DECLARATION

I hereby declare that the work incorporated in the present thesis "**Effect of Ionic Solutes on Amino Acids and Peptides from Thermodynamic, Volumetric and Transport Studies: Experiments and Correlations**" is original and is not been submitted to any other University / Institution for the award of a Diploma or Degree. I further declare that the results presented in the thesis and considerations made therein contribute in general to the advancement of knowledge in Chemistry and particularly to the field of Thermodynamics.

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CERTIFICATE

It is certified that the work incorporated in this thesis "**Effect of Ionic Solutes on Amino Acids and Peptides from Thermodynamic, Volumetric and Transport Studies: Experiments and Correlations**" submitted by Ms. Rohini Dhruva Badarayani, for the degree of **Doctor of Philosophy in Chemistry**, was carried out by the candidate under my supervision, in Physical Chemistry Division, National Chemical Laboratory, Pune, India. Materials obtained from other sources have been duly acknowledged in the thesis.

Date:

Dr. Anil Kumar

Research Guide

EFFECT OF IONIC SOLUTES ON AMINO ACIDS AND PEPTIDES FROM THERMODYNAMIC, VOLUMETRIC AND TRANSPORT STUDIES: EXPERIMENTS AND CORRELATIONS

A THESIS

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by

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Dedicated to

Aai and Baba

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Rohini Badarayani

CONTENTS

Ionic species play significant role in governing the physical, chemical and biological behavior of biological macromolecules like proteins, nucleic acids, etc. To explain the behavior of these biological molecules one must understand the ionic solutions in terms of ion-water and ion–ion interactions along with the biomolecules–water interactions and how these interactions are altered in the presence of proteins and other bio-molecules. These two aspects remain mystery for the physical and biological chemists and can be well understood by investigating the physico-chemical behavior of ionic species in biological systems.

1.1 Effect of electrolytes on biomolecules:

The biomolecules are composed of one or more linear polymer chains, each containing a number of chemically different monomer (residues) arranged in a particular genetically determined sequence and covalently linked end to end. The equilibrium conformation adopted by a given macromolecule is a sensitive function of residue composition, sequence and solvent environment. The number of different conformations can be divided into two major classes

1. The conformations for which chain – chain contacts are thermodynamically favored over chain - solvent contacts i.e. *native conformation*.
2. The conformations in which chain – solvent contacts are preferred leading to *random coil conformation*.

The energetic balance between native and random coil conformations includes many factors like chemical restrictions built into the covalent bonding of the back bone chains as well as hydrogen bonding, electrostatic interactions, hydrophobic bonding, London (dispersion) forces, etc. The net free energy difference which

stabilizes the native conformation against transition to other forms are small and can be easily overcome by relatively minor perturbations in the solvent environment e.g. temperature, pH, ionic strength or in the concentration of specific small molecular interactions.

The important contribution to conformational properties and structural stability of biological macromolecules comes from effect of neutral electrolytes, since biofluids too contains mixtures of electrolytes. The electrolytes, which are significantly soluble in water without bringing about a major change in the solution pH affect electrostatic interactions in macromolecules on a simple charge – shielding basis. First it will be of interest to know the effect of electrolytes on proteins.

1.1a: Effect of electrolytes on proteins:

The pioneering work on effect of electrolytes on proteins was carried out by von Hippel and coworkers[1]. He concluded that

- Ions such as ClO_4^-, SCN^- Ca^{2+} and guanidinium, (Gn^+) particularly decrease the stability of native conformation of fibrous or globular proteins in water and are termed as destabilizers.
- Ions such as Na^+, K^+, NH_4^+, SO_4^{2-} etc. stabilize the native conformation of proteins.

The effect of electrolytes on proteins can be studied in terms of T_m, melting temperature of proteins. von Hippel expressed this effect as:

$$T_m = T_m^0 + K\, c_S \qquad (1)$$

where T_m is the melting temperature of a particular protein at electrolyte concentration c_S (in moles per liter), $T_m^0 = T_m$ for the same protein at $c_S = 0$ and K is molar effectiveness of the electrolyte in perturbing T_m. $CaCl_2$ is a T_m depressor so K is negative. The linear dependence of T_m on electrolyte concentration has been found in the literature[2] for many proteins (e.g. calfskin, Ichthyocol, earthworm cuticle, etc.) in electrolytes. However, the slopes (K) obtained vary widely with electrolyte type. They range from large and negative values for electrolytes like $CaCl_2$, KSCN and $NaClO_4$ to substantially positive values for $(NH_4)_2SO_4$ and K_2HPO_4. Salts like $(CH_3)_4NCl$ and CH_3COONa yield values of K close to zero. GuSCN was found to be a much more potent destabilizer than GnCl[3]. On the other hand Gn_2SO_4 is found to be protein stabilizer[3]. Another group of electrolytes, which have striking effect on T_m are tetraalkylammonium salts[3]. The $(CH_3)_4N^+$ species has very little effect on T_m as the alkyl chain increases in length, the molar effect on Tm grows progressively larger and more negative. $(C_2H_5)_4N^+$ is among the most effective T_m depressors, $\Delta T_m \approx -30^0$ $mole^{-1}$. In the above studies, K was found to be insensitive for the protein concentration and pH. The effects of various electrolytes are additive in nature. The effects for the indivisual ions follow the Hofmeister series[4], so **equation (1)** can be modified as follows:

$$T_m = T_m^0 + \sum_i K_i c_{Si} \qquad (2)$$

where K_i and c_{Si} are the molar effectiveness and concentration of various ions, respectively. Recently Hagihara and Goto studied the GnHCl induced folding of proteins and observed that GnHCl at low concentrations refolds acid – unfolded apomyoglobin and cytochrome c, increase in GnHCl concentration above 1 molar (moles l^{-1}) caused co-operative unfolding of molten globule state[5]. Similar such peculiar effects were also observed by studying various thermodynamic properties of different proteins in several electrolytes and mixtures of electrolytes[6-8].

1.1b: Effect of electrolytes on DNA:

DNA consists of one negatively charged phosphate group per nucleotide unit, the addition of small quantities of neutral electrolytes moves the transition temperature to high levels, approaching 100^0 for DNA's of high G–C (guanine–cytosine) content. Schildkraut and Lifson demonstrated the dependence of NaCl concentration on DNA[9] as:

$$T_m = 16.6 \log c_S + 0.41 (G - C) + 81.5 \qquad (3)$$

Hamaguchi and Geiduschek have carried out extensive study on effect of high concentrations of uni–univalent salts on the stability of DNA helix[10]. The electrostatic destabilization of helical forms results from intermolecular electrostatic repulsion between charged groups, which form part of the macromolecule. Preferential binding affinity of native DNA with cations was observed to follow the series: $Li^+ > Na^+ > K^+ > (CH_3)_4N^+$ [11,12]. The interactions between DNA and electrolytes range

from weak effect of $(CH_3)_4N^+$ to complete neutralization by stoichiometric site binding e.g. Mg^{2+}, affecting the transition temperatures of the helical coils [13-15].

1.1c: Effect of electrolytes on activity of enzymes:

Effects of neutral salts on macromolecular structure also seem to be mirrored in effects on the activity of enzymes. These effects seem quite independent of enzyme type and concentration and operate in the usual one to several molar range of salt concentration.

Warren and Cheatum[16] and Warren et. al.[17] have published a study of effects of neutral salts on variety of enzymes, including myosin (ATPase), lactate dehydrogenase, trypsin, estradiol–17-β-dehydrogenase and fumarase. Order of increasing effectiveness on anions in producing the inhibition of enzymes studied was: $CH_3COO^- < Cl^- < NO_3^- < Br^- < I^- < SCN^- < ClO_4^-$ and $(CH_3)_4N^+ < Cs^+ < K^+ < Na^+ < Rb^+ < Li^+$ order of effectiveness as enzymes, as inhibitors of various anions and cations follow exactly Hofmeister or lyotropic series obtained for the destabilization of the folded conformation of macromolecules.

Although so many experiments have been performed to understand the biomolecule– electrolyte–water interactions, no satisfactory explanation is available yet for the anomalous behavior of biomolecules in the presence of electrolytes. To deduce the biomolecule–electrolyte–water interactions by measuring various thermodynamic properties is relatively difficult, since the nature and structure of biomolecules is complex, thus it is preferred to study properties of model compounds.

Amino acids are the building blocks of proteins. Amino acids also change their physical, chemical and biological behavior in the presence of electrolyte

solutions. A large number of experimental procedures that have been developed to understand ion–amino acid interactions are based on spectroscopic probes of one sort or another, but for many systems there are major difficulties in finding a suitable technique to monitor molecular interactions. The problems that arise can stem from either intrinsic insensitivity of spectroscopic probe or from the fact that many of the interactions of interest are weak. The thermodynamic methods, can offer vital information on molecular interactions. Thus, in order to better understand the effects of ionic species on amino acids in general, it will be of interest to investigate the thermodynamic, volumetric and transport properties like viscosity of the systems 'ions - amino acids', and 'ions – peptides' in aqueous medium. Some experimental and theoretical work has been reported on thermodynamics of amino acids in water and aqueous electrolytic solutions. Most of the data available are collected for amino acids in aqueous solutions, but there is lack of systematic data on amino acids in aqueous electrolyte solutions in full concentration range, at different temperatures and pressure. The information available on aqueous amino acids and in electrolyte solutions is summarized below.

1.2: Thermodynamics of amino acid – water system:

Amino acids and peptides are non-electrolytes, when dissolved in water they have the dipolar, zwitterionic form. The important interactions in aqueous amino acids are involving charged centers (COO^- and NH_3^+) and water molecules. Separation of COO^- and NH_3^+ groups by $-CH_2-$ groups enhances the intermolecular interactions involving cospheres of charged centers and suppressed hydrophobic interactions due to steric reasons. A through literature survey reveals that different

properties like free energy, entropy and enthalpy of mixing, activity, osmotic coefficients[18-37] and heat capacities[38-44] of aqueous α-amino acids, ω-amino acids or oligopeptides are reported in the past. It has been observed that the hydration number of various amino acids and oligopeptides in aqueous solution and their dependence on temperature and pressure are studied using apparent and partial molar volume, compressibility and expansibilities[45-94]. Along with the thermodynamic properties a few reports are also available of surface[95] and transport properties[96-101]. Some of the important contributions are discussed below.

A knowledge of thermodynamic properties such as activity coefficients for water - amino acid systems is prerequisite to design efficient separation and purification processes, and drying processes in food engineering as well. Many researchers[20,21,23,26,32] investigated the solubility of amino acids in terms of activity and osmotic coefficients in water. Solubility of amino acids as a function of temperature and pH was reported by Helgeson[33]. Few models are also available for correlation of the activity and osmotic coefficients[102-112] based on UNIFAC[102], UNIQUAC[37,103], perturbation theory [104-107] and Monte Carlo method[108].

Millero et al. studied apparent molar volumes, ϕ_{VAW} and compressibilities, ϕ_{KAW} of several aqueous amino acids at 298.15 K[48]. They have also reported the number of water molecules bonded to the charged centers of α-amino acids and various group contributions towards the limiting partial molar volumes and compressibilities.

Ahluwalia and coworkers reported apparent molar volumes and heat capacities of amino acids at 298.15 K and noted poor additivity of standard partial

molar quantities, which were attributed to ionization of NH_2 and COOH groups[39,57,58]. The group additivity due to presence of hydrophilic group in close proximity of α-amino acids decreased the functional group contribution as well as contribution due to hydrophobic hydration. The concentration dependence of apparent molar volume of amino acid in water was explained on the basis of combined effects of hydrophilic and hydrophobic solute–solute interactions mediated through typical water structure. For both amino acids and peptides positive slopes were observed for apparent molar volume *versus* amino acid concentration plots except for leucine and methionine. The positive slopes were explained on the basis of dominance of interactions involving charged moieties over apolar group–apolar group and apolar group–charged center interactions, which were also confirmed by increase in the slope values for ω-amino acids than α-amino acids. However negative volume contribution due to hydrophobic interactions cause a slope to decrease as side chain length increased.

Cabani et. al. reported the volumes, compressibilities, expansibilities and heat capacities of α-amino acids, ω-amino acids and polypeptides in the temperature range of 296.15 – 328.15 K[40,60,61]. The volume change in the formation of zwitterionic structures are estimated and correlated with distance between the NH_3^+ and COO^- groups and with the nature of the chain separating them. It was also shown that partial molar volumes of amino acids were less than those of neutral molecules were and approach those of ionic species of similar size. Similar studies on α, ω amino acids were also carried out by Chalikian et. al [55,56] and Shahidi and Farrell[51]. Chalikian et. al. obtained volume and compressibility contribution of $–CH_2$ group in α, ω-amino acids as 15.7×10^{-6} m^3 mol^{-1} and $–1.6 \times 10^{-15}$ m^3 mol^{-1} Pa^{-1}, respectively [55,56]. Shahidi

and Farrell correlated partial molar volumes of α, ω-amino acids with their van der Waals volumes[51]. The hydrophobic hydration of a $–CH_2$ group α to a COO^- group caused a volume decrease of 2.5 x 10^{-4} m^3 mol^{-1} due to effect of charge and a similar decrease of 3.5 x 10^{-4} m^3 mol^{-1} for a $–CH_2$ group α to an NH_3^+ group was also observed.

Jolicoeur and Boileau discussed apparent molar volumes and heat capacities of glycine, alanine, serine and their oligopeptides at 298.15 K[50]. The data were described in terms of contributions from amino acid side chains $–CH_3$ and $–CH_2OH$ and end group hydration effects. Yayanos reported the volumes and compressibilities of aqueous amino acids, at 298.15 K[46,47]. The volume change at 1000 atm. pressure was also reported and it was observed that apparent molar volume of dipolar amino acids increases with pressure. Electrostriction decreases with increasing pressure and appeared to be dependent on the dipole moment of amino acids.

Adiabatic compressibilities of aqueous amino acids were measured in the temperature range 288.15 – 343.15 K[52-55]. Partial compressibilities of atomic groups were also determined as a function of temperature, pH and interpreted in terms of hydration and intramolecular interactions between different parts of a molecule. The difference in behavior between charged, polar and non-polar atomic groups were considered and it was observed that atomic groups of different chemical nature could exert different actions on relaxation part of water compressibility as:

- Charged groups possess lowest negative partial molar compressibility and substantial decrease in the relaxation part of water compressibility observed under the action of electrostatic field of the charges.

- Bringing together oppositely charged atomic groups results in a compressibility increase as a result of overlapping of hydration shells leading to decrease of quantity of hydrated water.

It was also concluded that NH_3^+ group of glycine undergoes maximum hydration, while other amino acids show low hydration due to steric effects. The pH dependent volumetric study was also carried out by Rao et. al for aqueous amino acids at 293.15 K, which showed that the amino acid species with the highest number of charges had the lowest partial molar volume [63-66].

Along with the amino acids Hedwig[28, 73-82], Iqbal and Verrall[70], Iqbal and Ahmed[71], Makhatadze and coworkers[41-43] and Privalov and others [35,41-42,83] also studied thermodynamic properties of aqueous oligopeptides. Iqbal and Ahmed, and Iqbal and Verrall found the partial molar volume and compressibility of a glycyl unit in a peptide hypothetical infinite length contributed 37.51 x 10^{-6} m^3 mol^{-1} and –8.50 x 10^{-15} m^3 mol^{-1} Pa^{-1}, respectively. The peptide group (-CONH-) contributions at infinite dilution for volume and compressibility were found to be 20.61 x 10^{-6} m^3 mol^{-1} and –12.4 x 10^{-15} m^3 mol^{-1} Pa^{-1}, respectively. Important contribution on partial molar volume, isentropic compressibility, isentropic pressure coefficients at infinite dilution and isobaric expansion coefficients for peptides were added by Hedwig[28,73-82]. Pioneering work on entropy and free energy of aqueous peptides along with the heat capacities and partial molar volumes was carried out by Privalov[35,41,42,83]. A detailed account of heat capacities of amino acids is presented by Makhatadze in a review[43].

Devine and Lowe reported the viscosity B-coefficients for aqueous amino acids at 278.15 and 298.15 K[96]. Glycine and to a lesser extent β-alanine were found to be solvent structure-breakers, and 4-aminobutyric acid and 6-amino–n-hexanoic acid were found to be structure makers. The NH_3^+ and COO^- groups disrupt the water structure and in glycine and β-alanine their effect outweighs the structure promoting effect of $-CH_2$ groups, while in 4-aminobutyric acid and 6-aminohexanoic acid water structure enhancement by $–CH_2$ group is predominant. Viscosities of aqueous amino acids are also reported by many researchers[97-101]. A review by Lark and coworkers compiles the viscosity and B coefficients for different amino acids [99].

Leyendekkers developed a thermodynamic model for partial molar volume and partial molar compressibility of amino acids in water based on Kirkwood – Fuoss theory [72].

The thermodynamic, volumetric and transport properties of aqueous amino acids are important, as they play a key role in understanding the effect due to ions in terms of transfer properties.

1.3: Thermodynamics of electrolyte – water system

Inorganic salts when dissolved in water form aqueous electrolyte solutions. They play a significant role in chemical laboratories, industries and in Nature, in the form of geothermal systems and biological processes of living organisms. For past several years, interest in electrolyte phase equlibria has grown significantly and numerous articles have been published in literature on electrolyte – H_2O system.

The history of thermodynamic models for aqueous solutions of strong electrolyte solutions is described in brief here. The foundation of all the proposed models lies in the Debye – Hückel equation[113]. In 1887, Arrhenius presented theory of electrolytic dissociation, the partial dissociation of the solute into negatively and positively charged ions takes place, and his proposed method of calculating the degree of dissociation helped open the way for organised theoretical and experimental investigations of electrolyte solutions[114]. This theory was applied successfully to dilute solutions of weak electrolytes, but the contradiction with experimental results for strong electrolytes led to the realization that the electrostatic force between ions must be taken into account.

