
0.1511	108.75(±0.04)	111.60(±0.04)	112.61(±0.03)	113.17(±0.03)	115.19(±0.03)

Table 4.5. (*continued*)

m^a/(mol·kg^{-1})	T/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
	$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
	Cyclic alanylalanine in 0.0933 mol·kg^{-1} aqueous $ZnCl_2$ Solution				
0.0115	111.74(±0.50)	114.42(±0.49)	116.24(±0.48)	117.21(±0.48)	119.05(±0.47)
0.0253	111.23(±0.23)	114.07(±0.22)	115.73(±0.22)	117.02(±0.22)	118.70(±0.22)
0.0353	110.93(±0.16)	113.84(±0.16)	115.61(±0.16)	116.57(±0.16)	118.37(±0.16)
0.0762	110.01(±0.08)	112.85(±0.07)	114.64(±0.07)	115.53(±0.07)	117.61(±0.07)
0.1022	109.52(±0.06)	112.16(±0.06)	114.20(±0.06)	115.09(±0.05)	117.06(±0.05)
0.1260	109.05(±0.05)	111.76(±0.05)	113.83(±0.04)	114.49(±0.04)	116.67(±0.04)
0.1502	108.58(±0.04)	111.34(±0.04)	113.29(±0.04)	113.93(±0.04)	116.05(±0.04)

[a] The uncertainties in ϕ_v values are in parenthesis.

[b] m is the molality of cyclic alanylalanine in aqueous metal salt solutions. The experiment was carried out under atmosphere pressure.

Table 4.6. Least Squares Fit Parameters of the Equation $\phi_v = \phi_v^0 + S_v m$ for Cyclic Alanylalanine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6$ / (m^3·mol^{-1})	$S_v \cdot 10^6$/ (m^3·mol^{-2}·kg)	$\sigma \cdot 10^6$/ (m^3·mol^{-1})
	Cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $MnCl_2$ solution		
293.15	112.71(±0.04)	-17.25(±0.47)	0.1
298.15	114.81(±0.06)	-18.96(±0.72)	0.1
303.15	116.96(±0.06)	-21.56(±0.69)	0.1
308.15	119.28(±0.05)	-20.72(±0.61)	0.1
313.15	122.16(±0.03)	-19.21(±0.38)	0.1

Table 4.6. (*continued*)

T/K	$\phi_v^0 \cdot 10^6$ / ($m^3 \cdot mol^{-1}$)	$S_v \cdot 10^6$/ ($m^3 \cdot mol^{-2} \cdot kg$)	$\sigma \cdot 10^6$/ ($m^3 \cdot mol^{-1}$)
Cyclic alanylalanine in 0.1000 mol·kg^{-1} aqueous $CoCl_2$ Solution			
293.15	111.66(±0.19)	-21.09(±0.23)	0.1
298.15	116.24(±0.03)	-23.87(±0.03)	0.1
303.15	117.48(±0.14)	-25.84(±0.17)	0.1
308.15	121.48(±0.44)	-27.50(±0.54)	0.1
313.15	122.40(±0.11)	-28.28(±0.11)	0.1
Cyclic alanylalanine in 0.0981 mol·kg^{-1} aqueous $NiCl_2$ solution			
293.15	111.68(±0.07)	-19.43(±0.82)	0.1
298.15	113.84(±0.08)	-69.41(±0.94)	0.1
303.15	115.59(±0.04)	-20.01(±0.51)	0.1
308.15	116.58(±0.06)	-22.80(±0.76)	0.1
313.15	118.26(±0.05)	-20.66(±0.57)	0.1
Cyclic alanylalanine in 0.0933 mol·kg^{-1} aqueous $ZnCl_2$ Solution			
293.15	111.81(±0.07)	-22.08(±0.88)	0.1
298.15	114.62(±0.06)	-22.70(±0.70)	0.1
303.15	116.23(±0.06)	-19.58(±0.63)	0.1
308.15	117.48(±0.06)	-23.87(±0.73)	0.1
313.15	119.21(±0.04)	-20.85(±0.55)	0.1

[a]σ is the standard deviation of the fit.

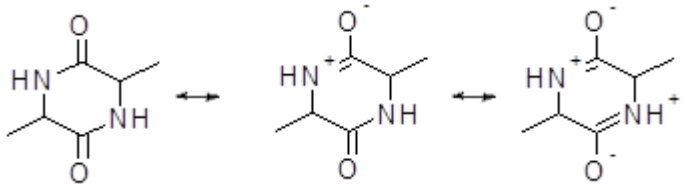

Figure 4.5. Resonance structures of cyclic alanylalanine molecule.

The interactions occurring among cyclic alanylalanine- MCl_2-water molecules can be explained taking account of following factors: The ionic interactions among M^{2+} and Cl^- ions with the polar groups present in the resonance structure of cyclic alanylalanine, the interactions among the hydrophilic groups of cyclic alanylalanine and water and the hydrophobic-hydrophilic interactions occurring among hydrophobic groups of cyclic alanylalanine and water.

Larger values of ϕ_v^0 for the systems: cyclic alanylalanine in aqueous MCl_2 than those in aqueous medium indicate the presence of interactions among ionic and hydrophilic groups as well as among the hydrophilic groups of the molecules. These interactions lead to release of electrostricted water molecules into the bulk which can be attributed by the increased ϕ_v^0 value for cyclic alanylalanine. The temperature dependence of ϕ_v^0 values of cyclic alanylalanine can be accounted to the size of primary and secondary solvation regions around the cyclic alanylalanine molecule. When the temperature increases, the secondary solvation layer releases the constituent water molecules into the bulk of the solvent thereby expanding the solution causing large change in ϕ_v^0 values.

A representative study of $CoCl_2$ in aqueous cyclic alanylalanine has been carried out to understand the behaviour of such systems. The experimental data for $CoCl_2$ in aqueous cyclic alanylalanine are presented in Table 4.7. The variation isentropic compressibility of this system with the cyclic alanylalanine concentration was found to be consistent with those obtained for other systems. This trend is depicted as Figure 4.6. The corresponding ϕ_v values calculated from Equation (3.1) are tabulated as Table 4.8 and fitted using the Equation (3.7). It is interesting to note the ϕ_v^0 values of $CoCl_2$ in aqueous cyclic alanylalanine solution. As per Table 4.9, these values were found to be negative and become more positive with the increase in temperature. This trend can be explained on the basis of following factors: When $CoCl_2$ enters the aqueous solution of cyclic alanylalanine the salt breaks up the open structure of water and contraction occurs due to electrostriction. The constituent ions of $CoCl_2$ become hydrated thereby decreasing the volume of the solution.

Table 4.7. Experimental Values of Density, ρ, Speed of Sound, c and Refractive Index, n_D of the System: $CoCl_2$ in 0.0500 mol·kg^{-1} Aqueous Cyclic Alanylalanine Solutions at Temperatures, T = (293.15 to 313.15) K

m^a/(mol·kg^{-1})	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
	T/K = 293.15		
0.0000	0.99990	1499.65	1.33510
0.0500	1.00800	1504.39	1.33628
0.0801	1.01282	1507.25	1.33752
0.1151	1.01850	1510.56	1.33912
0.1551	1.02490	1514.36	1.34059
0.2000	1.03210	1518.61	1.34201
0.2503	1.04020	1523.38	1.34393
0.3052	1.04900	1528.58	1.34531
0.4397	1.07084	1541.33	1.34920
0.5150	1.08311	1548.47	1.35084
	T/K = 298.15		
0.0000	0.99882	1509.50	1.33442
0.0500	1.00692	1514.08	1.33579
0.0801	1.01180	1516.84	1.33692
0.1151	1.01740	1520.05	1.33851
0.1551	1.02380	1523.72	1.34000
0.2000	1.03100	1527.84	1.34142
0.2503	1.03914	1532.45	1.34327
0.3052	1.04798	1537.49	1.34484
0.4397	1.06980	1549.82	1.34860
0.5150	1.08210	1556.73	1.35022
	T/K = 303.15		
0.0000	0.99748	1521.06	1.33372
0.0500	1.00550	1525.39	1.33519
0.0801	1.01033	1528.00	1.33622
0.1151	1.01594	1531.03	1.33783
0.1551	1.02236	1534.49	1.33944
0.2000	1.02956	1538.38	1.34075
0.2503	1.03763	1542.73	1.34266
0.3052	1.04644	1547.48	1.34417
0.4397	1.06801	1559.13	1.34801
0.5150	1.08009	1565.65	1.34955

Table 4.7. (*continued*)

m^a/(mol·kg $^{-1}$)	$\rho \cdot 10^{-3}$/(kg·m^{-3})	c/(m·s^{-1})	n_D
	T/K = 308.15		
0.0000	0.99618	1527.86	1.33312
0.0500	1.00414	1532.03	1.33452
0.0801	1.00893	1534.63	1.33548
0.1151	1.01451	1537.63	1.33709
0.1551	1.02088	1541.20	1.33873
0.2000	1.02803	1545.21	1.34005
0.2503	1.03604	1549.84	1.34205
0.3052	1.04479	1554.83	1.34330
0.4397	1.06621	1567.01	1.34733
0.5150	1.07820	1574.17	1.34871
	T/K = 313.15		
0.0000	0.99484	1535.86	1.33242
0.0500	1.00275	1540.12	1.33368
0.0801	1.00751	1542.81	1.33484
0.1151	1.01305	1545.95	1.33632
0.1551	1.01938	1548.99	1.33790
0.2000	1.02648	1552.99	1.33920
0.2503	1.03444	1557.80	1.34131
0.3052	1.04313	1563.82	1.34210
0.4397	1.06441	1576.52	1.34652
0.5150	1.07632	1584.02	1.34793

[a]m is the molality of $CoCl_2$ in aqueous cyclic alanylalanine solutions.
Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.025 kg·m^{-3}; for speed of sound u(u) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.05 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

4.2. HYDRATION EFFECTS

A comprehensive picture of hydration can be developed by volumetric measurements. This is particularly true when apparent molar volumes are combined with compression measurements; because ϕ_v is dominated by the intrinsic volume of the solute, rather than by volume changes produced by solute-solvent interactions. In low molecular weight compounds, however, the intrinsic compression of the solute can be regarded as negligible and as a result, the apparent molar isentropic compressions, ϕ_k is more sensitive to hydration effects (Bernal et al. 2000).

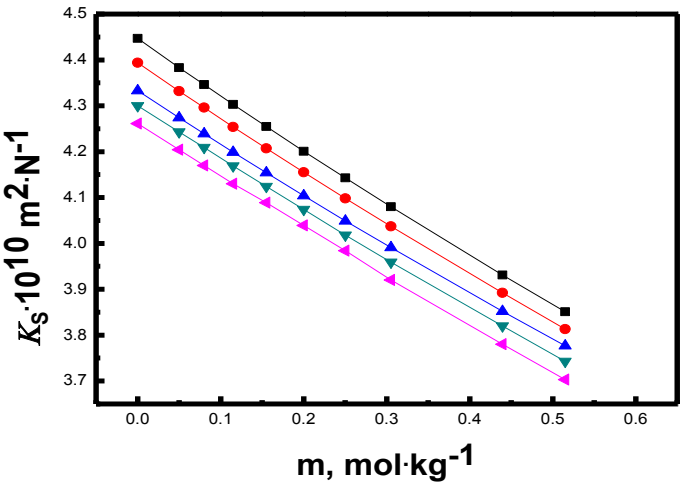

Figure 4.6. Isentropic compressibility, κ_S versus molal concentration, m of $CoCl_2$ in 0.0500 mol·kg^{-1}aqueous cyclic alanylalanine solutions at various temperatures. ■, T = 293.15 K; ●, T = 298.15 K; ▲, T = 303.15 K; ▼, T = 308.15 K; ◀, T = 313.15 K.

Table 4.8. Apparent Molar Volume, ϕ_v of $CoCl_2$ in 0.0500 mol·kg^{-1} Aqueous Cyclic Alanylalanine Solution at Temperatures, T = (293.15 to 313.15) K

m^a/(mol·kg^{-1})	$\phi_v \cdot 10^6$ /(m^3·mol^{-1})				
	T/K=293.15	T/K =298.15	T/K =303.15	T/K =308.15	T/K =313.15
0.0500	-31.92(±0.34)	-32.13(±0.34)	-30.80(±0.34)	-29.85(±0.33)	-29.10(±0.33)
0.0801	-31.08(±0.21)	-32.02(±0.21)	-30.67(±0.21)	-29.68(±0.21)	-28.94(±0.21)
0.1151	-31.20(±0.14)	-31.23(±0.14)	-30.46(±0.14)	-29.60(±0.14)	-28.82(±0.14)
0.1551	-30.60(±0.11)	-30.68(±0.11)	-30.30(±0.11)	-29.41(±0.11)	-28.65(±0.11)
0.2000	-30.21(±0.08)	-30.31(±0.08)	-30.08(±0.08)	-29.20(±0.08)	-28.43(±0.08)
0.2503	-29.98(±0.06)	-30.25(±0.06)	-29.85(±0.06)	-28.98(±0.06)	-28.22(±0.06)
0.3052	-29.60(±0.05)	-29.99(±0.05)	-29.61(±0.05)	-28.76(±0.05)	-28.00(±0.05)
0.4397	-29.43(±0.04)	-29.71(±0.04)	-29.00(±0.04)	-28.17(±0.04)	-27.44(±0.04)
0.5150	-29.31(±0.03)	-29.63(±0.03)	-28.68(±0.03)	-27.86(±0.03)	-27.13(±0.03)

[a]m is the molality of $CoCl_2$ in 0.0500 mol·kg^{-1}aqueous cyclic alanylalanine solutions.

Table 4.9. Least Squares Fit Parameters of the Equation $\phi_v = \phi_v^0 + S_v m$ for $CoCl_2$ in 0.0500 mol·kg^{-1}Aqueous Cyclic Alanylalanine Solutions at Temperatures T = (293.15 to 313.15) K

T/K	$\phi_v^0 \cdot 10^6$ /(m^3·mol^{-1})	$S_v \cdot 10^6$ /(m^3·mol^{-2}·kg)	$\sigma \cdot 10^6$ /(m^3·mol^{-1})
293.15	-31.58 (±0.23)	0.52(±0.08)	0.4
298.15	-31.89 (±0.28)	0.52(±0.10)	0.4
303.15	-31.01 (±0.02)	0.46(±0.01)	0.1
308.15	-30.06 (±0.01)	0.43(±0.01)	0.1
313.15	-29.29 (±0.01)	0.42(±0.01)	0.1

Equation 3.3 has been used to calculate the apparent molar isentropic compressions, ϕ_k of the solutions (Riyazuddeen and Usmani 2012) and the computed ϕ_k values are presented in Table 4.10 where the table clearly indicates the increase in molar isentropic compression of the system: cyclic alanylalanine-MCl_2 with solute concentration and temperature.

Table 4.10. Apparent Molar Isentropic Compression, ϕ_k of Cyclic Alanylalanine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.

m^a/(mol·kg^{-1})	T/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
	$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
	Cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0097	-24.75(±1.20)	-22.75(±1.19)	-20.01(±1.18)	-18.62(±1.17)	-17.43(±1.16)
0.0254	-23.69(±0.46)	-22.24(±0.45)	-19.73(±0.45)	-18.18(±0.45)	-17.30(±0.44)
0.0349	-23.41(±0.33)	-21.98(±0.33)	-19.39(±0.33)	-17.88(±0.33)	-16.93(±0.32)
0.0758	-21.88(±0.15)	-20.52(±0.15)	-18.59(±0.15)	-17.34(±0.15)	-16.55(±0.15)
0.0991	-21.08(±0.12)	-19.74(±0.12)	-18.13(±0.11)	-16.91(±0.11)	-16.12(±0.11)
0.1254	-19.97(±0.09)	-18.84(±0.09)	-17.33(±0.09)	-16.53(±0.09)	-15.81(±0.09)
0.1516	-19.08(±0.08)	-17.86(±0.08)	-17.07(±0.08)	-16.12(±0.08)	-15.47(±0.07)

Table 4.10. (*continued*)

m^a/(mol·kg^{-1})	*T*/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
	$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Cyclic alanylalanine in 0.1000 mol·kg^{-1}aqueous $CoCl_2$ solution					
0.0100	-23.22(±1.15)	-21.51(±1.13)	-20.88(±1.10)	-17.58(±1.08)	-16.91(±1.07)
0.0249	-23.39(±0.46)	-21.52(±0.45)	-21.24(±0.44)	-18.29(±0.43)	-15.95(±0.43)
0.0350	-23.59(±0.33)	-21.69(±0.32)	-21.74(±0.31)	-18.54(±0.31)	-15.99(±0.31)
0.0752	-24.16(±0.15)	-22.32(±0.15)	-22.45(±0.15)	-18.96(±0.15)	-16.51(±0.15)
0.0991	-24.61(±0.11)	-22.74(±0.11)	-22.84(±0.11)	-19.23(±0.11)	-17.08(±0.11)
0.1266	-25.05(±0.09)	-23.28(±0.09)	-23.34(±0.09)	-19.46(±0.08)	-17.70(±0.08)
0.1520	-25.52(±0.07)	-23.72(±0.07)	-23.81(±0.07)	-19.79(±0.07)	-18.32(±0.07)
Cyclic alanylalanine in 0.0981 mol·kg^{-1}aqueous $NiCl_2$ solution					
0.0112	-23.61(±1.05)	-21.15(±1.03)	-18.35(±1.01)	-16.99(±0.99)	-15.50(±0.97)
0.0246	-22.98(±0.48)	-20.79(±0.47)	-17.95(±0.46)	-16.67(±0.45)	-15.06(±0.44)
0.0353	-22.82(±0.33)	-20.54(±0.33)	-17.54(±0.32)	-16.31(±0.31)	-14.89(±0.31)
0.0735	-22.13(±0.16)	-20.12(±0.16)	-17.01(±0.15)	-15.56(±0.15)	-14.01(±0.15)
0.0987	-21.70(±0.12)	-19.51(±0.12)	-16.54(±0.11)	-14.94(±0.11)	-13.45(±0.11)
0.1261	-21.21(±0.09)	-18.85(±0.09)	-15.91(±0.09)	-14.34(±0.09)	-12.91(±0.09)
0.1511	-20.78(±0.08)	-18.17(±0.08)	-15.21(±0.07)	-13.95(±0.07)	-12.24(±0.07)
Cyclic alanylalanine in 0.0933 mol·kg^{-1} aqueous $ZnCl_2$ Solution					
0.0115	-23.52(±1.02)	-22.30(±1.00)	-19.52(±0.98)	-18.21(±0.96)	-16.38(±0.95)
0.0253	-22.88(±0.46)	-21.86(±0.46)	-18.83(±0.45)	-17.71(±0.44)	-16.02(±0.43)
0.0353	-22.34(±0.33)	-21.41(±0.33)	-18.54(±0.32)	-17.43(±0.31)	-15.65(±0.31)
0.0762	-19.68(±0.15)	-19.16(±0.15)	-17.14(±0.15)	-16.46(±0.14)	-15.05(±0.14)
0.1022	-18.07(±0.11)	-17.86(±0.11)	-16.28(±0.11)	-15.93(±0.11)	-14.58(±0.11)
0.1260	-16.83(±0.09)	-16.62(±0.09)	-15.44(±0.09)	-15.15(±0.09)	-14.06(±0.09)
0.1502	-15.47(±0.08)	-15.16(±0.08)	-14.75(±0.07)	-14.32(±0.07)	-13.57(±0.07)

[a]*m* is the molality of cyclic alanylalanine in aqueous metal salt solutions. The experiment was carried out under atmosphere pressure.

The method least-squares fit has been employed to fit ϕ_k values (Equation 3.8) for the present system. The extent of solute-solvent interaction can be attributed by the value of ϕ_k^0 obtained from this equation. The computed values of ϕ_k^0 and S_k along with their standard deviations are listed in Table 4.11.

Table 4.11. Least Squares Fit Parameters of the Equation $\phi_k = \phi_k^{\,0} + S_k m$ for Cyclic Alanylalanine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions at Temperatures T = (293.15 to 313.15) K.[a]

***T*/K**	$\phi_k^{\,0}$ **·10^{15}/ (Pa^{-1}·m^3·mol^{-1})**	S_k **·10^{15}/ (Pa^{-1}·m^3·mol^{-2}·kg)**	**σ·10^{15}/ (Pa^{-1}·m^3·mol^{-1})**
Cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $MnCl_2$ solution			
293.15	-24.85(±0.11)	38.58(±1.22)	0.2
298.15	-23.12(±0.03)	34.44(±0.32)	0.1
303.15	-20.20(±0.07)	21.49(±0.83)	0.1
308.15	-18.62(±0.07)	16.82(±0.80)	0.1
313.15	-17.55(±0.06)	13.87(±0.64)	0.1
Cyclic alanylalanine in 0.1000 mol·kg^{-1} aqueous $CoCl_2$ solution			
293.15	-23.02(±0.03)	-16.27(±0.32)	0.1
298.15	-21.06(±0.08)	-17.36(±1.00)	0.2
303.15	-20.97(±0.09)	-18.87(±0.97)	0.1
308.15	-17.84(±0.13)	-13.38(±1.56)	0.2
313.15	-15.26(±0.13)	-19.18(±1.43)	0.1
Cyclic alanylalanine in 0.0981 mol·kg^{-1} aqueous $NiCl_2$ solution			
293.15	-23.58(±0.09)	18.91(±1.03)	0.1
298.15	-22.09(±0.06)	26.07(±0.72)	0.1
303.15	-18.48(±0.09)	20.90(±1.04)	0.1
308.15	-17.17(±0.05)	21.95(±0.59)	0.1
313.15	-15.68(±0.03)	22.57(±0.43)	0.1

Table 4.11. (*continued*)

T/K	$\phi_k^0 \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-2}·kg)	$\sigma \cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})
Cyclic alanylalanine in 0.0933 mol·kg^{-1} aqueous $ZnCl_2$ Solution			
293.15	-24.29(±0.09)	59.41(±0.95)	0.1
298.15	-23.11(±0.10)	52.04(±1.06)	0.1
303.15	-19.77(±0.06)	34.00(±0.67)	0.1
308.15	-18.45(±0.09)	26.58(±0.95)	0.1
313.15	-16.50(±0.06)	19.38(±0.71)	0.1

[a]σ is the standard deviation of the fit.

The ϕ_k^0 values are negative for cyclic alanylalanine in aqueous MCl_2 solution which indicate the existence of a strong solute-solvent interaction in present systems.

One interesting feature of the system studied is the trend of the slopes of the concentration dependence of the apparent molar volumes. The S_v values are found to be negative, considerably indicating hydrophobic hydration in the system. The slopes are more negative suggesting an enhancement of the effect that leads to the volume and compression reduction. This indicates that water molecules in the vicinity of apolar groups such as CH_2 groups are less compressible than the bulk, but not quite as incompressible as electrostricted water (Riyazuddeen and Usmani 2012).

The volumetric properties and their temperature dependence are powerful tools to characterize hydration. The slopes of the concentration dependence, S_v of the apparent molar volumes are negative and become more negative with the increase in temperature. Thus one can conclude that both polar and nonpolar groups lead to a decrease in the mobility of the water molecules in the hydration shell, which in turn, leads to a reduction of the relaxation part of the compression.

The intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A) for the system, cyclic alanylalanine-MCl_2 have been calculated using the Equations 3.4, 3.5 and 3.6, respectively.

The corresponding values of L_f, Z and R_A are fitted using the following equation,

$$y = a + bm \qquad (4.1)$$

where *m* is the molality of the solution and *b* is the experimental slope. The coefficients of Equation (4.1) for the systems CAA-$MnCl_2$, CAA-$CoCl_2$, CAA-$NiCl_2$ and CAA-$ZnCl_2$ are reported as Tables 4.12, 4.13, 4.14 and 4.15, respectively.

Table 4.12. Coefficients of the Equation $y = a + bm$ for the System: Cyclic Alanylalanine in 0.0899 mol·kg^{-1} Aqueous $MnCl_2$ Solutions at Temperatures T = (293.15 to 313.15) K

T/K		L_f/Å	$\sigma \cdot 10^{-4}$/Å	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	$\sigma \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A[b]	$\sigma/10^{-4}$
293.15	a	0.4276	0.3	1513.10(±0.09)	0.1	0.9998	0. 5
	b	-0.0328(±0.0003)		140.05(±1.10))		0.0106(±0.0004)	
298.15	a	0.4306	0. 5	1515.20(±0.09)	0.1	0.9999	0. 8
	b	-0.0325(±0.0005)		138.32(±1.06)		0.0085(±0.0007)	
303.15	a	0.4329	0. 4	1520.00±0.04)	0.1	0.9999	0. 6
	b	-0.0327(0.0003)		137.48(±0.61)		0.0067(±0.0005)	
308.15	a	0.4359	0.4	1522.23(±0.02)	0.1	0.9999	0. 6
	b	-0.0331(±0.0004)		136.24(±0.47)		0.0041(±0.0006)	
313.15	a	0.4384	0. 3	1526.00(±0.03)	0.1	0.9996	0. 2
	b	-0.0335(±0.0002)		135.58(±0.40)		0.0023(±0.0005)	

[a] The standard errors for L_f are better than 0.0001Å.
[b]The standard errors for R_A are better than 0.0001.

Table 4.13. Coefficients of the Equation $y = a + bm$ for the System: Cyclic Alanylalanine in 0.1000 mol·kg^{-1} Aqueous $CoCl_2$ Solutions at Temperatures T = (293.15 to 313.15) K

T/K		L_f/Å	$\sigma \cdot 10^{-4}$/ Å	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	$\sigma \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A[b]	σ/10^{-4}
293.15	a	0.4260	0.3	1523.38(±0.04)	0.1	1.0000	0. 5
	b	-0.0358(±0.0002)		154.15(±0.53)		0.0084(±0.0004)	
298.15	a	0.4274	0. 2	1531.57(±0.04)	0.1	0.9999	0. 5
	b	-0.0361(±0.0001)		152.22(±0.55)		0.0040(±0.0002)	
303.15	a	0.4282	0. 3	1541.94(±0.04)	0.1	0.9999	0. 4
	b	-0.0367(0.0002)		154.09(±0.52)		0.0020(±0.0003)	
308.15	a	0.4296	0.2	1549.42(±0.02)	0.1	1.0000	0. 5
	b	-0.0352(±0.0001)		147.57(±0.31)		-0.0014(±0.0004)	
313.15	a	0.4317	0. 3	1553.79(±0.06)	0.1	0.9999	0. 7
	b	-0.0348(±0.0002)		145.02(±0.72)		-0.0009(±0.0005)	

[a] The standard errors for L_f are better than 0.0001Å.
[b]The standard errors for R_A are better than 0.0001.

Table 4.14. Coefficients of the Equation $y = a + bm$ for the System: Cyclic Alanylalanine in 0.0981 mol·kg^{-1} Aqueous $NiCl_2$ Solutions at Temperatures T = (293.15 to 313.15) K

T/K		L_f/Å	$\sigma \cdot 10^{-4}$/ Å	$Z \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	$\sigma \cdot 10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A[b]	σ/10^{-4}
293.15	a	0.4297	0.2	1507.32(±0.04)	0.1	0.9999	0. 5
	b	-0.0330±0.0002)		133.09(±0.53)		0.0144(±0.0004)	
298.15	a	0.4300	0. 4	1518.98(±0.06)	0.1	0.9999	0. 7
	b	-0.0326(±0.0004)		130.15(±0.75)		-0.0057(±0.0006)	
303.15	a	0.4307	0. 4	1529.08(±0.06)	0.1	0.9998	0. 8
	b	-0.0318(0.0004)		126.04(±0.73)		0.0057(±0.0003)	
308.15	a	0.4320	0.4	1537.38(±0.05)	0.1	0.9998	0. 5
	b	-0.0314(±0.0001)		124.36(±0.60)		-0.0056(±0.0007)	
313.15	a	0.4336	0. 4	1543.98(±0.06)	0.1	0.9998	0. 6
	b	-0.0309(±0.0003)		122.12(±0.72)		-0.0075(±0.0006)	

[a] The standard errors for L_f are better than 0.0001Å.
[b]The standard errors for R_A are better than 0.0001.

Table 4.15. Coefficients of the Equation $y = a + bm$ for the System: Cyclic Alanylalanine in 0.0933 mol·kg^{-1} Aqueous $ZnCl_2$ Solutions at Temperatures T = (293.15 to 313.15) K

T/K		L_f/Å	$\sigma\cdot10^{-4}$/ Å	$Z\cdot10^{-3}$/ (kg·m^{-2}·s^{-1})	$\sigma\cdot10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A[b]	σ/10^{-4}
293.15	a	0.4287	0.5	1510.75(±0.13)	0.2	0.9999	0. 8
	b	-0.0330±0.0002)		132.94(±1.54)		0.0133(±0.0004)	
298.15	a	0.4306	0. 3	1516.77(±0.14)	0.2	0.9998	0. 7
	b	-0.0309(±0.0003)		133.48(±1.58)		0.0103(±0.0006)	
303.15	a	0.4311	0. 3	1527.27(±0.08)	0.1	0.9999	0. 5
	b	-0.0318(0.0004)		134.14(±0.92)		0.0076(±0.0004)	
308.15	a	0.4324	0.5	1536.27(±0.08)	0.1	0.9998	0. 6
	b	-0.0318(±0.0005)		134.76(±0.96)		0.0070(±0.0007)	
313.15	a	0.4345	0. 3	1541.64(±0.05)	0.1	0.9999	0. 5
	b	-0.0320(±0.0003)		133.96(±0.62)		-0.0075(±0.0006)	

[a] The standard errors for L_f are better than 0.0001Å.
[b]The standard errors for R_A are better than 0.0001.

The decrease in intermolecular free length can be accounted to the solvent-solute interaction and dipole-dipole interaction (Masson 1929, Rao and Verrall 1987 and Regmi 2007). The increase in ultrasonic velocity with the solute concentration decreases intermolecular free length and vice versa (Canosa et al. 1997). It may be noted that the intermolecular free length shows an analogous variation as reflected by isentropic compressibility values which indicates that the molecules are closer in the system. The interdependence of L_f and c have been evolved from a model for sound propagation proposed by Eyring and Kincaid (1938). According to the proposed theory, the decrease in the value of κ_S and L_f with an increase in ultrasonic velocity further strengthens the process of complex formation between solute molecules through hydrogen bonding due to which structural arrangement is considerably altered (Fort and Moore 1965).

The specific acoustic impedance focusses on the molecular packing of the system. As we know there exists a strong intermolecular hydrogen bonding in cyclic alanylalanine (Benedetti et al. 1969), the increase in the specific acoustic impedance can be attributed to strong interaction among the constituents of the mixtures through hydrogen bonding (Yen and Woods 1966 and Munoz et al. 1999). Eucken's theory

(Munoz et al. 1999) proposed that there is a decrease in the number of aggregates of solvent molecules as the concentration and temperature of the solution increase. Consequently, as the temperature rises, water molecules start dissociating from the aggregate form. This effect is further enhanced by the introduction of an electrolyte into solvent environment. R_A is used to understand two types of effects taking place in a solution when a solute is added to it; the breaking of the solvent molecules on addition of solute to it and the simultaneous solvation of the solute by the solvent molecules (Sinha and Roy 2006). Relative association of the molecules increases with an increase in the amount of MCl_2 in aqueous cyclic alanylalanine solution (i.e. the second case) depicting a usual trend in the solvent aggregates dissociation (Yen and Woods 1966). While for the case of $CoCl_2$ in aqueous cyclic alanylalanine solutions, relative association values have been found to be almost independent of concentration and solvent composition. Similar results have been reported in literature (Nikam et al. 2004). This can be seen from Table 4.16.