It is generally more convenient in aqueous solution thermodynamics to describe the chemical potential (partial molar free energy) of a species, in terms of activity is a measure of difference between the components chemical potential at state of interest and at its standard state. For aqueous solutions in which the composition of solution is expressed in terms of molality, the standard state is hypothetical ideal solution of unit molality at the system temperature and pressure. It is chosen so that $\gamma_{\pm} \rightarrow 1$ as $m_i \rightarrow 0$ and the ratio $\gamma_i = a_i / m_i$ is called the activity coefficient, γ_i

In 1923, Debye and Hückel presented their theory of interionic attraction[113] applicable to electrolyte solutions. Since strong electrolytes are strongly dissociative in solution, the ion concentration is higher with resulting distance between them smaller than for weak electrolytes. This increase in concentration results in the tendency towards an orderly distribution of ions as the electrostatic forces cause mutual attraction between oppositely charged ions. The potential energy of the ionic

attraction must therefore be accounted in considering thermodynamics of electrolyte solutions. They proposed a simple equation for activity coefficients $\gamma_{\pm}$ as:

$$\log \gamma_{\pm} = -A \left| z_{+} z_{-} \right| I^{0.5} \qquad (4)$$

A is Debye – Hückel constant, which is a temperature dependent quantity and I is ionic strength. Due to assumptions and simplifications made in deriving the ionic atmosphere potential equation, the Debye – Hückel limiting law is valid only for very dilute solutions of ionic strength 0.01 mol kg^{-1} or less. They assumed the ions to be point charges. To overcome this limitation several models have been proposed. Some important developments in this direction are given below:

In 1935, Guggenheim and Turgeon proposed a modified version of Debye–Hückel equation on the mole fraction scale[115]. The mean activity coefficient for a single electrolyte can be obtained as:

$$\log \gamma_{\pm} = -A \left| z_{+} z_{-} \right| / (1 + I^{0.5}) + B\, m \qquad (5)$$

with a new interaction parameter B. Using this equation the $\gamma_{\pm}$ of 1-1, 1-2 and 2-1 electrolytes can be correlated successfully up to 0.1 ionic strength.

In 1972, Bromley suggested that though the ion–solvent interactions were of greater importance, specific ion–solvent interactions could be taken into account in concentrated solutions[116,117]. These interactions were taken into account by ionic

strength dependent constant B and proposed the following equation for the correlation of $\gamma_{\pm}$:

$$\log \gamma_{\pm} = (-A \left| z_{+} z_{-} \right| / (1 + I^{0.5})) + ((0.06+0.6\ B) \left| z_{+} z_{-} \right| I / (1+(1.5 / \left| z_{+} z_{-} \right|)) I^{2}) + B\ I \qquad (6)$$

Bromely noted that this equation gave good results for strong electrolytes to ionic strength of 6 mol kg^{-1}. Further he also suggested some modifications in his equation to compensate for strong ion associations.

A novel method was developed for correlation of reduced activity coefficient, Γ ($\Gamma = \gamma_{\pm}^{\ 1/\ z+z-}$) by Meissner[118-120]. He showed that a family of curves could be obtained by plotting Γ versus ionic strength. If one value of $\gamma_{\pm}$ above the Debye–Hückel concentration range is obtained then the $\gamma_{\pm}$ for any concentration (from low to saturated) could be graphically predicted. A method of dealing with temperature effects and handling of multicomponent systems was also proposed.

The non-ideality of the solutions can be attributed to the long–range and short–range interactions. The short–range interactions include molecule–molecule interactions, electrostatic forces between permanent dipoles or dispersion interactions between molecules and ion–molecule interactions such as ion–dipole electrostatic forces. These interactions are significant at close range and their effects drop rapidly as separation distance increases. The interionic electrostatic forces, long-range forces are significant over a much greater distance and thus, have dominant effect in dilute

solutions. As the concentration of solution increases, short–range effects become significant.

In all the above methods the ion–ion interactions are considered, while ion–molecule and molecule–molecule interactions, which are important in solutions of weak electrolytes, were ignored. In 1979 Chen et. al. presented a new set of equations considering molecular and ionic species, based on a concept of local composition, to account for short–range interactions between all species[121]. They proposed that the excess Gibbs free energy and activity coefficients could be expressed as sum of long–range and short– range contributions, which could be taken into account by Debye–Hückel term and modified Non Random Two Liquid model, NRTL proposed by Renon and Prausnitz[122]. In the modified NRTL model the local composition of solution was considered where the central ion attracts oppositely charged ions changing the overall mole fraction, but maintaining the electroneutrality of the solution. The short–range interactions are thus function of mole fractions of ions and molecules, (locally and overall) NRTL interaction parameter and Chen interaction parameters.

Most widely acclaimed of all these models is the Pitzer model[123]. Pitzer expanded the Debye–Hückel method by adding terms to account for the ionic strength dependence of the short–range forces effect in binary interaction. The approach has good theoretical basis. The short–range forces are accounted by virial coefficients. The coefficients depend on the ionic strength as well as temperature and pressure. The virial coefficients are evaluated empirically. This model is applicable for mixed electrolytes and for concentrated electrolyte solution up to 10 mol kg^{-1}. The basic

equation on the virial basis was postulated for the excess Gibbs energy from which other functions can be obtained from appropriate derivatives. The excess Gibbs free energy per kg of solvent can be obtained as:

$$G^{ex} / (n_w R T) = f(I) + \sum_i \sum_j \lambda_{ij}(I)\, m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk}\, m_i m_j m_k \qquad (7)$$

The long-range electrostatic forces lead to the Debye–Hückel term f (I). Short range inter particle potential effects were taken into account by virial coefficients, λ_{ij} for binary interactions, μ_{ijk} for ternary etc. The ternary interaction coefficient is independent of ionic strength and is required at only high concentrations. The working equations for osmotic, activity coefficients, entropy, heat capacity and volumetric properties could be derived from basic Pitzer **equation (7)**. For single electrolyte the activity and osmotic coefficient could be obtained as:

$$\ln \gamma_{\pm} = |z_+ z_-| f^{\gamma}(I) + m (2 \nu_+ \nu_- / \nu) B^{\gamma} + m^2 [2 (\nu_+ \nu_-)^{3/2} C^{\gamma}] \qquad (8)$$

$$\phi - 1 = |z_+ z_-| f^{\phi}(I) + m (2 \nu_+ \nu_- / \nu) B^{\phi} + m^2 [2 (\nu_+ \nu_-)^{3/2} C^{\phi}] \qquad (9)$$

where, the stoichiometry of an electrolyte is ν, $\nu = \nu_+ + \nu_-$ where ν_+ and ν_- are the number of cations and anions, respectively. B_{+-} is second virial coefficient and depends on ionic strength, I. The exact form of B^{γ} and B^{ϕ} could be determined on empirical basis. C^{ϕ} is the third virial coefficient.

McMillan and Mayer developed an exact theory of solutions and have described the thermodynamic properties of solutions in terms of certain integrals of radial distribution functions[124]. It provides some definite information about virial expansion. According to this theory, if the solvent is kept at unit activity (by applying a pressure equal to the osmotic pressure of solution) then it is possible to express the excess free energy of the solution in a form resembling the virial expansion. The extremely large deviations of ionic solutions from the laws of perfect solutions are partly to the long range of mutual electrostatic potentials, but also to the comparatively large value, which these potentials have.

Friedman proposed a simple statistical theory called Cluster Integral Expansion Theory for the quantification of interactions between like and unlike charged ions [125]. In order to derive the theory he used Mayer's Ionic Solution Theory[126]. It has been possible to compute the excess Gibbs free energy of mixing in terms of contributions made by pairs, triplets, quadruplets and high order mixing terms. The limiting laws of mixing of two ions of the same sign have been accurately derived and demonstrated successfully.

Numerous data are available on the thermodynamic, volumetric, surface and transport properties of aqueous electrolytes at different temperatures, pressure and compositions. Various compilations are available for the properties of various systems. The data of activity and osmotic coefficients of aqueous electrolytes at 298.15 K and at higher temperatures and for mixtures of electrolytes can be found in compilations of Robinson and Stokes[127] and Zemitis et. al.[128] Similarly for other thermodynamic properties the Horvath's[129] hand book can be referred.

1.4: Thermodynamics of amino acid – electrolyte - water system

Experimental measurements and modelling of thermodynamic properties of amino acids are of interest to the biophysical chemists for many years. Literature survey shows that electrolytes can influence the thermodynamic, surface and transport properties of amino acids. Reports are available on thermodynamic properties like excess free energy, enthalpy and entropy of mixing, solubility, activity and osmotic coefficients and heat capacities of mixtures of amino acids and aqueous electrolytes. No systematic study however exists on the volumetric properties of amino acids in concentrated electrolyte solutions.

The activity, γ and osmotic coefficients, ϕ of amino acids in aqueous electrolytes were studied by many researchers. A study of free energy relationships in some amino acids–NaCl–H_2O was studied by Schrier and Robinson by isopiestic vapour pressure method[130,131]. The amino acids were selected with increasing -CH_2- chain length. From the measured activity coefficients trace activity coefficients of amino acids were obtained and they were found to be slightly negative at low salt molalities. At higher salt molalities, the trace activity coefficients for glycine and β-alanine remained negative whereas those for β-aminobutyric acid and ε-aminocaproic acid became positive. The limiting interaction parameters were calculated for these systems using Kirkwood ion–dipole expression and an empirical term for the salt effect on non-polar portion of the molecule.

The activity coefficients for glycine - NaCl - H_2O system was reported by Phang and Steel from the e.m.f. measurements using cation responsive glass electrodes[132]. The free energy, enthalpy and entropy of amino acid transfer from H_2O

to aqueous electrolytic solutions were also calculated and it was found that all the three values are negative in 0.5 and 1 mol kg^{-1} NaCl. Wadi and Singh measured the activity coefficients of DL-alanine in aqueous KCl or RbCl at 308 K[133]. The results indicated net attractive interactions between electrolytes and DL–alanine.

Merida et. al. modified the Pitzer equations for amino acid–electrolyte–H_2O system[134]. The dependence of binary interaction parameter (amino acid–electrolyte) on both ionic strength and neutral species concentration was considered. To support this new equation he also measured the activity coefficients, γ_A of glycine, β-alanine and DL-α-aminobutyric acid in aqueous NaCl[134-137]. The γ_A of glycine decreases with the increase in concentration of glycine and NaCl. In case of DL-α-aminobutyric acid γ_A increases with concentration of amino acid and NaCl, while that of β-alanine initially decreases with NaCl and amino acid concentration and in concentrated solutions it starts increasing. The activity coefficient of NaCl, γ_J in all the three amino acids decreases in dilute solutions but in concentrated solutions γ_J starts increasing. The dependence of γ on pH was also checked, and it was found that amino acid concentration does not influence its protonation phenomenon. At low ionic strengths ion–ion interactions are most important but with increase of ionic strength in medium ion–solvent interactions (normal and hydrophobic) become prevailing. The solubility of amino acids was found to be dependent on pH, [138,139] for example the solubility of L-isoleucine increases till 1 mol l^{-1} of HCl, subsequent addition of Cl^- ions decreases the solubility. Amino acids show variable solubility in NaCl[140,141]. Solubility of glycine at various pH remains unaffected by NaCl concentration. L-cysteine solubility enhances with increase in NaCl concentration, while there is a decrease in

the solubility of L-tyrosine and L-leucine. From these observations one can see that if charges on amino acids increase its solubility in NaCl enhances.

Vera and coworkers studied activity coefficients of various amino acids in electrolyte solutions by e.m.f. method using electrochemical cells with two ion selective electrodes (a cation and anion selective electrode) and a double junction reference electrode[142-151]. They investigated amino acids with variable -CH_2- chain lengths and with different substituents like glycine, DL-alanine, DL-valine, DL-α-aminobutyric acid, DL-serine, DL-methionine and glycylglycine in aqueous electrolytic solutions of NaCl, NaBr, KCl, KBr, $NaNO_3$, KNO_3, HCl, HNO_3, NaOH and KOH. They have attempted to study the effect of cations, anions and pH on activity coefficients. From these measurements they concluded that solubility of amino acids depends on the nature of cation as well as anion. Solubility of all the amino acids increases with increase in KCl concentration. The solubility of glycine decreases in low concentration of NaCl or KCl but after concentration > 0.3 mol kg^{-1} the solubility of glycine shows enhancement. There are attractive interactions between molecules of glycine and $NaNO_3$ and repulsive interactions between DL-methionine and NaCl. Interactions between electrolytes and DL-α-aminobutyric acid are stronger in the presence of Br^- as anion compared to Cl^-. Solubility of amino acids is found to be more with NO_3^- anion as compared to Cl^- and higher in K^+ cation than with Na^+. The nature of anion shows major effect on glycylglycine than cation. The effect of electrolyte is larger for peptides than amino acids. The study of solubility at different pH shows that solubility of DL-alanine does not differ in presence of Na^+ or K^+ at high pH and Cl^- or NO_3^- at low pH values. However at higher concentrations of

acids or bases there is effect of counter ions on solubilities. For all amino acids solubility is higher in HNO_3 as compared to HCl and higher in KOH than in NaOH.

One of the important methods to analyse the amino acid–ion interactions is by studying the enthalpies of solution of amino acid - electrolyte - H_2O. The enthalpy of interaction between glycine and NaCl was calorimetrically measured and observed that the values differed qualitatively from values predicted from the classical Kirkwood's and other theories by Larson. From this observation the authors concluded that though, electrostatic theories account for the free energy of interaction between dipolar ions and electrolytes they do not even qualitatively account for enthalpy of interaction[152,153]. The enthalpy data for different amino acids–NaCl systems were also collected and the enthalpy of interaction of NaCl was found to be –211 cal mol^{-1} with glycine, 3 cal mol^{-1} with α-alanine, 112 cal mol^{-1} with valine, -120 cal mol^{-1} with serine, -78 cal mol^{-1} with β-alanine, -16 cal mol^{-1} with γ-aminobutyric acid and 161 cal mol^{-1} with ε-aminocaproic acid. The exothermic enthalpy of interaction indicated amino acid as net structure breaker, while endothermic values indicated net structure maker. A series of papers has reported the enthalpies of mixing amino acids with electrolytes[154-158]. The enthalpic interaction parameters for amino acids (glycine, α-alanine, α-aminobutyric acid) - NaI systems were also obtained at 298.15 K for understanding the effect of substituent hydrocarbon chain length. It was found that the binary interaction coefficients increased whereas the ternary interaction coefficients decreased as the hydrocarbon chain length increased. The effect of different cations was also studied on α-alanine and α-aminobutyric acid with LiCl, NaCl and KCl. The anionic effect was studied on α-alanine with KCl, KBr and KI

and for glycine with different Na halides. The enthalpy interaction parameters were found dependent on the ionic strength of electrolytes. The parameters are positive and their values increased with ionic strengths of electrolytes. The dependence of size of ions was discussed in terms of electrostatic and structural interactions. The enthalpy of interaction of L-cysteine with NaCl and $MgCl_2$ is recently reported[159]. The enthalpy or entropy of interaction between L-cystein and NaCl is negative, while between L-cystein and $MgCl_2$ is positive. The Gibbs free energy of interaction for both the systems is negative. Palecz measured enthalpies of α-alanine, DL-α-alanine, L-α-aminobutyric acid, L-α-valine, L-α-leucine, L-α-serine and L-α-threonine in water with aqueous LiCl, NaCl, KCl to study the effect of cation[160]. The standard dissolution enthalpies of α-alanine, DL-α-alanine, L-α-serine and L-α-threonine increase with increase in concentration of NaCl or LiCl and decrease in KCl. In the case of alanine, substitution of Na^+ with K^+ causes only inconsiderable changes in enthalpic interaction pair coefficients.

The enthalpy of interaction of amino acids in aqueous electrolytes have been studied in a series of papers[161-171]. The enthalpies of mixing aqueous glycine, oligopeptides of glycine β-alanine, γ-aminobutyric acids and ε-aminocaproic acid, norvaline, norleucine, serine, threonine, δ-aminovaleric acid with LiCl, NaCl, KF, KCl, KBr, KI, CsCl and $CaCl_2$. The pairwise enthalpy of interaction coefficients for theses systems were obtained using a microcalorimeter. The Lewis–Randall free energy coefficients, which represented pairwise interactions between ions of electrolytes and amino acid were also evaluated. The Lewis–Randall coefficients were transformed to McMillan–Mayer scale and then deconvoluted in an approximate

manner to give contributions arising from excluded volume (hard sphere) electrostatic (Kirkwood) and solvent recognisation effects. Excluded volume and solvent rcognisation effects are almost equal in magnitude but opposite is sign, so that the frequently used Kirkwood electrostatic model represents the net interaction well. The pairwise interaction coefficients for ions and glycine are negative indicating attractive interaction between electrolyte and glycine. They found little change in pairwise interaction parameter as the hydrocarbon side chain is extended for α, ω-acids the interactions with ions of electrolyte became increasingly attractive and more negative as homologous series is ascended, while the coefficients of α-amino acids remain constant after α-alanine. Interactions of ions and amino acid are localised at zwitterionic head groups of acid but there is also contribution of the net effect arising from perturbation of solvent peripheral to the amino acid. Peptides interact with ions in a more attractive way than amino acids. As molecules increase in size the attractive interaction between amino acid or peptide and ions increases. It is also observed that as the halide ion radius increases the enthalpic virial coefficients become increasingly negative i.e. the larger the anion, the more thermodynamically favourable is its interaction with amino acid. The interaction coefficients for different cations were found to be same. Thus, it can be concluded that mode of interaction at molecular level of the halide ions with amino acids is quite different from that for cation interacting with amino acid. The enthalpic virial coefficients consisted of two components electrostatic (estimated using Kirkwood approach) and specific (chemical) source.

The data on volumetric and transport properties of amino acids in electrolytes is scarce in the literature. Apparent molar volumes obtained from accurate density measurements and compressibilities from speed of sound measurements for glycine and DL-alanine have been obtained in aqueous Na_2SO_4 solution at 288.15, 298.15 and 308.15 K[172]. The results have been interpreted in terms of hydration of the hydrophobic and hydrophilic parts of amino acids. Na_2SO_4 is a strong structure maker. It has a salting in effect on the peptide group and a strong salting out effect on hydrophobic group. The hydration number of amino acid is found to decrease with increase in concentration of Na_2SO_4 and temperature. The authors also reported [173,174] apparent molar volumes and viscosities for amino acids at 288.15, 298.15 and 308.15 K in KSCN[173] solution and NH_4Cl [175]. The ions strongly interact with the charged centres of amino acids. Due to these interactions the electrostriction of water caused by charged centres of the amino acids reduces pushing the released water in bulk causing the volume to increase. The transfer volumes were positive and contributions from zwitterionic head groups and $-CH_2$ groups rationalised on basis of electrostatic and hydrophobic interactions between various groups by applying the transition state theory to the B-coefficient data and free energies of activation for the viscous flow obtained.

Partial molar heat capacities and volumes of transfer of some amino acids and peptides from water to aqueous NaCl and $CaCl_2$ were studied by Bhat and Ahluwalia[176,177]. The transfer properties were positive because of dominant interactions of Na^+, Ca^{2+} and Cl^- with charged centres of amino acids and peptides. The peptide group is strongly salted in or stabilised by $CaCl_2$ and less so by NaCl.