Table 4.16. Coefficients the of Equation $y = a + bm$ for the System: $CoCl_2$ in 0.0500 mol·kg^{-1}Aqueous Cyclic Alanylalanine Solutions at Temperatures, T = (293.15 to 313.15) K

T/K		L_f/Å	$\sigma\cdot10^{-4}$/ Å	$Z\cdot10^{-3}$/ (kg·m^{-2}·s^{-1})	$\sigma\cdot10^{-3}$/ (kg·m^{-2}·s^{-1})	R_A[b]	σ/10^{-4}
293.15	a	0.4294(±0.0001)	0.1	1498.63(±0.28)	0.5	1.0001	0.1
	b	-0.0576(±0.0003)		345.45(±1.01)		0.1390(±0.0001)	
298.15	a	0.4307(±0.0001)	0.1	1506.85(±0.28)	0.5	1.0001	0.1
	b	-0.0568(±0.0003)		343.79(±1.02)		0.1401(±0.0001)	
303.15	a	0.4317(±0.0001)	0.1	1516.48(±0.19)	0.3	1.0001	0.1
	b	-0.0551(±0.0001)		338.14(±0.69)		0.1405(±0.0002)	
308.15	a	0.4341(±0.0001)	0.1	1520.63(±0.30)	0.5	1.0002	0.1
	b	-0.0352(±0.0003)		341.65(±1.08)		0.1388(±0.0002)	
313.15	a	0.4361(±0.0001)	0.1	1526.05(±0.53)	0.8	1.0004	0.2
	b	-0.0575(±0.0002)		345.51(±1.89)		0.1372(±0.0004)	

[a] The standard errors for R_A are better than 0.0001.

With raise in temperature, the solvent aggregates start disassociating themselves thereby increasing the number of solvent molecules. The experimental R_A values were found to increase with an increase in the temperature i.e. from (293.15 to 303.15) K; later they decrease indicating simultaneous solvation of solute molecules at higher temperatures. This demonstrates that the degree of dissociation of aggregates of solvent molecules with increase in temperature in cyclic alanylalanine-MCl_2 systems follow polynomial trend than linear.

4.3. TRANSFER MOLAR QUANTITIES

The transfer molar properties at infinite dilution of cyclic alanylalanine from water to aqueous metal salt solutions have been calculated from Equation 3.9.

Table 4.17 represent the trends in transfer properties of cyclic alanylalanine from aqueous to aqueous metal salt solutions. It is evident from the table that the values of $\Delta_{tr}\phi_v^0$ and $\Delta_{tr}\phi_k^0$ are positive in aqueous metal salt solutions at all the temperatures and the overall values of $\Delta_{tr}\phi_v^0$ and $\Delta_{tr}\phi_k^0$ from water to aqueous $MnCl_2$ were found to be higher than those of aqueous cyclic alanylalanine system.

Another important observation of these chapters is that the transfer molar volume increases by increasing the temperature. This cannot be explained based on either electrostriction or hydrophobic hydration of the cyclic dipeptide since hydrophobic hydration decreases at higher temperatures due to release of some water molecules at higher temperatures thus causing negative contribution to ϕ_v^0 values (Chen et al. 2013).

Thermodynamically, cyclic alanylalanine behaves as a hydrophobic gas than a hydrophobic liquid or solid and the behaviour of hydrophobic gas can be attributed to its increasingly favourable enthalpic interaction with water; largely due to its size, hydrophobicity, etc. (Brady and Sharp 1997). Also, presence of strong cations such as Mn^{2+},Co^{2+}, Ni^{2+} or Zn^{2+} cause shrinkage in hydrogen bonding groups present in cyclic alanylalanine with water. This effect along with enthalpic interaction of cyclic alanylalanine with water at higher temperatures may explain the positive trend in

transfer molar quantities. Identical trend has been observed for cyclic alanylalanine - $CaCl_2$ and cyclic alanylalanine - $MgCl_2$ systems in the preceding chapter.

Table 4.17. TransferPartial Molar Volumes, $\Delta_{tr}\phi_v^0$ and Transfer Partial Molar Isentropic Compressions, $\Delta_{tr}\phi_k^0$ of Cyclic Alanylalanine from Water to Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions at Temperatures, T = (293.15 to 313.15) K.

***T*/K**	$\Delta_{tr}\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$\Delta_{tr}\phi_k^0 \cdot 10^{15}/(Pa^{-1} \cdot m^3 \cdot mol^{-1})$
	0.0899 mol·kg^{-1} aqueous $MnCl_2$ solution	
293.15	1.43	2.34
298.15	2.26	2.97
303.15	3.90	3.78
308.15	5.40	4.97
313.15	8.01	5.63
	0.1000 mol·kg^{-1} aqueous $CoCl_2$ solution	
293.15	0.38	4.17
298.15	3.69	5.03
303.15	4.42	3.01
308.15	7.60	5.75
313.15	7.79	7.92
	0.0981 mol·kg^{-1} aqueous $NiCl_2$ solution	
293.15	0.40	3.61
298.15	1.29	4.00
303.15	2.53	5.50
308.15	2.70	6.42
313.15	4.11	7.50
	0.0933 mol·kg^{-1} aqueous $ZnCl_2$ Solution	
293.15	0.53	2.90
298.15	2.07	2.98
303.15	3.17	4.21
308.15	3.60	5.14
313.15	5.06	6.68

The nature of transfer molar quantities with respect to temperature is depicted in Figures 4.7 and 4.8 wherein it is observed that the transfer molar quantities of cyclic alanylalanine in all the cases generally vary linearly with temperature.

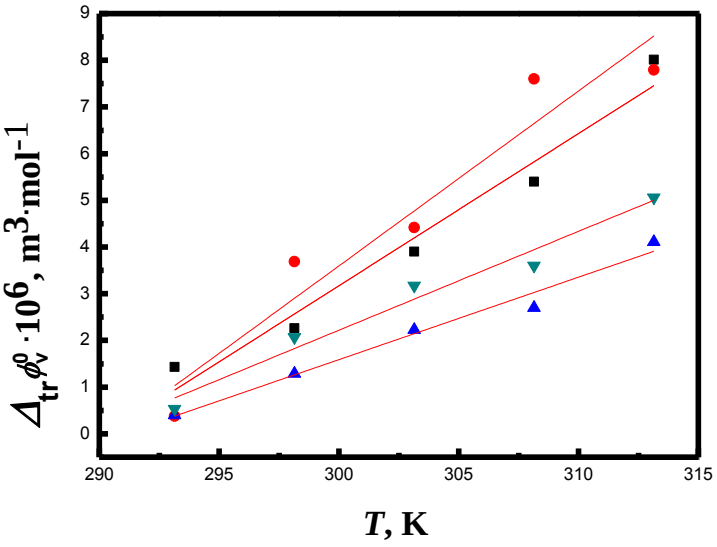

Figure 4.7. Transfer molar volume, $\Delta_{tr}\phi_v^0$ versus temperature, *T* for the systems: Cyclic alanylalanine-MCl_2 aqueous solutions. ●, M = Mn; ■, M = Co; ▲, M = Ni; ▼, M = Zn.

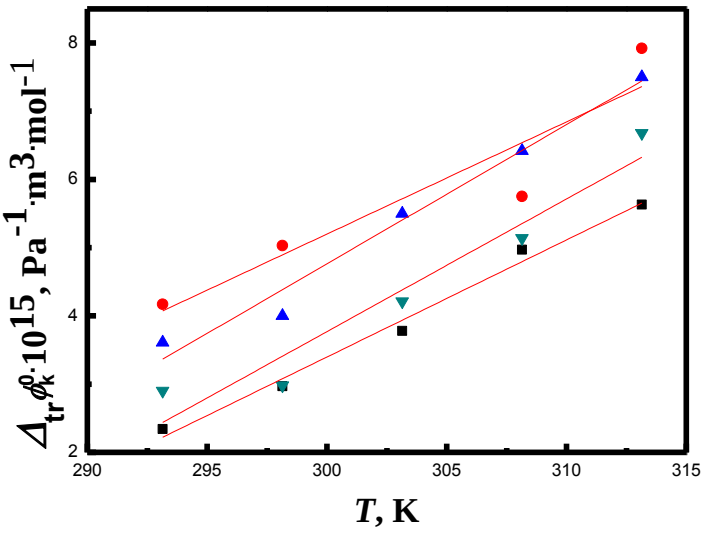

Figure 4.8. Transfer molar isentropic compression, $\Delta_{tr}\phi_k^0$ versus temperature, *T* for the systems: Cyclic alanylalanine-MCl_2 aqueous solutions. ●, M = Mn; ■, M = Co; ▲, M = Ni; ▼, M = Zn.

4.4. OPTICAL PROPERTIES

Experimental refractive indices, n_D of cyclic alanylalanine aqueous MCl_2 solutions have been measured as a function of the molality of the solute. The experimental n_D values were found to increase with the concentration of solute.

The molar Refraction, R_D, has been calculated from the refractive index data using the Lorentz–Lorenz equation, Equation 3.10.

The molar refraction values are fitted using equation 3.11. Table 4.18 presents the tabulated values of R_D° and B. As R_D is directly proportional to the molecular polarizability, the table shows that the overall polarizability of the cyclic alanylalanine solutions increases as the amount of solute increases in the mixture (Ali et. al. 2010).

Table 4.18. Values of Coefficients of the Equation $R_D = R_D^0 + Bx_i$ at T = (293.15 K to 313.15) K.

***T*/K**	**$R_D^\circ \cdot 10^6/(m^3 \cdot mol^{-1})$**	**$B \cdot 10^6/(m^3 \cdot mol^{-1})$**	**$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$**
Cyclic alanylalanine in 0.0899 mol·kg^{-1} aqueous $MnCl_2$ solution			
293.15	3.7926(±0.0008)	38.9471(±0.4174)	0.1
298.15	3.7907(±0.0009)	39.0010(±0.6336)	0.1
303.15	3.7897(±0.0009)	39.7036(±0.6644)	0.1
308.15	3.7894(±0.0009)	40.2257(±0.7256)	0.1
313.15	3.7890(±0.0009)	41.7714(±0.7540)	0.1
Cyclic alanylalanine in 0.1000 mol·kg^{-1} aqueous $CoCl_2$ solution			
293.15	3.7763(±0.0004)	34.9102(±0.4174)	0.1
298.15	3.7753(±0.0008)	34.9266(±0.5572)	0.1
303.15	3.7756(±0.0001)	33.4375(±0.0966)	0.1
308.15	3.7765(±0.0001)	32.7127(±0.0061)	0.1
313.15	3.7796(±0.0002)	32.2141(±0.1596)	0.1

Table 4.18. (*continued*)

T/K	$R_D^{\circ}\cdot10^6/(m^3\cdot mol^{-1})$	$B\cdot10^6/(m^3\cdot mol^{-1})$	$\sigma\cdot10^6/(m^3\cdot mol^{-1})$
	Cyclic alanylalanine in 0.0981 mol·kg^{-1} aqueous $NiCl_2$ solution		
293.15	3.7655(±0.0010)	31.2894(±0.7082)	0.1
298.15	3.7652(±0.0010)	32.5733(±0.6980)	0.1
303.15	3.7643(±0.0010)	33.0986(±0.6470)	0.1
308.15	3.7640(±0.0010)	32.5376(±0.6631)	0.1
313.15	3.7638(±0.0007)	32.9710(±0.4886)	0.1
	Cyclic alanylalanine in 0.0933 mol·kg^{-1} aqueous $ZnCl_2$ solution		
293.15	3.7775(±0.0002)	33.6051(±0.1518)	0.1
298.15	3.7766(±0.0004)	33.9266(±0.2643)	0.1
303.15	3.7745(±0.0003)	33.6970(±0.2519)	0.1
308.15	3.7721(±0.0004)	33.1853(±0.2862)	0.1
313.15	3.7670(±0.0003)	33.9145(±0.2600)	0.1
	$CoCl_2$ in 0.0500 mol·kg^{-1} aqueous Cyclic alanylalanine solution		
293.15	3.7438(±0.0017)	31.7337(±0.3227)	0.3
303.15	3.7426(±0.0026)	31.7450(±0.4607)	0.4
308.15	3.7440(±0.0026)	31.5706(±0.4704)	0.4
313.15	3.7451(±0.0068)	31.3851(±0.5345)	0.5

The polarizability can be seen as a combination of two contributions:

i. Measuring the ease with which the molecules are deformed by an electric field.

ii. The orientation of the molecular dipoles under the action of this field.

The first factor is independent of temperature whereas the second is temperature dependent. The orientation effects are important only for the molecules of higher electric dipole moment (Pineiro et al. 2002). Since the measured molar refraction values of molecules in this study are dependent on the temperature range, it can be predicted that the orientational effects have also included in polarizability. Molar refractions are

also related to internal forces present among the constituents of a liquid mixture, the dependence R_D values with the amount of cyclic alanylalanine or MCl_2 in the systems studied further strengthens the argument of interaction between solute and solvent molecules in the mixtures as indicated by the isentropic compressibility measurements.

CHAPTER 5

VOLUMETRIC STUDY OF GLYCINE BETAINE IN AQUEOUS NaCl, KCl, $CaCl_2$ AND $MgCl_2$ SOLUTIONS AT DIFFERENT TEMPERATURES

Chapter 5 describes the molecular interaction of glycine betaine (GB) in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at various temperatures. The solute-solvent interactions operative in these solutions have been expressed as a combination of electrostatic hydration of charged terminals of the zwitterion and the overlap of hydration co-spheres of these terminal groups with that of $–CH_2$ group of GB which contributes to enhanced partial molar volumes. In order to study the effect of NaCl on the solution properties of aqueous glycine betaine solutions, five different concentrations of NaCl have been considered.

5.1. PARTIAL MOLAR VOLUME AND PARTIAL MOLAR ISENTROPIC COMPRESSION STUDY OF GLYCINE BETAINE IN AQUEOUS AND AQUEOUS POTASSIUM CHLORIDE, CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE SOLUTIONS AT TEMPERATURES *T* = (288.15 TO 318.15) K

5.1.1. Isentropic Compressibility and Molar Volume Studies

Experimentally determined density, ρ and ultrasonic velocity, c and the refractive index, n_D for the systems; aqueous glycine betaine, glycine betaine in aqueous KCl, $CaCl_2$ and $MgCl_2$ solvents as a function of concentration of glycine betaine and temperature are reported in Table 5.1.The derived parameters have been calculated using these experimentally measured values.

The isentropic compressibilities κ_S have been calculated using Newton-Laplace equation (Apelblat et al. 2009),

$$\kappa_s = \frac{1}{\rho c^2} \qquad (5.1)$$

where ρ and c are the density and speed of sound in the solution, respectively. The isentropic compressibility values of aqueous glycine betaine solutions as a function of concentration of glycine betaine (at various temperatures) have also been included in Table 5.1. The κ_S values of glycine betaine in all aqueous solutions decrease with an increase in glycine betaine concentration and decrease with increasing temperature. The reduction in κ_S values of the system on increasing the concentration of glycine betaine

indicates that the water molecules which are in association with ionic groups of glycine betaine are less compressible than those water molecules in the bulk.

Table 5.1. Density, ρ, Speed of Sound, c, Refractive Index, n_D, and Isentropic Compressibility, κ_S, of Glycine Betaine in Aqueous, Aqueous KCl, $CaCl_2$ or $MgCl_2$ Solutions at Temperatures, T = 288.15 K to 318.15 K, as a Function of Glycine Betaine Molality.

m^a/(mol·kg^{-1})	T/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
				Aqueous glycine betaine			
ρ·10^{-3}/(kg·m^{-3})							
0.0000	0.9991	0.9982	0.9970	0.9957	0.9940	0.9922	0.9902
0.0482	1.0001	0.9991	0.9979	0.9966	0.9949	0.9931	0.9911
0.1063	1.0012	1.0002	0.9989	0.9976	0.9959	0.9941	0.9921
0.5027	1.0085	1.0072	1.0056	1.0042	1.0025	1.0007	0.9987
1.0023	1.0168	1.0151	1.0131	1.0116	1.0099	1.0079	1.0060
1.5040	1.0243	1.0221	1.0199	1.0180	1.0164	1.0144	1.0124
2.0048	1.0309	1.0281	1.0258	1.0235	1.0220	1.0199	1.0180
2.5190	1.0366	1.0336	1.0310	1.0284	1.0271	1.0250	1.0228
3.0081	1.0418	1.0385	1.0354	1.0328	1.0312	1.0291	1.0273
c/(m·s^{-1})							
0.0000	1465.94	1482.38	1496.46	1509.18	1519.44	1528.92	1536.42
0.0482	1471.08	1487.68	1501.58	1514.08	1524.16	1533.38	1540.78
0.1063	1477.36	1493.84	1507.64	1520.04	1529.88	1538.80	1545.98
0.5027	1517.62	1535.44	1547.16	1558.62	1567.52	1574.22	1580.32
1.0023	1562.82	1580.72	1593.10	1602.34	1610.16	1615.72	1620.88
1.5040	1599.74	1619.48	1629.96	1639.58	1648.12	1652.26	1656.66
2.0048	1628.10	1649.78	1656.82	1669.82	1679.78	1682.82	1688.28
2.5190	1648.92	1670.36	1674.46	1689.68	1699.96	1705.92	1713.78
3.0081	1658.30	1680.10	1698.92	1715.22	1726.55	1737.14	1743.74
n_D							
0.0000	1.33340	1.33302	1.33252	1.33194	1.33131	1.33059	1.32984
0.0482	1.33442	1.33396	1.33341	1.33274	1.33208	1.33134	1.33058
0.1063	1.33539	1.33493	1.33438	1.33377	1.33305	1.33234	1.33161
0.5027	1.34260	1.34209	1.34149	1.34081	1.33959	1.33876	1.33790
1.0023	1.35008	1.34942	1.34871	1.34797	1.34734	1.34664	1.34606
1.5040	1.36163	1.36321	1.35856	1.35778	1.35689	1.35607	1.35416
2.0048	1.36984	1.36919	1.36844	1.36763	1.36676	1.36580	1.36215
2.5190	1.37267	1.37193	1.37141	1.36955	1.36992	1.36900	1.36651
3.0081	1.37524	1.37442	1.37354	1.37263	1.37184	1.37127	1.37046

Table 5.1. (*continued*)

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
κ_S ·10^{10}/(m^2·N^{-1})							
0.0000	4.658	4.559	4.479	4.410	4.358	4.312	4.278
0.0482	4.620	4.522	4.444	4.377	4.327	4.283	4.250
0.1063	4.576	4.480	4.404	4.338	4.290	4.249	4.218
0.5027	4.305	4.211	4.154	4.099	4.060	4.034	4.011
1.0023	4.027	3.943	3.889	3.850	3.819	3.802	3.786
1.5040	3.815	3.730	3.691	3.654	3.622	3.612	3.601
2.0048	3.659	3.574	3.551	3.504	3.468	3.463	3.448
2.5190	3.548	3.468	3.459	3.406	3.369	3.353	3.329
3.0081	3.491	3.411	3.346	3.291	3.253	3.236	3.213
Glycine betaine in 0.3020mol·kg^{-1} aqueous KCl solution							
ρ.10^{-3}/(kg·m^{-3})							
0.0000	1.0199	1.0181	1.0169	1.0135	1.0085	1.0061	1.0034
0.0496	1.0207	1.0189	1.0177	1.0143	1.0094	1.0069	1.0042
0.1020	1.0215	1.0197	1.0185	1.0151	1.0102	1.0077	1.0050
0.4981	1.0273	1.0255	1.0242	1.0209	1.0161	1.0134	1.0108
0.9980	1.0337	1.0318	1.0306	1.0273	1.0226	1.0199	1.0172
1.4985	1.0391	1.0373	1.0361	1.0329	1.0282	1.0255	1.0228
1.9946	1.0437	1.0421	1.0407	1.0375	1.0330	1.0302	1.0277
2.5002	1.0476	1.0461	1.0449	1.0413	1.0371	1.0344	1.0320
2.9993	1.0511	1.0493	1.0481	1.0448	1.0406	1.0380	1.0356
c/(m·s^{-1})							
0.0000	1482.88	1500.76	1518.44	1537.82	1548.62	1558.82	1568.02
0.0496	1487.58	1505.30	1522.98	1542.42	1553.02	1563.12	1572.26
0.1020	1492.30	1510.10	1527.48	1546.89	1557.49	1567.54	1576.52
0.4981	1526.78	1545.26	1562.18	1580.98	1591.78	1600.88	1608.78
0.9980	1568.46	1585.49	1602.36	1620.78	1631.38	1639.98	1649.28
1.4985	1605.46	1622.36	1640.68	1658.56	1668.86	1678.72	1688.72
1.9946	1640.43	1656.39	1676.52	1693.82	1704.32	1714.85	1725.65
2.5002	1675.82	1689.78	1710.10	1729.86	1739.76	1750.98	1760.54
2.9993	1701.68	1721.63	1742.13	1764.36	1774.72	1785.36	1795.12

Table 5.1. (*continued*)

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
n_D							
0.0000	1.33669	1.33618	1.33562	1.33499	1.33426	1.33348	1.33268
0.0496	1.33777	1.33724	1.33665	1.33600	1.33530	1.33456	1.33381
0.1020	1.33866	1.33813	1.33813	1.33755	1.33616	1.33537	1.33452
0.4981	1.34523	1.34463	1.34399	1.34329	1.34263	1.34189	1.34110
0.9980	1.35301	1.35244	1.35175	1.35105	1.35024	1.34934	1.34852
1.4985	1.36018	1.35936	1.35864	1.35790	1.35724	1.35653	1.35586
1.9946	1.36695	1.36633	1.36557	1.36478	1.36394	1.36315	1.36204
2.5002	1.37315	1.37249	1.37173	1.37096	1.37010	1.36913	1.36785
2.9993	1.37847	1.37759	1.37671	1.37584	1.37501	1.37447	1.37360
κ_S ·10^{10}/(m^2·N^{-1})							
0.0000	4.459	4.361	4.265	4.172	4.135	4.090	4.053
0.0496	4.427	4.331	4.236	4.144	4.108	4.065	4.028
0.1020	4.396	4.300	4.208	4.117	4.081	4.039	4.003
0.4981	4.176	4.084	4.001	3.919	3.884	3.850	3.822
0.9980	3.932	3.855	3.779	3.706	3.674	3.646	3.614
1.4985	3.734	3.663	3.586	3.519	3.492	3.460	3.428
1.9946	3.560	3.498	3.419	3.360	3.333	3.301	3.268
2.5002	3.399	3.348	3.273	3.209	3.186	3.153	3.126
2.9993	3.285	3.215	3.144	3.075	3.051	3.022	2.997
Glycine betaine in 0.3088mol·kg^{-1} aqueous $CaCl_2$ solution							
ρ.10^{-3}/(kg·m^{-3})							
0.0000	1.0264	1.0253	1.0240	1.0224	1.0207	1.0168	1.0122
0.0509	1.0273	1.0262	1.0248	1.0232	1.0215	1.0176	1.0130
0.1019	1.0280	1.0269	1.0255	1.0239	1.0222	1.0183	1.0137
0.4839	1.0333	1.0322	1.0307	1.0291	1.0274	1.0235	1.0190
0.9712	1.0394	1.0381	1.0365	1.0349	1.0333	1.0293	1.0250
1.5111	1.0453	1.0435	1.0420	1.0405	1.0388	1.0349	1.0305
1.9505	1.0490	1.0474	1.0457	1.0442	1.0426	1.0387	1.0345
2.4892	1.0533	1.0514	1.0495	1.0480	1.0466	1.0425	1.0383
2.9351	1.0563	1.0542	1.0521	1.0505	1.0492	1.0450	1.0407

Table 5.1. (*continued*)

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
***c*/(m·s^{-1})**							
0.0000	1491.91	1513.74	1524.23	1535.43	1546.82	1554.62	1565.20
0.0509	1496.54	1518.46	1528.81	1539.98	1551.33	1559.05	1569.50
0.1019	1501.41	1523.44	1533.49	1544.65	1555.96	1563.60	1573.89
0.4839	1536.80	1559.20	1567.70	1578.96	1590.04	1596.82	1606.20
0.9712	1580.00	1602.90	1610.06	1621.62	1631.84	1638.50	1646.68
1.5111	1624.77	1648.44	1655.29	1666.12	1676.84	1682.60	1690.82
1.9505	1660.00	1682.04	1690.15	1701.54	1711.60	1717.29	1724.76
2.4892	1698.10	1718.48	1729.65	1742.60	1752.00	1758.69	1768.00
2.9351	1727.68	1748.64	1759.32	1771.56	1782.74	1788.35	1799.40
n_D							
0.0000	1.33691	1.33603	1.33551	1.33488	1.33423	1.33350	1.33278
0.0509	1.33767	1.33679	1.33627	1.33563	1.33497	1.33424	1.33351
0.1019	1.33843	1.33756	1.33702	1.33639	1.33572	1.33498	1.33425
0.4839	1.34262	1.34206	1.34148	1.34080	1.34013	1.33939	1.33865
0.9712	1.35167	1.35101	1.35038	1.34964	1.34885	1.34796	1.34683
1.5111	1.35937	1.35863	1.35792	1.35715	1.35639	1.35548	1.35489
1.9505	1.36818	1.36732	1.36650	1.36577	1.36504	1.36406	1.36355
2.4892	1.37390	1.37326	1.37242	1.37157	1.37073	1.36971	1.36867
2.9351	1.37915	1.37858	1.37770	1.37677	1.37587	1.37482	1.37350
κ_S ·10^{10}/(m^2·N^{-1})							
0.0000	4.377	4.256	4.203	4.149	4.095	4.069	4.033
0.0509	4.346	4.226	4.175	4.121	4.068	4.043	4.007
0.1019	4.315	4.196	4.147	4.093	4.041	4.017	3.982
0.4839	4.098	3.985	3.948	3.898	3.850	3.832	3.804
0.9712	3.854	3.749	3.722	3.675	3.634	3.619	3.598
1.5111	3.624	3.527	3.503	3.462	3.424	3.413	3.394
1.9505	3.459	3.375	3.348	3.308	3.274	3.265	3.249
2.4892	3.292	3.221	3.185	3.142	3.113	3.101	3.081
2.9351	3.172	3.102	3.071	3.033	2.999	2.992	2.968

Table 5.1. (*continued*)

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
Glycine betaine in 0.3012 mol·kg^{-1} aqueous $MgCl_2$ solution							
$\rho.10^{-3}$/(kg·m^{-3})							
0.0000	1.0247	1.0227	1.0203	1.0192	1.0171	1.0149	1.0126
0.0495	1.0254	1.0234	1.0210	1.0199	1.0178	1.0156	1.0133
0.0996	1.0261	1.0241	1.0216	1.0205	1.0184	1.0162	1.0139
0.4975	1.0313	1.0291	1.0264	1.0253	1.0232	1.0210	1.0187
0.9862	1.0370	1.0347	1.0316	1.0304	1.0284	1.0263	1.0239
1.4850	1.0421	1.0397	1.0363	1.0349	1.0332	1.0309	1.0285
1.9740	1.0464	1.0440	1.0402	1.0388	1.0369	1.0346	1.0323
2.4956	1.0505	1.0480	1.0437	1.0424	1.0403	1.0383	1.0358
3.0000	1.0538	1.0512	1.0462	1.0450	1.0431	1.0410	1.0385
c/(m·s^{-1})							
0.0000	1510.34	1518.62	1529.12	1540.04	1551.88	1563.02	1573.42
0.0495	1515.56	1523.78	1534.12	1544.94	1556.78	1567.80	1578.06
0.0996	1520.48	1528.72	1538.88	1549.62	1561.34	1572.42	1582.32
0.4975	1558.18	1566.94	1575.72	1586.16	1596.86	1607.50	1617.70
0.9862	1602.60	1611.38	1619.58	1627.82	1637.72	1649.30	1658.38
1.4850	1640.66	1650.32	1657.90	1667.96	1678.94	1688.46	1698.32
1.9740	1678.72	1685.68	1696.16	1705.36	1714.64	1725.76	1733.26
2.4956	1710.94	1720.24	1734.42	1744.10	1753.18	1762.18	1770.62
3.0000	1740.10	1750.24	1764.94	1775.16	1780.04	1790.54	1800.25
n_D							
0.0000	1.34072	1.34021	1.33966	1.33904	1.33836	1.33765	1.33696
0.0495	1.34199	1.34118	1.34052	1.34001	1.33902	1.33851	1.33828
0.0996	1.34359	1.34309	1.34212	1.34125	1.34023	1.33990	1.33921
0.4975	1.35011	1.34957	1.34894	1.34827	1.34744	1.34659	1.34561
0.9862	1.35770	1.35701	1.35631	1.35563	1.35496	1.35438	1.35355
1.4850	1.36458	1.36401	1.36412	1.36314	1.36254	1.36114	1.36052
1.9740	1.37153	1.37092	1.37018	1.36935	1.36844	1.36759	1.36637
2.4956	1.37734	1.37738	1.37624	1.37555	1.37442	1.37354	1.37225
3.0000	1.38266	1.38185	1.38099	1.38007	1.37923	1.37858	1.37776

Table 5.1. (*continued*)

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})							
0.0000	4.278	4.240	4.192	4.137	4.082	4.033	3.989
0.0495	4.246	4.208	4.162	4.108	4.054	4.006	3.963
0.0996	4.215	4.178	4.133	4.081	4.028	3.980	3.939
0.4975	3.994	3.958	3.924	3.877	3.833	3.790	3.751
0.9862	3.755	3.722	3.696	3.663	3.625	3.582	3.551
1.4850	3.565	3.531	3.511	3.473	3.434	3.403	3.371
1.9740	3.391	3.371	3.342	3.310	3.280	3.245	3.225
2.4956	3.252	3.224	3.185	3.154	3.127	3.102	3.079
3.0000	3.134	3.105	3.068	3.037	3.026	2.996	2.971

[a]*m* is the molality of glycine betaine in aqueous solutions.

Standard uncertainty for temperature u(*T*) = 0.01 K; for pressure u(*p*) = 5 kPa; for molality u(*m*) = 0.0001 mol·kg $^{-1}$; for density u(ρ) = 0.01 kg·m^{-3}; for speed of sound u(*u*) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.2 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.

The water–water interaction is predominantly present in the system which forms the typical three-dimensional cage-like structure of water. When glycine betaine molecule enters water's environment, water molecules from the solution bulk are attracted toward the zwitter ion- 'glycine betaine' due to the electrostrictive force. Thus, a decrease in the number of available water molecules for the next incoming molecule can be observed and hence, this process is called compression (Santosh et al. 2011). Since the solution compressibility is lower than that of the solvent, the volumetric concentration of the solution increases with a decrease in compressibility of the solvent. The reduction in the compressibility can be attributed to the electrostrictive forces causing a breakage in the water structure with increasing solute concentration. Hence compact packing occurs with the water molecules surrounding the solute which reduces the compressibility. In aqueous KCl, $CaCl_2$ or $MgCl_2$ solutions, the isentropic compressibilities decrease as the concentration of glycine betaine or temperature increases indicating strong solute-solvent interactions through dipole- dipole interactions of the –OH group of glycine betaine with the surrounding water molecules. Due to the sizes of hydrated ions in KCl, $CaCl_2$ or $MgCl_2$ solutions, the compressibility

values of glycine betaine are much lower in the case of aqueous $MgCl_2$ solvent than aqueous$CaCl_2$ or KCl solvents. This is because of lesser availability of number of water molecules for the incoming glycine betaine molecule in aqueous $MgCl_2$ solutions than $CaCl_2$ or KCl aqueous solutions.

Pitkänen et al. (2010) employed the following method to calculate the partial molar volume of glycine betaine.

Let V be the total solution volume which is dimerization equilibrium dependent. Also let n_1 and n_2 be the number of moles of solvent (water) and that of solute, respectively. Consider V_1, V_f and V_a be the partial molar volume of water, of the free and associated solute, respectively. It is considered that the partial molar volumes are assumed to be constant and independent of concentration in this approach. The if $2x$ is the number of moles of solute which associates into x moles of dimeric solute and if n_1 is the number of moles of solvent, then,

$$V = n_1V_1 + (n_2 - 2x)V_f + xV_a \tag{5.2}$$

Dividing the above equation by n_1 gives the Fucaloro's volume function, V^*(Fucaloro et al. 2007),

$$V^* = \left(\frac{V_m}{X_1}\right) + V_1 + rV_f + \left[\frac{2x}{n_1}\right]\left[\frac{V_a}{2} - V_f\right] \tag{5.3}$$

where $r=n_2/n_1$ and if the degree of association is given by $a=2x/n_2$, then,

$$V^* = V_1 + rV_f + \left[\left(\frac{a}{2}\right)r\right]\left[\frac{V_a}{2} - V_f\right] \tag{5.4}$$

The values of partial molar volumes at infinite dilution for solvent, V_1°, and free glycine betaine, V_f, may be calculated by fitting V^* to a polynomial function in r. For dilute or solution with no association, $V^*=f(r)$ gives a straight line and for concentrated solutions, the third term in Equation (5.4) is also needed since an association is likely to be present in those solutions. This equation may be approximated as,

$$V^* = A + Br + Cr^2 \tag{5.5}$$

where *A* is the molar volume of water, *B* is the molar volume of free glycine betaine, and *C* is the effect of molar volume from association of glycine betaine and other changes in the glycine betaine molecule in water.