The results were rationalised by co-sphere overlap model. Positive transfer compressibilities were also obtained in presence of NaCl and glucose solution by Banipal and Sehgal[178]. A detailed study of apparent molar volumes, compressibilities and refractive index of glycine (full concentration range) in aqueous NaCl, KCl, KNO_3 and $NaNO_3$ (0-1 mol kg^{-1} concentration) at 298.15 K was carried out [179,180]. The positive transfer properties obtained indicate glycine has larger size in aqueous electrolytes than in H_2O. This effect was attribute to doubly charged behaviour of glycine and formation of physically bonded ion–pairs between charged groups of glycine and ions. A model based on Pitzer formalism was developed to correlate activity coefficients, apparent molar volumes and compressibilities of glycine in aqueous NaCl. The model is only valid for glycine properties but it does not give NaCl properties.

Yan et. al. have collected volumetric data for different amino acids in organic salts like sodium acetate and sodium butyrate[181-183]. The partial molar volumes of amino acids at infinite dilution are composed of zwitterionic contribution and $-CH_2$ contribution. The volume at infinite dilution due to zwitterionic head groups increased with concentration of sodium acetate and those for $–CH_2-$ group remained almost constant. The transfer volume is found to increase and hydration number of amino acid decreases with increasing sodium acetate concentration showing strong interactions between Na^+ and CH_3COO^- and zwitterionic head groups. The volumetric interaction parameters are positive and decrease with increasing alkyl chain length. Sodium acetate and sodium butyrate have a stronger dehydration effect on amino acids, which have longer hydrophobic alkyl chains. The transfer volumes from water

to sodium acetate and butyrate and viscosity B-coefficients vary linearly with increasing number of C atoms in alkyl chain of amino acids and were split into contributions from charged end groups and CH_2 groups of amino acids.

Apparent molar volumes, compressibilities and expansibilities of amino acids have been determined at 298.15, 308.15 and 318.15 K in aqueous Li, K and Cs halide solutions by Basumallick and Mohanty[184,185]. The results were discussed in terms of Kirkwood model. Ogawa et. al. have reported apparent molar volumes, compressibilities and relative viscosities of amino acids in LiCl, NaCl and KCl[186]. The limiting values of apparent molar volumes, compressibilities and the extended Jones–Dole coefficients B and D were calculated using a least squares method. The transfer values obtained are positive. Alkali metal cation effect on amino acids was studied in terms of dehydration effect upon amino acids.

Viscosity and apparent molar volumes of glycine have been reported by Mishra and Gautam in transition metal chloride solutions[187]. All the electrolytes were observed to behave as structuremakers or promoters in order of Ni^{2+}> Co^{2+}>Zn^{2+}>Cu^{2+}.

Very few studies are available for the surface and transport properties of amino acids in aqueous electrolytic solutions. Viscosities of amino acids have been determined in sodium acetate solutions at 298.15 K and 308.15 K[188,189], and in alkali metal halides[186].

Surface tensions of amino acids in 0.1 M NaCl were measured by Bull et. al. at 303.15 K[190]. From experimental results the free energies of transfer of amino acid

residue from solution to surface have been calculated to yield a hydrophobic scale of the residues.

Urea and guanidinium salts are well known protein denaturants so most of the thermodynamic studies of amino acids have been carried out in the aqueous solutions of these denaturants. When amino acids are dissolved in water, they show a large excess free energy, indicating that they change the structure of surrounding water. The osmotic coefficients of amino acid solutions show evidence of these changes. Lapanje et. al. studied the interaction of some oligoglycines and oligoleucines in aqueous urea and GnCl[191]. The Gibbs energy of transfer of peptide backbone units and leucyl side chains from water to denaturant solutions were also calculated and it was found that Gibbs energy of transfer from water to 6 mol l^{-1} GnCl solution between diglycine and glycine is –97 cal mol^{-1} and between triglycine and diglycine is –496 cal mol^{-1}. The decrease in free energy with increase in -CH_2- chain indicates the stabilization of hydrophobic groups of peptides in denaturant solutions. Cussler Jr. reported activity coefficient of α-aminobutyric acid–urea–H_2O system by isopiestic vapour pressure measurements at 298.15 K[192]. The solubility of α-aminobutyric acid increases in aqueous urea solution. The solubility of amino acids with large hydrocarbon residues increases in urea solution, but decreases of those having small methyl and ethyl residues. Tanford also observed this conclusion[193-195]. Similar pattern of solubility of amino acids in GnCl was observed, although GnCl is 2 to 3 times more effective than urea at the same concentration. GnCNS also decreases the free energies of transfer of hydrophobic amino acid side chains and peptide bond from H_2O to GnCNS[196].

Kresheck and Bejamin reported calorimetric study of amino acids in aqueous urea[197]. They measured the partial molar heat capacities and enthalpies and the partial molar thermodynamic properties at infinite dilutions from water to 6 mol l^{-1} of urea solution. The excess heat capacity of transfer are negative for hydrocarbon residue and peptide bond and show that 40 – 50 % of excess heat capacity present in water solutions is absent in urea. From this the authors concluded that urea has a structure breaking effect on water associated with solute molecule. The excess enthalpy of transfer for amino acids depends on urea concentration and also on side chains of amino acids[198]. Leucine, alanine, threonine and phenylalanine side chains have positive values of transfer enthalpy that increase with urea concentration. Glutamine, tryptophan and aspargine side chains have negative values, which become more negative with urea concentration. The pair wise cross interaction term of the virial expansion of excess enthalpies increases with increasing length of alkyl chains of amino acids until a plateau is attained[199].

The volumetric properties of amino acids in presence of urea or Gn salts are also studied in literature[200-206]. The amino acids show positive transfer volumes when transferred from water to aqueous GnCl[200,201]. The positive values confirm the dominating interaction of GnCl with zwitterionic centres of amino acid over non-polar groups–GnCl interactions. Hakin et. al. reported apparent molar volumes and heat capacities of glycine and glycine peptides in concentrated urea solution[207]. The transfer properties were modelled using Helgeson, Kirkham and Flowers theory (HKF) theory[208].

Recently Yan et. al. have measured viscosity of amino acids in aqueous urea and GnCl[209]. The B-coefficients and activation parameters for the viscous flow were also obtained. The structure making or breaking effect of amino acids was studied on the basis of dB/dT values. The zwitterionic head groups have positive dB/dT values, while $-CH_2-$ groups have negative values. The amino acids have negative value for dB/dT suggesting dominance of non-polar part than charged. The B-coefficients in GnCl are larger than urea.

Some data are also available for the thermodynamic properties of amino acids in the presence of aqueous sugars. Uedaira reported the activity coefficients of α-aminobutyric acid and glycylglycine in aqueous sucrose[210]. Bhat et.al. measured densities and heat capacities of some amino acids and peptides in aqueous glucose[211]. It is found that at low concentration of solute salting in of amino acids takes place, whereas at higher concentrations salting out of amino acids predominates.

Some theoretical models have also been proposed in the past for correlation of activity or osmotic coefficients of amino acids in aqueous electrolytes. A molecular thermodynamic frame work for the representation of solubilities of amino acids and small peptides in aqueous solutions as a function of temperature, ionic strength, dipolar species concentration, solvent composition and pH was put forward by Chen et. al. [212]. The free energy of mixing amino acids with solvent was given as a combination of long range and short range interactions, which are accounted by Pitzer–Debye–Huckel term combined with Born equation and local interactions combine with NRTL, respectively. Talukdar et. al. used Scaled Particle Theory for correlation of excess free energy and entropy of mixing glycine, diglycine and

tryglycine from water to aqueous urea, glycerol or $NaNO_3$[213]. Kuramochi and workers used the UNIFAC model for correlation of activity coefficients of amino acids[214]. They also used the modified Pitzer–Debye–Hückel term for better correlation of activity coefficients.

Vera and coworkers attempted to correlate the results using Wilson equation, with satisfactory correlation obtained in concentrated region[142-151]. The model, however fails in dilute solutions. For correlation of most of the results Vera and coworkers have used a perturbed hard sphere thermodynamic model with electrostatic term. Model considers amino acid molecule as hard spheres with embedded charges. The electrostatic term, which accounts for electrostatic interactions of ions in water–electrolyte system is represented by a mean spherical approximation model. The energy of interaction terms incorporated in perturbed term of the model are those due to effect of dispersion forces, angle averaged charge – dipole interactions. The model can predict the experimental data of activity coefficients of amino acids in aqueous solutions at low electrolyte concentrations and can accurately correlate the results at higher electrolyte concentrations.

From the above survey, one can notice that there is lack of volumetric or viscometric data up to high concentration range of amino acids and electrolytes. No data are available for amino acids in mixed electrolyte systems. There is need of examining the effect of amino acids on the properties of electrolytes. There is also necessity of a unified model, which can correlate the thermodynamic and volumetric properties of amino acids as well as electrolytes. Till date no equations are available to describe the thermodynamic behaviour of these systems.

As illustrated in the first chapter it is preferred to study properties of model compounds like amino acids instead of complex bio-molecules. In order to understand the effects of ionic species on amino acids in general, various properties of amino acids in aqueous electrolyte solutions are studied. Similarly the effect of amino acids on electrolyte solutions has been examined. The thesis is aimed to seek the following objectives:

1. To measure the volumetric properties of amino acids or peptide in several aqueous electrolytic solutions and to study the effects of electrolytes on the properties of amino acids,
2. to estimate the effect of amino acids on the volumetric properties of electrolytes,
3. to measure the volumetric properties of amino acids or peptide in mixed electrolyte systems,
4. to investigate the effect of tetra-n-alkyl ammonium salts on amino acids and peptides,
5. to propose a thermodynamic model for excess Gibbs free energy of mixing amino acids or peptide with electrolytes in water in terms of the ion – amino acid interaction parameter,
6. To extend the model for correlating activity coefficient, osmotic coefficient, volume, compressibility and expansibility of amino acid with concentration in aqueous electrolytic solution,
7. to predict the properties of electrolytes in amino acids with a knowledge of ion – amino acid – water interaction parameter derived above,

8. to study viscous behaviour of the mixture containing amino acids or peptide, electrolyte and water system and to develop equations to describe the viscosity of such systems.

In order to achieve the above mentioned objectives following systems are studied: amino acids: glycine and L-alanine; peptide: glycylglycine; electrolytes: NaCl, NaBr, KCl, KBr, $MgCl_2$, Na_2SO_4, tetra-n-alkylammonium bromides ($(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$). The properties as mentioned in the following chapters have been investigated for these systems.

Details of the chemicals used in the experimentation and various experimental techniques are discussed in detail in this chapter.

3.1 Materials:

Summary of chemicals used during the experimental work:

No.	Name	Molar mass/(g mol^{-1})	Assay	Impurities as recorded on the labels	Supplier
1.	Glycine	75.07	Purified (>99%)	Cl<0.005%, SO_4<0.01%	Merck
2.	L-alanine	89.09	Biochemistry grade (>99%)	Heavy metals (as Pb) = 0.001%, NH_3 = 0.01%, foreign amino acids = 0.3%, other ninhydrin positive substances = 0.1%	LOBA Chemie
3.	Glycylglycine	132.12	Biochemistry grade	Cl = 0.005%, SO_4 = 0.005%, heavy metals (as Pb) = 0.0005%, Na = 0.01%, loss on drying = 1% at 105^0C	LOBA Chemie
4.	NaCl	58.44	Extra pure > 99.5%	Loss on drying (105^0C) = 1%, SO_4 = 0.02%, NH_3 = 0.002%, Fe = 0.002%, Pb	S. D. Fine Chem. Ltd.

				= 0.0005%	
5.	NaBr	102.90	Extra pure > 99.5%	BrO_3 = 0.001%, Cl = 0.2%, I = 0.02%, SO_4 = 0.005%, heavy metals (as Pb) = 0.001%, As = 0.0002%, Ca = 0.005%, Fe = 0.001%, Mg = 0.002%	LOBA Chemie
6.	Na_2SO_4	142.04	Purified L. R. (for synthesis) 99.0%	Loss on ignition at 300^0C = 0.5%, Cl = 0.01%, NO_3 = 0.01%, Fe = 0.002%, Pb = 0.002%	S. D. Fine Chem. Ltd.
7.	KCl	74.56	Pro analysi 99.5%	pH 5% w/v water = 5.5-8.5, Br = 0.01%, I = 0.002%, PO_4 = 0.005%, SO_4 = 0.03%, N = 0.01%, Ba = 0.001%, Ca = 0.001%, Heavy metals (as Pb) = 0.0005%, Fe = 0.0002%, Mg = 0.0005%, Na = 0.02%, loss on drying (130^0C) < 0.2%	Merck
8.	KBr	119.01	Pure 99%	Cl = 0.5%, I = 0.05%, SO_4	Merck

				= 0.01%, BrO_3 = 0.002%, heavy metals (as Pb) = 0.001%, Fe = 0.002%	
9.	$MgCl_2$	95.21	Synthesis grade >98%		Merck – Schuchardt
10.	Tetramehyl-ammonium bromide, $(CH_3)_4NBr$	154.06	Synthesis grade		Lancaster
11.	Tetraethyl-ammonium bromide, $(C_2H_5)_4NBr$	210.16	Pure >98%		SRL
12.	Tetra-n butylammonium bromide $(C_4H_9)_4NBr$	322.37	Extra pure A. R. > 99%	Sulphated ash = 0.1%	SRL

3.2 Composition of solutions:

All the solutions were prepared on the molality basis. The samples were weighed on a CONTECH CB – series electronic balance. The accuracy of the balance is ± 0.001 g. All the electrolytes were dried at 523 K (except tetra-n-alkylammonium bromide salts) for 3 h. prior to their use and then under vacuum for 30 min. Amino

acids and peptide were also dried under vacuum for 30 min before weighing. $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ were recrystallised once from 1:1 (v/v) mixture of methanol + ethanol, 1:3 (v/v) mixture of methanol + ethyl acetate and 20:1 (v/v) mixture of ethyl acetate + diethyl ether, respectively[163]. All the tetra-n-alkyl salts were dried in oven at T ≈360 K for 4-5 h and then dried under vacuum for 1 h. The specific conductivity of the water used was less than 0.055×10^{-6} S cm^{-1}. The deionised water was obtained from PURELAB CLASSIC, Elga Lab Water purification unit.

3.3 Measurement of density:

Densities of the solutions of glycine, L-alanine and glycylglycine in aqueous NaBr, Na_2SO_4, KCl, KBr and $MgCl_2$ were measured using a DMA 60 vibrating tube digital density meter supplied by, ANTON PAAR. Density determination is based on measuring the period of oscillation of a vibrating U shaped sample tube, which is filled with sample liquid or through which the sample liquid flows continuously as shown in **Figure 3.1**. The measuring principle is based on the change of natural frequency of hollow oscillator when filled with different concentrations of solutions. Oscillator consists of a hollow elastic glass tube, which is electronically excited, in an undamped harmonic fashion. Direction of oscillation is perpendicular to plane of U shaped sample tube. It is essential to ensure that the sample tube is completely filled, overfilling does not affect the measurement. Precaution was to avoid trapping micro air bubbles on wall of sample tube. The period of oscillation, τ for each solution is measured thrice. After each reading water and air reading was repeated. The instrument constant, K is calculated using the equation:

$$K = \rho_w / [(\tau_w / \tau_a)^2 - 1] \quad (1)$$

where τ_w and τ_a are the period of oscillations for water and air, respectively. The density of water, ρ_w is taken from literature[215]. The density of the experimental solution, ρ_{sample} is calculated using the instrument constant and τ_{sample} as:

$$\rho_{sample} = K [(\tau_{sample} / \tau_a)^2 - 1] \quad (2)$$

The density meter was calibrated using n-heptane[216], methanol[217], and aqueous NaCl[218] solution at different concentrations. The accuracy of the density meter was found to be ± 0.005 kg m^{-3}, while the precision was estimated as 0.002 kg m^{-3}, which can be seen from **Table 3.1**.

Table 3.1: Comparison of experimental and literature densities of standard solutions

System (298.15K)	$\rho_{experimental}$ / (kg m^{-3})	$\rho_{Literature}$ / (kg m^{-3})
Methanol	786.37	786.37
n-heptane	679.00	679.46
NaCl 0.2025 mol kg^{-1}	1005.31	1005.30
KCl 0.5089 mol kg^{-1}	1020.30	1020.29

The densities of glycine, L-alanine and glycylglycine in aqueous $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ solutions were measured using a DA 210 digital density meter supplied by, Kyoto electronics Japan. The density meter was calibrated daily by

measuring its vibrational period using dry air and distilled water to determine its calibration constant. Then the vibrational period of the tube containing the solution of interest was determined. All the vibrational periods were also measured three times. The density meter was also calibrated using aqueous NaCl solution[218]. The following relation was assumed between the density, ρ of the solution in the density meter tube and the measured vibrational period, τ at the experimental temperature:

$$\rho = K \tau^2 / (4 \pi V_0) - M_0 / V_0 \quad (3)$$

where K, V_0 and M_0 are the instrument constant, volume of sample in the cell (which is capacity of measuring cell) and the mass of the cell, respectively. The factor F was determined from the oscillation periods of air, τ_a and of water, τ_w using the density of air, ρ_a and water, ρ_w at specific temperature:

$$F = K (4 \pi^2 V_0) = (\rho_a - \rho_w) / (\tau_a^2 - \tau_w^2) \quad (4)$$

Then, the density of the solution of interest was determined from its measured oscillation period τ by using the following the relation:

$$\rho = \rho_w - F (\tau_a^2 - \tau_w^2) \quad (5)$$

The accuracy of the measured densities was found to be $\pm$ 0.005 kg m^{-3}, while the precision of the measurements was recorded as $\pm$ 0.002 kg m^{-3}.