One can also calculate the apparent molar volume of glycine betaine using the relation (Hedwig and Høiland 1991),

$$\phi_v = \frac{(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M_2}{\rho} \qquad (5.6)$$

where, ϕ_v and *m* are the apparent molar volume and molality of glycine betaine in aqueous solutions, M_2 is the molar mass of glycine betaine, ρ_0 and ρ are the densities of solvents (water, aqueous KCl, $CaCl_2$ or $MgCl_2$) and that of solutions, respectively. The calculated ϕ_v values are presented in Table 5.2 and these values have been fitted by using the method of least-squares described by the expression,

$$\phi_v = \phi_v^0 + S_v m \qquad (5.7)$$

Where ϕ_v^0 the partial molar volume of the solute at infinite dilution, S_v is the volumetric pairwise interaction coefficient and *m* is the molality of the solute.

The partial molar volumes of glycine betaine at infinite dilution calculated from Equation (5.5) as well as that from Equation (5.7) at various temperatures have been presented in Table 5.3 for comparison. As can be seen from the table that the partial molar volumes calculated using both the equations shows a good agreement. The calculated partial molar volumes differ slightly from the literature values. However the available literature do have such anomalies where Bhattacharya and Sengupta (1985) considered dilute solutions of glycine betaine and Pitkänen et al. (2011) studied the more concentrated solutions. But the present system deals with the moderately concentrated glycine betaine solutions.

The ϕ_v^0 values of glycine betaine in aqueous KCl, $CaCl_2$ and $MgCl_2$ solutions have been computed using the Equation (5.7) and the values are tabulated in Table 5.4. The observed partial molar volumes of glycine betaine in all the four cases can be attributed to the interactions occurring between it and the solvent molecules. Water

molecules around the vicinity of the solute differ in properties from those molecules in the bulk. These water molecules will be referred as coordinated water molecules.

Table 5.2. Apparent Molar Volume, ϕ_v of Glycine Betaine in Aqueous, Aqueous KCl, $CaCl_2$ or $MgCl_2$ Solutions at Temperatures, T = 288.15 to 318.15 K.

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
ϕ_v ·10^6/(m^3·mol^{-1})							
Aqueous glycine betaine							
0.0482	96.37(±2.09)[b]	98.53(±2.09)	98.63(±2.10)	98.73(±2.10)	98.87(±2.11)	99.01(±2.12)	99.18(±2.12)
0.1063	97.26(±0.95)	98.28(±0.95)	99.33(±0.95)	99.44(±0.96)	99.58(±0.96)	100.69(±0.96)	100.86(±0.97)
0.5027	97.60(±0.21)	98.51(±0.21)	99.43(±0.21)	99.75(±0.21)	99.89(±0.21)	100.88(±0.21)	101.05(±0.21)
1.0023	97.83(±0.11)	98.77(±0.11)	99.73(±0.11)	100.06(±0.11)	100.20(±0.11)	101.01(±0.11)	101.29(±0.11)
1.5040	98.00(±0.07)	99.04(±0.07)	99.89(±0.08)	100.45(±0.08)	100.52(±0.08)	101.13(±0.08)	101.45(±0.08)
2.0048	98.24(±0.06)	99.42(±0.06)	100.16(±0.06)	100.85(±0.06)	100.88(±0.06)	101.33(±0.06)	101.62(±0.06)
2.5190	98.64(±0.05)	99.72(±0.05)	100.50(±0.05)	101.24(±0.05)	101.19(±0.05)	101.59(±0.05)	101.81(±0.05)
3.0081	98.81(±0.04)	99.88(±0.04)	100.78(±0.04)	101.44(±0.04)	101.54(±0.04)	101.91(±0.04)	102.00(±0.04)
Glycine betaine in 0.3020 mol·kg^{-1} aqueous KCl solution							
0.0496	99.28(±1.95)	99.43(±1.95)	99.53(±1.96)	99.81(±1.97)	98.23(±1.99)	100.43(±2.00)	100.65(±2.01)
0.1020	99.63(±0.95)	99.78(±0.95)	99.88(±0.96)	100.16(±0.96)	99.61(±0.97)	100.78(±0.98)	101.01(±0.98)
0.4981	99.86(±0.20)	100.01(±0.20)	100.31(±0.20)	100.39(±0.20)	100.40(±0.21)	101.23(±0.21)	101.25(±0.21)
0.9980	100.21(±0.10)	100.47(±0.11)	100.57(±0.11)	100.76(±0.11)	100.86(±0.11)	101.39(±0.11)	101.62(±0.11)
1.4985	100.65(±0.07)	100.80(±0.07)	100.91(±0.07)	101.05(±0.07)	101.26(±0.07)	101.69(±0.07)	101.92(±0.07)
1.9946	101.04(±0.06)	101.08(±0.06)	101.29(±0.06)	101.47(±0.06)	101.62(±0.06)	102.06(±0.06)	102.18(±0.06)
2.5002	101.46(±0.05)	101.47(±0.05)	101.58(±0.05)	101.97(±0.05)	102.02(±0.05)	102.38(±0.05)	102.47(±0.05)
2.9993	101.75(±0.04)	101.91(±0.04)	102.01(±0.04)	102.27(±0.04)	102.38(±0.04)	102.68(±0.04)	102.79(±0.04)
Glycine betaine in 0.3088 mol·kg^{-1} aqueous $CaCl_2$ solution							
0.0509	97.27(±1.95)	97.35(±1.95)	98.88(±1.95)	99.34(±1.95)	99.47(±1.95)	99.93(±1.95)	100.32(±1.95)
0.1019	99.80(±0.97)	99.17(±0.97)	100.77(±0.97)	100.22(±0.97)	100.35(±0.97)	100.83(±0.97)	101.22(±0.97)
0.4839	99.93(±0.21)	100.02(±0.21)	100.59(±0.21)	100.54(±0.21)	100.68(±0.21)	101.16(±0.21)	101.34(±0.21)
0.9712	100.16(±0.11)	100.47(±0.11)	100.91(±0.11)	100.90(±0.11)	101.04(±0.11)	101.52(±0.11)	101.59(±0.11)
1.5111	100.42(±0.07)	101.01(±0.07)	101.28(±0.07)	101.26(±0.07)	101.33(±0.07)	101.82(±0.07)	102.07(±0.07)
1.9505	100.92(±0.06)	101.30(±0.06)	101.62(±0.06)	101.64(±0.06)	101.72(±0.06)	102.15(±0.06)	102.32(±0.06)
2.4892	101.23(±0.05)	101.70(±0.05)	102.09(±0.05)	102.09(±0.05)	102.19(±0.05)	102.63(±0.05)	102.85(±0.05)
2.9351	101.51(±0.04)	102.02(±0.04)	102.45(±0.04)	102.46(±0.04)	102.60(±0.04)	103.06(±0.04)	103.35(±0.04)

Table 5.2. (*continued*)

m^a/(mol·kg^{-1})	*T*/K						
	288.15	**293.15**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
ϕ_v ·10^6/(m^3·mol^{-1})							
Glycine betaine in 0.3012 mol·kg^{-1} aqueous $MgCl_2$ solution							
0.0495	100.79(±1.93)	100.96(±1.94)	101.17(±1.95)	101.26(±1.95)	101.44(±1.96)	101.63(±1.97)	101.83(±1.98)
0.0996	100.80(±0.96)	100.97(±0.97)	102.15(±0.97)	102.25(±0.98)	102.43(±0.98)	102.63(±0.98)	102.83(±0.99)
0.4975	101.04(±0.20)	101.61(±0.20)	102.43(±0.20)	102.53(±0.20)	102.71(±0.20)	102.91(±0.20)	103.11(±0.20)
0.9862	101.23(±0.11)	101.72(±0.11)	102.68(±0.11)	102.88(±0.11)	102.96(±0.11)	103.05(±0.11)	103.36(±0.11)
1.4850	101.44(±0.07)	101.91(±0.07)	102.86(±0.07)	103.18(±0.07)	103.07(±0.07)	103.34(±0.07)	103.62(±0.07)
1.9740	101.70(±0.06)	102.11(±0.06)	103.12(±0.06)	103.40(±0.06)	103.47(±0.06)	103.73(±0.06)	103.94(±0.06)
2.4956	101.91(±0.05)	102.33(±0.05)	103.44(±0.05)	103.63(±0.05)	103.83(±0.05)	103.93(±0.05)	104.24(±0.05)
3.0000	102.19(±0.04)	102.61(±0.04)	103.89(±0.04)	104.03(±0.04)	104.14(±0.04)	104.30(±0.04)	104.60(±0.04)

[a] *m* is the molality of glycine betaine in aqueous solutions.

[b] The uncertainties in ϕ_v values are in parenthesis.

Table 5.3. Comparison of Partial Molar Volumes of Glycine Betaine at Infinite Dilution Calculated from Equation (5.5) and Equation (5.7) at Temperatures, *T* = 288.15 to 318.15 K.

T/K	**Partial molar volumes of glycine betaine at infinite dilution**		
	From Equation (5.5) $^aV_f^0$ **·10^6/(m^3·mol^{-1})**	**From Equation (5.7)** $^b\phi_v^0$ **·10^6/(m^3·mol^{-1})**	**References**
288.15	97.31(±0.06)	97.26(±0.05)	97.91(±0.04)[c]
293.15	98.37(±0.14)	98.39(±0.06)	98.07(±0.06)[c]
298.15	99.10(±0.07)	99.20(±0.04)	98.43(±0.05)[c] 100[d]
303.15	99.60(±0.14)	99.38(±0.04)	98.72(±0.03)[c] 102[d]
308.15	99.59(±0.12)	99.52(±0.01)	103[d]
313.15	100.42(±0.14)	100.62(±0.05)	-
318.15	100.99(±0.09)	100.86(±0.02)	99.02(±0.02)[c] 103[d]

[a] V_f^0 is the partial molar volume of glycine betaine at infinite dilution calculated from Equation (5.5).

[b] ϕ_v^0 is the partial molar volume of glycine betaine at infinite dilution calculated from Equation (5.7).

[c] (Pitkänen et al. 2011)

[d] (Bhattacharya and Sengupta 1985)

The total volume of the coordinated water per solute molecule varies with concentration of solute. This volume decreases as the concentration of the solute increases, because the probability of interactions between neighbouring coordinated water regions reduces this volume. Thus the partial molar volumes of glycine betaine at infinite dilution are positive indicating glycine betaine as a structure breaking molecule. By considering the size of primary and secondary solvation layers around the zwitterion, glycine betaine, it is possible to explain the trend observed in the ϕ_v^0 values with respect to temperature. At higher temperatures, the water molecules from the secondary solvation layer of glycine betaine zwitterion are released into the bulk resulting in larger ϕ_v^0 values.

Table 5.4. Partial Molar Volume, ϕ_v^0 of Glycine Betaine in Aqueous KCl, $CaCl_2$ or $MgCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K Computed Using Equation (5.7).

***T*/K**	$\phi_v^0 \cdot 10^6$ **/(m^3·mol^{-1})**		
	Glycine betaine in 0.3020 mol·kg^{-1} aqueous KCl solution	**Glycine betaine in aqueous 0.3088 mol·kg^{-1} $CaCl_2$ solution**	**Glycine betaine in aqueous 0.3012 mol·kg^{-1} $MgCl_2$ solution**
288.15	99.51(±0.03)	99.54(±0.08)	100.77(±0.01)
293.15	99.69(±0.03)	99.69(±0.06)	101.35(±0.05)
298.15	99.87(±0.04)	100.13(±0.02)	102.09(±0.05)
303.15	100.02(±0.04)	100.26(±0.04)	102.24(±0.04)
308.15	100.05(±0.03)	100.42(±0.03)	102.36(±0.05)
313.15	100.79(±0.05)	100.75(±0.05)	102.56 (±0.04)
318.15	100.97(±0.02)	100.98(±0.09)	102.77(±0.02)

5.1.2. Partial Molar Isentropic Compression Studies

The apparent molar isentropic compression, ϕ_k of glycine betaine in aqueous, aqueous KCl, $CaCl_2$ or $MgCl_2$ solutions have been computed using the equation (Riyazuddeen and Usmani 2012),

$$\phi_k = \left[\frac{(\kappa_s - \kappa_0)}{m\rho^0}\right] + \kappa_s \phi_v \qquad (5.8)$$

where m is the solution molality, ρ_0 and κ_0 (=1/ $\rho_0 c_0^2$) are the density and the isentropic compressibility of the solvent, respectively and κ_S (=1/ρc^2) is the isentropic compressibility of the solution. The method least-squares fit has been employed to fit ϕ_k values,

$$\phi_k = \phi_k^0 + S_k m \qquad (5.9)$$

where ϕ_k^0 is the apparent molar isentropic compression at infinite dilution or the partial molar isentropic compression of the system and S_K is the experimental slope.

The calculated values of $\phi_k{}^0$ and S_K along with their standard deviations have been presented in Table 5.5. By the values of $\phi_k{}^0$ it is possible to predict the extent of solute-solvent interaction present in the system (Yan et al. 2003).

Table 5.5. Partial Molar Isentropic Compression, $\phi_k{}^0$, Standard Deviation (σ) in $\phi_k{}^0$ Values and the Experimental Slope, S_k of the Equation $\phi_k = \phi_k^0 + S_k m$ for the Systems: Glycine Betaine in Aqueous, Aqueous KCl, $CaCl_2$ or $MgCl_2$ Solutions at Temperatures T = 288.15 to 318.15 K.

T/K	$\phi_k{}^0 \cdot 10^{15}$/ **($Pa^{-1} \cdot m^3 \cdot mol^{-1}$)**	$S_k \cdot 10^{15}$ / **($Pa^{-1} \cdot m^3 \cdot mol^{-2} \cdot kg$)**	$\sigma \cdot 10^{15}$/ **($Pa^{-1} \cdot m^3 \cdot mol^{-1}$)**
	Aqueous glycine betaine		
288.15	-33.04(±0.04)	9.53(±0.03)	0.8
293.15	-31.75(±0.23)	9.09(±0.14)	0.4
298.15	-28.16(±0.35)	8.65 (±0.25)	0.6
303.15	-24.90(±0.14)	7.54(±0.10)	0.2
308.15	-21.88(±0.08)	6.01(±0.05)	0.1
313.15	-17.90(±0.25)	5.26(±0.18)	0.4
318.15	-15.30(±0.21)	4.23(±0.12)	0.3

Table 5.5. (*continued*)

T/K	$\phi_k^0 \cdot 10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-1}$)	$S_k \cdot 10^{15}$ / ($Pa^{-1}\cdot m^3\cdot mol^{-2}\cdot kg$)	$\sigma \cdot 10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-1}$)
Glycine betaine in 0.3020 mol·kg^{-1} aqueous KCl solution			
288.15	-16.35(±0.41)	3.90(±0.23)	0.6
293.15	-15.45(±0.37)	3.86(±0.22)	0.6
298.15	-13.08(±0.22)	2.90(±0.12)	0.3
303.15	-11.93(±0.40)	2.66(±0.22)	0.6
308.15	-11.63(±0.39)	2.58(±0.22)	0.6
313.15	-10.02(±0.28)	2.05(±0.17)	0.5
318.15	-8.46(±0.12)	1.36(±0.07)	0.2
Glycine betaine in 0.3088 mol·kg^{-1} aqueous $CaCl_2$ solution			
288.15	-16.86(±0.04)	3.08(±0.02)	0.1
293.15	-16.66(±0.08)	3.46(±0.05)	0.2
298.15	-13.10(±0.08)	2.28(±0.05)	0.1
303.15	-12.46(±0.11)	2.08(±0.07)	0.2
308.15	-11.55(±0.07)	1.91(±0.04)	0.1
313.15	-10.43(±0.08)	1.68(±0.05)	0.1
318.15	-8.74(±0.08)	1.15(±0.05)	0.2
Glycine betaine in 0.3012 mol·kg^{-1} aqueous $MgCl_2$ solution			
288.15	-18.31(±0.48)	4.54(±0.27)	0.7
293.15	-17.87(±0.41)	4.45(±0.23)	0.6
298.15	-14.66(±0.41)	3.38(±0.23)	0.6
303.15	-13.13(±0.41)	3.03(±0.23)	0.6
308.15	-11.90(±0.43)	2.91(±0.24)	0.6
313.15	-11.17(±0.38)	2.80(±0.21)	0.5
318.15	-9.40(±0.16)	2.27(±0.09)	0.2

The values S_K are positive for glycine betaine in aqueous solutions indicating the existence of a weak solute-solute interaction in present system (Pal and Chauhan 2011).

The dependence of ϕ_k^0 values of glycine betaine with temperature indicates the release of more number of water molecules from the secondary solvation layer of glycine betaine zwitterions into the bulk, rendering the solutions more compressible at higher temperatures (Riyazuddeen and Usmani 2012, Nain et al. 2011 and Mishra and Ahluwalia 1984).

The transfer molar properties at infinite dilution of glycine betaine from water to aqueous metal salt solutions have been calculated from:

$\Delta_{tr}Y = Y_{\phi}^0$ (in aqueous metal salt solutions) - Y_{ϕ}^0 (in pure water) (5.10)

Figure 5.1 and Figure 5.2 represent the trends in transfer properties of glycine betaine from aqueous to aqueous metal salt solutions. It is evident from the table that the values of $\Delta_{tr}\phi_v^0$ are positive in aqueous KCl, $CaCl_2$ and $MgCl_2$ solutions at all the temperatures. The constituent ions of the electrolytes interact with the zwitterion "glycine betaine" and reduce the electrostriction of the solvent thereby showing a positive trend in transfer volume. This further strengthens the argument of strong ionic group interactions between zwitterionic centres of glycine betaine and the weak interactions among the hydrophobic groups of glycine betaine with hydrophilic solvent molecules (water). The overall values of $\Delta_{tr}\phi_v^0$ from water to aqueous $MgCl_2$ were found to be slightly higher than those of aqueous $CaCl_2$ or KCl solutions. This can be explained by the larger size of hydrated Mg^{2+} ions in aqueous solution than that of Ca^{2+} or K^+ ions which contributes towards the positive volume of transfer. The dominance of hydrophilic-ionic interactions between glycine betaine and metal salts in aqueous medium is further supported by the positive values of $\Delta_{tr}\phi_k^0$. The refractive index measurements are also in concordance with the results obtained from the volumetric studies.

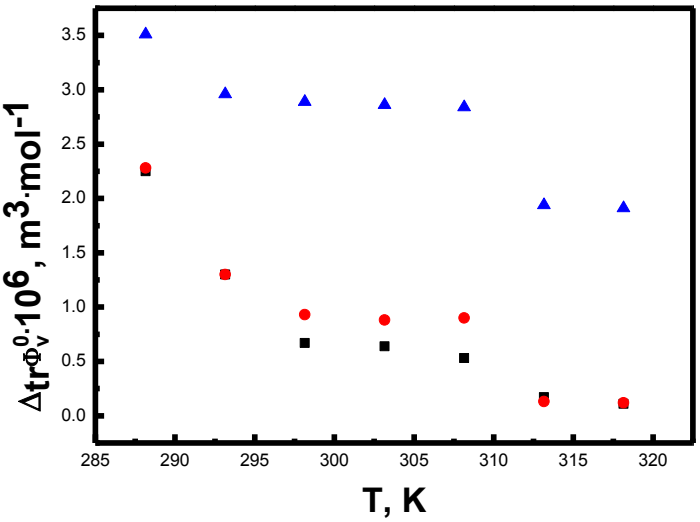

Figure 5.1. Plot of variation of transfer partial molar volumes, $\Delta_{tr}\phi_v^0$ of glycine betaine at temperatures T = 288.15 to 318.15 K in; ■, aqueous KCl, ●, aqueous $CaCl_2$ and ▲, $MgCl_2$ solutions.

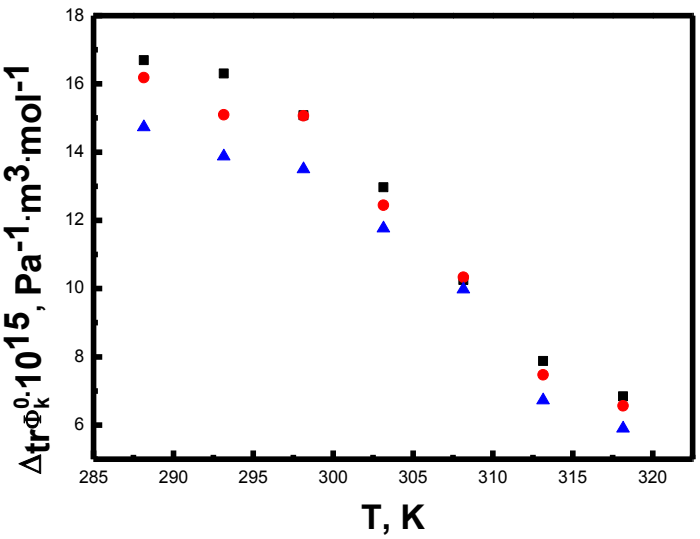

Figure 5.2. Plot of variation of transfer partial molar isentropic compressions, $\Delta_{tr}\phi_k^0$ of glycine betaine at temperatures T = 288.15 to 318.15 Kin; ■, aqueous KCl, ●, aqueous $CaCl_2$ and ▲, $MgCl_2$ solutions.

5.2. PARTIAL MOLAR VOLUMES AND COMPRESSIONS OF GLYCINE BETAINE IN AQUEOUS NaCl SOLUTIONS AT TEMPERATURES *T* = (288.15 TO 318.15) K

The results of the previous section show that the size of metal ions influences the solution properties of the solute to an appreciable extent. However the varying concentration of metal ion in such systems could also have an impact on the molecular interactions prevailing in the system. Thus in order to study the effect of NaCl on the solution properties of aqueous glycine betaine solutions, the present work has been carried out.

5.2.1. Apparent Molar Volumes and Compressions

The experimental density, speed of sound and refractive index of glycine betaine in aqueous NaCl solutions at temperatures *T* = (288.15 to 318.15) K are presented in Table 5.6.

The apparent molar volumes ϕ_v and apparent molar isentropic compression, ϕ_k of glycine betaine in aqueous NaCl solutions with different concentrations were calculated using the Equations 5.6 and 5.8, respectively:

The values of the apparent molar volume and apparent molar isentropic compression of glycine betaine in aqueous NaCl solutions at different temperatures are presented in Tables 5.7 and 5.8, respectively. The uncertainties of ϕ_v and ϕ_k were estimated using propagation of errors method (Hedwig and Høiland1991 and Marriot et al. 2001) and included in Tables 5.7 and 5.8. As can be seen from the tables, the values of ϕ_v and ϕ_k increase with the concentration of the solute at a fixed NaCl concentration.

Table 5.6. Density, ρ, Speed of Sound, c, and Refractive Index , n_D of Glycine Betaine in Aqueous NaCl Solutions at Temperatures, T = (288.15 K to 318.15) K, as a Function of Molality of Glycine Betaine.[a]

m_A[b]/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.1 mol·kg^{-1} aqueous NaCl solution				
ρ·10^{-3}/(kg·m^{-3})				
0.0000	1.0098	1.0074	1.0050	1.0025
0.0500	1.0107	1.0083	1.0059	1.0034
0.1002	1.0115	1.0091	1.0067	1.0042
0.5000	1.0178	1.0154	1.0130	1.0105
1.0020	1.0246	1.0222	1.0198	1.0172
1.5000	1.0305	1.0277	1.0253	1.0226
2.0000	1.0355	1.0323	1.0299	1.0272
2.5009	1.0396	1.0360	1.0338	1.0311
2.9990	1.0435	1.0389	1.0364	1.0339
c/(m·s^{-1})				
0.0000	1469.42	1499.24	1510.42	1525.98
0.0500	1473.98	1503.62	1514.80	1530.28
0.1002	1478.38	1508.08	1519.16	1534.62
0.5000	1513.80	1543.28	1553.60	1568.23
1.0020	1557.10	1584.96	1595.02	1610.82
1.5000	1594.04	1623.62	1631.64	1648.24
2.0000	1628.77	1658.87	1670.92	1688.35
2.5009	1661.50	1691.06	1702.00	1718.74
2.9990	1691.52	1722.95	1732.74	1748.00
n_D				
0.0000	1.33438	1.33377	1.33205	1.33032
0.0500	1.33634	1.33569	1.33395	1.33215
0.1002	1.33711	1.33646	1.33471	1.33290
0.5000	1.34206	1.34131	1.33956	1.33780
1.0020	1.35004	1.34927	1.34726	1.34478
1.5000	1.35502	1.35374	1.35223	1.35022
2.0000	1.36171	1.36068	1.35892	1.35743
2.5009	1.36790	1.36685	1.36484	1.36269
2.9990	1.37295	1.37185	1.36972	1.36728

Table 5.6. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.2 mol·kg^{-1} aqueous NaCl solution				
$\rho \cdot 10^{-3}$/(kg·m^{-3})				
0.0000	1.0109	1.0085	1.0061	1.0040
0.0487	1.0118	1.0094	1.0069	1.0048
0.1110	1.0128	1.0104	1.0079	1.0058
0.5000	1.0188	1.0164	1.0139	1.0116
0.9980	1.0256	1.0233	1.0207	1.0182
1.5000	1.0316	1.0291	1.0266	1.0239
1.9509	1.0363	1.0336	1.0312	1.0283
2.5050	1.0413	1.0384	1.0361	1.0332
2.9900	1.0451	1.0419	1.0400	1.0366
c/(m·s^{-1})				
0.0000	1480.15	1515.99	1523.62	1535.93
0.0487	1484.69	1520.17	1527.82	1540.03
0.1110	1490.19	1525.65	1533.18	1545.27
0.5000	1524.83	1558.97	1566.35	1577.64
0.9980	1564.63	1599.51	1607.00	1617.60
1.5000	1604.79	1637.94	1646.04	1656.49
1.9509	1635.52	1671.32	1678.33	1689.63
2.5050	1671.25	1706.81	1714.20	1727.79
2.9900	1700.47	1737.10	1743.94	1759.10
n_D				
0.0000	1.33483	1.33390	1.33308	1.33183
0.0487	1.33679	1.33582	1.33498	1.33366
0.1110	1.33756	1.33659	1.33584	1.33441
0.5000	1.34251	1.34144	1.33989	1.33831
0.9980	1.35049	1.34940	1.34859	1.34529
1.5000	1.35547	1.35382	1.35316	1.35073
1.9509	1.36216	1.36081	1.35925	1.35794
2.5050	1.36835	1.36698	1.36517	1.36420
2.9900	1.37340	1.37198	1.36995	1.36779

Table 5.6. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.3 mol·kg^{-1} aqueous NaCl solution				
$\rho \cdot 10^{-3}$/(kg·m^{-3})				
0.0000	1.0123	1.0105	1.0079	1.0063
0.0500	1.0132	1.0114	1.0087	1.0071
0.1100	1.0141	1.0123	1.0096	1.0080
0.5001	1.0201	1.0182	1.0154	1.0136
0.9948	1.0268	1.0247	1.0218	1.0199
1.5005	1.0327	1.0305	1.0275	1.0253
1.9419	1.0371	1.0349	1.0316	1.0295
2.5012	1.0420	1.0395	1.0363	1.0340
2.9829	1.0455	1.0430	1.0395	1.0374
c/(m·s^{-1})				
0.0000	1496.40	1530.24	1542.42	1557.98
0.0500	1500.94	1534.53	1546.66	1562.05
0.1100	1506.44	1539.70	1551.57	1566.96
0.5001	1541.08	1573.00	1583.45	1598.66
0.9948	1580.88	1612.76	1622.83	1636.96
1.5005	1621.04	1650.99	1660.64	1675.28
1.9419	1651.77	1683.57	1690.83	1706.31
2.5012	1687.50	1721.06	1728.00	1746.48
2.9829	1716.72	1751.35	1760.64	1779.04
n_D				
0.0000	1.33532	1.33464	1.33437	1.33249
0.0500	1.33728	1.33656	1.33627	1.33432
0.1100	1.33805	1.33733	1.33703	1.33507
0.5001	1.34300	1.34218	1.34188	1.33997
0.9948	1.35098	1.35014	1.34958	1.34695
1.5005	1.35596	1.35521	1.35455	1.35239
1.9419	1.36265	1.36155	1.36124	1.35960
2.5012	1.36884	1.36772	1.36716	1.36486
2.9829	1.37389	1.37272	1.37204	1.36945

Table 5.6. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.4 mol·kg^{-1} aqueous NaCl solution				
$\rho \cdot 10^{-3}$/(kg·m^{-3})				
0.0000	1.0145	1.0120	1.0100	1.0071
0.0500	1.0153	1.0128	1.0108	1.0079
0.0989	1.0160	1.0135	1.0115	1.0086
0.4990	1.0217	1.0192	1.0171	1.0141
0.9960	1.0280	1.0255	1.0232	1.0201
1.5010	1.0338	1.0311	1.0286	1.0253
1.9589	1.0383	1.0356	1.0328	1.0293
2.5020	1.0432	1.0402	1.0373	1.0335
2.9900	1.0464	1.0435	1.0406	1.0365
c/(m·s^{-1})				
0.0000	1516.61	1549.26	1559.44	1582.50
0.0487	1521.15	1553.62	1563.52	1586.54
0.1110	1525.65	1557.96	1567.58	1590.53
0.5000	1561.29	1591.95	1600.16	1622.81
0.9980	1601.62	1632.25	1639.44	1661.30
1.5000	1641.25	1670.64	1677.86	1699.26
1.9509	1671.98	1703.78	1711.25	1731.87
2.5050	1707.71	1739.64	1748.48	1770.26
2.9900	1736.80	1769.67	1780.90	1802.52
n_D				
0.0000	1.33633	1.33565	1.33458	1.33340
0.0487	1.33829	1.33757	1.33648	1.33523
0.1110	1.33906	1.33834	1.33724	1.33598
0.5000	1.34401	1.34319	1.34209	1.34088
0.9980	1.35199	1.35115	1.34979	1.34786
1.5000	1.35697	1.35662	1.35476	1.35330
1.9509	1.36366	1.36256	1.36145	1.36051
2.5050	1.36985	1.36873	1.36737	1.36577
2.9900	1.37490	1.37373	1.37225	1.37036

Table 5.6. (*continued*)

m_A[b]/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.5 mol·kg^{-1} aqueous NaCl solution				
$\rho \cdot 10^{-3}$/(kg·m^{-3})				
0.0000	1.0190	1.0161	1.0131	1.0102
0.0489	1.0197	1.0168	1.0138	1.0109
0.1090	1.0205	1.0176	1.0146	1.0117
0.4950	1.0255	1.0226	1.0196	1.0167
0.9970	1.0313	1.0283	1.0253	1.0224
1.5000	1.0364	1.0333	1.0305	1.0274
2.0000	1.0408	1.0379	1.0349	1.0316
2.4970	1.0447	1.0420	1.0391	1.0356
3.0001	1.0481	1.0455	1.0429	1.0386
c/(m·s^{-1})				
0.0000	1525.40	1561.24	1573.42	1601.98
0.0489	1529.86	1565.59	1577.57	1606.00
0.1090	1535.38	1570.92	1582.60	1610.98
0.4950	1570.04	1604.81	1614.60	1642.48
0.9970	1612.28	1646.20	1654.72	1682.82
1.5000	1650.64	1685.22	1692.79	1721.24
2.0000	1684.77	1719.57	1728.53	1758.35
2.4970	1716.50	1754.06	1762.57	1792.74
3.0001	1745.72	1782.00	1794.74	1828.01
n_D				
0.0000	1.33638	1.33592	1.33473	1.33447
0.0489	1.33834	1.33796	1.33663	1.33630
0.1090	1.33911	1.33860	1.33739	1.33705
0.4950	1.34406	1.34356	1.34224	1.34195
0.9970	1.35204	1.35136	1.34994	1.34893
1.5000	1.35702	1.35681	1.35491	1.35437
2.0000	1.36371	1.36292	1.36160	1.36158
2.4970	1.36990	1.36921	1.36752	1.36684
3.0001	1.37495	1.37417	1.37240	1.37143

[a]Standard uncertainty for temperature u(*T*) = 0.01 K; for pressure u(*p*) = 5 kPa; for molality u(*m*) = 0.0001 mol·kg^{-1}; for density u(ρ) = 0.1 kg·m^{-3}; for speed of sound u(*c*) = 0.2 m·s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.2 kg·m^{-3}; $U_c(c)$ = 0.4 m·s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.
[b] m_A is the molality of glycine betaine in aqueous NaCl solutions.