3.4 Measurement of sound speed:

The speed of sound was measured using the ultrasonic interferometer supplied by M/S Mittal Enterprises, New Delhi. The instrument is based on interference method. This method was developed by Pierce[219]. The schematic diagram is shown in **Figure 3.2.** The source of the ultrasonic waves is a quartz crystal transducer mounted at the base of cylindrical sample cell made of stainless steel. Quartz crystal is attached to a heavy base plate of interferometer by means of three bolts, which permit adjustment to exact parallelism with the perpendicular reflector. This is the prime criterion for the measurement. The crystal of the transducer has an exposed radiating surface 1cm in diameter and is in direct contact with the solution. A radio frequency oscillator excites the crystal. The lower face of the crystal is air loaded. The crystal circuit is carefully packed and is operated closed to fundamental resonance frequency. Interchangeable crystal holders permit operation at various frequencies between 0.5 and 12 MHz. Micrometer screw is attached to a hollow cylinder and a reflector. Due to reflection from the reflector a system of stationary waves is formed with nodes and antinodes. The reflected waves react on the quartz source and change the plate current or the tank current of the oscillator supplying the voltage to the quartz crystal. The plate current or tank current depends on the amplitude of vibration of the crystal. Depending on the position of the reflector, the reflected vibrations will reach the crystal. If the vibrations are out of phase vibrations of the crystal will be damped or if they are in phase vibrations of the crystal will be enhanced, this will be reflected in the change of plate current or tank current of oscillator. Consequently, the plate or tank current will go through a cycle of values as the reflector plate is moved through

half a wavelength. The speed of sound can be determined by noting the positions of current maxima or minima on the micrometer screw. By taking the average of the difference between two successive readings as the position of successive maxima or minima, the value of $\lambda / 2$ i.e. wavelength of the sound wave can be obtained. The speed of sound, u can be obtained from wavelength and frequency, f of the wave using the relation $u = f \lambda$. The speed of sound can also be measured by plotting a graph between the change of plate or tank current and the position of the piston as noted in the micrometer screw. From the positions of successive maxima or minima the value of $\lambda / 2$ can be obtained and further u can be obtained.

The interferometer was calibrated using the speed of sound of water[215] and aqueous NaCl[220] data at 298.15 K. A cell with 4 MHz. frequency was used to measure the speed of sound. The cell was filled by 7-8 ml solution and was allowed to equilibrate for ½ h. before taking the readings. Average of 10 readings was taken as a final value. The measured speed of sound values are accurate, to ± 0.05%. The precession of sound speed based on 10 readings was calculated as ± 0.02%. The experimental speed of sound in water at 298.15, 308.15, 318.15 K were observed to be in good agreement with literature values as 1496.0 (1496.7), 1520.0 (1519.8), 1536.0 (1536.4) m s^{-1}, respectively (values in parenthesis are the literature values)[215]. The speed of sound data obtained in 2 mol l^{-1}aqueous NaCl is 1616.0 m s^{-1}, whereas the literature value is 1616.2 m s^{-1} [220].

3.5 Measurement of viscosity:

Viscosity was measured using a ubbelhodde viscometer. Time required for the flow of water at 298.15 K was 129.51 s. Time was measured using a Racer digital

stopwatch having accuracy ± 0.01 s. Average of five readings was taken as the value of time. The difference in the readings was not more than 0.05 s. The viscometer was calibrated with deionised water[221], aqueous KCl[222] and Na_2SO_4[221]. The accuracy in the measurements of viscosity is 0.01 %. The change in density of 0.01 kg m^{-3} was found to change viscosity by only ± 0.002%.

Viscosity of the solution, η is given by following equation:

$$\eta / \rho = C\,t - K / t \qquad (6)$$

where t is the flow time (s), ρ is density of the solution and C and K are the viscometer constants, which were obtained by the measurements of flow time for water at 283.15, 293.15, 298.15, 303.15, 313.15 and 413.15 K as shown in **Figure 3.3**. The values of C and K obtained are 6.924 x 10^{-6} mPa s m^3 kg^{-1} and 1.390 x 10^{-4} mPa s^2 m^3 kg^{-1}, respectively. The density and viscosity of water at different temperatures were taken from literature [215,221].

A constant temperature bath supplied by Julabo (F 25) was used to control the temperature up to ± 0.05 K. Distilled water was used as a circulating fluid between the temperature range 273 to 303 K. To prevent loss of heat from tubings proper insulation of the tubings was done. The experimental solutions were allowed to equilibrate for 30 min. before taking reading.

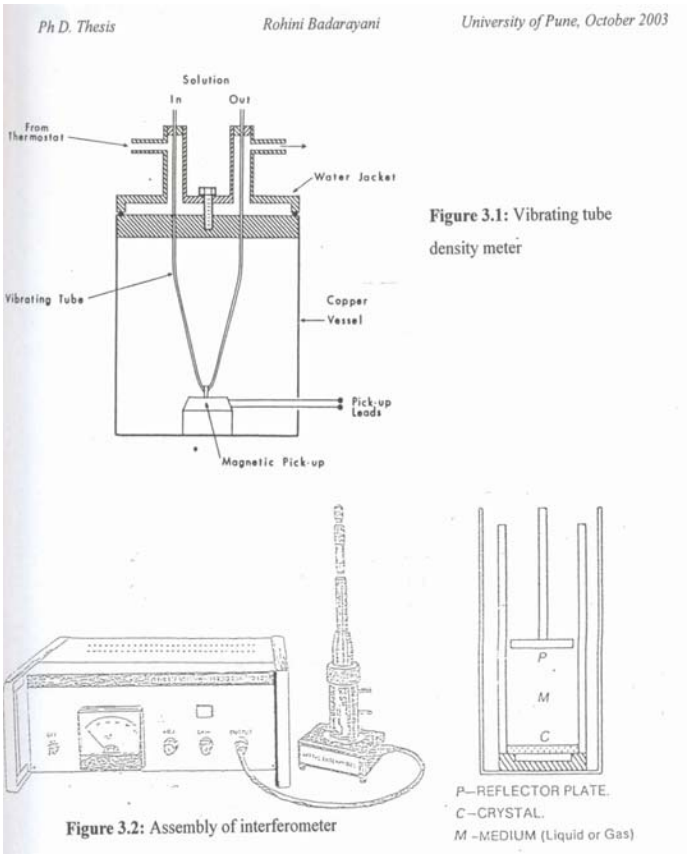


Figure 3.1: Vibrating tube density meter

Figure 3.2: Assembly of interferometer

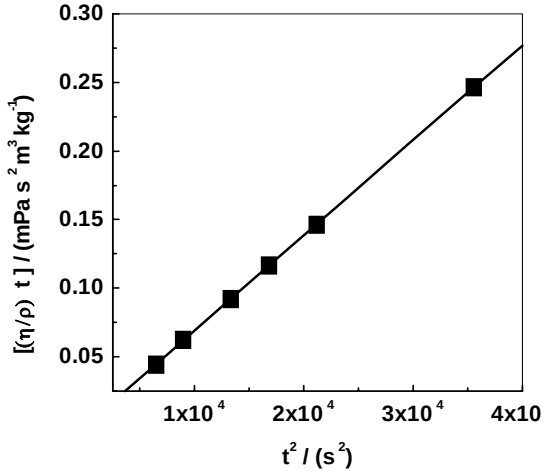


Figure 3.3 Plot of $[(\eta/\rho)\ t]$ versus flow time measured, t^2 to obtain calibration constants of viscometer, C and K.

The partial and apparent molar volumes and expansibilities, obtained from the experimentally measured densities of amino acid-electrolyte-water systems are discussed in detail in this chapter. The partial or apparent molar volumes have been used to study the intermolecular and inter-ionic interactions in solutions. The values at infinite dilution provide information about solute–solvent interactions and concentration dependence reflects solute–solute interactions.

4.1: Preface:

The partial molar volume of an electrolyte can be defined as the change in the volume of solvent or solution, upon the addition of 1 mol of electrolyte to the large reservoir of solvent or solution. The partial molar volume, V_2, of a solute, 2 having number of moles n_2 at constant temperature, T and pressure, P can be presented as:

$$V_2 = (\partial V / \partial n_2)_{T,P,n1} \qquad (1)$$

However, it is not possible to determine the partial molar volume using the above form of expression. This can be done as shown below by using apparent molar volume. Apparent molar volume is defined as:

$$\phi_V = (V - n_1 V_1^*) / n_2 \qquad (2)$$

In **equation (2)**, n_1 and n_2 are the number of moles of solvent and solute, respectively. V_1^* is the molar volume of solvent. The apparent molar volume and partial molar volumes can be related using **equation (3),** as:.

$$V_2 = \phi_V + 0.5\, m^{0.5} (\partial\phi_V / \partial m^{0.5})$$

$$V_2 = \phi_V + m\, (\partial\phi_V / \partial m) \qquad (3)$$

From **equation (3)** it can be seen that partial and apparent molar volumes become equal at infinite dilution.

The experimentally measured densities, ρ can be converted into apparent molar volumes, ϕ_V of amino acid, A (ϕ_{VAJW}) in aqueous electrolytic solution or of electrolytes, J in aqueous amino acids (ϕ_{VJAW}) using the following equation:

$$\phi_V = \{(\rho^0 - \rho) / m \rho^0 \rho\} + M / \rho \qquad (4)$$

where m and M are the molality and molar mass of the solute in question. ρ^0 is the density of the solvent. The solvent is water, W (ρ^0 = 997.04 kg m^{-3} at 298.15 K)[215] for binary solutions (A–W or J–W). Aqueous electrolytic solution is considered as solvent for calculating ϕ_{VAJW} while, aqueous amino acid solution for calculating ϕ_{VJAW} in the mixtures. The probable errors in ϕ_V can be obtained as:

$$\sigma\phi_V \approx (M_2/\rho^2 + 1/ m \rho^2) (\sigma \rho)^2 \qquad (5)$$

In dilute solutions error in ϕ_V is enlarged due to error in molality. The density measurements in dilute solutions should therefore be measured carefully.

4.2 Study of glycine + electrolytes + water system:

The experimentally measured densities of glycine in aqueous NaBr, KCl, KBr and $MgCl_2$ are listed in **Table 4.1**. The influence of different electrolytes on apparent molar volume, ϕ_{VAJW} of glycine in different electrolytes is depicted in **Figures 4.1 (a-d)**. The ϕ_{VAJW} of glycine increases from 43 to 54 x 10^6 m^3 mol^{-1} in the presence of different electrolytes. At neutral pH amino acids exist as zwitterions. The solution of amino acid in water shows an overall decrease in the volume of water. This is due to the electrostriction of water by charged end groups of amino acids. Addition of electrolytes will affect the hydration spheres of the charged end groups. As a result of cation-COO^- and anion-NH_3^+ interactions, the hydrated water molecules are allowed to relax to the bulk state and cause increase in the volume. Glycine contains H as substituents along with the COO^- and NH_3^+ groups. Thus the ions are only interacting with the head groups of glycine. The ϕ_{VAJW} versus m_A plots show positive slopes in the presence of all the studied electrolytes, but as concentration of electrolytes increases the value of slope decreases and in concentrated electrolytic solutions (concentration>2 mol kg^{-1}) the slopes become negative. In dilute electrolytic solution with the increase in amino acid concentration the ions of electrolyte interact with charged centers and release more and more water molecules to bulk water showing positive slopes. As the concentration of electrolyte as well as amino acid increases less water molecules are available around the charged centers of glycine and release of water molecules to bulk also decreases causing the slopes to be negative or almost zero.

Table 4.1: Experimental densities of aqueous glycine in different electrolytes at 298.15 K.

m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})
NaBr							
m_A = 0.5006 mol kg^{-1}		m_A = 1.0006 mol kg^{-1}		m_A = 2.0004 mol kg^{-1}		m_A = 3.0012 mol kg^{-1}	
0.5010	1049.65	0.5010	1062.63	0.4986	1085.95	0.5015	1107.38
0.9991	1085.21	0.9999	1097.11	1.0010	1118.57	0.9996	1137.57
1.9986	1153.11	2.0006	1163.02	1.9991	1179.06	2.0011	1196.12
3.0020	1217.06	2.9993	1225.16	2.9990	1237.94	3.0001	1251.32
4.0008	1276.97	4.0001	1282.89	4.0003	1293.29	4.0010	1303.14
KCl							
m_A = 0.5002 mol kg^{-1}		m_A = 0.9985 mol kg^{-1}		m_A = 2.0004 mol kg^{-1}		m_A = 3.0002 mol kg^{-1}	
1.0004	1054.74	1.0001	1067.21	0.9993	1089.66	0.5004	1093.41
2.0002	1093.14	1.9995	1103.99	2.0001	1123.86	1.0003	1110.07
3.0008	1128.46	3.0011	1137.88	3.0005	1155.31	2.0002	1141.59
4.0007	1161.78	4.0004	1168.44	4.0006	1184.24	3.0003	1170.91

KBr

m_A = 0.4998 mol kg^{-1}		m_A = 1.0010 mol kg^{-1}		m_A = 2.0001 mol kg^{-1}		m_A = 3.0004 mol kg^{-1}	
0.5017	1052.23	0.5018	1065.24	0.5013	1088.15	0.5017	1109.48
1.0009	1089.85	2.0002	1170.27	1.0004	1122.81	1.0015	1141.73
1.9995	1160.07	3.0010	1231.38	2.0015	1186.54	2.0013	1202.71
2.9979	1226.06	4.0008	1291.57	3.0006	1247.29	3.0006	1258.75
4.0117	1286.27	5.0013	1346.37	4.0008	1302.67	4.0027	1311.96

$MgCl_2$

m_A = 0.5004 mol kg^{-1}		m_A = 1.0005 mol kg^{-1}		m_A = 2.0006 mol kg^{-1}		m_A = 3.0002 mol kg^{-1}	
0.1005	1019.74	0.0995	1033.82	0.1005	1058.99	0.1005	1081.67
0.5006	1047.81	0.5002	1060.28	0.5002	1083.54	0.4974	1104.24
1.0008	1080.90	0.9996	1092.08	0.9995	1113.11	0.9999	1131.88
1.5007	1112.52	1.5013	1122.61	1.4992	1141.04		

The apparent molar volume of electrolytes, ϕ_{VJAW} are also affected due to glycine. The change in ϕ_{VJAW} of different electrolytes as a function of m_J are depicted in **Figures 4.2 (a-d)**. The ϕ_{VJAW} of NaBr changes from 28 to 40 x 10^{-6} m^3 mol^{-1}, KCl changes from 29 to 39 x 10^{-6} m^3 mol^{-1}, while, KBr and $MgCl_2$ change from 38 to 52 x 10^{-6} m^3 $mol^{-1}$and 15 to 40 x 10^{-6} m^3 mol^{-1}, respectively. The slopes of ϕ_{VJAW} versus m_J plots also show positive slopes in low concentrations of glycine and in concentrated solution (m_A>1 mol kg^{-1}) the plots show negative slopes.

The solute-solvent interactions observed are also supported with the transfer volume of glycine at infinite dilution from water to electrolytic solutions, $\phi_V^0{}_{tr.AJW}$ ($\phi_V^0{}_{tr.AJW} = \phi_V^0{}_{AJW} - \phi_V^0{}_{AW}$). The $\phi_V^0{}_{tr.AJW}$ of glycine in NaBr, KCl, KBr and $MgCl_2$ as a function of m_J are plotted in **Figure 4.3**. The transfer volumes of glycine are

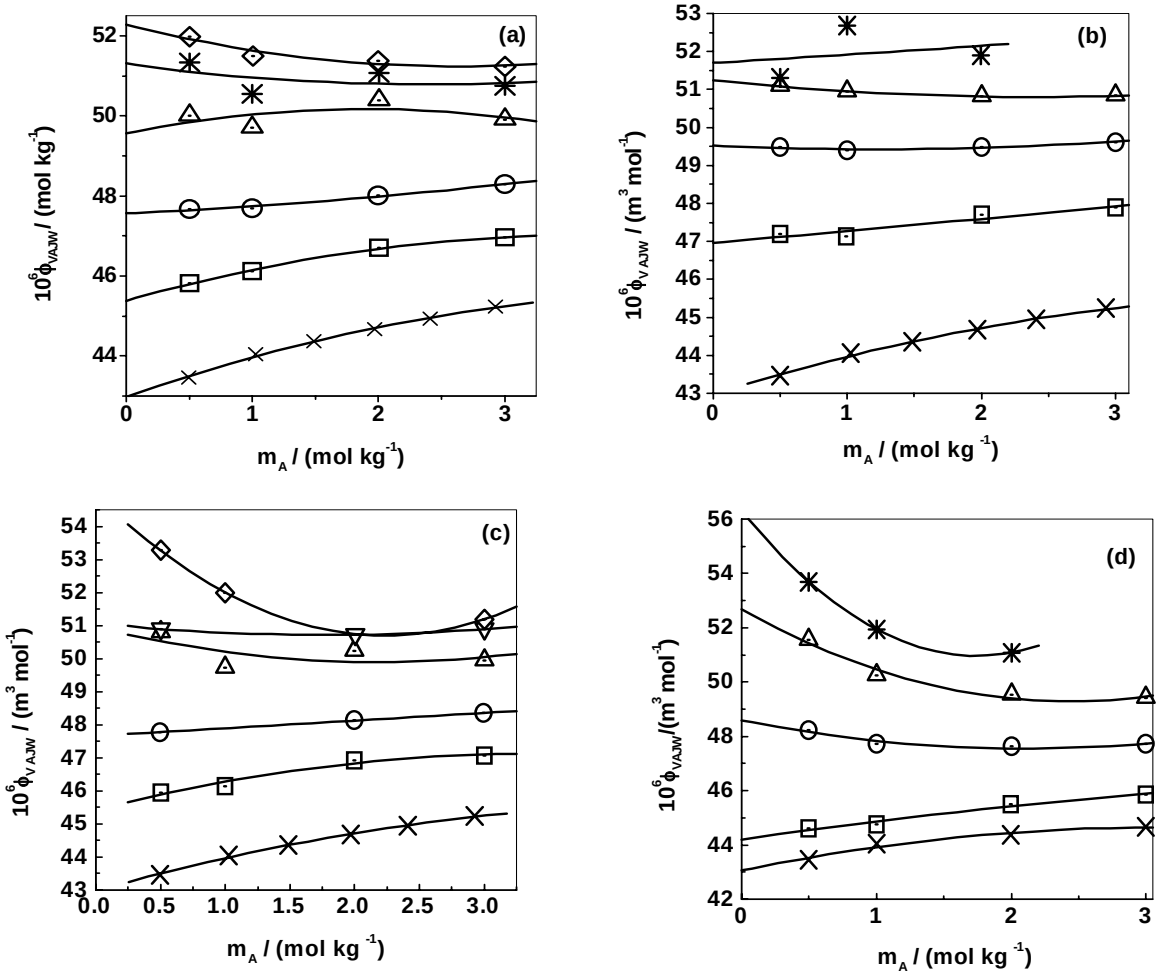


Figure 4.1: Plots of ϕ_{VAJW} *vs.* m_A of glycine in H_2O (X) **(a)** NaBr: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (T), 4 mol kg^{-1} (Γ); **(b)** KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (T); **(c)** KBr: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (∇), 4 mol kg^{-1} (Γ); **(d):** $MgCl_2$: 0.1 mol kg^{-1}(o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (T)

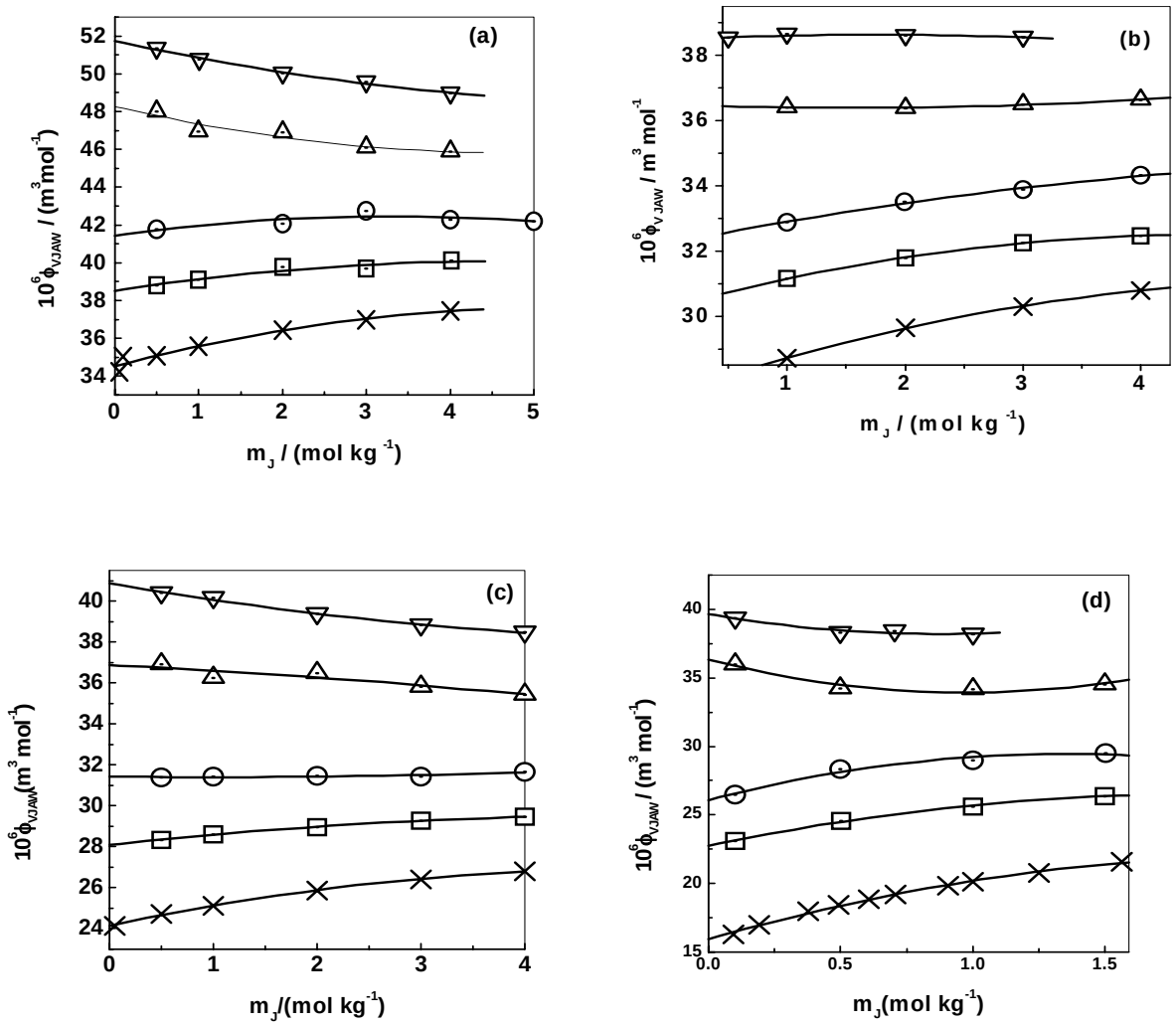


Figure 4.2: Plots of ϕ_{VJAW} *vs.* m_J of **(a)** NaBr **(b)** KCl **(c)** KBr **(d)** $MgCl_2$: in H_2O (X), 0.5 mol kg^{-1} glycine (o), 1 mol kg^{-1} glycine (O), 2 mol kg^{-1} glycine (Δ), 3 mol kg^{-1} glycine (∇)

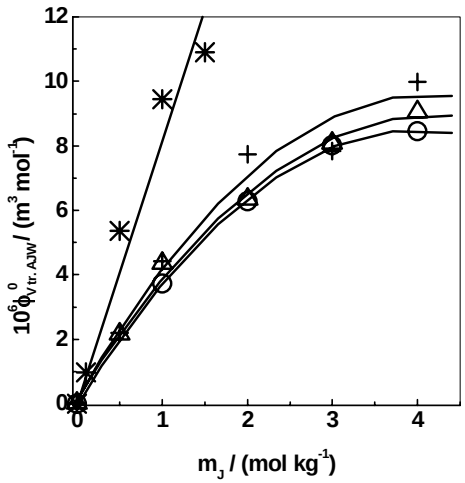


Figure 4.3: Plots of $\phi_V^0{}_{tr.AJW}$ of glycine *vs.* m_J in NaBr (Δ), KCl (O), KBr (+) and $MgCl_2$ (Σ)

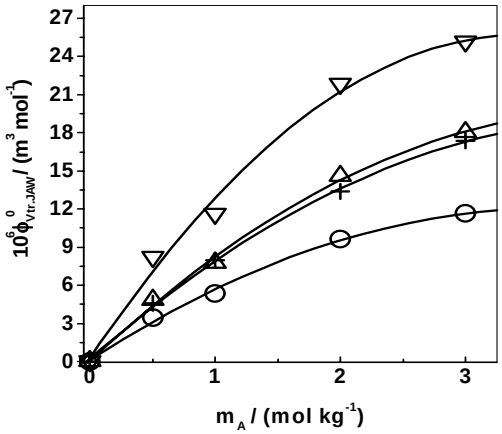


Figure 4.4: Plots of $\phi_V^0{}_{tr.JAW}$ of glycine *vs.* m_A in NaBr (+), KCl (O), KBr (Δ) and $MgCl_2$ (∇)

positive in the presence of all the electrolytes. The slopes of $\phi_V^0{}_{tr.AJW}$ *versus* m_J plots at 1 mol kg^{-1} of J are higher in the presence of $MgCl_2$, (9.23 x 10^{-6} m^3 mol^{-1}) than for 1-1 electrolytes (≈ 3.93 x 10^{-6} m^3 mol^{-1}). Mg^{2+} cation being smaller in size (r = 0.065nm) undergoes higher electrostriction compared to 1-1 electrolytes. The transfer volumes of electrolytes, $\phi_V^0{}_{tr.JAW}$ are plotted as a function of m_A in **Figure 4.4**. The transfer volumes are positive for all the electrolytes. The $(\partial\phi_V^0{}_{tr.JAW}/\partial m_A)$ values observed for different electrolytes at 1 mol kg^{-1} glycine are, NaBr = 7.91 x 10^{-6} m^3 mol^{-1}, KCl = 5.68 x 10^{-6} m^3 mol^{-1}, KBr = 8.24 x 10^{-6} m^3 mol^{-1} and $MgCl_2$ = 12.87 x 10^{-6} m^3 mol^{-1}. $MgCl_2$ shows higher effect of glycine than any 1-1 electrolytes does. From the above slopes it can be observed that the effect of glycine on electrolytes depends both on cations and anions.

4.3 Study of L-alanine + electrolytes + water system:

In **Table 4.2** are listed the experimentally measured densities of L-alanine in aqueous NaBr, KCl, KBr and $MgCl_2$. The apparent molar volume of L-alanine, ϕ_{VAJW} in aqueous electrolytes changes from 60 to 70 x 10^{-6} m^3 mol^{-1}. The variation of ϕ_{VAJW} with m_A in different concentrations of electrolytes is shown in **Figures 4.5 (a-c)**. L-alanine is having a $–CH_3$ group along with the charged centers. The $–CH_3$ group is hydrophobic in nature. Along with the end groups water molecules are also interacting with $–CH_3$ group. The release of water molecules due to interaction with ions is thus reduced resulting in negative or almost zero slopes. The ϕ_{VAJW} increases in the presence of NaBr and KBr. The effect of L-alanine on electrolyte volume is depicted in **Figures 4.6 (a-c)**. The ϕ_{VJAW} of KCl changes from 29 to 34 x 10^{-6} m^3

mol^{-1}, and that of $MgCl_2$ changes from 20 to 30 x 10^{-6} m^3 mol^{-1}. KCl and $MgCl_2$ show positive slopes for ϕ_{VJAW} versus m_J plots.

Transfer volumes of L-alanine in electrolytes are plotted in **Figure 4.7** as a function of m_J. L-alanine shows positive transfer volumes in all electrolytes studied. The $(\partial\phi_V{}^0{}_{tr.JAW}/\partial m_J)$ values of L-alanine in 1 mol kg^{-1} $MgCl_2$ (6.83 x 10^{-6} m^3 mol^{-1}) is almost 1.5 times more than that in KCl (4.45 x 10^{-6} m^3 mol^{-1}). Dominance of $MgCl_2$ on $\phi_V{}^0{}_{tr.AJW}$ can be clearly seen in **Figure 4.7**. The transfer volumes of electrolytes from water to aqueous L-alanine are shown in **Figure 4.8**. The effect of L-alanine on $\phi_V{}^0{}_{JAW}$ of $MgCl_2$ is almost twice than that on KCl, which is reflected in $(\partial\phi_V{}^0{}_{tr.JAW}/m_A)$ values. The $(\partial\phi_V{}^0{}_{tr.JAW}/m_J)$ values for $MgCl_2$ and KCl in 1 mol kg^{-1} L-alanine are 12.81 x 10^{-6} m^3 mol^{-1} and 5.88 x 10^{-6} m^3 mol^{-1}, respectively.

Table 4.2: Densities, ρ at different molality of L-alanine, m_A, and electrolyte, m_J, at 298.15 K.

m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})
NaBr			
m_A = 0.5001 mol kg^{-1}		m_A = 1.0001 mol kg^{-1}	
0.0501	1014.59	0.0500	1027.08
0.5001	1047.65	0.5001	1058.82
1.0004	1083.13	1.0001	1092.92
2.0004	1150.62	2.0004	1157.81
2.9998	1213.97	3.0002	1218.94
4.0000	1273.67	4.0004	1276.37

KCl

m_A = 0.0505 mol kg^{-1}		m_A = 0.5004 mol kg^{-1}	
1.0017	1042.72	1.0021	1052.98
2.0037	1082.68	2.0029	1091.12
3.0022	1119.39	3.0039	1126.60
4.0036	1153.27	4.0008	1159.01
m_A = 0.1001 mol kg^{-1}		m_A = 0.9999 mol kg^{-1}	
1.0068	1044.07	1.0008	1063.57
2.0073	1083.74	1.9997	1100.03
3.0035	1120.16	3.0014	1133.75
4.0021	1153.86	4.0006	1164.96

KBr

m_A = 0.5001 mol kg^{-1}		m_A = 1.0003 mol kg^{-1}	
0.0500	1014.84	0.0504	1027.38
0.5001	1050.16	0.5000	1061.25
1.0001	1087.72	1.0002	1097.34
2.0004	1158.22	2.0002	1165.02
3.0003	1223.14	3.0006	1227.57
4.0000	1283.16	4.0004	1285.95

$MgCl_2$

m_A = 0.1007 mol kg^{-1}		m_A = 0.7503 mol kg^{-1}	
0.0511	1003.74	0.0505	1020.79
0.4984	1036.39	0.4984	1051.27

0.9954	1070.39	1.0018	1084.04
1.5112	1104.72	1.5017	1114.56
	m_A = 0.5007 mol kg^{-1}		m_A = 1.0005 mol kg^{-1}
0.1011	1017.99	0.0516	1026.99
0.5023	1046.10	0.4995	1056.75
0.9989	1079.27	0.9997	1088.59
1.4961	1111.21	1.5006	1118.35

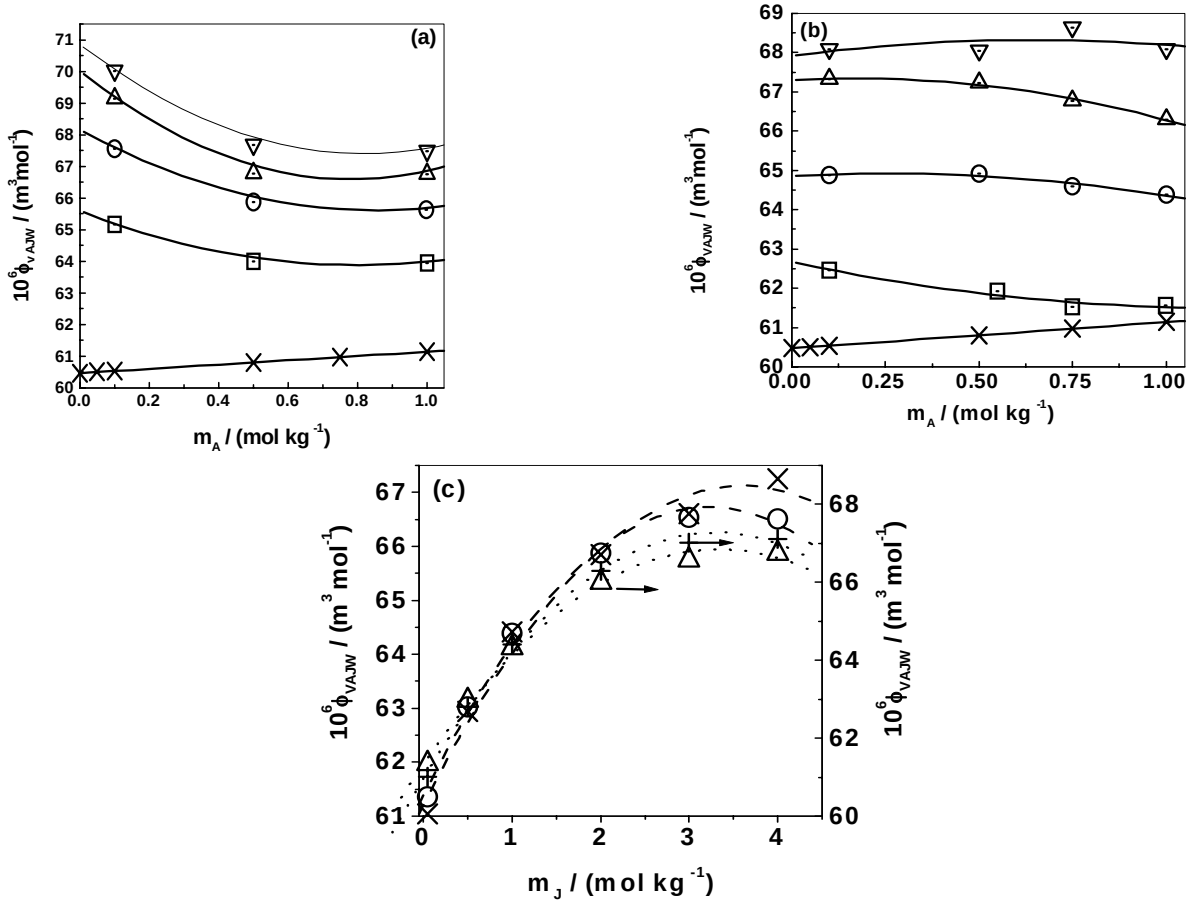


Figure 4.5: Plots of ϕ_{VAJW} of L-alanine *vs.* m_A in H_2O (X), **(a)** in KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (∇); **(b)** in $MgCl_2$: 0.05 mol kg^{-1} (o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (∇); **(c)** Plots of ϕ_{VAJW} of L-alanine versus m_J in NaBr: + 0.5 mol kg^{-1} L-alanine (+), + 1 mol kg^{-1} L-alanine (Δ), KBr: + 0.5 mol kg^{-1} L-alanine (X), + 1 mol kg^{-1} L-alanine (O)

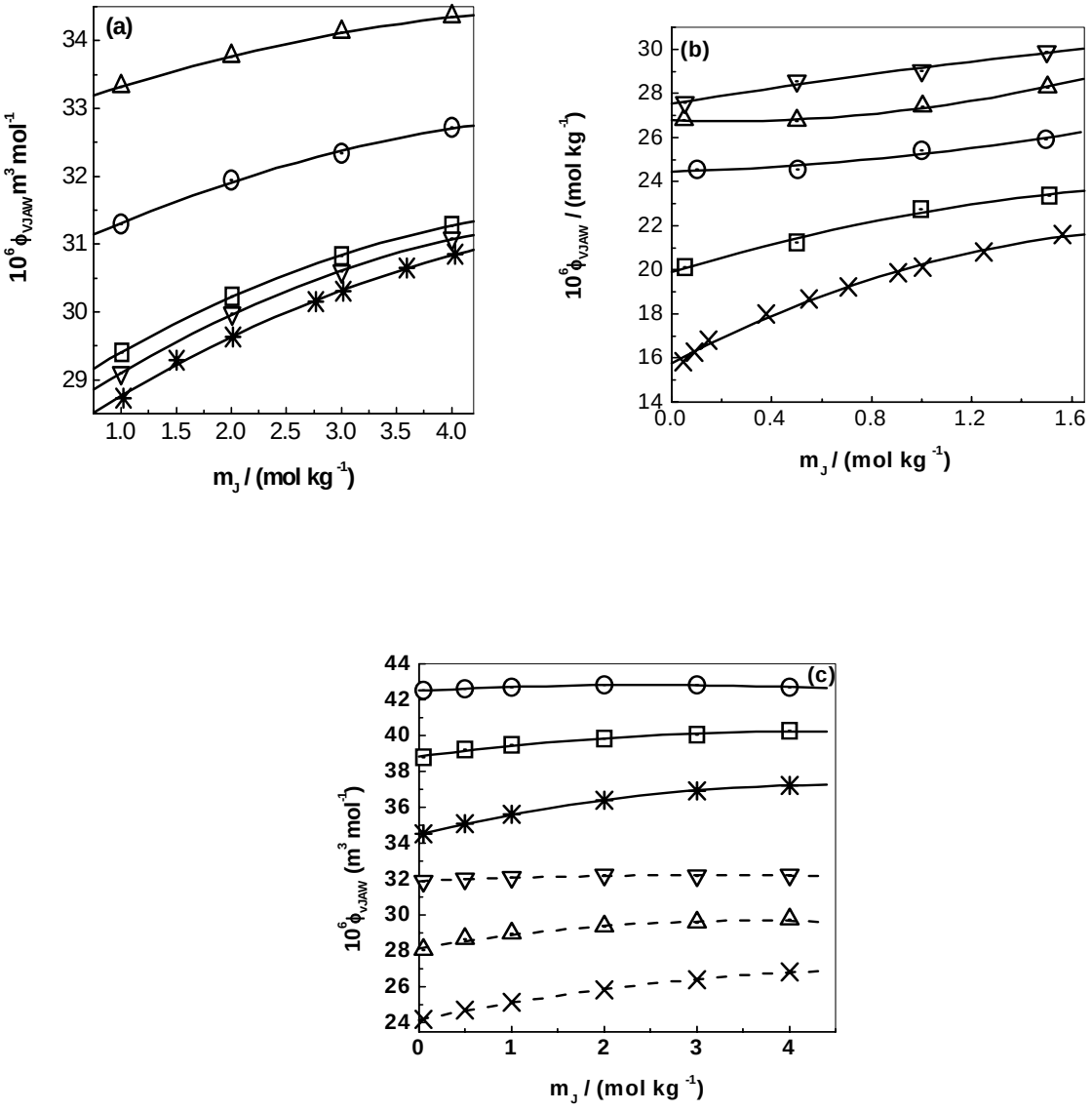


Figure 4.6: Plots of ϕ_{VJAW} vs. m_J in **(a)** KCl: + H_2O (T), 0.05 mol kg^{-1} + L- alanine (∇), 0.1 mol kg^{-1} L- alanine (o), 0.5 mol kg^{-1} L- alanine (O), 1 mol kg^{-1} L- alanine (Δ); **(b)** in H_2O (X), 0.1 mol kg^{-1} $MgCl_2$ (o), 0.5 mol kg^{-1} $MgCl_2$ (O), 0.75 mol kg^{-1} $MgCl_2$ (Δ), 1 mol kg^{-1} $MgCl_2$ (∇); **(c)** in NaBr: + H_2O (X), + 0.5 mol kg^{-1} L-alanine (Δ), + 1 mol kg^{-1} L-alanine (∇), in KBr: + H_2O (T), 0.5 mol kg^{-1} L-alanine (o), + 1 mol kg^{-1} L-alanine (O)