Table 5.7. Apparent Molar Volumes, ϕ_v of Glycine Betaine in Aqueous NaCl Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a](mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.1 mol·kg^{-1} aqueous NaCl solution				
0.0500	98.27(±1.97)[b]	98.46(±1.98)	98.66(±1.99)	98.86(±2.00)
0.1002	99.21(±0.99)	99.40(±0.99)	99.60(±1.00)	99.81(±1.00)
0.5000	99.53(±0.20)	99.73(±0.21)	99.93(±0.21)	100.14(±0.21)
1.0020	100.06(±0.11)	100.26(±0.11)	100.46(±0.11)	100.78(±0.11)
1.5000	100.42(±0.07)	100.92(±0.07)	101.13(±0.07)	101.49(±0.07)
2.0000	100.84(±0.06)	101.51(±0.06)	101.72(±0.06)	102.05(±0.06)
2.5009	101.34(±0.05)	102.12(±0.05)	102.24(±0.05)	102.55(±0.05)
2.9990	101.60(±0.04)	102.73(±0.04)	102.98(±0.04)	103.21(±0.04)
Glycine betaine in 0.2 mol·kg^{-1} aqueous NaCl solution				
0.0487	97.72(±2.02)	97.90(±2.03)	100.13(±2.04)	100.31(±2.05)
0.1110	98.95(±0.89)	99.15(±0.89)	100.24(±0.90)	100.42(±0.90)
0.5000	99.65(±0.20)	99.85(±0.20)	100.25(±0.21)	100.84(±0.21)
0.9980	100.02(±0.11)	100.11(±0.11)	100.53(±0.11)	101.14(±0.11)
1.5000	100.33(±0.07)	100.60(±0.07)	100.88(±0.07)	101.51(±0.07)
1.9509	100.62(±0.06)	101.00(±0.06)	101.20(±0.06)	101.86(±0.06)
2.5050	100.97(±0.05)	101.42(±0.05)	101.58(±0.05)	102.15(±0.05)
2.9900	101.27(±0.04)	101.81(±0.04)	101.81(±0.04)	102.54(±0.04)
Glycine betaine in 0.3 mol·kg^{-1} aqueous NaCl solution				
0.0500	98.07(±1.96)	98.22(±1.97)	100.40(±1.98)	100.54(±1.98)
0.1100	98.58(±0.90)	99.73(±0.90)	100.85(±0.90)	100.98(±0.91)
0.5001	99.74(±0.20)	100.09(±0.20)	100.72(±0.21)	101.27(±0.21)
0.9948	100.07(±0.11)	100.54(±0.11)	101.08(±0.11)	101.54(±0.11)
1.5005	100.44(±0.07)	100.88(±0.07)	101.40(±0.07)	101.99(±0.07)
1.9419	100.79(±0.06)	101.18(±0.06)	101.82(±0.06)	102.26(±0.06)
2.5012	101.17(±0.05)	101.66(±0.05)	102.18(±0.05)	102.65(±0.05)
2.9829	101.54(±0.04)	101.98(±0.04)	102.59(±0.04)	102.94(±0.04)

Table 5.7. (*continued*)

m_A[a]/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.4 mol·kg^{-1} aqueous NaCl solution				
0.0500	99.85(±1.95)	100.06(±1.96)	100.23(±1.97)	100.47(±1.98)
0.0989	100.59(±0.99)	100.80(±1.00)	100.97(±1.00)	101.22(±1.01)
0.4990	100.74(±0.20)	100.95(±0.20)	101.33(±0.21)	101.79(±0.21)
0.9960	100.96(±0.11)	101.18(±0.11)	101.67(±0.11)	102.14(±0.11)
1.5010	101.06(±0.07)	101.42(±0.07)	101.96(±0.07)	102.52(±0.07)
1.9589	101.29(±0.06)	101.63(±0.06)	102.27(±0.06)	102.88(±0.06)
2.5020	101.46(±0.05)	101.92(±0.05)	102.52(±0.05)	103.22(±0.05)
2.9900	101.91(±0.04)	102.29(±0.04)	102.84(±0.04)	103.60(±0.04)
Glycine betaine in 0.5 mol·kg^{-1} aqueous NaCl solution				
0.0489	101.11(±1.98)	101.36(±1.99)	101.62(±2.00)	101.87(±2.01)
0.1090	101.56(±0.89)	101.81(±0.90)	102.08(±0.90)	102.33(±0.91)
0.4950	101.67(±0.20)	101.92(±0.20)	102.19(±0.21)	102.44(±0.21)
0.9970	101.85(±0.11)	102.21(±0.11)	102.48(±0.11)	102.74(±0.11)
1.5000	102.05(±0.07)	102.45(±0.07)	102.57(±0.07)	102.98(±0.07)
2.0000	102.28(±0.06)	102.54(±0.06)	102.80(±0.06)	103.29(±0.06)
2.4970	102.47(±0.05)	102.63(±0.05)	102.85(±0.05)	103.40(±0.05)
3.0001	102.69(±0.04)	102.83(±0.04)	102.93(±0.04)	103.77(±0.04)

[a]m_A is the molality of glycine betaine in aqueous NaCl solutions.

[b]Estimated uncertainty for each ϕ_v is in brackets. The experiment was carried out under atmosphere pressure.

Table 5.8. Apparent Molar Isentropic Compressions, ϕ_k of Glycine Betaine in Aqueous NaCl Solutions at Temperatures, T = (288.15 to 318.15) K.

m^a/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
ϕ_k ·10^{15}/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.1 mol·kg^{-1} aqueous NaCl solution				
0.0500	-19.40(±0.25)[b]	-15.59(±0.23)	-15.10(±0.23)	-13.51(±0.22)
0.1002	-17.43(±0.12)	-15.11(±0.12)	-14.05(±0.11)	-12.82(±0.11)
0.5000	-16.53(±0.02)	-14.61(±0.02)	-13.19(±0.02)	-11.54(±0.02)
1.0020	-15.16(±0.01)	-12.67(±0.01)	-11.64(±0.01)	-11.08(±0.01)
1.5000	-12.31(±0.01)	-10.73(±0.01)	-9.25(±0.01)	-8.96(±0.01)
2.0000	-10.14(±0.01)	-8.74(±0.01)	-8.60(±0.01)	-8.46(±0.01)
2.5009	-8.32(±0.01)	-6.85(±0.01)	-6.54(±0.01)	-6.24(±0.01)
2.9990	-6.82(±0.01)	-5.54(±0.01)	-4.99(±0.01)	-4.52(±0.01)
Glycine betaine in 0.2 mol·kg^{-1} aqueous NaCl solution				
0.0487	-20.30(±0.25)	-14.06(±0.23)	-12.28(±0.23)	-10.66(±0.22)
0.1110	-17.49(±0.11)	-13.65(±0.10)	-12.12(±0.10)	-10.55(±0.10)
0.5000	-16.04(±0.02)	-12.40(±0.02)	-11.70(±0.02)	-9.82(±0.02)
0.9980	-12.93(±0.01)	-10.93(±0.01)	-10.45(±0.01)	-8.81(±0.01)
1.5000	-11.78(±0.01)	-9.34(±0.01)	-9.22(±0.01)	-7.88(±0.01)
1.9509	-9.73(±0.01)	-8.27(±0.01)	-7.90(±0.01)	-6.94(±0.01)
2.5050	-7.81(±0.01)	-6.41(±0.01)	-6.20(±0.01)	-5.84(±0.01)
2.9900	-6.40(±0.01)	-5.22(±0.01)	-5.04(±0.01)	-4.83(±0.01)
Glycine betaine in 0.3 mol·kg^{-1} aqueous NaCl solution				
0.0500	-17.38(±0.23)	-12.86(±0.22)	-10.23(±0.21)	-7.86(±0.21)
0.1100	-16.30(±0.10)	-11.70(±0.10)	-9.00(±0.10)	-7.63(±0.09)
0.5001	-14.91(±0.02)	-11.10(±0.02)	-8.56(±0.02)	-7.35(±0.02)
0.9948	-12.12(±0.01)	-9.44(±0.01)	-7.74(±0.01)	-6.30(±0.01)
1.5005	-10.82(±0.01)	-8.01(±0.01)	-6.62(±0.01)	-5.54(±0.01)
1.9419	-9.02(±0.01)	-7.14(±0.01)	-5.31(±0.01)	-4.66(±0.01)
2.5012	-7.04(±0.01)	-5.69(±0.01)	-4.22(±0.01)	-4.14(±0.01)
2.9829	-5.67(±0.01)	-4.62(±0.01)	-3.65(±0.01)	-3.57(±0.01)

Table 5.8. (*continued*)

m^a/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$ /(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.4 mol·kg^{-1} aqueous NaCl solution				
0.0500	-14.47(±0.22)	-11.06(±0.21)	-7.81(±0.21)	-6.67(±0.20)
0.0989	-14.16(±0.11)	-10.85(±0.11)	-7.58(±0.10)	-6.28(±0.10)
0.4990	-12.94(±0.02)	-9.51(±0.02)	-7.04(±0.02)	-5.78(±0.02)
0.9960	-10.54(±0.01)	-8.29(±0.01)	-6.29(±0.01)	-4.90(±0.01)
1.5010	-9.32(±0.01)	-7.03(±0.01)	-5.55(±0.01)	-4.22(±0.01)
1.9589	-7.38(±0.01)	-6.07(±0.01)	-4.85(±0.01)	-3.47(±0.01)
2.5020	-5.99(±0.01)	-4.76(±0.01)	-4.00(±0.01)	-2.95(±0.01)
2.9900	-4.55(±0.01)	-3.63(±0.01)	-3.32(±0.01)	-2.30(±0.01)
Glycine betaine in 0.5 mol·kg^{-1} aqueous NaCl solution				
0.0489	-12.69(±0.22)	-9.99(±0.21)	-7.54(±0.20)	-5.35(±0.21)
0.1090	-12.49(±0.10)	-9.55(±0.09)	-6.87(±0.10)	-5.19(±0.09)
0.4950	-11.65 (±0.02)	-9.13(±0.02)	-6.41(±0.02)	-4.91(±0.02)
0.9970	-9.97(±0.01)	-7.65(±0.01)	-5.58(±0.01)	-4.57(±0.01)
1.5000	-8.10(±0.01)	-6.42(±0.01)	-4.79(±0.01)	-3.91(±0.01)
2.0000	-6.23(±0.01)	-4.93(±0.01)	-3.92(±0.01)	-3.35(±0.01)
2.4970	-4.78(±0.01)	-4.18(±0.01)	-3.29(±0.01)	-2.74(±0.01)
3.0001	-3.40(±0.01)	-2.67(±0.01)	-2.60(±0.01)	-2.30(±0.01)

[a]*m* is the molality of glycine betaine in aqueous NaCl solutions.

[b]Estimated uncertainty for each ϕ_k is in brackets. The experiment was carried out under atmosphere pressure.

The method least-squares fit (Equations 5.7 and 5.9) has been employed to fit ϕ_v and ϕ_k values. The values of ϕ_v^0 and ϕ_k^0 along with the slopes are listed in Tables 5.9 and 5.10, respectively. So obtained values have been compared with those available in the literature. The infinite dilution properties (or partial molar quantities) are important because these values describe solely the interactions between glycine betaine and the solvent molecules, as the interactions among glycine betaine molecules are negligible at infinite dilution (Soto et al. 2004).

Table 5.9. Least Squares Fit Parameters of the Equation, $\phi_v = \phi_v^0 + S_v m$ for the System: Glycine Betaine in Aqueous NaCl Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6$/ $(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6$/ $(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6$/ $(m^3 \cdot mol^{-1})$
	Glycine betaine in 0.1 mol·kg^{-1} aqueous NaCl solution		
288.15	99.15(±0.04)	0.84(±0.02)	0.1
298.15	99.18(±0.05)	1.16(±0.03)	0.1
308.15	99.38(±0.05)	1.17(±0.03)	0.1
318.15	99.63(±0.04)	1.19(±0.03)	0.1
	Glycine betaine in 0.2 mol·kg^{-1} aqueous NaCl solution		
288.15	99.35(±0.02)	0.64(±0.01)	0.1
298.15	99.39(±0.05)	0.81(±0.02)	0.1
308.15	100.00(±0.05)	0.61(±0.02)	0.1
318.15	100.37(±0.04)	0.73(±0.02)	0.1
	Glycine betaine in 0.3 mol·kg^{-1} aqueous NaCl solution		
288.15	99.42(±0.03)	0.70(±0.02)	0.1
298.15	99.70(±0.03)	0.78(±0.02)	0.1
308.15	100.34(±0.02)	0.74(±0.01)	0.1
308.15	100.91(±0.02)	0.69(±0.01)	0.1

Table 5.9. (*continued*)

***T*/K**	$\phi_v^0 \cdot 10^6$/ **($m^3 \cdot mol^{-1}$)**	$S_v \cdot 10^6$/ **($m^3 \cdot mol^{-2} \cdot kg$)**	$\sigma \cdot 10^6$/ **($m^3 \cdot mol^{-1}$)**
	Glycine betaine in 0.4 mol·kg^{-1} aqueous NaCl solution		
288.15	100.51(±0.06)	0.42(±0.03)	0.1
298.15	100.70(±0.04)	0.50(±0.02)	0.1
308.15	100.99(±0.04)	0.63(±0.02)	0.1
318.15	101.30(±0.06)	0.79(±0.04)	0.1
	Glycine betaine in 0.5 mol·kg^{-1} aqueous NaCl solution		
288.15	101.48(±0.02)	0.40(±0.01)	0.1
298.15	101.81(±0.05)	0.35(±0.03)	0.1
308.15	102.09(±0.05)	0.31(±0.03)	0.1
318.15	102.24(±0.04)	0.50(±0.02)	0.1
288.15	101.48(±0.02)	0.40(±0.01)	0.1

[a]Standard deviations are in parentheses.

Table 5.10. Least Squares Fit Parameters of the Equation, $\phi_k = \phi_k^{\,0} + S_k m$ for the System: Glycine Betaine in Aqueous NaCl Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_k^{\,0}\cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})	$S_k\cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-2}·kg)	$\sigma\cdot 10^{15}$/ (Pa^{-1}·m^3·mol^{-1})
	Glycine betaine in 0.1 mol·kg^{-1} aqueous NaCl solution		
288.15	-18.71(±0.35)	4.09(±0.21)	0.6
298.15	-15.89(±0.19)	3.50(±0.11)	0.3
308.15	-14.79(±0.23)	3.28(±0.13)	0.3
318.15	-13.42(±0.27)	2.84(±0.16)	0.4
	Glycine betaine in 0.2 mol·kg^{-1} aqueous NaCl solution		
288.15	-17.60(±0.33)	3.89(±0.19)	0.4
298.15	-13.99(±0.09)	2.98(±0.05)	0.1
308.15	-12.68(±0.16)	2.50(±0.10)	0.2
318.15	-10.79(±0.02)	1.98(±0.01)	0.1
	Glycine betaine in 0.3 mol·kg^{-1} aqueous NaCl solution		
288.15	-16.82(±0.29)	3.90(±0.18)	0.5
298.15	-12.36(±0.21)	2.67 (±0.12)	0.3
308.15	-9.74(±0.22)	2.14(±0.13)	0.3
308.15	-7.87(±0.10)	1.51(±0.06)	0.1

Table 5.10. (*continued*)

T/K	$\phi_k^{\,0}\cdot10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-1}$)	$S_k\cdot10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-2}\cdot kg$)	$\sigma\cdot10^{15}$/ ($Pa^{-1}\cdot m^3\cdot mol^{-1}$)
Glycine betaine in 0.4 mol·kg^{-1} aqueous NaCl solution			
288.15	-14.43(±0.18)	3.41(±0.11)	0.3
298.15	-10.95(±0.11)	2.50(±0.06)	0.1
308.15	-7.80(±0.03)	1.51(±0.02)	0.1
318.15	-6.49(±0.09)	1.45(±0.06)	0.1
Glycine betaine in 0.5 mol·kg^{-1} aqueous NaCl solution			
288.15	-12.98(±0.12)	3.25(±0.07)	0.2
298.15	-10.07(±0.12)	2.44(±0.07)	0.2
308.15	-7.25(±0.11)	1.60(±0.07)	0.2
318.15	-5.42(±0.06)	1.04(±0.03)	0.1

[a]Standard deviations are in parentheses.

A close perusal of Tables 5.9 and 5.10 suggests that values of ϕ_v^0 and ϕ_k^0 are large and positive and are much larger than the values of S_v and S_k thereby, indicating the presence of strong solute–solvent interactions in the present systems. The variation of these derived properties of glycine betaine at different concentrations of NaCl is shown in Figures 5.3 and 5.4. As depicted by the figures, with the temperature, ϕ_v^0 and ϕ_k^0 values follow an increasing trend. Further, the partial molar volumes and compressions of glycine betaine in 0.4 and 0.5 mol·kg^{-1} NaCl aqueous solutions were found to be more positive than those in lower NaCl concentrations which hints much stronger solute-solvent interactions at higher NaCl concentrations.

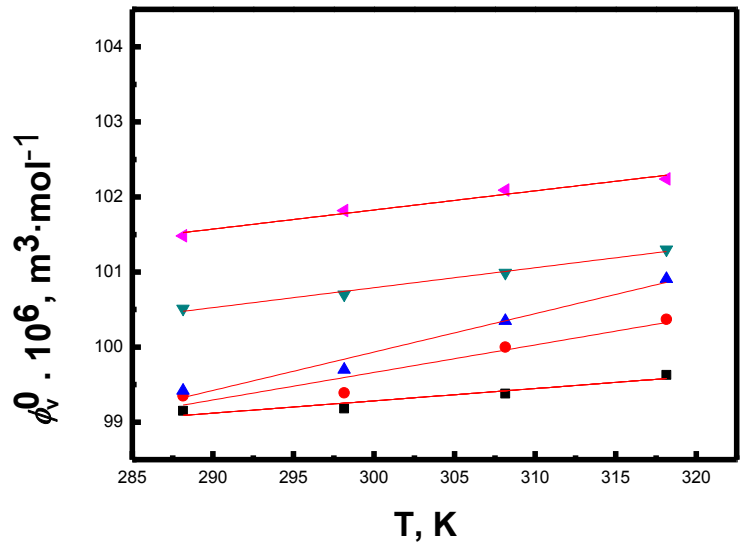

Figure 5.3. Variation of ϕ_v^0 of glycine betaine in aqueous NaCl solutions with respect to temperature at different concentration of NaCl.■, 0.1 mol·kg^{-1}; ●, 0.2 mol·kg^{-1}; ▲, 0.3 mol·kg^{-1}; ▼, 0.4 mol·kg^{-1}; ◄, 0.5 mol·kg^{-1}.

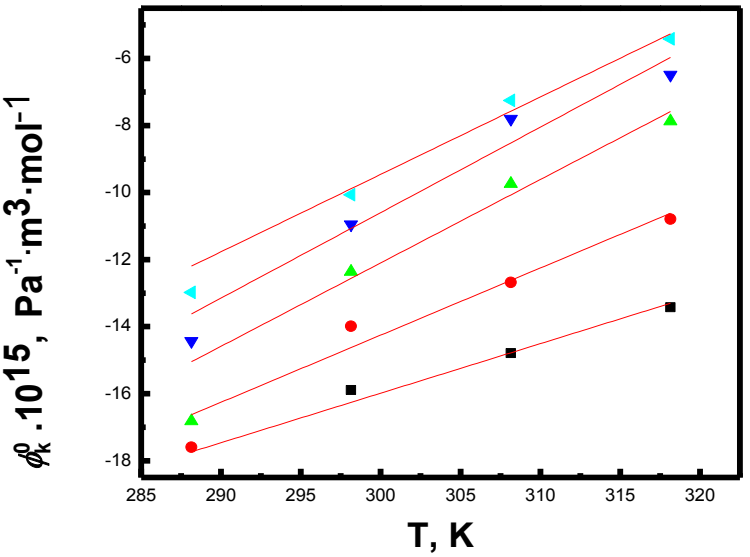

Figure 5.4. Variation of ϕ_k^0 of glycine betaine in aqueous NaCl solutions with respect to temperature at different concentration of NaCl.■, 0.1 mol·kg^{-1}; ●, 0.2 mol·kg^{-1}; ▲, 0.3 mol·kg^{-1}; ▼, 0.4 mol·kg^{-1}; ◄, 0.5 mol·kg^{-1}.

Glycine betaine can be regarded as a 'doubly charged' derivative of a peptide-'glycine' whose all the three hydrogen atoms in amino group are replaced by (-CH_3) groups. As a result of dissociation of amino and carboxyl groups of the molecule, it essentially behaves as a zwitterion. The solute-solvent interactins operative in this case can be explained as: (i) electrostatic hydration of charged terminals of the zwitter ion, and (ii) the overlap of hydration co-spheres of these terminal groups with that of –CH_2 group of glycine betaine thus contributing enhanced ϕ_v^0 values (Nain and Pal 2013). At higher temperatures, water molecules from the secondary solvation layer of betaine zwitterions are released into the bulk resulting in larger ϕ_v^0 values and rendering the solutions more compressible. Thus, increasing temperature favours the process of releasing water molecules rather than binding to the charged end groups (Riyazuddeen and Afrin 2012).

Water molecules in the vicinity of the solute differ in properties from those molecules in the bulk. Water molecules which are in direct contact with the peptide surface are said to constitute a hydration co-sphere. The interactions among the constituent ions of the solvent (i.e. sodium and chloride) and the charged groups of peptides influence the hydration co-sphere of peptides. These charged groups in turn influence the water molecules in the hydration co-sphere to exhibit different physicochemical characteristics as compared to bulk water. The partial molar isentropic compression values were negative and can be attributed to the electrostriction at the terminals of the zwitterion that reduces the mobility of the hydration water. Also, its contribution to the relaxation part of the compression has a decreasing effect on the total compression. The positive values of S_v and S_k suggest that the pairwise interaction is dominated by the interaction of the charged functional groups (of glycine betaine) with ions of the solvent (Na^+/Cl^-); (Shekaari and Jebali 2010) thus, both the volumetric and compression results complement each other.

Further, it has also been found that the effect of glycine betaine concentration on the ϕ_k^0 values decreases at higher NaCl concentrations owing to the reduction in the magnitude of the electrostatic interactions between the glycine betaine and water

molecules; because at higher NaCl concentrations, the charged groups of peptides are surrounded by a large concentration of oppositely charged sodium and chloride ions.

5.2.2. Transfer Thermodynamic Properties

Transfer thermodynamic properties of biomolecules provide qualitative and quantitative information regarding the co-solvent-solute interactions without take into account the effects of solute-solute interactions. A thermodynamic transfer function may be defined as the change in an apparent molar thermodynamic property obtained at infinite dilution when one mole of a solute is transferred from one solvent system to another solvent system (Hakin et al. 2003). The transfer molar volumes, $\Delta_{tr}\phi_v^0$ and transfer molar isentropic compressions, $\Delta_{tr}\phi_k^0$ of glycine betaine from water to aqueous NaCl solutions have been calculated from Equation 5.10. The values of transfer properties are presented in Table 5.11.

As can be seen from the table, the transfer properties increase with the molar concentration of the NaCl solutions. The negative values of $\Delta_{tr}\phi_v^0$ at 0.1 mol·kg^{-1} (298.15 K and 318.15 K) and at 0.2 mol·kg^{-1} (318.15 K) can be explained based on dehydration of glycine betaine in NaCl solution. At these concentrations, mutual interaction between molecules and ions of the electrolyte may cause some water molecules to squeeze out from the hydration co-sphere into typical bulk water (Palecz and Piekarski 1999). With the increase in the NaCl concentration in the solution, the direct interaction between glycine betaine and salt ions strengthens and contributes a positive volume transfer. Also, the electrostriction of water decreases and causes the release of water molecules into the bulk solution leading to an increase in volume (Riyazuddeen and Afrin 2012). Thus the structure-breaking tendency of the ions diminishes accordingly.

It has been reported that the amino group causes more electrostriction than the carboxyl group (Edsall and Wyman 1935). Similarly, smaller ions such as Na^+ ions produce larger electrostriction of the solvent due to their stronger electrical fields near the ions, and hence cause increased compression and orientation effects. Thus, in the present study, the strong interactions of NaCl with glycine betaine results in an

increased volume and the positive values of ϕ_v^0 (Tyrrell and Kennerley 1968, Millero et al. 1978, Kikuchi et al. 1995, Kharakoz 1997, Yan et al. 1998 and Thakur et al. 2013). However, the interaction between the ionic groups of the solvent NaCl and the nonpolar (-CH_2 and-CH_3) groups of the glycine betaine molecule should have caused a decrease in the volume transfer of glycine betaine. But the positive volume transfers of glycine betaine in this work indicate that, the electrostatic charge–charge interactions (among Na^+, Cl^-, amino and carboxylic groups of betaine glycine molecules) are predominant than the ionic–hydrophobic interactions (i.e. among Na^+, Cl^-, -CH_2 or -CH_3 groups of the glycine betaine) in aqueous solutions.

Table 5.11. Transfer Partial Molar Volumes, $\Delta_{tr}\phi_v^0$ and Transfer Partial Molar Isentropic Compressions, $\Delta_{tr}\phi_k^0$ of Glycine Betaine in Aqueous NaCl Solution sat Temperatures, T = (288.15 to 318.15) K.

***T*/K**	**$^a m_B$/(mol·kg^{-1})**				
	0.1	**0.2**	**0.3**	**0.4**	**0.5**
$\Delta_{tr}\phi_v^0 \cdot 10^6$/(m^3·mol^{-1})					
288.15	1.89	2.09	2.16	3.25	4.22
298.15	-0.02	0.19	0.50	1.50	2.61
308.15	-0.14	0.48	0.82	1.47	2.57
318.15	-1.23	-0.49	0.05	0.44	1.38
$\Delta_{tr}\phi_k^0 \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})					
288.15	14.33	15.44	16.22	18.61	20.06
298.15	12.27	14.17	15.80	17.21	18.09
308.15	7.09	9.20	12.14	14.08	14.63
318.15	1.88	4.51	7.43	8.81	9.88

$^a m_B$ is the molar concentration of NaCl solution.

5.2.3. Comparison of Partial Molar Volumes and Partial Molar Isentropic Compressions in Different Metal Salt Solutions

It is interesting to compare the results of the present study to have an idea of the effect of metal ions on the volumetric and compression parameters of glycine betaine in aqueous solutions. The $\Delta_{tr}\phi_v^0$ values of glycine betaine in aqueous metal salt solutions (at 0.3 mol·kg^{-1}) roughly follow the order $\Delta_{tr}\phi_v^0(KCl) < \Delta_{tr}\phi_v^0(NaCl) < \Delta_{tr}\phi_v^0(CaCl_2) < \Delta_{tr}\phi_v^0(MgCl_2)$. This trend may be due to greater hydrophilic-ionic interactions in aqueous $MgCl_2$ solutions owing to the size of the metal ions. However $\Delta_{tr}\phi_k^0$ values follow different trend $\Delta_{tr}\phi_k^0(NaCl) > \Delta_{tr}\phi_k^0(KCl) > \Delta_{tr}\phi_k^0(CaCl_2) > \Delta_{tr}\phi_k^0(MgCl_2)$. Since K^+ is a structure breaker, Na^+ and Ca^{2+} are borderline and Mg^{2+} is a structure maker ion, the dehydration of glycine betaine molecules in aqueous KCl is more difficult than in other solutions. This is due to the large size of K^+ ions than Na^+, Ca^{2+} or Mg^{2+} ions (Wang et al. 2009 and Jerome and Snell 1969). Similar type of observations based on enthalpic pairwise coefficient studies have been reported by W. Shen et al. (2011) for glycine betaine in NaCl or KCl solutions.

The refractive indices, n_D of glycine betaine in aqueous NaCl solutions were recorded as a function of the molar concentration of the solute and are presented in Table 5.7. The values of n_D were found to increase with the solute concentration in all the cases. The characteristics of n_D shows that the dipole in the compounds lies perpendicular to the long axis of the molecules and is responsible for the intermolecular attractions (Thakur et al. 2013).This behaviour is consistent with the results obtained for the effect of glycine betaine and NaCl concentrations on the apparent molar volume and the isentropic compression, indicating that the refractive index is directly related to the interactions in the solution.

CHAPTER 6

INVESTIGATION OF SOLUTION BEHAVIOUR OF GLYCINE BETAINE IN AQUEOUS SOLUTIONS OF SOME TRANSITION METAL CHLORIDES AT DIFFERENT TEMPERATURES

Chapter 6 presents a detailed study on the interactions in glycine betaine - transition metal chloride aqueous solutions. The transition metal salts employed in the study are, $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$.

6.1. VOLUMETRIC STUDIES

Size and nature of transition metal ions influence the volumetric properties of amino acids, peptides and their derivatives. Study of such biomolecules-electrolyte systems by means of molar volumes and compressions can provide greater insight into the structural and unfolding nature of globular proteins. In order to understand the volumetric behaviour of glycine betaine in aqueous transition metal salt solutions with equal charge, the present work has been carried-out. Thus, the isentropic compressibility, partial molar volume, partial molar isentropic compression and transfer molar quantities of glycine betaine in aqueous solutions of $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ at various temperatures have been reported.

The experimental densities, ρ, speed of sound, c and calculated isentropic compressibilities, κ_S of glycine betaine in aqueous solutions of $MnCl_2$, $CoCl_2$ and $NiCl_2$ (of concentration between 0.1 and 0.5 $mol \cdot kg^{-1}$ with 0.1 $mol \cdot kg^{-1}$ intervals) at temperatures T = (288.15, 298.15, 308.15 and 318.15) K are presented as Tables 6.1, 6.2 and 6.3, respectively. Also, the basic data for the system: glycine betaine in aqueous zinc chloride solution (of concentration 0.0971 $mol \cdot kg^{-1}$) have been given in Table 6.4. Higher concentrations in case of $ZnCl_2$ have been omitted due to precipitation constraints. Representative plots namely, Figure 6.1, Figure 6.2 and Figure 6.3 depict variation of density, ρ of the solutions with respect to molality of glycine betaine in approximately 0.3 $mol \cdot kg^{-1}$ aqueous of $MnCl_2$, $CoCl_2$ and $NiCl_2$, respectively at different temperatures. Similarly, Figure 6.4 shows the density variation with respect to solute concentration at different temperatures for the system glycine betaine in 0.0971 $mol \cdot kg^{-1}$ zinc chloride aqueous solution.