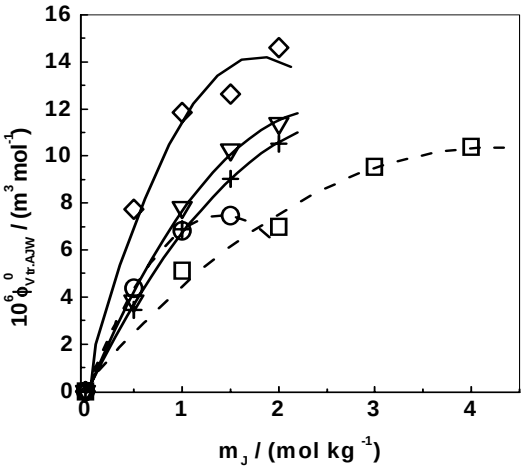


Figure 4.7: Plots of $\phi_V^0{}_{tr.AJW}$ *vs.* m_J of L-alanine in KCl (o), $MgCl_2$ (O); of glycylglycine in KCl (+), KBr (∇), Na_2SO_4 (◊)

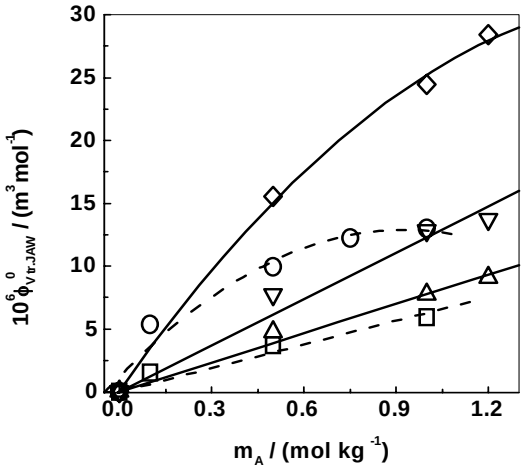


Figure 4.8: Plots of $\phi_V^0{}_{trJAW}$ *vs.* m_A of L-alanine in KCl (o), $MgCl_2$ (O); of glycylglycine in KCl (Δ), KBr (∇), Na_2SO_4 (◊)

4.4 Study of glycylglycine + electrolytes + water system:

Apparent molar volume of glycylglycine, ϕ_{VAJW} calculated from experimentally measured densities, (listed in **Table 4.3**) in different electrolytes are plotted in **Figure 4.9 (a-c)**. The ϕ_{VAJW} value changes from 76 to 90 x 10^{-6} m^3 mol^{-1} in KCl, KBr and Na_2SO_4. The transfer volumes of glycylglycine from water to aqueous KCl, KBr and $MgCl_2$ are plotted in **Figure 4.7**. Glycylglycine also shows positive transfer volumes in aqueous electrolytes like amino acids. The effect is prominent in glycylglycine than amino acids.

In **Figure 4.10 (a-c)** the effect of glycylglycine on the apparent molar volume of the aqueous electrolytes, ϕ_{VJAW} is shown. The ϕ_{VJAW} of KCl changes from 26 to 37 x 10^{-6} m^3 mol^{-1}, while that of KBr and Na_2SO_4 change from 33 to 50 x 10^{-6} m^3 mol^{-1} and 11 to 44 x 10^{-6} m^3 mol^{-1}. Significant increase in the ϕ_{VJAW} due to glycylglycine is seen in Na_2SO_4 as compared to KCl and KBr. If glycylglycine has any influence on the electrolytes, it should be also witnessed in the ${\phi_V}^0_{JAW}$ values. In the case of Na_2SO_4, though the effect is due to SO_4^{2-}, glycylglycine demonstrates strong influence in altering the ion – water interactions from 11.59 x 10^{-6} m^3 mol^{-1} (${\phi_V}^0_{JW}$ of Na_2SO_4 in pure water)[223] to about 41 x 10^{-6} m^3 mol^{-1} when glycylglycine is added from 0.5 to 1.2 mol kg^{-1}. Such effects though were seen on addition of glycine; they however are more prominent in the case of glycylglycine owing to its high dipole moment. The transfer volumes of electrolytes from water to aqueous glycylglycine are plotted as a function of m_A in **Figure 4.18**. The ${\phi_V}^0_{tr.JAW}$ values are positive. The value $(\partial {\phi_V}^0_{tr.JAW} / \partial m_A)$ for KCl, KBr and Na_2SO_4 at 1 mol kg^{-1} glycylglycine are 7.93 x 10^{-6} m^3 mol^{-1}, 12.65 x 10^{-6} m^3 mol^{-1} and 25.23 x 10^{-6} m^3 mol^{-1}, respectively. The

effect of glycylglycine is higher in Na_2SO_4 as compared to KCl or KBr (1:1 electrolytes).

Table 4.3: Experimental densities, ρ of aqueous glycylglycine in different electrolytes at 298.15 K.

m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})
KCl					
m_A = 0.5 mol kg^{-1}		m_A = 1.0 mol kg^{-1}		m_A = 1.2 mol kg^{-1}	
0.5007	1044.45	0.5001	1066.81	0.5001	1074.45
0.9999	1064.26	1.0008	1085.34	1.0002	1093.15
1.5001	1083.33	1.5002	1103.19	1.5007	1110.48
2.0001	1101.64	1.9997	1120.09	2.0010	1127.08
KBr					
0.5005	1061.96	0.4996	1083.40	0.4997	1089.79
0.9995	1098.89	1.0001	1118.50	1.0006	1125.81
1.5007	1134.16	1.4995	1151.70	1.5002	1158.30
2.0002	1167.89	2.0010	1183.74	2.0001	1189.15
Na_2SO_4					
0.5001	1079.56	0.5002	1099.74	0.4993	1106.97
0.9994	1131.07	1.0004	1148.26	1.0002	1154.49
1.5014	1179.22	1.5004	1193.84	1.5001	1199.21
2.0040	1224.46	2.0001	1236.27	2.0007	1240.43

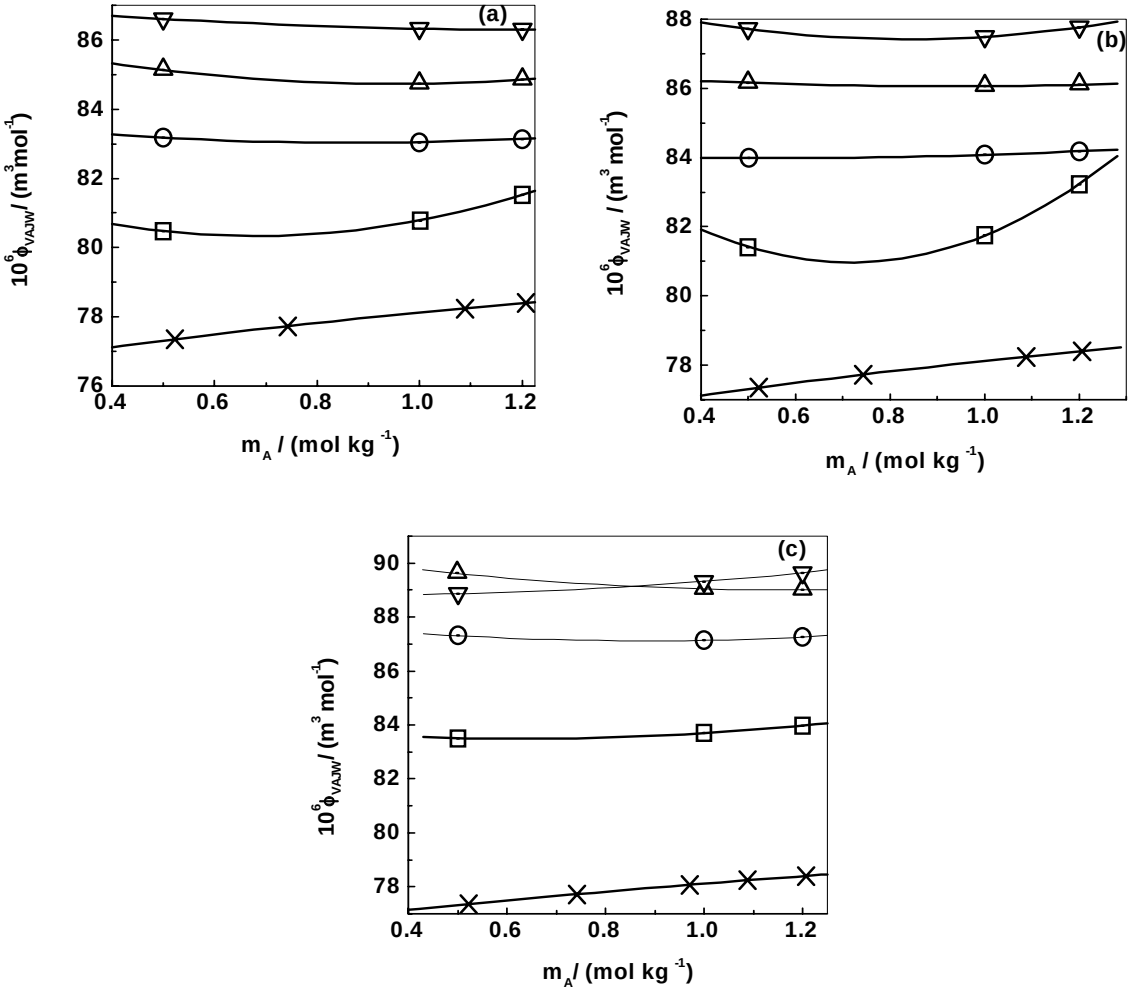


Figure 4.9: Plots of ϕ_{VAJW} of glycylglycine vs. m_A in **(a)** H_2O (X), KCl: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (∇) **(b)** H_2O (X), KBr 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (∇) **(c)** H_2O (X), Na_2SO_4 KBr 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (∇)

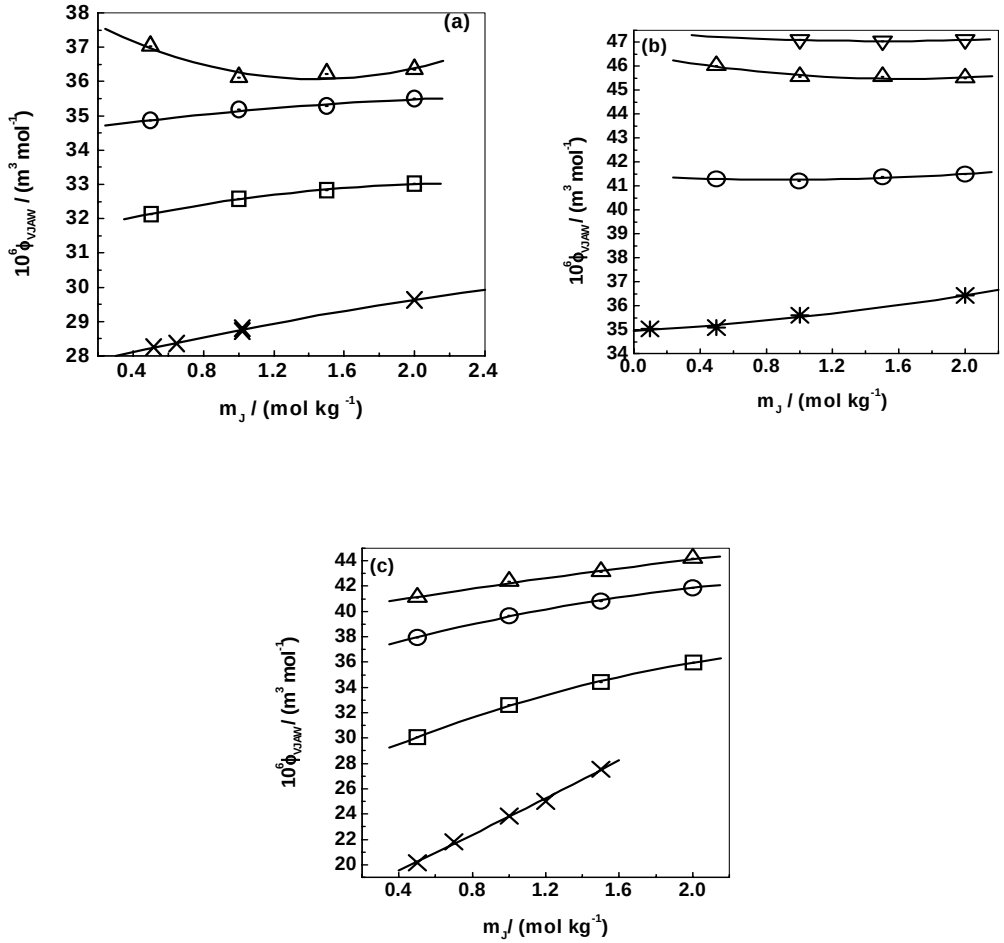


Figure 4.10: Plots of ϕ_{VJAW} *vs.* m_J (a) KCl in H_2O (X), in 0.5 mol kg^{-1} glycylglycine (o), 1 mol kg^{-1} glycylglycine (O), 1.2 mol kg^{-1} glycylglycine (Δ); (b) KBr in H_2O (T), in 0.5 mol kg^{-1} glycylglycine (O), 1 mol kg^{-1} glycylglycine (Δ), 1.2 mol kg^{-1} glycylglycine (∇); (c) Na_2SO_4 in H_2O (X), in 0.5 mol kg^{-1} glycylglycine (o), 1 mol kg^{-1} glycylglycine (O), 1.2 mol kg^{-1} glycylglycine (Δ)

4.5 Study of expansibility of L-alanine – KCl – water system:

For complete understanding of the influence of electrolytes on amino acids, knowledge of the apparent molar expansibility in addition to volume measurements is required. Thus, the temperature dependent determinations of apparent molar volume of L-alanine in concentrated KCl, in the temperature range 283.15 to 313.15 K is reported.

In **Table 4.4** are listed the experimental ρ values for the aqueous L-alanine - KCl system at different temperatures and concentrations of KCl. The densities of aqueous KCl were taken from literature[224] and that of aqueous L-alanine were experimentally measured at different temperatures. The variation of apparent molar volume, ϕ_{VAJW} of amino acid with the temperature is shown in **Figure 4.11**. The ϕ_{VAJW} *versus* temperature plots show positive slopes at all the concentrations of KCl. The positive slopes shown by alanine in KCl are in accordance with the positive slopes shown by alanine in guanidinium hydrochloride[181] and KSCN[173]. The concentration of KCl does not show a drastic effect on the slopes. The average slope of ϕ_{VAJW} *versus* temperature plot is 3.046 x 10^{-8} m^3 mol^{-1} K^{-1}.

Table 4.4: The densities, ρ of the L-alanine - KCl in water at different temperatures.

T / K	ρ / (kg m^{-3})	ρ / (kg m^{-3})	ρ / (kg m^{-3})	ρ / (kg m^{-3})
		m_A = 0.5 mol·kg^{-1}		
m_J / (mol kg^{-1})	1	2	3	4
283.15	1056.99	1096.13	1131.80	1164.64
288.15	1055.79	1094.57	1130.03	1162.58

298.15	1052.98	1091.20	1126.60	1159.01
308.15	1049.16	1087.03	1121.78	1153.93
313.15	1046.91	1084.78	1119.45	1151.53
		m_A=1 mol·kg^{-1}		
m_J / (mol·kg^{-1})	1	2	3	4
283.15	1067.93	1105.03	1139.20	1067.93
288.15	1066.59	1103.49	1137.39	1066.59
298.15	1063.57	1100.03	1133.75	1164.96
308.15	1059.64	1095.69	1129.07	1059.64
313.15	1057.61	1093.56	1126.80	1057.61

There is an increase in the ϕ_{VAJW} from 63 x 10^{-6} to 68 x 10^{-6} m^3 mol^{-1} due to addition of KCl and increase in the temperature from 283.15 to 313.15 K. The change in the ϕ_{VAJW} as a function of molality of KCl at different temperatures is shown in **Figures 4.12**. The increase in the temperature favors the relaxation of water molecules than binding them to charged end groups which is seen in the form of the positive slopes of ϕ_{VAJW} *versus* temperature and ϕ_{VAJW} versus molality of KCl.

Since the temperature effect on ϕ_{VAJW} in the presence of KCl is studied it would be of interest to check the thermal expansion of KCl as modified by L-alanine. The variation of apparent molar volume, ϕ_{VJAW} with the temperature is shown in **Figures 4.13**. The ϕ_{VJAW} varies from 30 x 10^{-6} to 35 x 10^{-6} m^3 mol^{-1}. The dependence of ϕ_{VJAW} on m_J is illustrated in **Figures 4.14**.