Table 6.1. Density, ρ, Speed of Sound, c, and Isentropic Compressibility, κ_S of Glycine Betaine in Aqueous $MnCl_2$ solutions at Temperatures, T = (288.15 K to 318.15) K as a Function of Molality of Glycine Betaine.[a]

m_A[b]/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.0903 mol·kg^{-1} aqueous $MnCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0095	1.0065	1.0049	1.0019
0.0499	1.0104	1.0074	1.0058	1.0028
0.1000	1.0112	1.0082	1.0066	1.0035
0.5049	1.0177	1.0146	1.0129	1.0095
1.0070	1.0249	1.0218	1.0199	1.0163
1.5000	1.0311	1.0280	1.0259	1.0223
2.0066	1.0367	1.0337	1.0315	1.0278
2.5010	1.0415	1.0388	1.0362	1.0326
3.0014	1.0459	1.0430	1.0406	1.0370
c/(m·s^{-1})				
0.0000	1478.38	1505.20	1531.23	1557.15
0.0499	1483.49	1510.17	1536.20	1561.75
0.1000	1488.52	1515.29	1541.32	1566.52
0.5049	1528.19	1554.71	1581.02	1603.66
1.0070	1574.40	1600.18	1625.20	1647.82
1.5000	1619.98	1641.05	1663.44	1689.26
2.0066	1659.98	1677.46	1696.00	1725.88
2.5010	1688.08	1708.44	1721.62	1754.95
3.0014	1715.82	1732.12	1746.95	1785.62
$\kappa_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.532	4.385	4.244	4.116
0.0499	4.497	4.353	4.213	4.088
0.1000	4.463	4.320	4.182	4.061
0.5049	4.208	4.078	3.950	3.852
1.0070	3.936	3.822	3.712	3.624
1.5000	3.696	3.612	3.523	3.428
2.0066	3.501	3.438	3.370	3.266
2.5010	3.369	3.298	3.256	3.144
3.0014	3.248	3.196	3.149	3.024

Table 6.1. (*continued*)

m_A^b/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.2001 mol·kg^{-1} aqueous $MnCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0219	1.0177	1.0135	1.0093
0.0487	1.0227	1.0185	1.0143	1.0101
0.1110	1.0236	1.0194	1.0152	1.0110
0.4973	1.0292	1.0250	1.0207	1.0163
0.9944	1.0356	1.0314	1.0270	1.0225
1.5101	1.0416	1.0374	1.0322	1.0279
1.9894	1.0466	1.0424	1.0362	1.0323
2.4890	1.0510	1.0468	1.0401	1.0362
2.9859	1.0551	1.0509	1.0432	1.0396
c/(m·s^{-1})				
0.0000	1488.83	1514.04	1538.63	1562.99
0.0487	1493.95	1519.10	1543.67	1567.59
0.1110	1500.31	1525.49	1550.20	1573.63
0.4973	1539.81	1564.62	1589.38	1610.43
0.9944	1587.39	1610.00	1636.00	1655.10
1.5101	1634.04	1656.70	1678.35	1697.70
1.9894	1667.56	1690.87	1711.57	1733.78
2.4890	1698.04	1716.25	1737.25	1764.05
2.9859	1728.74	1746.95	1766.15	1792.75
$\kappa_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.415	4.287	4.168	4.056
0.0487	4.381	4.255	4.137	4.029
0.1110	4.340	4.215	4.099	3.994
0.4973	4.098	3.985	3.878	3.794
0.9944	3.832	3.740	3.638	3.570
1.5101	3.596	3.512	3.439	3.375
1.9894	3.436	3.355	3.294	3.223
2.4890	3.300	3.243	3.186	3.101
2.9859	3.171	3.118	3.073	2.993

Table 6.1. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0330	1.0303	1.0272	1.0243
0.0500	1.0336	1.0309	1.0278	1.0249
0.1000	1.0341	1.0314	1.0283	1.0254
0.5007	1.0382	1.0355	1.0324	1.0296
0.9722	1.0425	1.0398	1.0368	1.0339
1.4535	1.0464	1.0437	1.0407	1.0380
1.9312	1.0498	1.0470	1.0441	1.0413
2.4216	1.0530	1.0500	1.0472	1.0443
3.0009	1.0559	1.0528	1.0501	1.0474
c/(m·s^{-1})				
0.0000	1497.80	1524.90	1552.43	1579.02
0.0500	1503.41	1530.38	1557.77	1584.15
0.1000	1508.87	1535.81	1563.24	1589.36
0.5007	1552.15	1578.89	1605.13	1629.80
0.9722	1599.28	1626.87	1650.80	1674.45
1.4535	1645.61	1671.85	1692.58	1717.88
1.9312	1685.70	1710.51	1727.36	1757.80
2.4216	1719.67	1742.96	1757.25	1785.22
3.0009	1757.79	1782.44	1793.78	1824.12
$\kappa_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.315	4.174	4.039	3.916
0.0500	4.280	4.142	4.009	3.888
0.1000	4.248	4.111	3.980	3.861
0.5007	3.998	3.874	3.760	3.656
0.9722	3.750	3.634	3.539	3.450
1.4535	3.529	3.428	3.354	3.265
1.9312	3.352	3.264	3.210	3.108
2.4216	3.211	3.135	3.092	3.005
3.0009	3.065	2.990	2.960	2.869

Table 6.1. (*continued*)

m_A^b/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.3772 mol·kg^{-1} aqueous $MnCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0372	1.0355	1.0342	1.0327
0.0510	1.0378	1.0361	1.0348	1.0333
0.0999	1.0382	1.0365	1.0352	1.0337
0.4823	1.0418	1.0400	1.0387	1.0372
0.9679	1.0458	1.0440	1.0426	1.0411
1.4850	1.0495	1.0477	1.0462	1.0447
1.9439	1.0523	1.0506	1.0489	1.0475
2.5020	1.0552	1.0536	1.0518	1.0504
2.8991	1.0569	1.0555	1.0535	1.0521
c/(m·s^{-1})				
0.0000	1507.61	1528.29	1550.37	1570.50
0.0510	1513.15	1533.76	1555.86	1575.65
0.0999	1518.65	1539.15	1561.09	1580.74
0.4823	1560.29	1580.37	1600.56	1619.20
0.9679	1608.62	1628.66	1643.92	1665.30
1.4850	1656.25	1668.84	1690.93	1710.26
1.9439	1692.98	1706.52	1724.89	1741.87
2.5020	1728.71	1740.17	1754.04	1772.26
2.8991	1749.80	1762.12	1776.78	1798.52
$\kappa_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.242	4.135	4.023	3.926
0.0510	4.208	4.103	3.992	3.898
0.0999	4.176	4.073	3.964	3.872
0.4823	3.943	3.850	3.758	3.677
0.9679	3.695	3.611	3.549	3.464
1.4850	3.473	3.427	3.343	3.273
1.9439	3.316	3.268	3.204	3.146
2.5020	3.171	3.134	3.090	3.031
2.8991	3.090	3.051	3.007	2.938

Table 6.1. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.4653 mol·kg^{-1} aqueous $MnCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0406	1.0392	1.0371	1.0351
0.0512	1.0411	1.0397	1.0376	1.0356
0.1050	1.0416	1.0402	1.0381	1.0361
0.5000	1.0451	1.0436	1.0416	1.0396
1.0000	1.0489	1.0475	1.0455	1.0435
1.5008	1.0522	1.0509	1.0489	1.0470
1.9980	1.0549	1.0536	1.0516	1.0498
2.5008	1.0572	1.0559	1.0539	1.0521
3.0000	1.0591	1.0578	1.0559	1.0540
c/(m·s^{-1})				
0.0000	1516.86	1539.29	1563.62	1585.75
0.0512	1522.37	1544.48	1568.80	1590.88
0.1050	1528.15	1549.92	1574.18	1596.25
0.5000	1569.54	1588.72	1612.80	1634.45
1.0000	1617.87	1634.26	1657.86	1679.42
1.5008	1662.35	1677.14	1700.18	1720.51
1.9980	1701.23	1715.22	1736.44	1757.12
2.5008	1729.96	1744.17	1767.29	1787.68
3.0000	1760.05	1775.12	1795.03	1817.77
$\kappa_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.177	4.061	3.944	3.842
0.0512	4.144	4.032	3.916	3.815
0.1050	4.111	4.002	3.887	3.788
0.5000	3.884	3.796	3.691	3.601
1.0000	3.642	3.574	3.480	3.398
1.5008	3.439	3.383	3.298	3.227
1.9980	3.275	3.226	3.154	3.085
2.5008	3.161	3.113	3.038	2.974
3.0000	3.048	3.000	2.939	2.871

Table 6.2. Density, ρ, Speed of Sound, c, and Isentropic Compressibility, κ_S of Glycine Betaine in Aqueous $CoCl_2$ solutions at Temperatures, T = (288.15 K to 318.15) K, as a Function of Molality of Glycine Betaine.[a]

m_A[b]/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.1083 mol·kg^{-1} aqueous $CoCl_2$ solution				
ρ·10^{-3} /(kg·m^{-3})				
0.0000	1.0126	1.0096	1.0066	1.0036
0.0500	1.0135	1.0105	1.0075	1.0045
0.1020	1.0144	1.0113	1.0083	1.0052
0.5049	1.0209	1.0176	1.0146	1.0112
1.0017	1.0280	1.0244	1.0215	1.0178
1.5000	1.0343	1.0304	1.0276	1.0238
2.0066	1.0396	1.0357	1.0330	1.0292
2.5190	1.0444	1.0403	1.0377	1.0341
3.0005	1.0484	1.0439	1.0413	1.0382
c/(m·s^{-1})				
0.0000	1483.42	1506.22	1535.16	1558.68
0.0500	1488.50	1511.06	1539.94	1563.25
0.1020	1493.74	1516.15	1545.08	1568.30
0.5049	1533.90	1555.00	1582.90	1605.76
1.0017	1580.05	1600.06	1627.00	1649.03
1.5000	1620.52	1643.22	1666.37	1688.61
2.0066	1656.82	1679.20	1702.10	1724.60
2.5190	1691.02	1708.88	1732.10	1756.80
3.0005	1710.82	1731.82	1757.00	1780.16
κ_S ·10^{10} /(m^2·N^{-1})				
0.0000	4.488	4.366	4.215	4.101
0.0500	4.453	4.334	4.185	4.074
0.1020	4.418	4.302	4.154	4.045
0.5049	4.163	4.064	3.934	3.835
1.0017	3.896	3.813	3.698	3.613
1.5000	3.682	3.594	3.505	3.426
2.0066	3.504	3.424	3.341	3.267
2.5190	3.348	3.292	3.212	3.133
3.0005	3.259	3.194	3.111	3.039

Table 6.2. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.2140 mol·kg^{-1} aqueous $CoCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0241	1.0215	1.0188	1.0161
0.0510	1.0250	1.0223	1.0196	1.0169
0.1000	1.0256	1.0230	1.0203	1.0176
0.5000	1.0312	1.0286	1.0259	1.0229
1.0000	1.0373	1.0347	1.0318	1.0288
1.4980	1.0424	1.0398	1.0368	1.0338
2.0050	1.0469	1.0444	1.0413	1.0382
2.5000	1.0504	1.0479	1.0448	1.0417
3.0000	1.0534	1.0510	1.0478	1.0447
c/(m·s^{-1})				
0.0000	1499.72	1515.12	1540.70	1561.10
0.0510	1504.94	1520.40	1545.80	1566.00
0.1000	1510.24	1525.38	1550.70	1570.64
0.5000	1552.20	1566.00	1590.36	1608.80
1.0000	1601.02	1612.05	1637.08	1651.58
1.4980	1645.28	1654.27	1680.18	1694.20
2.0050	1681.50	1694.56	1717.28	1729.69
2.5000	1712.80	1725.88	1749.50	1761.00
3.0000	1735.40	1750.65	1774.97	1793.94
$K_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.341	4.264	4.135	4.038
0.0510	4.308	4.232	4.105	4.010
0.1000	4.275	4.201	4.076	3.984
0.5000	4.025	3.964	3.854	3.777
1.0000	3.761	3.719	3.616	3.563
1.4980	3.544	3.514	3.417	3.370
2.0050	3.378	3.334	3.256	3.219
2.5000	3.245	3.204	3.127	3.096
3.0000	3.152	3.105	3.029	2.974

Table 6.2. (*continued*)

m_A^b/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0370	1.0342	1.0314	1.0286
0.0492	1.0376	1.0348	1.0320	1.0292
0.0997	1.0381	1.0353	1.0325	1.0297
0.4885	1.0421	1.0393	1.0365	1.0337
0.9786	1.0466	1.0438	1.0409	1.0381
1.4702	1.0506	1.0475	1.0446	1.0420
1.9535	1.0539	1.0506	1.0476	1.0451
2.4675	1.0571	1.0536	1.0503	1.0478
2.9524	1.0596	1.0559	1.0525	1.0498
c/(m·s^{-1})				
0.0000	1513.44	1524.48	1550.07	1563.46
0.0492	1519.00	1529.80	1555.25	1568.50
0.0997	1524.61	1535.28	1560.56	1573.65
0.4885	1566.32	1576.51	1600.46	1612.52
0.9786	1614.90	1625.59	1646.34	1658.14
1.4702	1657.48	1669.33	1687.18	1700.03
1.9535	1691.94	1701.83	1723.71	1736.60
2.4675	1725.24	1738.68	1758.12	1771.56
2.9524	1747.50	1760.78	1786.07	1800.36
$K_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.210	4.161	4.035	3.977
0.0492	4.177	4.129	4.006	3.949
0.0997	4.144	4.098	3.977	3.922
0.4885	3.911	3.871	3.767	3.720
0.9786	3.664	3.625	3.544	3.504
1.4702	3.465	3.426	3.363	3.321
1.9535	3.315	3.286	3.213	3.173
2.4675	3.178	3.140	3.080	3.041
2.9524	3.090	3.055	2.978	2.939

Table 6.2. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.4014 mol·kg^{-1} aqueous $CoCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0454	1.0427	1.0400	1.0373
0.0500	1.0459	1.0432	1.0405	1.0379
0.1002	1.0464	1.0437	1.0410	1.0383
0.4998	1.0501	1.0474	1.0447	1.0420
0.9960	1.0541	1.0514	1.0487	1.0460
1.5010	1.0576	1.0547	1.0519	1.0494
1.9880	1.0602	1.0575	1.0546	1.0522
2.5000	1.0627	1.0598	1.0567	1.0544
2.9980	1.0645	1.0617	1.0586	1.0564
c/(m·s^{-1})				
0.0000	1519.64	1533.79	1553.94	1568.09
0.0500	1525.20	1539.27	1559.37	1573.20
0.1002	1530.61	1544.62	1564.58	1578.44
0.4998	1572.52	1586.49	1606.30	1618.31
0.9960	1623.10	1636.08	1654.24	1666.84
1.5010	1666.13	1682.00	1697.48	1710.91
1.9880	1702.37	1719.28	1734.78	1748.48
2.5000	1734.73	1751.08	1766.06	1781.19
2.9980	1758.43	1774.40	1794.47	1808.92
$K_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.142	4.077	3.982	3.921
0.0500	4.110	4.046	3.952	3.893
0.1002	4.079	4.016	3.924	3.866
0.4998	3.851	3.793	3.710	3.664
0.9960	3.601	3.553	3.485	3.441
1.5010	3.406	3.351	3.299	3.255
1.9880	3.255	3.199	3.151	3.109
2.5000	3.127	3.077	3.034	2.989
2.9980	3.038	2.992	2.934	2.893

Table 6.2. (*continued*)

m_A^b/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.5024 mol·kg^{-1} aqueous $CoCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0567	1.0541	1.0515	1.0489
0.0509	1.0572	1.0546	1.0520	1.0494
0.1020	1.0576	1.0550	1.0524	1.0498
0.5020	1.0607	1.0581	1.0555	1.0530
1.0000	1.0641	1.0615	1.0588	1.0563
1.5000	1.0670	1.0642	1.0616	1.0591
2.0100	1.0694	1.0668	1.0638	1.0614
2.5000	1.0713	1.0685	1.0655	1.0631
2.9985	1.0728	1.0702	1.0670	1.0645
c/(m·s^{-1})				
0.0000	1525.60	1541.08	1560.23	1572.62
0.0509	1531.16	1546.34	1565.40	1577.66
0.1020	1536.68	1551.70	1570.60	1582.78
0.5020	1579.48	1592.20	1611.23	1621.27
1.0000	1630.06	1640.45	1659.15	1668.58
1.5000	1674.09	1685.27	1703.44	1712.58
2.0100	1711.33	1726.22	1744.74	1752.54
2.5000	1745.60	1762.04	1778.02	1790.85
2.9985	1768.50	1784.86	1805.43	1818.88
$K_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.066	3.995	3.907	3.855
0.0509	4.035	3.966	3.879	3.829
0.1020	4.004	3.937	3.852	3.802
0.5020	3.779	3.728	3.649	3.613
1.0000	3.537	3.501	3.431	3.400
1.5000	3.344	3.309	3.246	3.219
2.0100	3.193	3.146	3.088	3.068
2.5000	3.063	3.014	2.969	2.933
2.9985	2.980	2.933	2.875	2.840

Table 6.3. Density, ρ, Speed of Sound, c, and Isentropic Compressibility, κ_S of Glycine Betaine in Aqueous $NiCl_2$ solutions at Temperatures, T = (288.15 K to 318.15) K, as a Function of Molality of Glycine Betaine.[a]

m_A[b]/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.1108 mol·kg^{-1} aqueous $NiCl_2$ solution				
ρ·10^{-3} /(kg·m^{-3})				
0.0000	1.0176	1.0146	1.0130	1.0100
0.0478	1.0184	1.0155	1.0139	1.0108
0.1121	1.0194	1.0164	1.0148	1.0117
0.5091	1.0254	1.0224	1.0208	1.0174
1.0007	1.0321	1.0291	1.0275	1.0238
1.5020	1.0382	1.0352	1.0337	1.0297
2.0050	1.0437	1.0408	1.0393	1.0350
2.5230	1.0489	1.0460	1.0445	1.0400
2.9989	1.0532	1.0503	1.0488	1.0441
c/(m·s^{-1})				
0.0000	1483.42	1506.22	1527.16	1548.68
0.0478	1488.42	1510.90	1531.66	1553.06
0.1121	1494.80	1517.54	1538.00	1559.10
0.5091	1533.90	1555.95	1574.90	1595.50
1.0007	1580.05	1600.26	1619.00	1639.03
1.5020	1620.52	1643.22	1658.37	1678.61
2.0050	1656.82	1679.20	1694.10	1714.60
2.5230	1691.02	1708.88	1724.10	1746.80
2.9989	1710.82	1731.82	1749.00	1770.16
κ_S ·10^{10} /(m^2·N^{-1})				
0.0000	4.466	4.344	4.233	4.128
0.0478	4.432	4.314	4.204	4.102
0.1121	4.390	4.272	4.166	4.066
0.5091	4.145	4.040	3.950	3.861
1.0007	3.881	3.795	3.713	3.636
1.5020	3.668	3.578	3.518	3.447
2.0050	3.490	3.407	3.353	3.287
2.5230	3.334	3.274	3.221	3.151
2.9989	3.244	3.175	3.117	3.057

Table 6.3. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.2021 mol·kg^{-1} aqueous $NiCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0287	1.0245	1.0203	1.0161
0.0491	1.0295	1.0253	1.0211	1.0169
0.0999	1.0302	1.0260	1.0218	1.0175
0.4998	1.0358	1.0317	1.0275	1.0230
1.0011	1.0422	1.0381	1.0340	1.0292
1.4998	1.0479	1.0439	1.0398	1.0347
2.0010	1.0530	1.0491	1.0449	1.0397
2.4850	1.0575	1.0536	1.0494	1.0440
2.9999	1.0618	1.0580	1.0535	1.0480
c/(m·s^{-1})				
0.0000	1489.72	1514.68	1530.70	1551.10
0.0491	1494.94	1519.60	1535.56	1555.66
0.0999	1500.18	1524.58	1540.58	1560.62
0.4998	1541.02	1563.20	1579.36	1597.96
1.0011	1587.02	1608.05	1623.08	1641.58
1.4998	1630.28	1648.27	1663.18	1683.44
2.0010	1667.50	1686.56	1701.28	1718.69
2.4850	1700.38	1716.88	1729.50	1750.00
2.9999	1723.40	1741.65	1758.97	1776.94
$K_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.380	4.254	4.183	4.091
0.0491	4.346	4.224	4.153	4.063
0.0999	4.313	4.193	4.123	4.035
0.4998	4.065	3.967	3.902	3.828
1.0011	3.810	3.725	3.671	3.606
1.4998	3.591	3.526	3.477	3.410
2.0010	3.415	3.351	3.307	3.256
2.4850	3.271	3.220	3.186	3.128
2.9999	3.171	3.116	3.068	3.022

Table 6.3. (*continued*)

m_A^b/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.3031 mol·kg^{-1} aqueous $NiCl_2$ solution				
$\rho \cdot 10^{-3}$/(kg·m^{-3})				
0.0000	1.0392	1.0354	1.0322	1.0282
0.0510	1.0398	1.0360	1.0328	1.0288
0.0998	1.0403	1.0365	1.0333	1.0293
0.4886	1.0443	1.0405	1.0373	1.0333
0.9789	1.0487	1.0449	1.0418	1.0378
1.4850	1.0526	1.0489	1.0458	1.0419
1.9966	1.0560	1.0524	1.0493	1.0452
2.4865	1.0591	1.0553	1.0522	1.0482
2.9282	1.0616	1.0577	1.0544	1.0506
c/(m·s^{-1})				
0.0000	1495.88	1523.07	1550.12	1570.32
0.0510	1501.52	1528.45	1555.48	1575.64
0.0998	1506.95	1533.55	1560.56	1580.55
0.4886	1549.10	1573.70	1600.00	1619.80
0.9789	1597.36	1621.04	1648.49	1665.14
1.4850	1643.69	1666.02	1690.27	1710.57
1.9966	1683.78	1707.68	1729.05	1750.49
2.4865	1717.75	1741.13	1763.94	1780.91
2.9282	1740.87	1762.61	1795.00	1809.81
$\kappa_S \cdot 10^{10}$/(m^2·N^{-1})				
0.0000	4.300	4.163	4.032	3.944
0.0510	4.266	4.132	4.002	3.915
0.0998	4.233	4.102	3.974	3.889
0.4886	3.990	3.881	3.766	3.689
0.9789	3.737	3.642	3.532	3.475
1.4850	3.516	3.435	3.347	3.280
1.9966	3.340	3.258	3.188	3.122
2.4865	3.200	3.126	3.054	3.008
2.9282	3.108	3.043	2.944	2.906

Table 6.3. (*continued*)

m_A^b/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.4004 mol·kg^{-1} aqueous $NiCl_2$ solution				
$\rho \cdot 10^{-3}$ /(kg·m^{-3})				
0.0000	1.0477	1.0460	1.0447	1.0432
0.0502	1.0483	1.0465	1.0452	1.0438
0.1000	1.0487	1.0470	1.0456	1.0442
0.4990	1.0524	1.0505	1.0492	1.0477
0.9956	1.0565	1.0544	1.0531	1.0515
1.5030	1.0601	1.0579	1.0567	1.0549
1.9882	1.0630	1.0607	1.0594	1.0576
2.4977	1.0658	1.0632	1.0618	1.0602
2.9982	1.0682	1.0653	1.0640	1.0623
c/(m·s^{-1})				
0.0000	1505.69	1526.46	1553.94	1572.09
0.0502	1511.20	1531.86	1559.37	1577.20
0.1000	1516.76	1537.05	1564.58	1582.44
0.4990	1560.04	1579.60	1606.30	1622.48
0.9956	1607.17	1628.43	1654.24	1670.84
1.5030	1653.50	1673.41	1697.48	1714.91
1.9882	1693.59	1712.07	1734.78	1752.48
2.4977	1727.56	1746.52	1769.06	1785.19
2.9982	1762.68	1778.00	1808.47	1822.92
$K_S \cdot 10^{10}$ /(m^2·N^{-1})				
0.0000	4.210	4.103	3.964	3.879
0.0502	4.177	4.072	3.935	3.851
0.1000	4.145	4.043	3.907	3.824
0.4990	3.904	3.815	3.694	3.626
0.9956	3.664	3.576	3.470	3.407
1.5030	3.450	3.376	3.284	3.223
1.9882	3.280	3.216	3.137	3.079
2.4977	3.144	3.083	3.009	2.960
2.9982	3.013	2.969	2.874	2.833

Table 6.3. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.5121 mol·kg^{-1} aqueous $NiCl_2$ solution				
$\rho \cdot 10^{-3}$/(kg·m^{-3})				
0.0000	1.0596	1.0582	1.0561	1.0541
0.0510	1.0601	1.0587	1.0566	1.0546
0.1033	1.0605	1.0591	1.0570	1.0550
0.5001	1.0637	1.0621	1.0600	1.0580
0.9987	1.0671	1.0654	1.0634	1.0613
1.4988	1.0702	1.0683	1.0662	1.0642
2.0088	1.0728	1.0706	1.0686	1.0667
2.4988	1.0750	1.0727	1.0706	1.0685
2.9978	1.0770	1.0743	1.0724	1.0702
c/(m·s^{-1})				
0.0000	1577.62	1560.23	1542.36	1514.94
0.0510	1582.88	1565.64	1547.84	1520.55
0.1033	1588.08	1571.10	1553.36	1526.28
0.5001	1627.27	1611.23	1594.80	1569.29
0.9987	1673.58	1660.04	1644.33	1617.42
1.4988	1717.58	1706.44	1689.31	1662.75
2.0088	1757.54	1747.74	1728.97	1703.84
2.4988	1795.85	1781.02	1760.42	1739.81
2.9978	1828.88	1818.43	1798.90	1774.93
$K_S \cdot 10^{10}$/(m^2·N^{-1})				
0.0000	4.112	3.972	3.890	3.812
0.0510	4.080	3.943	3.861	3.785
0.1033	4.048	3.913	3.833	3.758
0.5001	3.817	3.702	3.634	3.569
0.9987	3.582	3.471	3.412	3.364
1.4988	3.380	3.280	3.221	3.185
2.0088	3.211	3.125	3.064	3.035
2.4988	3.073	3.008	2.945	2.902
2.9978	2.947	2.876	2.820	2.794

Table 6.4. Density, ρ, Speed of Sound, c, and Isentropic Compressibility, κ_S of Glycine Betaine in Aqueous $ZnCl_2$ solutions at Temperatures, T = (288.15 K to 318.15) K, as a Function of Molality of Glycine Betaine.[a]

m_A[b]/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
Glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solution				
ρ·10^{-3} /(kg·m^{-3})				
0.0000	1.0124	1.0089	1.0055	1.0020
0.0515	1.0132	1.0097	1.0063	1.0028
0.1018	1.0139	1.0104	1.0070	1.0035
0.4948	1.0193	1.0158	1.0124	1.0089
0.9830	1.0253	1.0219	1.0183	1.0149
1.5250	1.0312	1.0279	1.0241	1.0208
1.9702	1.0355	1.0321	1.0281	1.0249
2.4400	1.0395	1.0362	1.0320	1.0288
2.9322	1.0435	1.0399	1.0359	1.0323
c/(m·s^{-1})				
0.0000	1465.94	1496.70	1519.83	1536.42
0.0515	1471.05	1501.71	1524.62	1540.95
0.1018	1476.12	1506.69	1529.36	1545.47
0.4948	1514.45	1544.50	1565.61	1580.02
0.9830	1559.72	1589.12	1609.10	1621.88
1.5250	1605.98	1635.30	1654.79	1666.62
1.9702	1640.99	1670.53	1690.27	1702.05
2.4400	1675.08	1705.10	1724.50	1738.94
2.9322	1705.24	1736.82	1758.54	1776.52
κ_S ·10^{10} /(m^2·N^{-1})				
0.0000	4.596	4.425	4.306	4.228
0.0515	4.561	4.392	4.275	4.200
0.1018	4.526	4.360	4.246	4.172
0.4948	4.277	4.127	4.030	3.970
0.9830	4.009	3.875	3.793	3.746
1.5250	3.760	3.638	3.566	3.527
1.9702	3.586	3.472	3.404	3.368
2.4400	3.429	3.319	3.258	3.214
2.9322	3.296	3.188	3.122	3.069

[a]Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg^{-1}; for density u(ρ) = 0.1 kg m^{-3} and for speed of sound u(c) = 0.2 m s^{-1}. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.2 kg m^{-3} and $U_c(c)$ = 0.4 m s^{-1} with 0.95 level of confidence. The experiment was carried-out under laboratory pressure.

[b] m_A is the molality of glycine betaine in aqueous metal salt solutions.

The isentropic compressibility (κ_S) of the systems has been calculated employing Equation 5.1. As can be seen from the table that the κ_S values of glycine betaine in aqueous metal salt solutions decrease with an increase in its concentration and decrease with the increasing temperature. This indicates that the water molecules which are in association with ionic groups of glycine betaine are less compressible than those water molecules in the bulk. The reduction in the compressibility can also be attributed to the electrostrictive forces causing a breakage in the water network with increasing solute concentration and occurrence of compact packing of water molecules around the solute.

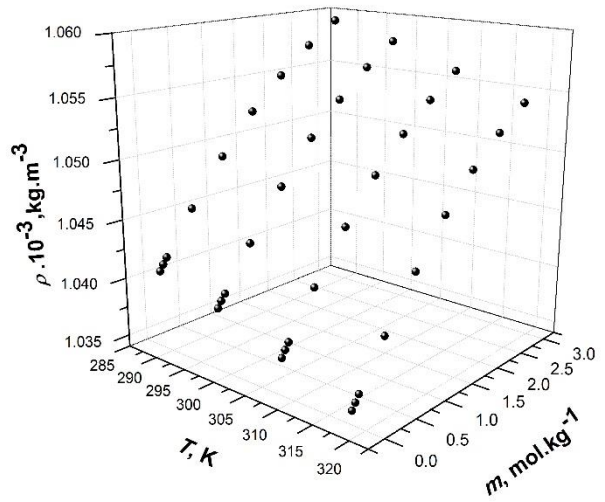

Figure 6.1. Variation of density, ρ versus molal concentration, m of glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solutions at various temperatures.

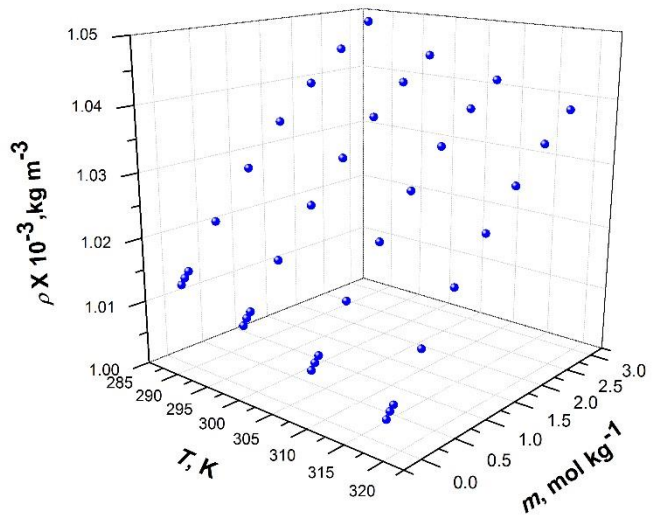

Figure 6.2. Variation of density, ρ versus molal concentration, m of glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solutions at various temperatures.

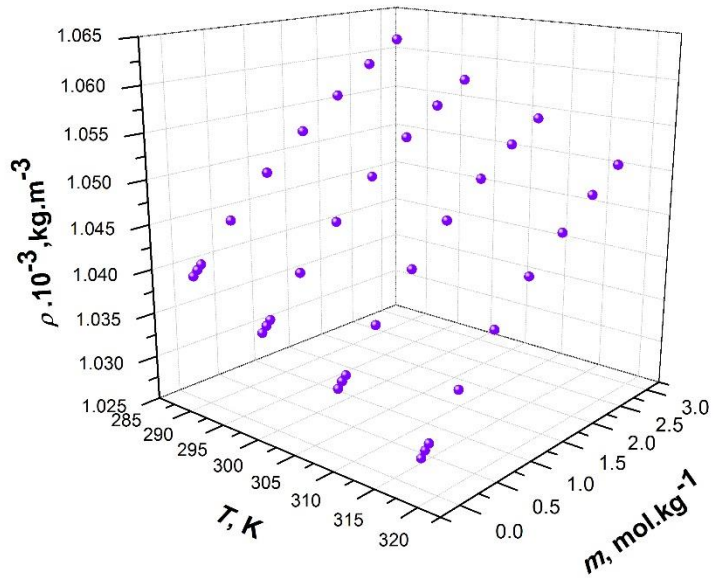

Figure 6.3. Variation of density, ρ versus molal concentration, m of glycine betaine in 0.3262 mol·kg^{-1} aqueous $NiCl_2$ solutions at various temperatures.

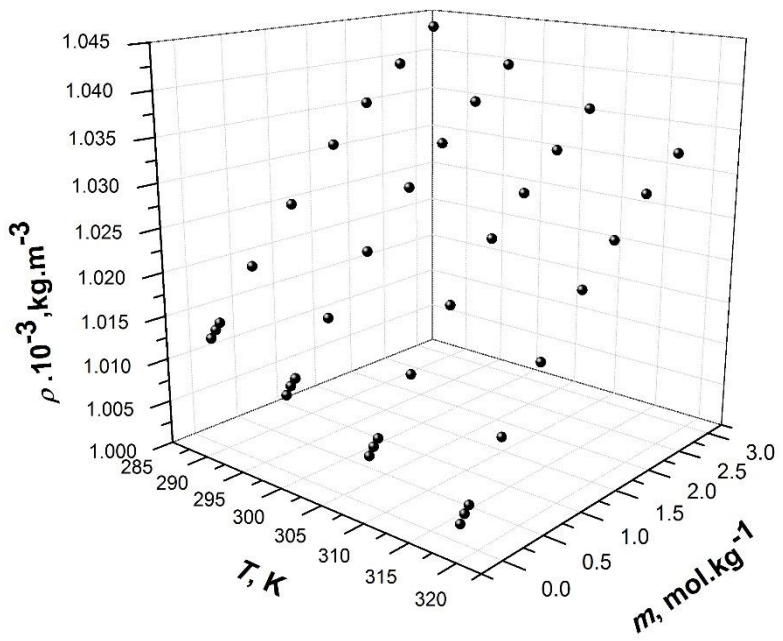

Figure 6.4. Variation of density, ρ versus molal concentration, m of glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solutions at various temperatures.

6.2. APPARENT MOLAR VOLUME AND APPARENT MOLAR ISENTROPIC COMPRESSION

The apparent molar volumes ϕ_v and apparent molar isentropic compression, ϕ_k of glycine betaine in aqueous solutions of $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ aqueous solutions at different temperatures have been calculated using the Equations 5.7 and 5.9, respectively for the present system.

The ϕ_v values of glycine betaine in aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions are presented in Tables 6.5-6.8. Similarly the ϕ_k values of glycine betaine in aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions are presented in Tables 6.9-6.12. The uncertainties in the calculation of ϕ_v and ϕ_k values were estimated using propagation of errors method (Hedwig and Høiland 1991 and Marriott et al. 2001). As can be seen from the tables, the ϕ_v and ϕ_k values increase with the concentration of the solute at a fixed metal salt concentration. Also, these values were found to increase

with the increase in concentration of $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ in each of the aqueous solutions.

Table 6.5. Apparent Molar Volumes, ϕ_v of Glycine Betaine in Aqueous $MnCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.0903 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0499	98.26(±1.97)[b]	98.50(±1.99)	98.63(±1.99)	98.87(±2.00)
0.1000	99.20(±0.99)	99.40(±1.00)	99.58(±1.00)	100.83(±1.00)
0.5049	99.30(±0.20)	99.75(±0.20)	100.09(±0.20)	101.16(±0.21)
1.0070	99.52(±0.11)	99.88(±0.11)	100.33(±0.11)	101.23(±0.11)
1.5000	99.78(±0.07)	100.11(±0.07)	100.61(±0.07)	101.32(±0.08)
2.0066	100.05(±0.06)	100.30(±0.06)	100.78(±0.06)	101.45(±0.06)
2.5010	100.31(±0.05)	100.42(±0.05)	101.04(±0.05)	101.59(±0.05)
3.0014	100.52(±0.04)	100.74(±0.04)	101.20(±0.04)	101.71 (±0.04)
Glycine betaine in 0.2001 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0487	98.83(±1.97)	99.17(±1.99)	99.52(±1.99)	99.87(±2.02)
0.1110	99.81(±0.87)	100.16(±0.88)	100.51(±0.88)	100.87(±0.89)
0.4973	99.87(±0.20)	100.22(±0.20)	100.78(±0.20)	101.55(±0.21)
0.9944	100.10(±0.10)	100.46(±0.11)	101.03(±0.11)	101.71(±0.11)
1.5101	100.22(±0.07)	100.57(±0.07)	101.66(±0.07)	102.10(±0.07)
1.9894	100.33(±0.06)	100.68(±0.06)	102.19(±0.06)	102.39(±0.06)
2.4890	100.58(±0.05)	100.94(±0.05)	102.50(±0.05)	102.72(±0.05)
2.9859	100.72(±0.04)	101.08(±0.04)	102.89(±0.04)	103.02(±0.04)
Glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0500	102.10(±1.98)	102.34(±1.89)	102.62(±1.90)	102.74(±1.91)
0.1000	102.99(±0.95)	103.23(±0.95)	103.51(±0.96)	103.78(±0.96)
0.5007	103.16(±0.20)	103.40(±0.20)	103.68(±0.20)	103.81(±0.20)
0.9722	103.30(±0.11)	103.54(±0.11)	103.72(±0.11)	103.98(±0.11)
1.4535	103.43(±0.07)	103.67(±0.07)	103.88(±0.07)	104.00(±0.07)
1.9312	103.57(±0.06)	103.87(±0.06)	104.04(±0.06)	104.25(±0.06)
2.4216	103.66(±0.05)	104.05(±0.05)	104.19(±0.05)	104.46(±0.05)
3.0009	103.95(±0.04)	104.36(±0.04)	104.49(±0.04)	104.67(±0.04)

Table 6.5. (*continued*)

m_A[a]/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
ϕ_v ·10^6/(m^3·mol^{-1})				
Glycine betaine in 0.3772 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0510	101.95(±1.83)	102.10(±1.84)	102.22(±1.84)	102.35(±1.85)
0.0999	103.54(±0.94)	103.70(±0.94)	103.82(±0.95)	103.95(±0.95)
0.4823	103.62(±0.19)	103.98(±0.20)	104.10(±0.20)	104.24(±0.20)
0.9679	103.83(±0.11)	104.09(±0.11)	104.31(±0.11)	104.45(±0.11)
1.4850	104.02(±0.07)	104.24(±0.07)	104.51(±0.07)	104.65(±0.07)
1.9439	104.21(±0.06)	104.37(±0.06)	104.72(±0.06)	104.80(±0.06)
2.5020	104.45(±0.05)	104.56(±0.05)	104.91(±0.05)	105.01(±0.05)
2.8991	104.64(±0.04)	104.68(±0.04)	105.09(±0.04)	105.19(±0.04)
Glycine betaine in 0.4653 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0512	103.51(±1.81)	103.64(±1.82)	103.83(±1.83)	104.01(±1.83)
0.1050	103.68(±0.89)	103.81(±0.89)	104.00(±0.89)	104.19(±0.90)
0.5000	103.82(±0.19)	104.14(±0.19)	104.14(±0.20)	104.32(±0.20)
1.0000	104.08(±0.10)	104.21(±0.10)	104.30(±0.10)	104.49(±0.10)
1.5008	104.28(±0.07)	104.34(±0.07)	104.46±0.07)	104.57(±0.07)
1.9980	104.53(±0.06)	104.61(±0.06)	104.75(±0.06)	104.82(±0.06)
2.5008	104.78(±0.05)	104.86(±0.05)	105.01(±0.05)	105.11(±0.05)
3.0000	105.02(±0.04)	105.11(±0.04)	105.23(±0.04)	105.37(±0.04)

[a]m_A is the molality of glycine betaine in aqueous $MnCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_v is in brackets.

Table 6.6. Apparent Molar Volumes, ϕ_v of Glycine Betaine in Aqueous $CoCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.1083 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0500	98.05(±1.96)[b]	98.29(±1.97)	98.53(±1.98)	98.77(±1.99)
0.1020	98.31(±0.96)	99.52(±0.97)	99.76(±0.98)	100.99(±0.98)
0.5049	98.85(±0.20)	99.70(±0.20)	99.95(±0.20)	101.02(±0.21)
1.0017	99.19(±0.11)	100.07(±0.11)	100.19(±0.11)	101.22(±0.11)
1.5000	99.45(±0.07)	100.36(±0.07)	100.47(±0.07)	101.32(±0.07)
2.0066	99.91(±0.06)	100.67(±0.06)	100.75(±0.06)	101.47(±0.06)
2.5190	100.23(±0.05)	101.01(±0.05)	101.07(±0.05)	101.62(±0.05)
3.0005	100.50(±0.04)	101.38(±0.04)	101.47(±0.04)	101.77(±0.04)
Glycine betaine in 0.2140 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0510	97.48(±1.88)	99.57(±1.89)	99.80(±1.90)	100.02(±1.91)
0.1000	99.94(±0.96)	100.16(±0.97)	100.39(±0.97)	100.62(±0.98)
0.5000	100.16(±0.20)	100.38(±0.20)	100.61(±0.20)	101.44(±0.20)
1.0000	100.51(±0.10)	100.73(±0.11)	101.17(±0.10)	101.72(±0.11)
1.4980	100.94(±0.07)	101.16(±0.07)	101.62(±0.07)	102.07(±0.07)
2.0050	101.30(±0.06)	101.46(±0.06)	101.93(±0.06)	102.39(±0.06)
2.5000	101.75(±0.05)	101.93(±0.05)	102.36(±0.05)	102.79(±0.05)
3.0000	102.16(±0.04)	102.31(±0.04)	102.75(±0.04)	103.16(±0.04)
Glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0492	101.57(±1.90)	101.81(±1.91)	102.06(±1.92)	102.31(±1.93)
0.0997	102.60(±0.94)	102.85(±0.95)	103.10(±0.95)	103.35(±0.96)
0.4885	102.76(±0.20)	103.01(±0.20)	103.26(±0.20)	103.51(±0.20)
0.9786	102.90(±0.11)	103.15(±0.11)	103.50(±0.11)	103.76(±0.11)
1.4702	103.02(±0.07)	103.49(±0.07)	103.81(±0.07)	103.92(±0.07)
1.9535	103.24(±0.06)	103.78(±0.06)	104.15(±0.06)	104.24(±0.06)
2.4675	103.39(±0.05)	103.97(±0.05)	104.47(±0.05)	104.59(±0.05)
2.9524	103.59(±0.04)	104.22(±0.04)	104.72(±0.04)	104.94(±0.04)

Table 6.6. (*continued*)

m_A[a]/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.4014 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0500	102.86(±1.84)	103.11(±1.85)	103.35(±1.86)	101.73(±1.87)
0.1002	102.83(±0.92)	103.07(±0.93)	103.32(±0.93)	103.56(±0.94)
0.4998	102.99(±0.19)	103.24(±0.19)	103.48(±0.19)	103.73(±0.20)
0.9960	103.21(±0.10)	103.46(±0.10)	103.70(±0.10)	103.95(±0.10)
1.5010	103.42(±0.07)	103.80(±0.07)	104.12(±0.07)	104.23(±0.07)
1.9880	103.78(±0.06)	104.03(±0.06)	104.39(±0.06)	104.47(±0.06)
2.5000	104.01(±0.05)	104.35(±0.05)	104.79(±0.05)	104.85(±0.05)
2.9980	104.33(±0.04)	104.62(±0.04)	105.03(±0.04)	105.08(±0.04)
Glycine betaine in 0.5024 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0509	102.02(±1.77)	102.25(±1.78)	102.48(±1.79)	102.71(±1.79)
0.1020	102.87(±0.89)	103.11(±0.89)	103.34(±0.90)	103.58(±0.90)
0.5020	103.34(±0.19)	103.57(±0.19)	103.81(±0.19)	103.86(±0.19)
1.0000	103.51(±0.10)	103.75(±0.10)	104.09(±0.10)	104.23(±0.10)
1.5000	103.70(±0.07)	104.08(±0.07)	104.32(±0.07)	104.49(±0.07)
2.0100	103.96(±0.06)	104.20(±0.06)	104.65(±0.06)	104.79(±0.06)
2.5000	104.19(±0.05)	104.53(±0.05)	104.95(±0.05)	105.10(±0.05)
2.9985	104.46(±0.04)	104.71(±0.04)	105.19(±0.04)	105.39(±0.04)

[a]m_A is the molality of glycine betaine in aqueous $CoCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_v is in brackets.

Table 6.7. Apparent Molar Volumes, ϕ_v of Glycine Betaine in Aqueous $NiCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.1108 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0478	98.88(±2.03)[b]	97.09(±2.04)	97.21(±2.05)	99.50(±2.06)
0.1121	99.44(±0.87)	99.69(±0.87)	99.82(±0.88)	100.95(±0.88)
0.5091	99.56(±0.20)	99.81(±0.20)	99.95(±0.20)	101.00(±0.20)
1.0007	99.71(±0.10)	99.96(±0.11)	100.09(±0.11)	101.09(±0.11)
1.5020	99.86(±0.07)	100.11(±0.07)	100.17(±0.07)	101.16(±0.07)
2.0050	99.99(±0.06)	100.18(±0.06)	100.26(±0.06)	101.26(±0.06)
2.5230	100.07(±0.05)	100.27(±0.05)	100.36(±0.05)	101.32(±0.05)
2.9989	100.16(±0.04)	100.37(±0.04)	100.46(±0.04)	101.42(±0.04)
Glycine betaine in 0.2021 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0491	98.41(±1.93)	98.75(±1.95)	99.09(±1.96)	99.43(±1.98)
0.0999	99.55(±0.95)	99.90(±0.96)	100.25(±0.97)	101.58(±0.98)
0.4998	99.77(±0.20)	99.92(±0.20)	100.27(±0.20)	101.23(±0.20)
1.0011	99.83(±0.10)	100.08(±0.10)	100.33(±0.10)	101.31(±0.11)
1.4998	99.92(±0.07)	100.13(±0.07)	100.41(±0.07)	101.43(±0.07)
2.0010	100.04(±0.06)	100.23(±0.06)	100.58(±0.06)	101.51(±0.06)
2.4850	100.13(±0.05)	100.34(±0.05)	100.70(±0.05)	101.63(±0.05)
2.9999	100.23(±0.04)	100.43(±0.04)	100.90(±0.04)	101.80(±0.04)
Glycine betaine in 0.3031 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0510	101.78(±1.82)	102.11(±1.84)	102.39(±1.85)	102.75(±1.87)
0.0998	102.42(±0.94)	102.75(±0.94)	103.04(±0.95)	103.40(±0.96)
0.4886	102.56(±0.20)	102.90(±0.20)	103.19(±0.20)	103.55(±0.20)
0.9789	102.80(±0.10)	103.15(±0.10)	103.33(±0.10)	103.69(±0.11)
1.4850	103.05(±0.07)	103.32(±0.07)	103.54(±0.07)	103.83(±0.07)
1.9966	103.27(±0.06)	103.50(±0.06)	103.74(±0.06)	104.16(±0.06)
2.4865	103.34(±0.05)	103.69(±0.05)	103.93(±0.05)	104.30(±0.05)
2.9282	103.42(±0.04)	103.81(±0.04)	104.14(±0.04)	104.43(±0.04)

Table 6.7. (*continued*)

m_A[a]/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.4004 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0502	100.87(±1.82)	102.85(±1.83)	102.96(±1.83)	101.26(±1.84)
0.1000	102.61(±0.92)	102.76(±0.92)	103.80(±0.93)	103.01(±0.93)
0.4990	102.77(±0.19)	103.31(±0.19)	103.43(±0.19)	103.57(±0.19)
0.9956	102.90(±0.10)	103.46(±0.10)	103.57(±0.10)	103.81(±0.10)
1.5030	103.08(±0.07)	103.58(±0.07)	103.63(±0.07)	103.98(±0.07)
1.9882	103.30(±0.06)	103.78(±0.06)	103.90(±0.06)	104.20(±0.06)
2.4977	103.43(±0.05)	103.99(±0.05)	104.16(±0.05)	104.34(±0.05)
2.9982	103.56(±0.04)	104.19(±0.04)	104.31(±0.04)	104.53(±0.04)
Glycine betaine in 0.5121 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0510	101.78(±1.76)	101.90(±1.76)	102.09(±1.77)	102.27(±1.77)
0.1033	102.71(±0.87)	102.84(±0.87)	103.03(±0.88)	103.21(±0.88)
0.5001	102.86(±0.19)	103.36(±0.19)	103.55(±0.19)	103.74(±0.19)
0.9987	103.14(±0.10)	103.56(±0.10)	103.66(±0.10)	103.94(±0.10)
1.4988	103.23(±0.07)	103.70(±0.07)	103.89(±0.07)	104.08(±0.07)
2.0088	103.42(±0.05)	103.98(±0.05)	104.12(±0.05)	104.25(±0.05)
2.4988	103.57(±0.04)	104.10(±0.04)	104.29(±0.04)	104.52(±0.05)
2.9978	103.69(±0.04)	104.32(±0.04)	104.44(±0.04)	104.70(±0.04)

[a]m_A is the molality of glycine betaine in aqueous $NiCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_v is in brackets.

Table 6.8. Apparent Molar Volumes, ϕ_v of Glycine Betaine in Aqueous $ZnCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_v \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solution				
0.0515	100.48(±1.90)[b]	100.78(±1.91)	101.06(±1.92)	101.36(±1.92)
0.1018	101.19(±0.97)	101.49(±0.97)	101.78(±0.97)	102.09(±0.98)
0.4948	101.42(±0.21)	101.72(±0.21)	102.02(±0.21)	102.32(±0.21)
0.9830	101.62(±0.11)	101.81(±0.11)	102.33(±0.11)	102.53(±0.11)
1.5250	101.80(±0.07)	101.96(±0.07)	102.55(±0.07)	102.71(±0.07)
1.9702	101.95(±0.06)	102.20(±0.06)	102.85(±0.06)	102.99(±0.06)
2.4400	102.14(±0.05)	102.35(±0.05)	103.05(±0.05)	103.22(±0.05)
2.9322	102.23(±0.04)	102.58(±0.04)	103.14(±0.04)	103.49(±0.04)

Table 6.9. Apparent Molar Isentropic Compressions, ϕ_k of Glycine Betaine in Aqueous $MnCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m^a/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.0903 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0499	-25.65(±0.24)[b]	-22.25(±0.23)	-20.65(±0.22)	-15.35(±0.21)
0.1000	-24.13(±0.12)	-22.12(±0.11)	-20.52(±0.11)	-14.53(±0.10)
0.5049	-21.94(±0.02)	-19.87(±0.02)	-18.52(±0.02)	-13.33(±0.02)
1.0070	-19.46(±0.01)	-17.40(±0.01)	-15.33(±0.01)	-12.14(±0.01)
1.5000	-18.38(±0.01)	-15.05(±0.01)	-12.42(±0.01)	-11.08(±0.01)
2.0066	-15.91(±0.01)	-12.42(±0.01)	-9.37(±0.01)	-9.14(±0.01)
2.5010	-12.26(±0.01)	-10.07(±0.01)	-6.42(±0.01)	-6.85(±0.01)
3.0014	-9.75(±0.01)	-7.19(±0.01)	-4.45(±0.01)	-5.55(±0.01)
Glycine betaine in 0.2001 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0487	-24.29(±0.24)	-22.07(±0.23)	-20.49(±0.22)	-14.62(±0.21)
0.1110	-22.38(±0.10)	-20.76(±0.10)	-20.01(±0.10)	-14.50(±0.09)
0.4973	-21.40(±0.02)	-19.58(±0.02)	-18.35(±0.02)	-13.62(±0.02)
0.9944	-18.97(±0.01)	-16.39(±0.01)	-15.82(±0.01)	-12.07(±0.01)
1.5101	-17.04(±0.01)	-15.07(±0.01)	-12.64(±0.01)	-10.17(±0.01)
1.9894	-13.67(±0.01)	-12.21(±0.01)	-9.66(±0.01)	-8.50(±0.01)
2.4890	-10.64(±0.01)	-8.45(±0.01)	-6.28(±0.01)	-6.14(±0.01)
2.9859	-8.81(±0.01)	-6.94(±0.01)	-4.55(±0.01)	-4.43(±0.01)
Glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0500	-23.33(±0.22)	-20.20(±0.21)	-17.23(±0.20)	-13.87(±0.19)
0.1000	-21.70(±0.11)	-19.18(±0.10)	-17.16(±0.10)	-13.56(±0.10)
0.5007	-20.05(±0.02)	-18.12(±0.02)	-15.45(±0.02)	-12.59(±0.02)
0.9722	-17.49(±0.01)	-16.32(±0.01)	-13.37(±0.01)	-10.91(±0.01)
1.4535	-15.86(±0.01)	-14.28(±0.01)	-11.06(±0.01)	-9.78(±0.01)
1.9312	-13.55(±0.01)	-11.81(±0.01)	-8.42(±0.01)	-8.42(±0.01)
2.4216	-10.84(±0.01)	-9.02(±0.01)	-5.85(±0.01)	-5.34(±0.01)
3.0009	-8.46(±0.01)	-7.10(±0.01)	-4.11(±0.01)	-4.00(±0.01)

Table 6.9. (*continued*)

m^a/mol·kg^{-1}	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.3772 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0510	-20.31(±0.21)	-18.36(±0.20)	-17.31(±0.20)	-13.05(±0.19)
0.0999	-19.95(±0.11)	-17.77(±0.10)	-15.85(±0.10)	-12.53(±0.10)
0.4823	-18.93(±0.02)	-16.98(±0.02)	-13.94(±0.02)	-11.59(±0.02)
0.9679	-16.08(±0.01)	-14.65(±0.01)	-10.29(±0.01)	-10.09(±0.01)
1.4850	-13.76(±0.01)	-10.28(±0.01)	-9.33(±0.01)	-8.36(±0.01)
1.9439	-11.39(±0.01)	-8.92(±0.01)	-7.15(±0.01)	-5.86(±0.01)
2.5020	-8.14(±0.01)	-5.84(±0.01)	-3.62(±0.01)	-2.81(±0.01)
2.8991	-5.96(±0.01)	-4.15(±0.01)	-2.29(±0.01)	-2.08(±0.01)
Glycine betaine in 0.4653 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0512	-17.48(±0.21)	-13.07(±0.20)	-11.86(±0.19)	-10.47(±0.18)
0.1050	-17.26(±0.10)	-12.86(±0.10)	-11.44(±0.09)	-10.25(±0.09)
0.5000	-15.88(±0.02)	-11.44(±0.02)	-10.33(±0.02)	-9.04(±0.02)
1.0000	-13.43±0.01)	-9.60(±0.01)	-8.42(±0.01)	-7.41(±0.01)
1.5008	-11.35(±0.01)	-8.19(±0.01)	-7.03(±0.01)	-5.87(±0.01)
1.9980	-9.11(±0.01)	-6.47(±0.01)	-5.09(±0.01)	-4.25(±0.01)
2.5008	-5.93(±0.01)	-3.84(±0.01)	-3.02(±0.01)	-2.26(±0.01)
3.0000	-4.14(±0.01)	-2.50(±0.01)	-1.36(±0.01)	-1.00(±0.01)

[a]*m* is the molality of glycine betaine in aqueous $MnCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_k is in brackets.

Table 6.10. Apparent Molar Isentropic Compressions, ϕ_k of Glycine Betaine in Aqueous $CoCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.1083 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0500	-24.55(±0.24)[b]	-20.37(±0.23)	-18.11(±0.22)	-14.76(±0.21)
0.1020	-24.00(±0.12)	-19.58(±0.11)	-17.94(±0.11)	-14.45(±0.10)
0.5049	-22.35(±0.02)	-18.69(±0.02)	-16.11(±0.02)	-13.75(±0.02)
1.0017	-19.66(±0.01)	-16.52(±0.01)	-14.26(±0.01)	-11.99(±0.01)
1.5000	-16.46(±0.01)	-14.88(±0.01)	-11.87(±0.01)	-10.19(±0.01)
2.0066	-13.40(±0.01)	-12.01(±0.01)	-9.60(±0.01)	-8.29(±0.01)
2.5190	-11.11(±0.01)	-8.99(±0.01)	-7.10(±0.01)	-6.45(±0.01)
3.0005	-7.70(±0.01)	-6.31(±0.01)	-5.00(±0.01)	-4.33(±0.01)
Glycine betaine in 0.2140 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0510	-22.82(±0.22)	-20.98(±0.21)	-17.67(±0.21)	-14.68(±0.20)
0.1000	-22.24(±0.11)	-19.93(±0.11)	-17.15(±0.10)	-13.84(±0.10)
0.5000	-21.50(±0.02)	-18.98(±0.02)	-16.40(±0.02)	-13.10(±0.02)
1.0000	-18.88(±0.01)	-15.94(±0.01)	-14.33(±0.01)	-10.49(±0.01)
1.4980	-16.21(±0.01)	-13.47(±0.01)	-12.35(±0.01)	-9.51(±0.01)
2.0050	-12.69(±0.01)	-11.58(±0.01)	-9.82±0.01)	-7.23(±0.01)
2.5000	-9.80(±0.01)	-8.88(±0.01)	-7.56(±0.01)	-5.30(±0.01)
3.0000	-6.51(±0.01)	-6.09(±0.01)	-5.05(±0.01)	-4.22(±0.01)
Glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0492	-22.61(±0.22)	-19.44(±0.21)	-16.59(±0.20)	-14.57(±0.20)
0.0997	-21.18(±0.11)	-18.65(±0.10)	-15.70(±0.10)	-13.62(±0.10)
0.4885	-18.77(±0.02)	-17.36(±0.02)	-14.44(±0.02)	-12.59(±0.02)
0.9786	-16.14(±0.01)	-15.48(±0.01)	-11.94(±0.01)	-10.70(±0.01)
1.4702	-13.20(±0.01)	-12.87(±0.01)	-9.42(±0.01)	-8.91(±0.01)
1.9535	-9.98(±0.01)	-9.16(±0.01)	-7.36(±0.01)	-6.96(±0.01)
2.4675	-7.47(±0.01)	-7.36(±0.01)	-5.35(±0.01)	-5.09±0.01)
2.9524	-4.55(±0.01)	-4.38(±0.01)	-3.52(±0.01)	-3.35(±0.01)

Table 6.10. (*continued*)

m_A[a]/mol·kg^{-1}	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.4014 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0500	-19.16 (±0.21)	-17.58(±0.20)	-16.04(±0.20)	-13.77(±0.19)
0.1002	-18.26(±0.10)	-16.82(±0.10)	-14.87(±0.10)	-12.86(±0.10)
0.4998	-16.07(±0.02)	-15.23(±0.02)	-13.96(±0.02)	-11.40(±0.02)
0.9960	-14.81(±0.01)	-13.65(±0.01)	-11.88(±0.01)	-10.66(±0.01)
1.5010	-11.69(±0.01)	-11.56(±0.01)	-9.38(±0.01)	-8.79(±0.01)
1.9880	-8.93(±0.01)	-9.06±0.01)	-7.31(±0.01)	-6.89(±0.01)
2.5000	-6.32(±0.01)	-6.23(±0.01)	-4.66(±0.01)	-4.57(±0.01)
2.9980	-3.53(±0.01)	-3.42(±0.01)	-2.81(±0.01)	-2.65(±0.01)
Glycine betaine in 0.5024 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0509	-17.19(±0.20)	-13.52(±0.19)	-11.83(±0.19)	-10.15(±0.18)
0.1020	-16.18(±0.10)	-13.22(±0.10)	-11.21(±0.09)	-9.77(±0.09)
0.5020	-15.05(±0.02)	-11.76(±0.02)	-10.86(±0.02)	-8.44(±0.02)
1.0000	-13.47(±0.01)	-10.53(±0.01)	-9.54(±0.01)	-7.90(±0.01)
1.5000	-10.87(±0.01)	-8.95(±0.01)	-8.01(±0.01)	-6.76(±0.01)
2.0100	-7.91(±0.01)	-7.28(±0.01)	-6.42(±0.01)	-5.21(±0.01)
2.5000	-6.03(±0.01)	-5.69(±0.01)	-4.52(±0.01)	-4.33(±0.01)
2.9985	-3.13(±0.01)	-2.87(±0.01)	-2.47(±0.01)	-2.36(±0.01)

[a]*m* is the molality of glycine betaine in aqueous $CoCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_k is in brackets.

Table 6.11. Apparent Molar Isentropic Compressions, ϕ_k of Glycine Betaine in Aqueous $NiCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.1108 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0478	-24.91(±0.25)[b]	-21.42(±0.24)	-18.13(±0.23)	-14.08(±0.22)
0.1121	-22.53(±0.10)	-20.85(±0.10)	-17.29(±0.10)	-13.57(±0.09)
0.5091	-20.67(±0.02)	-18.59(±0.02)	-15.43(±0.02)	-12.93(±0.02)
1.0007	-18.73(±0.01)	-16.22(±0.01)	-14.11(±0.01)	-11.95(±0.01)
1.5020	-15.58(±0.01)	-14.51(±0.01)	-11.77(±0.01)	-10.06(±0.01)
2.0050	-12.91(±0.01)	-11.92(±0.01)	-9.72(±0.01)	-8.28(±0.01)
2.5230	-10.72(±0.01)	-9.00(±0.01)	-7.27(±0.01)	-6.41(±0.01)
2.9989	-7.54(±0.01)	-6.59(±0.01)	-5.42(±0.01)	-4.38(±0.01)
Glycine betaine in 0.2021 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0491	-24.38(±0.23)	-19.53(±0.22)	-18.12(±0.21)	-14.00(±0.21)
0.0999	-22.41(±0.11)	-17.92(±0.11)	-17.08(±0.10)	-13.50(±0.10)
0.4998	-20.68(±0.02)	-16.59(±0.02)	-16.04(±0.02)	-12.91(±0.02)
1.0011	-17.38(±0.01)	-14.31(±0.01)	-13.29(±0.01)	-11.15(±0.01)
1.4998	-15.31(±0.01)	-12.10(±0.01)	-11.25(±0.01)	-10.05(±0.01)
2.0010	-12.71(±0.01)	-10.48(±0.01)	-9.67(±0.01)	-7.99(±0.01)
2.4850	-10.66(±0.01)	-8.33(±0.01)	-7.25(±0.01)	-6.35(±0.01)
2.9999	-7.41(±0.01)	-5.75(±0.01)	-5.47(±0.01)	-4.29(±0.01)
Glycine betaine in 0.3031 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0510	-22.07(±0.22)	-17.75(±0.22)	-16.14(±0.20)	-14.83(±0.19)
0.0998	-21.66(±0.11)	-16.94(±0.11)	-15.36(±0.10)	-13.44(±0.10)
0.4886	-20.13(±0.02)	-15.95(±0.02)	-13.90(±0.02)	-12.68(±0.02)
0.9789	-16.95(±0.01)	-13.88(±0.01)	-12.95(±0.01)	-10.55(±0.01)
1.4850	-14.57(±0.01)	-11.90(±0.01)	-10.04(±0.01)	-9.43(±0.01)
1.9966	-11.79(±0.01)	-10.05(±0.01)	-7.89(±0.01)	-7.51(±0.01)
2.4865	-9.52(±0.01)	-7.89(±0.01)	-6.34(±0.01)	-5.24±0.01)
2.9282	-7.03(±0.01)	-5.36(±0.01)	-5.35(±0.01)	-4.13(±0.01)

Table 6.11. (*continued*)

m_A[a]/mol·kg^{-1}	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.4004 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0502	-20.68 (±0.21)	-16.82(±0.20)	-15.63(±0.19)	-13.15(±0.19)
0.1000	-19.69(±0.11)	-16.02(±0.10)	-14.10(±0.10)	-12.60(±0.10)
0.4990	-18.36(±0.02)	-15.73(±0.02)	-13.61(±0.02)	-11.02(±0.02)
0.9956	-14.61(±0.01)	-13.55(±0.01)	-11.56(±0.01)	-10.08(±0.01)
1.5030	-12.69(±0.01)	-11.30(±0.01)	-9.26(±0.01)	-8.28(±0.01)
1.9882	-10.78(±0.01)	-9.25±0.01)	-7.25(±0.01)	-6.48(±0.01)
2.4977	-8.23(±0.01)	-6.96(±0.01)	-5.24(±0.01)	-4.39(±0.01)
2.9982	-6.91(±0.01)	-5.21(±0.01)	-4.84(±0.01)	-3.83(±0.01)
Glycine betaine in 0.5121 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0510	-18.08(±0.20)	-15.30(±0.19)	-13.80(±0.18)	-11.68(±0.18)
0.1033	-17.18(±0.10)	-14.09(±0.10)	-12.67(±0.09)	-10.22(±0.09)
0.5001	-16.34(±0.02)	-12.87(±0.02)	-10.80(±0.02)	-8.93(±0.02)
0.9987	-13.13(±0.01)	-11.46(±0.01)	-9.88(±0.01)	-7.55(±0.01)
1.4988	-11.23(±0.01)	-9.64(±0.01)	-8.79(±0.01)	-6.50(±0.01)
2.0088	-9.14(±0.01)	-7.40(±0.01)	-7.04(±0.01)	-5.04(±0.01)
2.4988	-7.41(±0.01)	-5.16(±0.01)	-5.10(±0.01)	-4.21(±0.01)
2.9978	-6.11(±0.01)	-4.54(±0.01)	-4.34(±0.01)	-2.97(±0.01)

[a]*m* is the molality of glycine betaine in aqueous $NiCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_k is in brackets.