The apparent molar expansibility of L-alanine, ϕ_{EAJW} in KCl may be defined as:

$$\phi_{EAJW} = (\partial\phi_{VAJW} / \partial T)_P \quad (6)$$

The values of ϕ_{EAJW} in different concentrations of KCl are listed in **Table 4.5**. In **Figure 4.15** is illustrated the variation of ϕ_{EAJW} with respect to m_J. The apparent molar expansibility of KCl in the presence of L-alanine, ϕ_{EJAW} is calculated using equation analogous to **equation (6)** and the values are listed in **Table 4.5**.

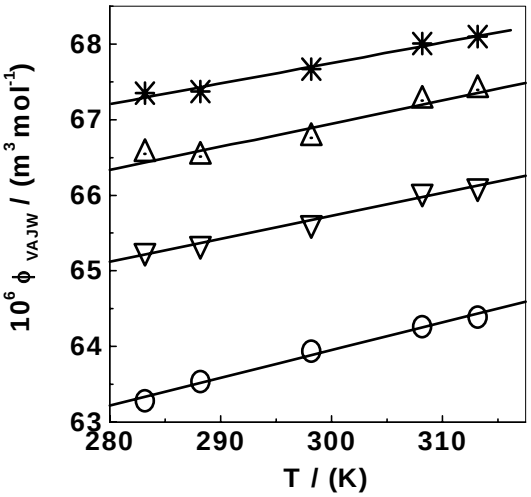


Figure 4.11: Plots of ϕ_{VAJW} vs. temperature, T in several mixtures: 0.5 mol kg^{-1} L-alanine + 3 mol kg^{-1} KCl (Δ), + 4 mol kg^{-1} KCl (T); 1 mol kg^{-1} L-alanine + 2 mol kg^{-1} KCl (∇), + 1 mol kg^{-1} KCl (O)

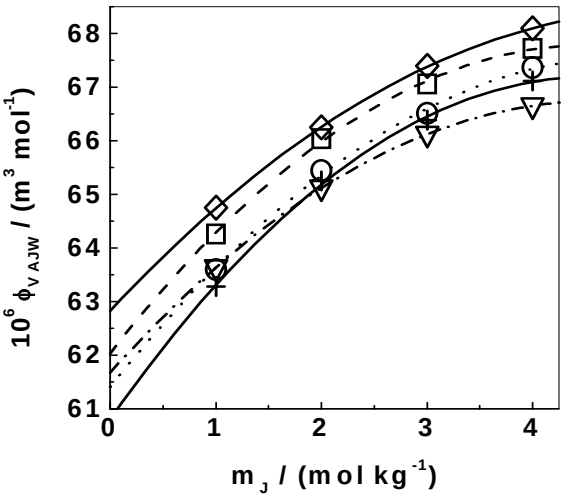


Figure 4.12: Plots of ϕ_{VAJW} vs. m_J, in 0.5 mol kg^{-1} L-alanine at 288.15 K (O) with dotted line, 313.15 K (Γ); and 1 mol kg^{-1} L-alanine at 283.15 K (+), 298.15 K (∇) with dash dot dash line, 308.15 K (o) with dashed line.

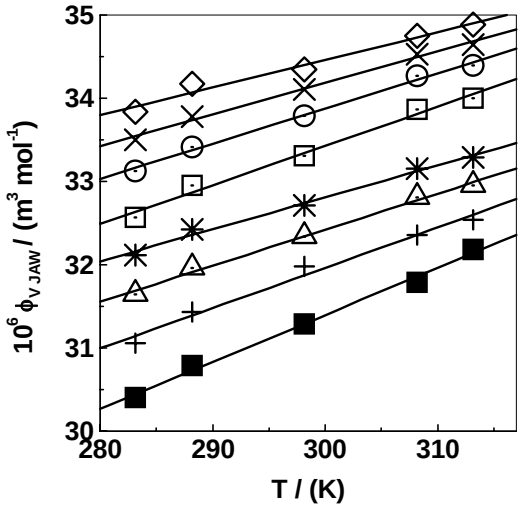


Figure 4.13: Plots of ϕ_{VJAW} vs. temperature, T in 0.5 mol kg^{-1} L-alanine+1 mol kg^{-1} KCl (ν), + 2 mol kg^{-1} KCl (+), + 3 mol kg^{-1} KCl (Δ), + 4 mol kg^{-1} KCl (T); 1 mol kg^{-1} L-alanine + 1 mol kg^{-1} KCl (o), + 2 mol kg^{-1} KCl (O), + 3 mol kg^{-1} KCl (X), + 4 mol kg^{-1} KCl (Γ)

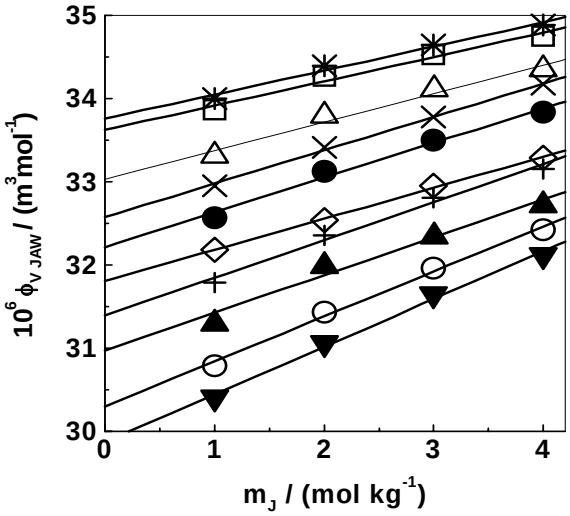


Figure 4.14: Plots of ϕ_{VJAW} *vs.* m_J, in 0.5 mol kg^{-1} L-alanine at 283.15 K (τ), 288.15 K (O), 298.15 K (σ), 308.15 K (+), 313.15 K (Γ); and 1 mol kg^{-1} L-alanine at 283.15 K (λ), 288.15 K (X), 298.15 K (Δ), 308.15 K (ο), 313.15 K (T)

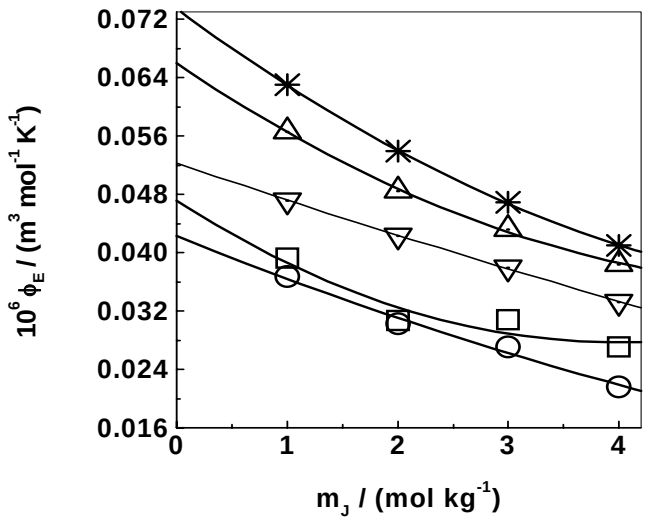


Figure 4.15: Plots of ϕ_E *vs.* m_J of 0.5 mol kg^{-1} L-alanine (ο), of 1 mol kg^{-1} L-alanine (O), of KCl in H_2O (T), 0.5 mol kg^{-1} L-alanine (Δ), 1 mol kg^{-1} L-alanine (∇)

Table 4.5: Apparent molar expansibilities of L-alanine and KCl in L-alanine - KCl - water system

m_J / (mol kg^{-1})	$10^8\,\phi_{EAJW}$ / ($m^3\,mol^{-1}\,K^{-1}$)		$10^8\,\phi_{EJAW}$ / ($m^3\,mol^{-1}\,K^{-1}$)	
	m_A = 0.5 mol kg^{-1}	m_A = 1 mol kg^{-1}	m_A = 0.5 mol kg^{-1}	m_A = 1 mol kg^{-1}
1	3.92	3.67	5.65	4.71
2	3.07	3.03	4.84	4.23
3	3.08	2.71	4.32	3.79
4	2.71	2.16	3.84	3.32

4.6 Effect of mixed ions on aqueous amino acids:

In the biological fluids mixtures of electrolytes are present, so the effect of combinations of ions on amino acids must also be considered. So far no reference is available on the study of amino acid volumetric properties in the mixture of ions. The volumetric properties of glycine and L-alanine in KCl (1) - NaCl (2) and KCl (1) – $MgCl_2$ (2) mixtures at ionic strengths, I = 1 and 3 mol kg^{-1} are reported for the first time.

The measured ρ values are listed at different concentrations of electrolytes in 0.5 mol kg^{-1} of L-alanine and glycine in **Tables 4.6 and 4.7**, respectively. The densities of the solvents, KCl–NaCl–H_2O and KCl–$MgCl_2$–H_2O required for calculation of ϕ_{VAJW} were taken from literature[225,226] and L-alanine–H_2O and glycine–H_2O were experimentally measured. The change ϕ_{VAJW} values in the presence of

mixtures of electrolytes is shown in **Figures 4.16 (a,b)** as a function of ionic strength fraction of KCl, y_{J1}. The ϕ_{VAJW} of L-alanine in KCl-NaCl, KCl -$MgCl_2$ and of glycine in KCl-NaCl passes through a minima (at 0.5 y_{J1}) as the concentration of KCl starts increasing, but ϕ_{VAJW} of glycine in KCl -$MgCl_2$ passes through a maxima with the increase in KCl concentration.

The effect of amino acid - electrolyte on ϕ_{VJAW} are shown in **Figures 4.17 (a-c)**. The change in volume of electrolyte is prominent at ionic strength 3 mol kg^{-1}. In case of ϕ_{VJAW} of NaCl, L-alanine changes the volume predominantly than glycine, while in case of $MgCl_2$ the volume increase is higher due to glycine than L-alanine. The change in ϕ_{VJAW} of KCl does not show any dependence on amino acid. The change in volume due of KCl in the presence of amino acid - NaCl is more that that in amino acid + $MgCl_2$.

Table 4.6: The experimental densities of L-alanine in mixture of electrolytes at 298.15K.

m_1 / (mol kg^{-1})	m_2/ (mol kg^{-1})	ρ / (kg m^{-3})	m_1/ (mol kg^{-1})	m_2/ (mol kg^{-1})	ρ / (kg m^{-3})
L-alanine-KCl -NaCl -H_2O					
m_A = 0.5002 mol kg^{-1}					
0	1.0004	1113.78	0	2.9986	1047.87
0.1999	0.8002	1116.42	0.6003	2.3995	1048.93
0.3997	0.5999	1118.80	1.2001	1.8005	1049.90

0.6002	0.4004	1151.22	1.8001	1.2005	1050.89
0.8002	0.2002	1123.79	2.4005	0.5999	1051.84
1.0021	0	1126.60	3.0039	0	1052.98
m_1 / (mol kg^{-1})	m_3/ (mol kg^{-1})	ρ / (kg m^{-3})	m_1/ (mol kg^{-1})	m_3/ (mol kg^{-1})	ρ / (kg m^{-3})
L-alanine - KCl - $MgCl_2$ - H_2O					
m_A = 0.5006 mol kg^{-1}					
0	0.3335	1034.45	0	0.9989	1079.27
0.2007	0.2665	1038.03	0.6007	0.8006	1088.86
0.4013	0.2005	1041.97	1.4993	0.5005	1103.35
0.6001	0.1344	1045.68	1.8013	0.4010	1108.22
0.8002	0.0675	1049.33	2.1014	0.3011	1112.68
1.0021	0	1052.98	2.3991	0.1985	1116.86
			3.0039	0	1126.60

Table 4.7: The experimental densities of glycine in mixture of electrolytes at 298.15K.

m_1 / (mol kg^{-1})	m_2/ (mol kg^{-1})	ρ / (kg m^{-3})	m_1/ (mol kg^{-1})	m_2/ (mol kg^{-1})	ρ / (kg m^{-3})
Glycine - KCl - NaCl - H_2O					
m_A = 0.5001 mol kg^{-1}					
0	1.0010	1049.80	0	3.0002	1116.09
0.2001	0.7991	1050.69	0.5993	2.3999	1118.61

0.4001	0.6009	1051.83	1.2001	1.8001	1121.23
0.5994	0.4001	1052.70	1.8001	1.2002	1123.65
0.8001	0.2002	1053.83	2.4001	0.6001	1126.13
1.0002	0	1054.74	3.0008	0	1128.46
m_1 / (mol kg^{-1})	m_3/ (mol kg^{-1})	ρ / (kg m^{-3})	m_1/ (mol kg^{-1})	m_3/ (mol kg^{-1})	ρ / (kg m^{-3})

Glycine - KCl - $MgCl_2$ - H_2O

m_A = 0.5002 mol kg^{-1}

0	0.3330	1036.14	0	1.0008	1080.90
0.2007	0.2670	1039.84	0.6007	0.8001	1087.88
0.4008	0.2001	1043.31	1.1987	0.6001	1098.55
0.6006	0.1322	1047.30	1.8001	0.4005	1109.54
0.8014	0.0681	1051.13	2.4009	0.2005	1118.72
1.0001	0	1054.74	3.0008	0	1128.46

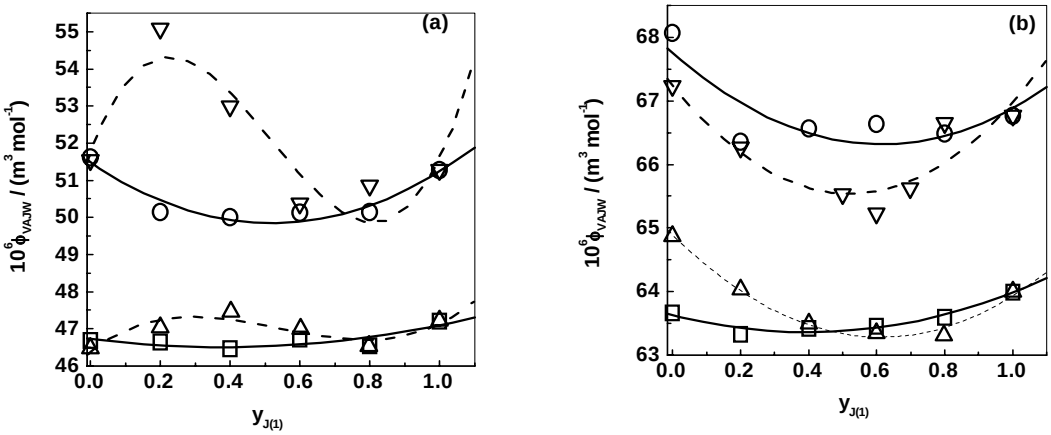


Figure 4.16: Plots of ϕ_{VAJW} vs. y_{J1} in KCl - NaCl: I = 1 mol kg^{-1} (o), I = 3 mol kg^{-1} (μ); in KCl – $MgCl_2$: I = 1 mol kg^{-1} (Δ), I = 3 mol kg^{-1} (∇); **(a)** of glycine **(b)** of L-alanine

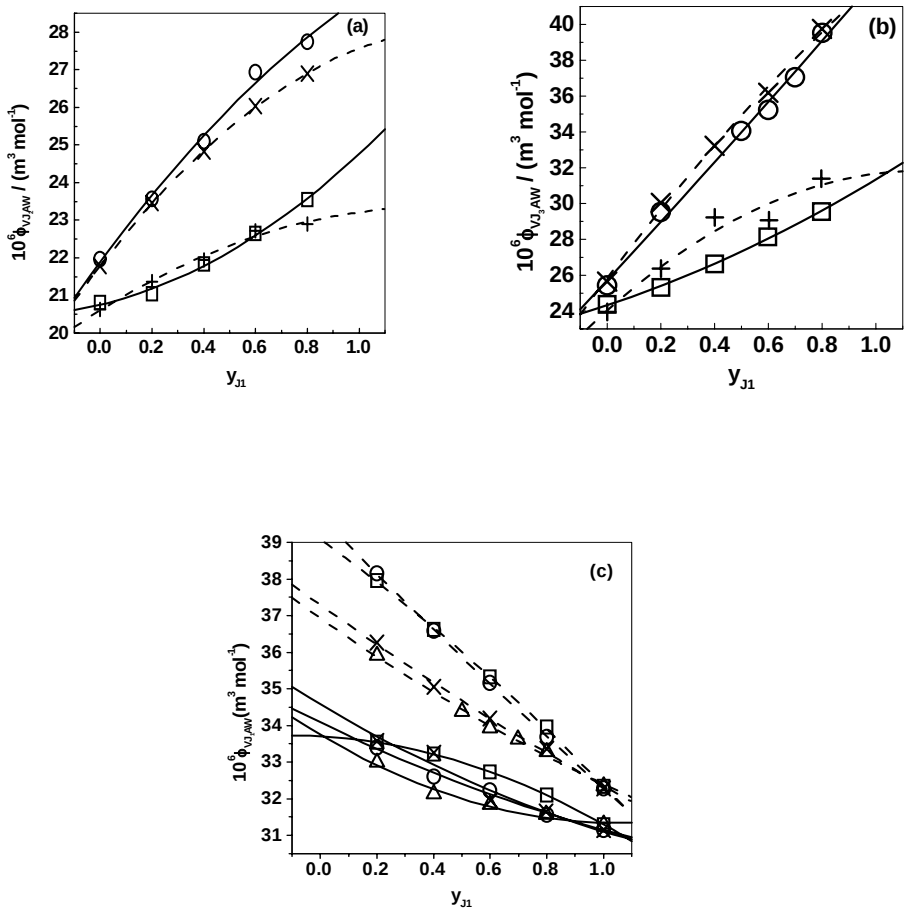


Figure 4.16: Plots of ϕ_{VJAW} *vs.* y_{J1} of **(a)** of NaCl in glycine + KCl: I = 1 mol kg^{-1} (+), I = 3 mol kg^{-1} (X); in + L-alanine + KCl: I = 1 mol kg^{-1} (o), I = 3 mol kg^{-1} (O**); (b)** of $MgCl_2$ in glycine + KCl: I = 1 mol kg^{-1} (+), I = 3 mol kg^{-1} (X); in + L-alanine + KCl: I = 1 mol kg^{-1} (o), I = 3 mol kg^{-1} (O) **(c)** of KCl in glycine + NaCl: (O), in L-alanine + NaCl (o), in glycine + $MgCl_2$ (X); in L-alanine + $MgCl_2$ (Δ) ; For I = 1 mol kg^{-1}(____) and I = 3 mol kg^{-1} (__ __ __)

4.7 Study of amino acids – tetra-n-alkylammonium bromides – water:

It was found that electrolytes like KCl, KBr, NaBr, $MgCl_2$ and Na_2SO_4 increase the apparent molar volumes of amino acids or peptides. This increase could be attributed to the interaction of the ions of the electrolytes and zwitterionic head groups of amino acids, causing the relaxation of hydrated water molecules to the bulk state. Similar effect was seen on the apparent molar volumes of electrolytes in the presence of amino acids or peptide. The electrolytes mentioned above are smaller in size and show hydrophilic hydration. The structure making or breaking capacities of these smaller ions are also less, which can be seen from their B-coefficient values. The B-coefficients for Na^+, K^+, Mg^{2+} and Cl^- are +0.086, -0.007, +0.385 and -0.007 l mol^{-1}, respectively[223]. Thus it will be of interest to study a separate class of electrolytes like tetra-n-alkylammonium salts, R_4NBr (R = $((CH_4)_4$, $(C_2H_5)_4$,$(C_4H_9)_4$), which are bulky in nature and are known to orient the water molecules around them depending on their alkyl chain. The R_4N^+ cations are strong structure makers because of their large sizes, weak charges and inability to break down the tetrahedral structure of water. The B-coefficients for these cations are +0.12, +0.38 and 1.28 l mol^{-1} for $(CH_4)_4N^+$, $(C_2H_5)_4N^+$ and $(C_4H_9)_4N^+$, respectively[223]. The aqueous solutions of these salts have been found to be highly viscous[227] and bear high apparent molal heat capacities[228,229] apparent molar volumes[230] and peculiar activity coefficients[231,232]. It will be therefore important to study the effect of these tetra-n-alkylammonium salts on the volumetric properties of aqueous amino acids.