Table 6.12. Apparent Molar Isentropic Compressions, ϕ_k of Glycine Betaine in Aqueous $ZnCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

m_A[a]/mol·kg^{-1}	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\phi_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solution				
0.0515	-22.22(±0.24)[b]	-19.17(±0.23)	-15.52(±0.22)	-12.03(±0.21)
0.1018	-22.01(±0.12)	-19.00(±0.11)	-15.23(±0.11)	-11.93(±0.11)
0.4948	-20.28(±0.02)	-17.69(±0.02)	-14.32(±0.02)	-11.30(±0.02)
0.9830	-18.26(±0.01)	-15.97(±0.01)	-13.07(±0.01)	-10.53(±0.01)
1.5250	-15.90(±0.01)	-14.04(±0.01)	-11.67(±0.01)	-9.65(±0.01)
1.9702	-14.08(±0.01)	-12.45(±0.01)	-10.47(±0.01)	-8.87(±0.01)
2.4400	-12.26(±0.01)	-10.92±0.01)	-9.11(±0.01)	-8.27(±0.01)
2.9322	-10.13(±0.01)	-9.11(±0.01)	-7.96(±0.01)	-7.66(±0.01)

[a]m is the molality of glycine betaine in aqueous $ZnCl_2$ solutions. The experiment was carried-out under atmospheric pressure.

[b]Estimated uncertainty for each ϕ_k is in brackets.

6.3. PARTIAL MOLAR VOLUME AND PARTIAL MOLAR ISENTROPIC COMPRESSION

The least-squares fit method has been employed to fit ϕ_v and ϕ_k values using Equations 5.8 and 5.10. The coefficients of Equation (5.8) for the systems; glycine betaine in aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions are tabulated in Table 6.13, 6.14, 6.15 and 6.16, respectively. Similarly, the values of ϕ_k^0 and S_k along with the standard deviations (for all the cases) are given in Table 6.17-6.20.

Table 6.13. Least Squares Fit Parameters of the Equation, $\phi_v = \phi_v^0 + S_v m$ for the System: Glycine Betaine in Aqueous $MnCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
	Glycine betaine in 0.0903 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	99.09(±0.03)	0.48(±0.02)	0.1
298.15	99.46(±0.04)	0.41(±0.02)	0.1
308.15	99.72(±0.08)	0.52(±0.05)	0.2
318.15	100.92(±0.05)	0.27(±0.03)	0.1
	Glycine betaine in 0.2001 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	99.75(±0.03)	0.32(±0.01)	0.1
298.15	100.09(±0.03)	0.32(±0.02)	0.1
308.15	100.35(±0.07)	0.86(±0.04)	0.1
308.15	101.18(±0.04)	0.61(±0.02)	0.1
	Glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	102.98(±0.03)	0.31(±0.01)	0.1
298.15	103.18(±0.03)	0.37(±0.02)	0.1
308.15	103.46(±0.04)	0.32(±0.02)	0.1
308.15	103.64(±0.06)	0.32(±0.03)	0.1

Table 6.13. (*continued*)

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
	Glycine betaine in 0.3772 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	103.45(±0.02)	0.40(±0.01)	0.1
298.15	103.75(±0.03)	0.32(±0.02)	0.1
308.15	103.85(±0.03)	0.43(±0.02)	0.1
318.15	103.99(±0.06)	0.42(±0.02)	0.1
	Glycine betaine in 0.4653 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	103.57(±0.02)	0.48(±0.01)	0.1
298.15	103.80(±0.05)	0.41(±0.03)	0.1
308.15	103.87(±0.03)	0.44(±0.02)	0.1
318.15	104.06(±0.04)	0.41(±0.02)	0.1

[a]Standard deviations are in parentheses.

Table 6.14. Least Squares Fit Parameters of the Equation, $\phi_v = \phi_v^0 + S_v m$ for the System: Glycine Betaine in Aqueous $CoCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6$/(m^3·mol^{-1})	$S_v \cdot 10^6$/(m^3·mol^{-2}·kg)	$\sigma \cdot 10^6$/(m^3·mol^{-1})
Glycine betaine in 0.1083 mol·kg^{-1} aqueous $CoCl_2$solution			
288.15	98.38(±0.07)	0.73(±0.04)	0.1
298.15	99.41(±0.03)	0.64(±0.01)	0.1
308.15	99.64(±0.04)	0.58(±0.02)	0.1
318.15	100.92(±0.02)	0.28(±0.03)	0.1
Glycine betaine in 0.2140 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	99.79(±0.04)	0.78(±0.02)	0.1
298.15	100.02(±0.03)	0.75(±0.02)	0.1
308.15	100.29(±0.04)	0.83(±0.02)	0.1
308.15	101.05(±0.04)	0.69(±0.02)	0.1
Glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	102.57(±0.02)	0.34(±0.01)	0.1
298.15	102.77(±0.04)	0.49(±0.02)	0.1
308.15	102.98(±0.03)	0.59(±0.02)	0.1
308.15	103.23(±0.05)	0.55(±0.03)	0.1

Table 6.14. (*continued*)

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
Glycine betaine in 0.4014 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	102.72(±0.04)	0.52(±0.02)	0.1
298.15	102.97(±0.02)	0.54(±0.01)	0.1
308.15	103.18(±0.04)	0.62(±0.02)	0.1
318.15	103.46(±0.03)	0.54(±0.02)	0.1
Glycine betaine in 0.5024 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	102.96(±0.06)	0.50(±0.03)	0.1
298.15	103.32 (±0.05)	0.47(±0.02)	0.1
308.15	103.41(±0.06)	0.61(±0.03)	0.1
318.15	103.55(±0.02)	0.62(±0.01)	0.1

[a]Standard deviations are in parentheses.

Table 6.15. Least Squares Fit Parameters of the Equation, $\phi_v = \phi_v^0 + S_v m$ for the System: Glycine Betaine in Aqueous $NiCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
Glycine betaine in 0.1108 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	99.44(±0.02)	0.25(±0.02)	0.1
298.15	99.70(±0.03)	0.23(±0.01)	0.1
308.15	99.84(±0.02)	0.21(±0.01)	0.1
318.15	100.92(±0.01)	0.16(±0.01)	0.1
Glycine betaine in 0.2021 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	99.60(±0.03)	0.22(±0.02)	0.1
298.15	99.86(±0.02)	0.19(±0.01)	0.1
308.15	100.15(±0.04)	0.22(±0.02)	0.1
308.15	101.10(±0.03)	0.22(±0.01)	0.1
Glycine betaine in 0.3031 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	102.42(±0.05)	0.37(±0.03)	0.1
298.15	102.74(±0.02)	0.38(±0.01)	0.1
308.15	102.98(±0.02)	0.38(±0.01)	0.1
308.15	103.35(±0.03)	0.38(±0.02)	0.1

Table 6.15. (*continued*)

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
Glycine betaine in 0.4004 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	102.59(±0.02)	0.33(±0.01)	0.1
298.15	102.78(±0.04)	0.39(±0.02)	0.1
308.15	103.10(±0.03)	0.35(±0.02)	0.1
318.15	103.41(±0.03)	0.38(±0.01)	0.1
Glycine betaine in 0.5121 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	102.96(±0.06)	0.50(±0.03)	0.2
298.15	103.17 (±0.03)	0.38(±0.02)	0.1
308.15	103.33(±0.03)	0.38(±0.02)	0.2
318.15	103.53(±0.03)	0.38(±0.02)	0.1

[a]Standard deviations are in parentheses.

Table 6.16. Least Squares Fit Parameters of the Equation, $\phi_v = \phi_v^0 + S_v m$ for the System: Glycine Betaine in Aqueous $ZnCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_v^0 \cdot 10^6/(m^3 \cdot mol^{-1})$	$S_v \cdot 10^6/(m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^6/(m^3 \cdot mol^{-1})$
Glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solution			
288.15	101.22(±0.03)	0.36(±0.02)	0.1
298.15	101.46(±0.03)	0.37(±0.02)	0.1
308.15	101.79(±0.05)	0.50(±0.03)	0.1
318.15	102.04(±0.03)	0.48(±0.01)	0.1

[a]Standard deviations are in parentheses.

Table 6.17. Least Squares Fit Parameters of the Equation, $\phi_k = \phi_k^0 + S_k m$ for the System: Glycine Betaine in Aqueous $MnCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_k^0 \cdot 10^{15}/(Pa^{-1} \cdot m^3 \cdot mol^{-1})$	$S_k \cdot 10^{15}/(Pa^{-1} \cdot m^3 \cdot mol^{-2} \cdot kg)$	$\sigma \cdot 10^{15}/(Pa^{-1} \cdot m^3 \cdot mol^{-1})$
Glycine betaine in 0.0903 mol·kg^{-1} aqueous $MnCl_2$solution			
288.15	-25.10(±0.42)	5.00(±0.25)	0.7
298.15	-22.54(±0.07)	5.06(±0.04)	0.1
308.15	-21.06(±0.18)	5.70(±0.11)	0.3
318.15	-15.25(±0.23)	3.19(±0.14)	0.4
Glycine betaine in 0.2001 mol·kg^{-1} aqueous $MnCl_2$ solution			
288.15	-23.93(±0.36)	5.11(±0.22)	0.6
298.15	-21.93(±0.36)	5.08(±0.21)	0.6
308.15	-20.59(±0.20)	5.60(±0.12)	0.3
318.15	-15.16(±0.20)	3.51(±0.12)	0.3

Table 6.17. (*continued*)

T/K	$\phi_k^0 \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-2}·kg)	σ·10^{15}/(Pa^{-1}·m^3·mol^{-1})
	Glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	-22.66(±0.29)	4.80(±0.17)	0.4
298.15	-20.25(±0.24)	4.41(±0.15)	0.4
308.15	-17.64(±0.19)	4.64(±0.12)	0.3
308.15	-14.19(±0.27)	3.36(±0.17)	0.4
	Glycine betaine in 0.3772 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	-20.87(±0.22)	5.03(±0.13)	0.3
298.15	-18.79(±0.35)	5.11(±0.21)	0.6
308.15	-16.54(±0.44)	5.03(±0.26)	0.7
318.15	-13.43(±0.31)	3.94(±0.19)	0.5
	Glycine betaine in 0.4653 mol·kg^{-1} aqueous $MnCl_2$ solution		
288.15	-17.95(±0.19)	4.60(±0.11)	0.3
298.15	-13.30(±0.16)	3.60(±0.09)	0.2
308.15	-12.02(±0.10)	3.53(±0.06)	0.1
318.15	-10.65(±0.07)	3.25(±0.04)	0.1

[a]Standard deviations are in parentheses.

Table 6.18. Least Squares Fit Parameters of the Equation, $\phi_k = \phi_k^{\,0} + S_k m$ for the System: Glycine Betaine in Aqueous $CoCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_k^{\,0} \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-2}·kg)	$\sigma \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})
Glycine betaine in 0.1083 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	-24.93(±0.19)	5.64(±0.11)	0.3
298.15	-20.82(±0.37)	4.61(±0.22)	0.6
308.15	-18.45(±0.09)	4.46(±0.05)	0.1
318.15	-15.19(±0.19)	3.49(±0.11)	0.3
Glycine betaine in 0.2140 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	-23.65(±0.41)	5.50(±0.24)	0.7
298.15	-20.98(±0.22)	4.88(±0.13)	0.3
308.15	-18.16(±0.26)	4.22(±0.15)	0.4
318.15	-14.53(±0.23)	3.56(±0.14)	0.4
Glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	-22.09(±0.25)	6.01(±0.15)	0.4
298.15	-19.78(±0.31)	5.12(±0.19)	0.5
308.15	-16.49(±0.21)	4.50(±0.12)	0.3
308.15	-14.39(±0.13)	3.76(±0.08)	0.2

Table 6.18. (*continued*)

T/K	$\phi_k^0 \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-2}·kg)	σ·10^{15}/(Pa^{-1}·m^3·mol^{-1})
Glycine betaine in 0.4014 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	-19.18(±0.26)	5.14(±0.15)	0.4
298.15	-17.67(±0.21)	4.40(±0.13)	0.3
308.15	-15.97(±0.20)	4.41(±0.12)	0.3
318.15	-13.70(±0.27)	3.57(±0.16)	0.4
Glycine betaine in 0.5024 mol·kg^{-1} aqueous $CoCl_2$ solution			
288.15	-17.37(±0.28)	4.60(±0.17)	0.4
298.15	-13.74(±0.24)	3.38(±0.14)	0.4
308.15	-12.16(±0.27)	3.04(±0.16)	0.4
318.15	-10.13(±0.19)	2.45(±0.11)	0.3

[a]Standard deviations are in parentheses.

Table 6.19. Least Squares Fit Parameters of the Equation, $\phi_k = \phi_k^{\,0} + S_k m$ for the System: Glycine Betaine in Aqueous $NiCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_k^{\,0} \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-2}·kg)	$\sigma \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})
Glycine betaine in 0.1108 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	-23.39(±0.25)	5.17(±0.14)	0.3
298.15	-21.43 (±0.18)	4.89(±0.11)	0.3
308.15	-17.99(±0.09)	4.19(±0.19)	0.2
318.15	-14.47(±0.27)	3.19(±0.16)	0.4
Glycine betaine in 0.2021 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	-22.94(±0.22)	5.10(±0.12)	0.2
298.15	-18.51(±0.16)	4.16(±0.13)	0.2
308.15	-17.86(±0.21)	4.20(±0.12)	0.3
318.15	-14.28(±0.21)	3.19(±0.12)	0.3
Glycine betaine in 0.3031 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	-22.32(±0.12)	5.21(±0.07)	0.2
298.15	-17.83(±0.20)	4.08(±0.12)	0.3
308.15	-15.99(±0.27)	3.80(±0.16)	0.5
308.15	-14.08(±0.23)	3.40(±0.13)	0.3

Table 6.19. (*continued*)

T/K	$\phi_k^0 \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-2}·kg)	σ·10^{15}/(Pa^{-1}·m^3·mol^{-1})
Glycine betaine in 0.4004 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	-20.25(±0.37)	4.70(±0.22)	0.6
298.15	-17.11(±0.24)	3.96(±0.14)	0.4
308.15	-15.13(±0.36)	3.70(±0.21)	0.6
318.15	-13.01(±0.22)	3.22(±0.13)	0.3
Glycine betaine in 0.5121 mol·kg^{-1} aqueous $NiCl_2$ solution			
288.15	-17.82(±0.31)	4.12(±0.18)	0.5
298.15	-14.91(±0.28)	3.64(±0.17)	0.4
308.15	-13.11(±0.31)	3.05(±0.18)	0.5
318.15	-10.70(±0.33)	2.68(±0.20)	0.5

[a]Standard deviations are in parentheses.

Table 6.20. Least Squares Fit Parameters of the Equation, $\phi_k = \phi_k^0 + S_k m$ for the System: Glycine Betaine in Aqueous $ZnCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K.[a]

T/K	$\phi_k^0 \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})	$S_k \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-2}·kg)	σ·10^{15}/(Pa^{-1}·m^3·mol^{-1})
Glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solution			
288.15	-22.39(±0.04)	4.19(±0.02)	0.1
298.15	-19.37(±0.02)	3.49(±0.01)	0.1
308.15	-15.60(±0.04)	2.62(±0.03)	0.1
318.15	-12.06(±0.05)	1.55(±0.03)	0.1

[a]Standard deviations are in parentheses.

The partial molar quantities are sensitive towards the structural reorganizations arising when non-electrolyte and electrolyte are dissolved in water, changes in parameters such as concentration and temperature (Korolev and Serebryakova 2011). Further these values solely concern the interactions between glycine betaine and solvent molecules, as at infinite dilution, the interactions among glycine betaine molecules are negligible (Soto et al. 2004). As seen by the table, ϕ_k^0 values of glycine betaine in aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions are large and positive, while the ϕ_k^0 values are negative indicating the presence of strong solute-solvent interactions in the systems considered. The partial molar volumes of glycine betaine in $MnCl_2$ were found to be higher than those in other metal salt solutions at all the temperatures of the study.

The observed trend in partial molar quantities can be discussed in view of the nature of solute and solvent. Properties of water molecules in the vicinity of the solute differ compared to those in the bulk. Water molecules which are in direct contact with the glycine betaine surface are said to constitute a hydration co-sphere. The charged groups of glycine betaine influence the water molecules in the hydration co-sphere to exhibit different physicochemical characteristics as compared to bulk water. These co-spheres are also influenced by the constituent ions of the solvent (i.e. Mn^{2+}, Co^{2+}, Ni^{2+} or Zn^{2+} and Cl^-) and various molecular interactions will come into picture.

The observed trend can also be analysed by taking into account of cosphere overlap model; Glycine betaine essentially behaves as a zwitterion since it is the derivative of a peptide-'glycine' whose all the three hydrogen atoms at amino group have been replaced by ($-CH_3$) groups. As a result of dissociation of amino and carboxyl groups of the molecule in aqueous solvent, the water molecules orient around the solute and solvent constituents depending on their strength. The solute-solvent interactions present in the solutions studied can be explained as (i) electrostatic hydration of charged end groups of the zwitter ion, and (ii) the overlap of hydration co-spheres of these terminal groups with that of $-CH_2$ group of glycine betaine contributing towards ϕ_v^0 values (Nain and Pal 2013). As the temperature increases, water molecules from the secondary solvation layer of glycine betaine are released into the bulk resulting in larger ϕ_v^0 values and rendering the solutions more compressible. Thus, at higher temperature

the process of releasing water molecules favours rather than to bind the charged end groups of glycine betaine. Similar trends in ϕ_v^0 values have been observed in chapter 5, i.e. on volumetric properties of glycine betaine in aqueous NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions. It is known that the non-additive perturbation of hydrogen bonded network of solvent water is absent in glycine betaine (Michele et al. 2006). But the perturbation seems to be present in aqueous metal salt solutions. In view of this, pertaining to the glycine betaine molecule, the restructure of water network is the result of two effects: (i) the hydrophobic hydration of -CH_3 and-CH- portions of the molecules (ii) hydrophilic hydration of net charges present in the molecule. But it is concluded in the literature that the disturbing effect of the ionic carboxylate group on the ice-like water is prevalent compared to the structuring effect due to hydrophobic hydration (Michele et al. 2006).

The ϕ_k^0 values of glycine betaine in aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions are negative. This can be attributed to the electrostriction at the terminals of the zwitterion. Such electrostriction reduces the mobility of the hydration water and its contribution to the relaxation part of the compression has a decreasing effect on the total compression. The positive values of the slopes S_v and S_k suggest that the pairwise interaction is influenced by the interaction of the charged functional groups (of glycine betaine) with ions of the solvent (Mn^{2+}/Co^{2+}/Ni^{2+}/Zn^{2+}/ Cl^-); hence, both the volumetric and compression results complement each other. The higher ϕ_v^0 and ϕ_k^0 values of glycine betaine in $MnCl_2$ than other metal salts can be attributed to the different bond distance of M^{2+}-H_2O in water (where M= Mn/Co/Ni/Zn). The Ni^{2+}-water, Zn^{2+}-water, Co^{2+}-water and Mn^{2+}-water bond distances due to cation hydration from the X-ray diffraction studies are 206.2 pm, 209.6 pm, 210.0 pm and 220.0 pm, respectively (Bol et al. 1970 and Ohtaki and Radnai 1993). The Mn^{2+}-OH_2 bond distance is longer in comparison to that of Co^{2+}-water, Ni^{2+}-water and Zn^{2+}-water, the same trend can be observed in the partial molar volume and partial molar isentropic compression of glycine betaine in these solvents.

At higher concentrations of metal slats, the effect of glycine betaine concentration on the ϕ_k^0 values decreases due to the reduction in the magnitude of the

electrostatic interactions. This may be attributed to the accumulation of large concentration of oppositely charged M^{2+} and chloride ions around the glycine betaine molecules in concentrated metal salt solutions.

6.4. TRANSFER MOLAR PROPERTIES

Transfer thermodynamic properties of biomolecules are important due to qualitative and quantitative information they furnish on the co-solvent-solute interactions without taking account of the effects of solute-solute interactions. A thermodynamic transfer function is defined as the change in an apparent molar thermodynamic property obtained at infinite dilution when one mole of a solute is transferred from one solvent system to another (Hakin et al. 2003). The transfer molar volumes, $\Delta_{tr}\phi_v^0$ and transfer molar isentropic compressions, $\Delta_{tr}\phi_k^0$ of glycine betaine from water to aqueous $MnCl_2/CoCl_2/NiCl_2/ZnCl_2$ solutions have been calculated using the Equation 5.11.

The calculated values of transfer properties are presented in Table 6.21. According to this table, the transfer properties roughly decrease with the temperature of the study. The effect of concentrations of $MnCl_2$, $CoCl_2$ and $NiCl_2$ in aqueous solutions on transfer volumes have been plotted as Figures 6.5, 6.6 and 6.7, respectively. Similarly, the effect of concentrations of $MnCl_2$, $CoCl_2$ and $NiCl_2$in aqueous solutions on transfer partial molar isentropic compressions have been plotted as Figures 6.8, 6.9 and 6.10, respectively.

Table 6.21. Transfer Partial Molar Volumes, $\Delta_{tr}\phi_v^0$ and Transfer Partial Molar Isentropic Compressions, $\Delta_{tr}\phi_k^0$ of Glycine Betaine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, T = (288.15 to 318.15) K.

$^a m_B$/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
$\Delta_{tr}\phi_v^0 \cdot 10^6$/(m^3·mol^{-1})				
Glycine betaine in aqueous $MnCl_2$ solutions				
0.0903	1.83	0.26	0.20	0.06
0.2001	2.49	0.89	0.83	0.32
0.3224	5.72	3.98	3.94	2.78
0.3772	6.19	4.55	4.33	3.13
0.4653	6.31	4.60	4.35	3.20
Glycine betaine in aqueous $CoCl_2$ solutions				
0.1083	1.12	0.21	0.12	0.06
0.2140	2.53	0.82	0.77	0.19
0.3262	5.31	3.57	3.46	2.37
0.4014	5.46	3.77	3.66	2.60
0.5024	5.70	4.12	3.89	2.69
Glycine betaine in aqueous $NiCl_2$ solutions				
0.1108	2.18	0.50	0.32	0.06
0.2021	2.34	0.66	0.63	0.24
0.3031	5.16	3.54	3.46	2.49
0.4004	5.33	3.58	3.58	2.55
0.5121	5.70	3.97	3.81	2.67
Glycine betaine in aqueous $ZnCl_2$ solutions				
0.0971	3.96	2.66	2.27	1.18

$^a m_B$ is the molar concentration of metal salt solution.

Table 6.21. (*continued*)

$^{a}m_B$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
$\Delta_{tr}\phi_v^0 \cdot 10^{15}$/(Pa^{-1}·m^3·mol^{-1})				
Glycine betaine in aqueous $MnCl_2$ solutions				
0.0903	7.94	5.62	0.82	0.05
0.2001	9.11	6.23	1.29	0.14
0.3224	10.38	7.91	4.24	1.11
0.3772	12.17	9.37	5.34	1.87
0.4653	15.09	14.86	9.86	4.65
Glycine betaine in aqueous $CoCl_2$ solutions				
0.1083	8.11	7.30	3.43	0.11
0.2140	9.39	7.18	3.72	0.77
0.3262	10.95	8.38	5.39	0.91
0.4014	13.86	10.49	5.91	1.60
0.5024	15.67	14.42	9.72	5.17
Glycine betaine in aqueous $NiCl_2$ solutions				
0.1108	9.65	6.73	3.89	0.83
0.2021	10.10	9.65	4.02	1.02
0.3031	10.72	10.33	5.89	1.22
0.4004	12.79	11.05	6.75	2.29
0.5121	15.22	12.25	8.77	4.60
Glycine betaine in aqueous $ZnCl_2$ solutions				
0.0971	3.96	2.66	2.27	1.18

$^{a}m_B$ is the approximate molar concentration of metal salt solution.

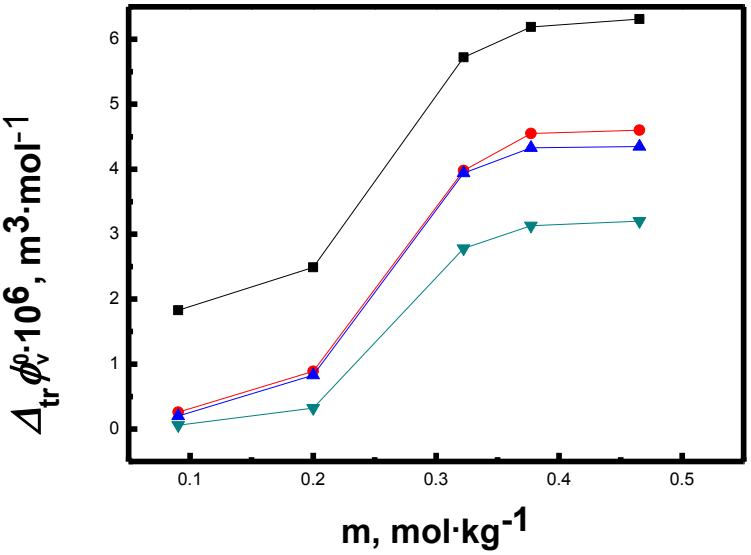

Figure 6.5. Plot of variation of transfer partial molar volumes, $\Delta_{tr}\phi_v^0$ of glycine betaine from aqueous to aqueous $MnCl_2$ solutions with respect to solvent concentration. At temperatures, ■, T = 288.15 K; ●, T = 298.15 K; ▲, T = 308.15 K; ▼, T = 318.15 K.

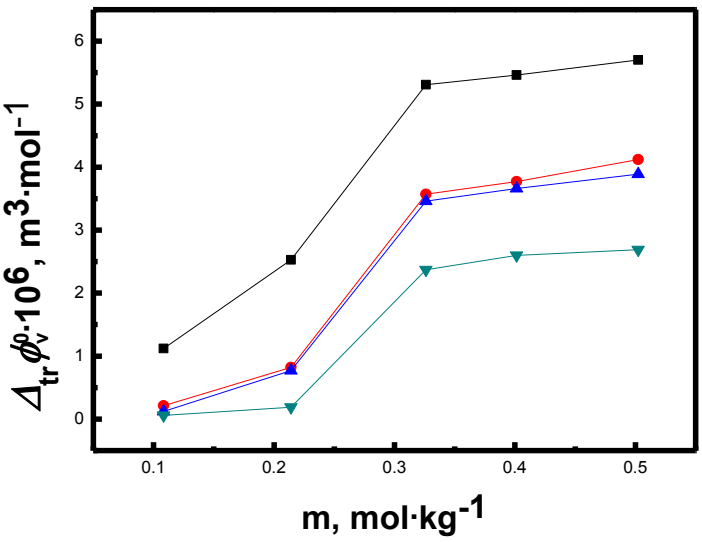

Figure 6.6. Plot of variation of transfer partial molar volumes, $\Delta_{tr}\phi_v^0$ of glycine betaine from aqueous to aqueous $CoCl_2$ solutions with respect to solvent concentration. At temperatures, ■, T = 288.15 K; ●, T = 298.15 K; ▲, T = 308.15 K; ▼, T = 318.15 K.

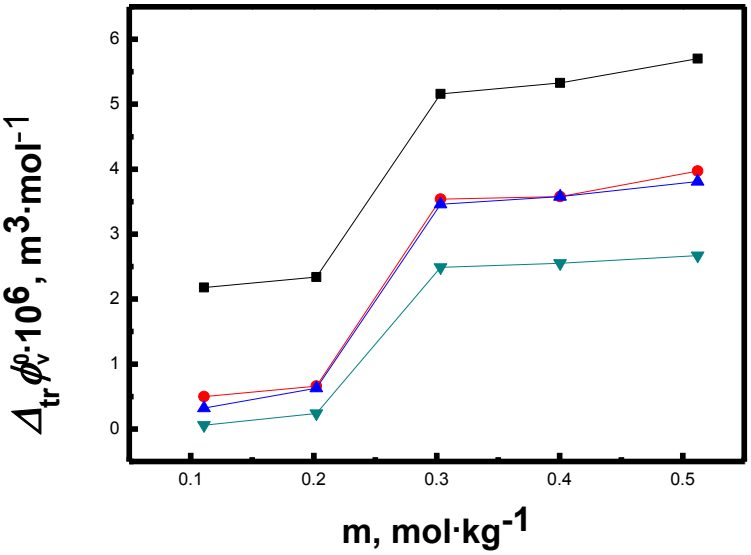

Figure 6.7. Plot of variation of transfer partial molar volumes, $\Delta_{tr}\phi_v^0$ of glycine betaine from aqueous to aqueous $NiCl_2$ solutions with respect to solvent concentration. At temperatures, ■, T = 288.15 K; ●, T = 298.15 K; ▲, T = 308.15 K; ▼, T = 318.15 K.

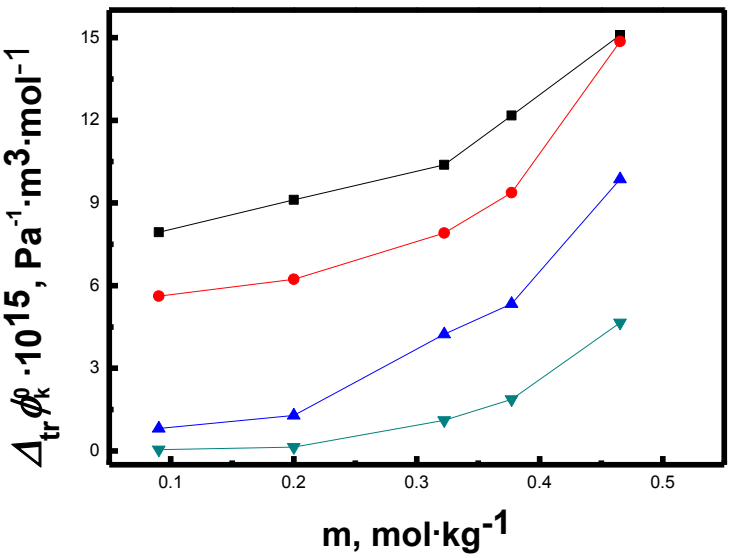

Figure 6.8. Plot of variation of transfer partial molar isentropic compressions, $\Delta_{tr}\phi_k^0$ of glycine betaine from aqueous to aqueous $MnCl_2$ solutions with respect to solvent concentration. At temperatures, ■, T = 288.15 K; ●, T = 298.15 K; ▲, T = 308.15 K; ▼, T = 318.15 K.

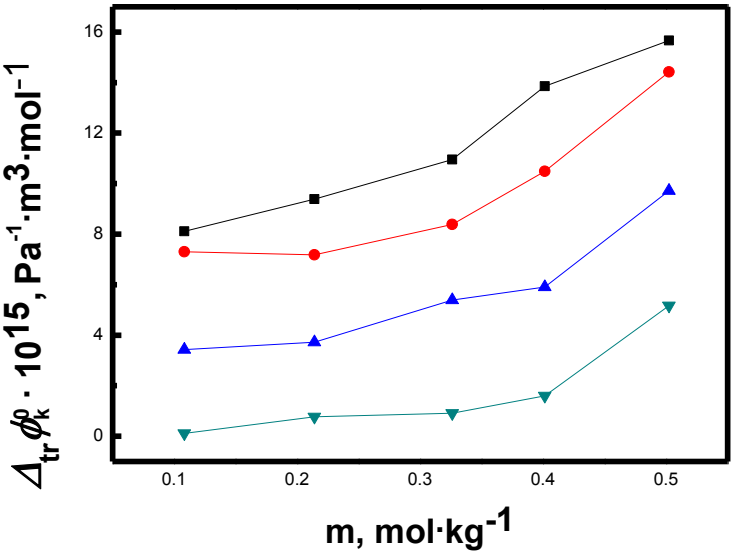

Figure 6.9. Plot of variation of transfer partial molar isentropic compressions, $\Delta_{tr}\phi_k^0$ of glycine betaine from aqueous to aqueous $CoCl_2$ solutions with respect to solvent concentration. At temperatures, ■, T = 288.15 K; ●, T = 298.15 K; ▲, T = 308.15 K; ▼, T = 318.15 K.

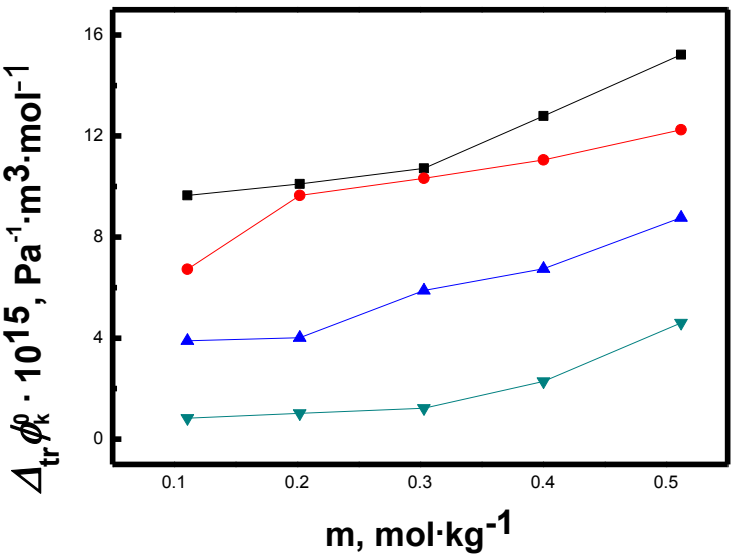

Figure 6.10. Plot of variation of transfer partial molar isentropic compressions, $\Delta_{tr}\phi_k^0$ of glycine betaine from aqueous to aqueous $NiCl_2$ solutions with respect to solvent concentration. At temperatures, ■, T = 288.15 K; ●, T = 298.15 K; ▲, T = 308.15 K; ▼, T = 318.15 K.

As depicted by the figures, the transfer molar quantities increase with concentrations of $MnCl_2$, $CoCl_2$ and $NiCl_2$ in aqueous solutions.

The positive and increasing values of $\Delta_{tr}\phi_v^0$ and $\Delta_{tr}\phi_k^0$ may be attributed to the larger electrostriction by metal ions in aqueous solutions. Further, in glycine betaine molecule, there is a greater effect of electrostriction of the amino group than the carboxyl group (Edsall and Wyman 1935).

The stronger electrical fields near the ions cause increased compression and orientation effects in the solutions. Thus, there will be an increase in volume and hence positive values of $\Delta_{tr}\phi_v^0$ for glycine betaine in aqueous metal salt solutions due to strong interactions of constituents of the solvent with glycine betaine molecule (Tyrrell and Kennerley 1968, Millero et al. 1978, Kikuchi et al 1995, Kharakoz 1997, Yan et al. 1998 and Thakur et al. 2013). Also, the positive volume transfers of glycine betaine in this work indicate that, the electrostatic charge-charge interactions (among Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cl^-, amino and carboxylic groups of glycine betaine) are predominant over the ionic–hydrophobic interactions (among Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cl^-, $-CH_2$ or $-CH_3$ groups of glycine betaine) in aqueous solutions.

Further, there is a surge in transfer partial properties of these system with electrolyte concentrations more than 0.3 mol·kg^{-1}. This effect can be understood by taking into account of increased cohesion due to increase in number of ions in the solutions.

The temperature dependence of ϕ_v^0 can be expressed by the equation (Pal and Chauhan 2012),

$$\phi_V^0 = a + b(T - T_m) + c(T - T_m)^2 \qquad (6.1)$$

where T_m is the midpoint of the temperature range used (T_m = 303.15 K). The parameters *a*, *b* and *c* were obtained by the least square fitting of Equation (6.1). So obtained values are given in Table 6.22 along with their uncertainties. As can be seen from the table, values of the coefficient *a* are positive indicating the presence of solute-solvent interaction in the present systems.

Table 6.22. The Polynomial Coefficients of Equation (6.1) for the System: Glycine Betaine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions at Temperatures, T = (288.15 to 318.15) K.

$^{a}m_B$/(mol·kg^{-1})	$a\cdot10^6$/(m^3·mol^{-1})	$b\cdot10^7$ /(m^3·mol^{-1}·K^{-1})	$c\cdot10^{10}$/(m^3·mol^{-1}·K^{-2})
Glycine betaine in aqueous $MnCl_2$ solutions			
0.0903	99.54(±0.18)	0.5744(±0.1054)	20.4(±11.8)
0.2001	100.19(±0.12)	0.4550(±0.0683)	12.1(±7.6)
0.3224	103.32(±0.03)	0.2273(±0.0174)	-0.25(±1.9)
0.3772	103.81(±0.04)	0.1727 (±0.0237)	-3.79(±2.6)
0.4653	103.84(±0.05)	0.1542(±0.0290)	-1.34(±3.2)
Glycine betaine in aqueous $CoCl_2$ solutions			
0.1083	99.51(±0.33)	0.7850(±0.0185)	6.25(±2.07)
0.2140	100.12(±0.08)	0.4050(±0.0045)	13.3(±5.03)
0.3262	102.87(±0.03)	0.2190(±0.0003)	1.25(±0.33)
0.4014	103.07(±0.02)	0.2430(±0.0011)	0.75(±1.2)
0.5024	103.38(±0.05)	0.1860(±0.0032)	-5.50(±3.5)
Glycine betaine in aqueous $NiCl_2$ solutions			
0.1108	99.78(±0.18)	0.4580(±0.0106)	20.0(±1.19)
0.2021	99.96(±0.11)	0.4790(±0.0063)	17.2(±0.70)
0.3031	102.85(±0.03)	0.3031(±0.0002)	12.5(±0.25)
0.4004	102.93(±0.03)	0.2782(±0.0014)	3.00(±1.2)
0.5121	103.26(±0.05)	0.2590(±0.0033)	-6.25(±3.6)
Glycine betaine in aqueous $ZnCl_2$ solutions			
0.0971	101.62(±0.01)	0.2815(±0.0006)	0.23(±0.73)

$^{a}m_B$ is the molar concentration of metal salt solution.

The partial molar isobaric expansion at infinite dilution, E_2^0 can be obtained by the differentiating Equation (6.7) with respect to temperature at constant pressure,

$$E_2^0 = (\partial\phi_V^0 / \partial T)_P = b + 2c(T - T_m) \tag{6.2}$$

This relation can be utilized to compute Hepler's coefficient $(\partial^2\phi_V^0 / \partial T^2)$,

$$\left(\partial C_P^0 / \partial P\right)_T = -T(\partial^2\phi_v^0 / \partial T^2)_P \tag{6.3}$$

where C_P^0 is the heat capacity of the solute at infinite dilution. Calculated values of $(\partial^2\phi_v^0/\partial T^2)$ are presented in Table 6.23.

Table 6.23. Values of Hepler's Coefficient for the Systems: Glycine Betaine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions.

$^a m_B$/(mol·kg^{-1})	$(\partial^2\phi_v^0/\partial T^2)\cdot 10^{10}$/(m^3·mol^{-1}·K^{-2})
Glycine betaine in aqueous $MnCl_2$ solutions	
0.0903	40.8
0.2001	24.2
0.3224	-0.50
0.3772	-7.58
0.4653	-2.68
Glycine betaine in aqueous $CoCl_2$ solutions	
0.1083	12.5
0.2140	26.6
0.3262	2.50
0.4014	1.50
0.5024	-11.0
Glycine betaine in aqueous $NiCl_2$ solutions	
0.1108	41.0
0.2021	34.4
0.3031	2.50
0.4004	0.06
0.5121	-12.5
Glycine betaine in aqueous $ZnCl_2$ solutions	
0.0971	0.46

$^a m_B$ is the molar concentration of metal salt solution.

From the positive values of Hepler's coefficients, it can be proposed that glycine betaine acts as a structure-maker in aqueous $CoCl_2$, $NiCl_2$ and $ZnCl_2$ solution under the experimental conditions.

Glycine betaine molecule can be visualized as a tetramethylammonium moiety in aqueous solutions (Bhattacharya and Sengupta 1985). The tetramethylammonium moiety should therefore, increase the extent of structure braking character of the glycine betaine molecule. This effect is suppressed by the presence of acetate groups at the other end of the molecule. The localized positive charge facilitates the separation of proton through the inductive effect and this further enhanced by the presence of co-solute metal salt. Thus due to the solute-co-solute interaction, glycine betaine behaves as the structure maker glycinium cation which is evident from the positive $(\partial^2\phi_v^0 / \partial T^2)_P$ values (Hepler 1969 and Pal and Kumar 2004). However in concentrated $MnCl_2$, $CoCl_2$ and $NiCl_2$ solutions it behaves as a structure breaker. This particular behaviour needs further explorations as one of the probable reasons may be that the hydrophobic-ionic interactions between hydrophobic parts of the glycine betaine molecule with constituent ions of metal salt solutions increase at higher concentration of metal salt. The same effect can be related to negative value of Hepler's constant for glycine betaine in aqueous solutions as reported by Krakowiak et al. (2013) where glycine betaine behaves as a structure breaker. The co-solute-glycine betaine interactions at lower metal salt concentration may fecilitate for structure making property of the molecule which later decreases as metal salt concentration increases.

The refractive index values of all the above systems are presented in Table 6.24. The values of n_D were found to increase with the solute concentration in all the cases. This behaviour is consistent with the results obtained from apparent molar volume and the isentropic compressibility values of glycine betaine in aqueous metal salt solutions is directly related to the interactions in the solutions.

Table 6.24. Refractive Index, n_D, of the Systems: Glycine Betaine in Aqueous $MnCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ Solutions at Temperatures, T = (288.15 K to 318.15) K

$m_A{}^b$/(mol·kg^{-1})	T/K			
	288.15	**298.15**	**308.15**	**318.15**
n_D				
Glycine betaine in 0.0903 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0000	1.33651	1.33553	1.33454	1.33442
0.0499	1.33732	1.33632	1.33556	1.33514
0.1000	1.33821	1.33721	1.33688	1.33671
0.5049	1.34525	1.34446	1.34367	1.34285
1.0070	1.35257	1.35158	1.35043	1.34931
1.5000	1.35829	1.35740	1.35672	1.35660
2.0066	1.36492	1.36403	1.36271	1.36259
2.5010	1.37104	1.37015	1.36899	1.36858
3.0014	1.37592	1.37503	1.37368	1.37256
Glycine betaine in 0.2001 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0000	1.33790	1.33715	1.33654	1.33630
0.0487	1.33932	1.33894	1.33809	1.33785
0.1110	1.34021	1.33974	1.33889	1.33865
0.4973	1.34605	1.34507	1.34395	1.34371
0.9944	1.35377	1.35203	1.35125	1.35101
1.5101	1.35949	1.35775	1.35679	1.35655
1.9894	1.36612	1.36466	1.36331	1.36307
2.4890	1.37224	1.37035	1.36931	1.36907
2.9859	1.37712	1.37588	1.37504	1.37480
Glycine betaine in 0.3224 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0000	1.34282	1.34195	1.34093	1.34049
0.0500	1.34426	1.34345	1.34238	1.34193
0.1000	1.34493	1.34408	1.34301	1.34251
0.5007	1.35002	1.34919	1.34815	1.34771
0.9722	1.35765	1.35666	1.35554	1.35512
1.4535	1.36275	1.36191	1.36084	1.36045
1.9312	1.37046	1.36954	1.36856	1.36799
2.4216	1.37420	1.37299	1.37191	1.37126
3.0009	1.38330	1.38198	1.38101	1.38042

Table 6.24. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
n_D				
Glycine betaine in 0.3772 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0000	1.34457	1.34336	1.34187	1.34050
0.0510	1.34520	1.34397	1.34260	1.34104
0.0999	1.34581	1.34462	1.34311	1.34174
0.4823	1.35054	1.34933	1.34788	1.34644
0.9679	1.35655	1.35534	1.35394	1.35247
1.4850	1.36295	1.36170	1.36033	1.35876
1.9439	1.36863	1.36742	1.36601	1.36454
2.5020	1.37554	1.37430	1.37281	1.37134
2.8991	1.38046	1.37925	1.37782	1.37635
Glycine betaine in 0.4653 mol·kg^{-1} aqueous $MnCl_2$ solution				
0.0000	1.34608	1.34446	1.34278	1.34170
0.0512	1.34661	1.34508	1.34350	1.34214
0.1050	1.34734	1.34572	1.34408	1.34294
0.5000	1.35205	1.35063	1.34871	1.34774
1.0000	1.35809	1.35644	1.35484	1.35369
1.5008	1.36446	1.36280	1.36133	1.35999
1.9980	1.37024	1.36862	1.36691	1.36554
2.5008	1.37705	1.37545	1.37391	1.37234
3.0000	1.38199	1.38035	1.37852	1.37725
Glycine betaine in 0.1083 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0000	1.34054	1.33950	1.33819	1.33656
0.0500	1.34308	1.34198	1.34065	1.33891
0.1020	1.34375	1.34265	1.34131	1.33957
0.5049	1.34897	1.34774	1.34649	1.34502
1.0017	1.35753	1.35623	1.35455	1.35253
1.5000	1.36200	1.36061	1.35905	1.35743
2.0066	1.36978	1.36830	1.36666	1.36488
2.5190	1.37528	1.37368	1.37196	1.37043
3.0005	1.38015	1.37846	1.37670	1.37542

Table 6.24. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
n_D				
Glycine betaine in 0.2140 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0000	1.34085	1.33981	1.33850	1.33687
0.0510	1.34339	1.34229	1.34096	1.33922
0.1000	1.34406	1.34296	1.34162	1.33988
0.5000	1.34928	1.34805	1.34680	1.34533
1.0000	1.35784	1.35654	1.35486	1.35284
1.4980	1.36231	1.36092	1.35936	1.35774
2.0050	1.37009	1.36861	1.36697	1.36519
2.5000	1.37559	1.37399	1.37227	1.37074
3.0000	1.38046	1.37877	1.37701	1.37573
Glycine betaine in 0.3262 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0000	1.34153	1.34049	1.33918	1.33755
0.0492	1.34407	1.34297	1.34164	1.33990
0.0997	1.34474	1.34364	1.34230	1.34056
0.4885	1.34996	1.34873	1.34748	1.34601
0.9786	1.35852	1.35722	1.35554	1.35352
1.4702	1.36299	1.36160	1.36004	1.35842
1.9535	1.37077	1.36929	1.36765	1.36587
2.4675	1.37627	1.37467	1.37295	1.37142
2.9524	1.38114	1.37945	1.37769	1.37641
Glycine betaine in 0.4014 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0000	1.34267	1.34163	1.34032	1.33869
0.0500	1.34521	1.34411	1.34278	1.34104
0.1002	1.34588	1.34478	1.34344	1.34170
0.4998	1.35110	1.34987	1.34862	1.34715
0.9960	1.35966	1.35836	1.35668	1.35466
1.5010	1.36413	1.36274	1.36118	1.35956
1.9880	1.37191	1.37043	1.36879	1.36701
2.5000	1.37741	1.37581	1.37409	1.37256
2.9980	1.38228	1.38059	1.37883	1.37755

Table 6.24. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
n_D				
Glycine betaine in 0.5024 mol·kg^{-1} aqueous $CoCl_2$ solution				
0.0000	1.34319	1.34221	1.34080	1.33919
0.0509	1.34573	1.34469	1.34326	1.34154
0.1020	1.34641	1.34536	1.34397	1.34215
0.5020	1.35162	1.35038	1.34915	1.34760
1.0000	1.36028	1.35894	1.35721	1.35511
1.5000	1.36465	1.36332	1.36171	1.36001
2.0100	1.37243	1.37093	1.36929	1.36756
2.5000	1.37799	1.37631	1.37462	1.37311
2.9985	1.38286	1.38107	1.37936	1.37810
Glycine betaine in 0.1108 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0000	1.33850	1.33754	1.33684	1.33648
0.0478	1.33914	1.33818	1.33747	1.33710
0.1121	1.33999	1.33904	1.33831	1.33794
0.5091	1.34528	1.34433	1.34353	1.34311
1.0007	1.35182	1.35089	1.34998	1.34951
1.5020	1.35850	1.35758	1.35657	1.35604
2.0050	1.36519	1.36429	1.36318	1.36259
2.5230	1.37209	1.37121	1.36998	1.36934
2.9989	1.37843	1.37756	1.37623	1.37554
Glycine betaine in 0.2021 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0000	1.34021	1.33945	1.33861	1.33837
0.0491	1.34085	1.34008	1.33923	1.33899
0.0999	1.34152	1.34073	1.33988	1.33964
0.4998	1.34680	1.34586	1.34498	1.34474
1.0011	1.35341	1.35229	1.35137	1.35113
1.4998	1.35999	1.35869	1.35773	1.35749
2.0010	1.36660	1.36512	1.36412	1.36388
2.4850	1.37298	1.37132	1.37029	1.37005
2.9999	1.37977	1.37793	1.37685	1.37661

Table 6.24. (*continued*)

$m_A{}^b$/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
n_D				
Glycine betaine in 0.3031 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0000	1.34460	1.34380	1.34274	1.34231
0.0510	1.34527	1.34447	1.34340	1.34297
0.0998	1.34592	1.34511	1.34404	1.34361
0.4886	1.35105	1.35018	1.34912	1.34867
0.9789	1.35751	1.35658	1.35553	1.35505
1.4850	1.36419	1.36319	1.36214	1.36163
1.9966	1.37094	1.36986	1.36883	1.36829
2.4865	1.37740	1.37626	1.37523	1.37466
2.9282	1.38323	1.38202	1.38101	1.38041
Glycine betaine in 0.4004 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0000	1.34577	1.34456	1.34312	1.34167
0.0502	1.34638	1.34517	1.34373	1.34228
0.1000	1.34699	1.34577	1.34433	1.34289
0.4990	1.35183	1.35061	1.34917	1.34772
0.9956	1.35785	1.35664	1.35520	1.35374
1.5030	1.36401	1.36279	1.36136	1.35989
1.9882	1.36990	1.36868	1.36724	1.36576
2.4977	1.37608	1.37486	1.37343	1.37194
2.9982	1.38215	1.38093	1.37950	1.37800
Glycine betaine in 0.5121 mol·kg^{-1} aqueous $NiCl_2$ solution				
0.0000	1.34726	1.34569	1.34403	1.34290
0.0510	1.34788	1.34631	1.34465	1.34351
0.1033	1.34851	1.34694	1.34529	1.34414
0.5001	1.35333	1.35175	1.35009	1.34891
0.9987	1.35938	1.35779	1.35613	1.35490
1.4988	1.36545	1.36385	1.36219	1.36091
2.0088	1.37165	1.37003	1.36836	1.36703
2.4988	1.37760	1.37597	1.37430	1.37292
2.9978	1.38365	1.38201	1.38034	1.37891

Table 6.24. (*continued*)

m_A[b]/(mol·kg^{-1})	*T*/K			
	288.15	**298.15**	**308.15**	**318.15**
n_D				
Glycine betaine in 0.0971 mol·kg^{-1} aqueous $ZnCl_2$ solution				
0.0000	1.33707	1.33588	1.33468	1.33349
0.0515	1.33832	1.33737	1.33652	1.33595
0.1018	1.33899	1.33803	1.33722	1.33664
0.4948	1.34404	1.34328	1.34242	1.34183
0.9830	1.35044	1.34974	1.34885	1.34820
1.5250	1.35750	1.35696	1.35602	1.35533
1.9702	1.36334	1.36289	1.36188	1.36116
2.4400	1.36946	1.36913	1.36806	1.36735
2.9322	1.37591	1.37570	1.37457	1.37378

[a]Standard uncertainty for temperature u(T) = 0.01 K; for pressure u(p) = 5 kPa; for molality u(m) = 0.0001 mol·kg $^{-1}$; for refractive index u(n_D) = 0.00011 kg m^{-3} and the combined expanded uncertainty $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried-out under laboratory pressure.
[b] m_A is the molality of glycine betaine in aqueous metal salt solutions.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Chapter 7 presents the summary and conclusions of the present study. This chapter also includes scope for further research in the current field.

7.1. SUMMARY

Most of the natural chemical processes take place in solution medium. The investigation of the kinetics and thermodynamics of these reactions is crucial for the reason that these reactions are mainly biological. Proteins are the extensively studied biomolecules owing to their role in physiological processes. The studies on the stability, conformations and solubility of proteins are of fundamental importance for many biological phenomena. Due to the large size and complex nature of these biomolecules, it is somewhat difficult to analyse them in their native form. Hence, it has been in practice that scientists consider relatively simpler biomolecules with low molecular weights which mimic some specific aspects of protein structures in aqueous solutions. Volumetric and compression studies of these protein model compounds are very useful to have an insight of solute-solute and solute-solvent interactions taking place in such solutions. Since water in biochemical environment is not pure always and may contain some other additives, it is equally important to understand the effects of additives on solution parameters. Salt solutions are known to produce remarkable effects on the conformation as well as properties of proteins and are equally important in biology.

The present work has been undertaken to study the solution behaviour of two important biomolecules namely, cyclic alanylalanine and glycine betaine in aqueous as well as aqueous metal salt solutions. Biologically important metal chlorides such as sodium chloride, potassium chloride, calcium chloride, magnesium chloride, manganese chloride, cobalt chloride, nickel chloride and zinc chloride have been chosen for the present study. Choice of chloride can be attributed to the fact that it lies in middle of the Hofmeister series and hence one could directly investigate the effect of cations on the physico-chemical properties of present systems.

Density, ρ, speed of sound, c, and refractive index measurements of different sets of biomolecule-metal salt solutions have been carried out under experimental conditions. So obtained results have been utilized to calculate various derived parameters such as isentropic compressibility, molar volumes, compressions, specific

acoustic impedance, relative association, transfer molar quantities etc. to explain the probable interactions present in the systems.

The present thesis consists of seven chapters. The **Chapter 1** titled 'Introduction' gives general introduction to the subject of peptides, electrolytes, solvents, volumetric, acoustical and refractometric properties**.** It also gives literature review, problem definition, scope and objectives of the present investigation.

Chapter 2 presents a brief description of the materials and experimental methods used in this study. The source, purity and CAS number of the chemicals along with the characterization methods followed have been included. The instruments used, uncertainties estimated in various measurements, laboratory conditions, concentration range, etc. have been provided in this chapter.

Chapter 3 outlines a detailed study of density, speed of sound and refractive index of cyclic alanylalanine (CAA) in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at different temperatures. By the values of isentropic compressibility, apparent molar volume, apparent molar isentropic compression, molar refraction, transfer molar quantities, specific acoustic impedance, intermolecular free length and relative association the characteristics and structural properties of the systems have been discussed.

Chapter 4 concerns with the volumetric, optical and compression study of cyclic alanylalanine (CAA) in some transition metal chloride aqueous solutions. A representative study on variation of metal chloride concentration in aqueous cyclic alanylalanine has also been carried out to understand the behaviour of such systems. The results have been utilised to have an insight of nature of all the systems under the experimental conditions.

Chapter 5 describes the molecular interaction of glycine betaine (GB) in water and in aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ at various temperatures. The solute-solvent interactions operative in these solutions have been expressed as a combination of electrostatic hydration of charged terminals of the zwitterion and the overlap of hydration co-spheres of these terminal groups with that of $–CH_2$ group of GB which contributes to enhanced partial molar volumes.

Chapter 6 comprises of the study of solution parameters of glycine betaine (GB) in aqueous transition metal chloride solutions such as $MnCl_2$, $CoCl_2$, $NiCl_2$ and

$ZnCl_2$. The effect of concentration of metal chlorides on the volumetric properties of glycine betaine has been elucidated by considering solvents of different concentrations. The concentration range of 0.1 to 0.5 $mol \cdot kg^{-1}$ has been chosen for this purpose. The study on glycine betaine-$ZnCl_2$ has been carried out only at 0.1 $mol \cdot kg^{-1}$ due to precipitation constraints. The general trend in the compressibility values suggested the influence of M^{2+} to water (where M=Mn, Co, Ni or Zn) bond distances on these values. The hydration sphere overlap model best described the interaction between GB and metal chlorides.

7.2. CONCLUSIONS

Based on the results obtained from the present study, the following conclusions have been drawn.

- From the volumetric and compression study of all the above systems, it can be concluded that these molecules can be regarded as the protein model compounds.
- In cyclic alanylalanine-aqueous metal salt systems (NaCl/KCl/$CaCl_2$/$MgCl_2$), the partial molar volume of cyclic alanylalanine in the metal salt solutions varied in the sequence: KCl<NaCl<$CaCl_2$<$MgCl_2$ which accounts for the variation of sizes of these ions in aqueous solutions.
- In the fourth chapter, where the solution behaviour of cyclic alanylalanine-aqueous transition metal salt systems was studied, the dominance of hydrophobic hydration in the molar volume contribution has been indicated by the trends of the slopes of the concentration dependence of the apparent molar volumes.
- In glycine betaine-aqueous metal salt systems (NaCl/KCl/$CaCl_2$/$MgCl_2$), zwitterionic interaction contributes to enhanced partial molar volumes. As in the case of chapter 3, the volumetric parameters were highly influenced by the metal ion sizes.
- From chapter 6 concerning glycine betaine (GB)-aqueous transition metal salt systems, it has been found that cohesive forces increase in the solution above certain concentration (0.3 $mol \cdot kg^{-1}$) of the metal salt. Positive values of Hepler's coefficient suggest that: in GB-$CoCl_2$, GB-$NiCl_2$ and GB- $ZnCl_2$ systems, GB behaves as a structure-maker under the experimental conditions.

7.3. SCOPE FOR FUTURE WORK

Transfer properties of a large set of amino acids and their derivatives in aqueous or non-aqueous media in the presence of electrolytes can provide appropriate deductions regarding the nature of amino acid or their derivatives. From the literature study, it is clear that thermodynamic transfer properties are required for a much larger set of amino acid side chains as well. Thus, it is imperative to include more number of small peptide molecules in order to have a realistic model for the thermodynamic transfer studies. Following experiments can be carried out in future to endure the present work.

- An investigation involving other cyclic peptides and betaine molecules in aqueous solutions can be carried out.
- The present study can be extended to non-aqueous solvents such as ethanol, methanol, etc.
- Interactions of some other biologically important metal salts with cyclic alanylalanine and glycine betaine in aqueous as well as non-aqueous solutions can be considered.
- Side chain contributions of amino acid derivative to the overall thermodynamic properties can be ascertained.

RESEARCH PUBLICATIONS

Research papers in international journals

1. Karanth, V.R. and Bhat, D.K. (2013). "Volumetric, Acoustic and Refractometric Study of Cyclic Alanylalanine in Aqueous Cobalt Chloride Solutions at Temperatures T = (293.15 to 313.15) K." *J. Chem. Eng. Data*, 58, 271-278.

2. Karanth, V.R. and Bhat, D.K. (2013). "Partial Molar Volume and Partial Molar Isentropic Compressibility Study of Glycine Betaine in Aqueous and Aqueous KCl or $MgCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K." *Thermochim. Acta,* 572, 23-29.

3. Karanth, V.R. and Bhat, D.K. (2014). "Partial molar volumes and compressibilities of glycine betaine in aqueous NaCl solutions at temperatures T = (288.15 to 318.15) K." *Fluid Phase Equilib.*, 375, 18–22.

4. Karanth, V.R. and Bhat, D.K. (2014). "Volumetric Properties of Cyclic Alanylalanine in Aqueous Solutions of $MnCl_2$, $NiCl_2$ and $ZnCl_2$ at Temperatures T = (293.15 to 313.15) K."*Thermochim. Acta,* (Under review).

5. Karanth, V.R. and Bhat, D.K. (2014). "Volumetric and ultrasonic studies of glycine betaine in aqueous solutions of $MnCl_2$ or $CoCl_2$ at different temperatures." *J. Chem. Sci.*, (Communicated).

6. Karanth, V.R., Akshay, H. and Bhat, D.K. (2014). "Study of solute-solvent interactions of glycine betaine in aqueous $NiCl_2$ solutions at different temperatures." *Int. J. Thermophys.* (Communicated).

7. Karanth, V.R. and Bhat, D.K. (2014). "Solution behaviour of glycine betaine-$CaCl_2$ and glycine betaine-$ZnCl_2$ aqueous systems at T = (288.15 to 318.15) K." *Fluid Phase Equilib*. (Communicated).

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1. Karanth, V.R. and Bhat, D.K. (2012). "Effect of Temperature on Molecular Interactions in Aqueous Betaine-KCl Solutions." *7th National Conference on Thermodynamics of Chemical, Biological and Environmental Processes-2012*, Sri Venkateswara University, Tirupati.

2. Karanth, V.R. and Bhat, D.K. (2013). "Isentropic Compressibility, Partial Molar Volumes and Partial Molar Isentropic Compressibility of Betaine in Aqueous $MgCl_2$ Solutions." *International Conference on Recent Advances in Material Science and Technology-2013*, National Institute of Technology Karnataka, Surathkal.

3. Karanth, V.R. and Bhat, D.K. (2013). "Molecular Interactions in Aqueous Glycine Betaine-$ZnCl_2$ Solutions: A Volumetric and Acoustic Approach." *CRSI Mid-Year Symposium-2013*, National Institute of Technology Karnataka, Surathkal.

4. Karanth, V.R. and Bhat, D.K. (2014). "A Volumetric and Acoustic Study of Molecular Interactions in Aqueous Glycine Betaine-KCl or NaCl Solutions." *Two day national conference on World's Emerging Advancements in Chemical Technology 2014*, Govinda Dasa First Grade College, Surathkal.

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Education and Qualifications

2007-2009	M. Sc. in Chemistry in Mangalore University, Mangalore. With 72.5%.
2004-2007	B. Sc. in Govinda Dasa First Grade College, Surathkal with 79.4%.
2002-2004	P.U.C. in Govinda Dasa Pre-University College, Surathkal with 73.0%.
2002	S.S.C. in Manjunath Vidyalay, Dombivli (E), Mumbai with 75.9%.

Work Experience

- Conducted classes for M. Sc. Chemistry (Kuvempu University Distance Education) students in Govinda Dasa College Surathkal (One semester).
- Conducted lab for M.Sc. Chemistry and B. Tech students in NITK for (Eight semesters).

Research Publications

- Karanth, V.R., Bhat, D.K. (2013). "Volumetric, Acoustic and Refractometric Study of Cyclic Alanylalanine in Aqueous Cobalt Chloride Solutions at Temperatures *T* = (293.15 to 313.15) K." *J. Chem. Eng. Data*. 58, 271-278.
- Karanth, V.R., Bhat, D.K. (2013). "Partial Molar Volume and Partial Molar Isentropic Compressibility Study of Glycine Betaine in Aqueous and Aqueous KCl or $MgCl_2$ Solutions at Temperatures T = (288.15 to 318.15) K." *Thermochim. Acta.* 572, 23-29.
- Karanth, V.R., Bhat, D.K. (2014). "Partial molar volumes and compressibilities of glycine betaine in aqueous NaCl solutions at temperatures T = (288.15 to 318.15) K." *Fluid Phase Equilib.*, 375, 18-22.
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- Karanth, V.R., Bhat, D.K. (2014). "A Volumetric and Acoustic Study of Molecular Interactions in Aqueous Glycine Betaine-KCl or NaCl Solutions." *Two day national conference on World's Emerging Advancements in Chemical Technology 2014*, Govinda Dasa First Grade College, Surathkal.

Additional Qualification

- Confident with a range of IT packages including Word, Excel, Power Point and Origin.

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I certify that all the information provided above is true to best of my knowledge and belief.

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