The experimentally measured densities of amino acids and tetra-n-alkylammonium bromides are reported in **Tables 4.8, 4.9 and 4.10.** The ϕ_{VAJW} values are plotted as a function of their respective molalities, m_A in different R_4NBr salts in

Figure 4.17 (a-c), 4.18 (a-c) and 4.19. The ϕ_{VAJW} values of glycine, L-alanine and glycylglycine increase with m_A as well as with m_J. Both the amino acids and peptide show positive slopes for ϕ_{VAJW} versus m_A plots. The ϕ_{VAJW} of glycine varies from 43.6 to 46.0 x 10^{-6} m^3 mol^{-1}, that of L-alanine changes from 60.4 to 62·0 x 10^{-6} m^3 mol^{-1} and glycylglycine shows variation from 76.8 to 79.2 x 10^{-6} m^3 mol^{-1}. The $(\partial\phi_{VAJW} / \partial m_A)_{mJ}$ value for glycine in the 0.2580 mol kg^{-1} solution of $(CH_3)_4NBr$ is 0.723 x 10^{-6} m^3 kg mol^{-2}, which increases to 0.800 x 10^{-6} m^3 kg mol^{-2} in 0.2709 mol· kg^{-1} $(C_4H_9)NBr$.

Table 4.8: Densities, ρ of the amino acid or peptide – $(CH_3)_4NBr$ – H_2O system at 298.15 K

m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})
Glycine - $(CH_3)_4NBr$ - H_2O					
m_J = 0.2580 mol kg^{-1}		m_J = 0.5320 mol kg^{-1}		m_J = 0.8239 mol kg^{-1}	
0	1006.83	0	1016.59	0	1026.24
0.4978	1022.00	0.4982	1031.55	0.4956	1026.24
1.0001	1036.32	0.7446	1038.63	1.4981	1067.99
1.5012	1049.60	0.9923	1045.43	1.9990	1079.86
1.9993	1061.93	1.4966	1058.69		
m_J = 1.1339 mol kg^{-1}		m_J = 1.8386 mol kg^{-1}			
0	1036.07	0	1046.90		
0.4923	1050.56	0.4908	1060.86		

1.4852	1076.63	0.9921	1074.04
1.9891	1087.22	1.4891	1086.21
2.1861	1091.58		

L-alanine – $(CH_3)_4NBr$ - H_2O

m_J = 0.2581 mol kg^{-1}		m_J = 0.5325 mol kg^{-1}		m_J = 0.8239 mol kg^{-1}	
0	1006.90	0	1016.59	0.4927	1039.23
0.1005	1009.70	0.4967	1029.85	0.7507	1045.60
0.4985	1020.65	0.7467	1036.13	0.9905	1050.77
0.7511	1026.90	0.9967	1042.18		
1.0010	1032.98				
m_J = 1.1339 mol kg^{-1}		m_J = 1.8386 mol kg^{-1}			
0.0965	1038.31	0.0975	1049.43		
0.4884	1048.45	0.4981	1059.31		
0.7338	1054.35	0.7479	1065.09		
0.9873	1060.21	0.9883	1070.31		

Glycylglycine - $(CH_3)_4NBr$ - H_2O

m_J = 0.2579 mol kg^{-1}		m_J = 0.5322 mol kg^{-1}		m_J = 0.8105 mol kg^{-1}	
0	1006.85	0	1016.42	0	102586
0.1014	1012.36	0.5023	1042.43	0.0985	1031.10
0.5001	1032.93	0.7445	1053.98	0.4962	1051.30
0.7495	1044.94			0.7464	1063.09
m_J = 1.1342 mol kg^{-1}					
0	1035.72				

0.0991	1040.98
0.4966	1060.90
0.7393	1072.24

Table 4.9: Densities, ρ of the amino acid or peptide – $(C_2H_5)_4NBr$ – H_2O system at 298.15 K

m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})
Glycine - $(C_2H_5)_4NBr$ - H_2O							
m_J = 0.1020 mol kg^{-1}		m_J = 0.4023 mol kg^{-1}		m_J = 0.5490 mol kg^{-1}		m_J = 1.2115 mol kg^{-1}	
0	1000.71	0	1006.20	0	1015.83	0	1035.67
0.4979	1016.01	0.4964	1026.00	0.4957	1030.73	0.4928	1050.08
0.7540	1023.46	0.7502	1033.31	0.7450	1037.82	0.7416	1056.92
1.0001	1303.47	0.9317	1040.25	1.0005	1044.84	0.9898	1063.55
1.5055	1043.88	1.5126	1053.70	1.4951	1057.76	1.4877	1076.22
L-alanine – $(C_2H_5)_4NBr$ - H_2O							
m_J =0.1020 mol kg^{-1}		m_J =0.2622 mol kg^{-1}		m_J = 0.5490 mol kg^{-1}		m_J = 1.2115 mol kg^{-1}	
0.1005	1003.56	0.0984	1008.98	0.1003	1018.59	0.4902	1048.46
0.5053	1014.60	0.4999	1019.83	0.4939	1029.13	0.7383	1054.53
0.7539	1021.04	0.7534	1026.34	0.7463	1035.55	0.9900	1060.38
1.0013	1027.16	0.9974	1032.36	0.9907	1041.50		
Glycylglycine - $(C_2H_5)_4NBr$ - H_2O							

m_J = 0.1020 mol kg^{-1}		m_J = 0.2623 mol kg^{-1}		m_J = 0.5491 mol kg^{-1}		m_J = 1.2122 mol kg^{-1}	
0.1012	1006.34	0.1011	1011.83	0.0997	1021.17	0	1035.35
0.5054	1027.29	0.5059	1032.74	0.4958	1041.47	0.4958	1060.52
0.7534	1039.28	0.7482	1044.40	0.7457	1053.34	0.7446	1072.02

Table 4.10: Densities, ρ of the amino acid or peptide – $(C_4H_9)_4NBr$ – H_2O system at 298.15 K

m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})	m_A/ (mol kg^{-1})	ρ / (kg m^{-3})

Glycine - $(C_4H_9)_4NBr$ – H_2O

m_J = 0.0509 mol kg^{-1}		m_J = 0.1034 mol kg^{-1}		m_J = 0.2709 mol kg^{-1}	
0	998.20	0	999.39	0	1003.18
0.4985	1013.54	0.4968	1014.60	0.5026	1018.47
0.7473	1020.83	0.7508	1021.99	0.7537	1025.68
1.0058	1028.06	1.0041	1029.08	1.0058	1032.67
1.5035	1041.41	1.5055	1042.49	1.5083	1045.93

m_J = 0.5890 mol kg^{-1}		m_J = 0.7318 mol kg^{-1}	
0	1010.09	0	1013.27
0.5002	1024.93	0.4973	1027.84
0.7499	1031.99	0.7496	1034.87
0.9967	1038.69	0.9999	1041.61
1.4941	1051.57	1.4993	1054.39

L-alanine - $(C_4H_9)_4NBr$ - H_2O

m_J = 0.1034 mol kg^{-1}		m_J = 0.2709 mol kg^{-1}		m_J = 0.5890 mol kg^{-1}		m_J = 0.7318 mol kg^{-1}	
0.1009	1002.27	0.1001	1005.99	0.1010	1012.88	0.0989	1015.99
0.5006	1013.19	0.5007	1016.90	0.4995	1023.57	0.4978	1026.55
0.7487	1019.62	0.7545	1023.46	0.7508	1029.90	0.7496	1032.84
		1.0017	1029.58	0.9996	1035.95		

Glycylglycine - $(C_4H_9)_4NBr$ - H_2O

m_J = 0.0509 mol kg^{-1}		m_J = 0.2710 mol kg^{-1}		m_J = 0.5889 mol kg^{-1}	
0.1012	1003.78	0.1013	1008.75	0.0999	1015.56
0.5022	1024.63	0.5013	1029.31	0.4988	1035.87
0.7538	1036.79	0.7516	1041.35	0.7538	1047.91

The apparent molar volumes, ϕ_{VJW} of R_4NBr in aqueous and non-aqueous solvents have been a topic of interest since a long time. In aqueous solution the volumes of these salts appear to be a sensitive function of concentration, temperature and pressure. Electrolytes like NaCl, KCl show that the value of ϕ_{VJW} at very low concentration (<0.1 mol kg^{-1}) increases with the concentration of NaCl or KCl in accordance with the Debye – Hückel limiting slope of 1.86 at 298.15 K and the value of ϕ_{VJW} keeps increasing with concentration at least up to a concentration of about 4 mol kg^{-1}. However except $(CH_4)_4NBr$, R_4NBr ϕ_{VJW} *versus* m_J plots show negative slopes. At higher concentrations the plot of $(C_4H_9)_4NBr$ *versus* m_J goes through a minimum and then turns upward.

The possible reasons for the anomalous behavior in volumetric properties of tetra-n-alkyl ammonium salts can be due to large cation undergoing hydrophobic

hydration or due to caging effect of water molecules[230]. The bulky tetra-n-alkyl ammonium cations do not interact electrostatically with water molecules. The cations are hydrophobic in nature so to avoid contact with water the R_4N^+ cation sits in the cavities created by the tetrahedrally arranged water molecules, resulting in a tighter packing than would have occurred and causing a volume decrease. The water molecules are not sufficient to cage the $(C_4H_9)_4N^+$ in concentrated solutions making its volume to increase in concentrated solutions.

The amino acids and peptide alter the ϕ_{VJAW} significantly, as shown in **Figure 4.20 (a-c), 4.21 (a-c) and 4.22 (a-c).** In **Figures 4.20 – 4.22** ϕ_{VJAW} are plotted as a function of m_J. The ϕ_{VJAW} of $(CH_3)_4NBr$ increases with m_J as shown in from 114 x 10^{-6} m^3 mol^{-1} to 121 x 10^{-6} m^3 mol^{-1} in the presence of 1 mol kg^{-1} glycine and L-alanine. There is a competition between hydrophilic hydration with increase in the volume of solution and hydrophobic hydration with decrease in volume of solutions. The nature of hydration of an ion depends on its size and charge besides the dielectric constant of solvent. The $(CH_4)_4N^+$ being a smaller cation (with a radii 0.280 nm) interacts with the head groups of glycine and L-alanine and releases water molecules to the bulk water causing increase in the volume showing dominance of hydrophilic hydration, while glycylglycine being bulky molecule restricts the interaction making the increase in the apparent molar volume of $(CH_4)_4NBr$ of 0.5 x 10^{-6} m^3 mol^{-1} only. $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ with larger cations (with radii $(C_2H_5)_4N^+$ = 0.337 nm and $(C_4H_9)_4N^+$ = 0.413 nm) show decrease in ϕ_{VJAW} with m_J, as these cations undergo hydrophobic hydration.

The effect of solvent (i.e. aqueous R_4NBr solution) on amino acid or peptide and of aqueous amino acid or peptide on R_4NBr can be studied by studying the transfer volumes. The change in the ${\phi_V}^0_{tr\ .AJW}$ as a function of R_4NBr concentration is depicted in **Figure 4.23**. The transfer volumes are positive for all the systems. The $(\partial {\phi_V}^0_{tr\ AJW} / \partial m_J)$ for glycine, L-alanine and glycylglycine are almost double in $(C_4H_9)NBr$ (e.g. $\partial {\phi_V}^0_{tr\ AJW} / \partial m_J$ value for glycine in $(C_4H_9)_4NBr$ = 1.722 10^{-6} m^3 kg mol^{-2}) than that in $(CH_3)_4NBr$ or $(C_2H_5)_4NBr$, which are almost equal. (e.g. $\partial {\phi_V}^0_{tr.AJW} / \partial m_J$ values for glycine in $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ are 0.839 and 0.873 x 10^{-6} m^3 kg mol^{-2}, respectively). The increasing $\partial {\phi_V}^0_{tr.\ AJW}$ of glycine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ are supported by the B coefficients of these ions. The values of $(\partial {\phi_V}^0_{tr.AJW} / \partial m_J)$ of glycine in the presence of 1 mol kg^{-1} solution of KCl, KBr and $MgCl_2$ have been noted as 3.71 x 10^{-6}, 4.42 x 10^{-6} and 8.20 x 10^{-6} m^3 kg mol^{-2}, respectively. From the above comparison it appears that ions undergoing hydrophilic hydration show significant effect on the amino acid $(\partial {\phi_V}^0_{tr.AJW} / \partial m_J)$ than ions undergoing hydrophobic hydration. Higher transfer volumes also indicate the dominance of the interactions of glycine with hydrophilic ions as compared to those with hydrophobic ones. The transfer volumes, ${\phi_V}^0_{tr.JAW}$ are plotted as a function of m_A in **Figure 4.24**. All the systems show negative slopes. The slopes observed for different systems are listed in **Table 4.11**. It can be observed from these slopes that the values decrease in the order of $(CH_3)_4NBr<(C_2H_5)_4NBr<(C_4H_9)_4NBr$ for L-alanine, glycine and glycylglycine.

Table 4.11: The $(\partial {\phi_V}^0_{tr.JAW} / \partial m_A)$ 10^6 m^3 kg mol^{-2} for different systems (values in the parenthesis are the standard errors in slope values)

System	Glycine	L-alanine	Glycylglycine
$(CH_3)_4NBr$	-0.33 (0.18)	-1.59 (0.62)	-1.30 (0.04)
$(C_2H_5)_4NBr$	-2.14 (0.10)	-2.93 (0.13)	-4.15 (0.33)
$(C_4H_9)_4NBr$	-5.37 (0.22)	-7.30 (0.09)	-7.66 (0.30)

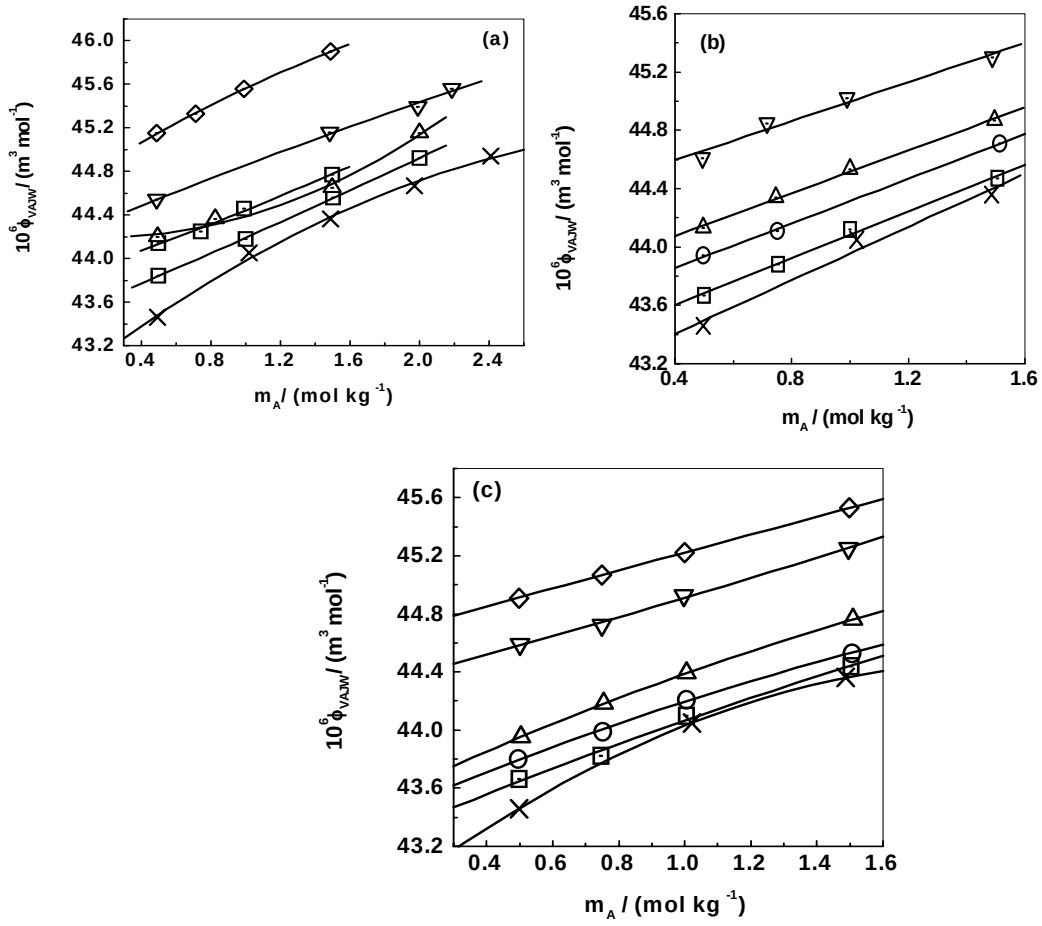


Figure 4.17: Plots of ϕ_{VAJW} *vs.* m_A of glycine in **(a)** H_2O (X), $(CH_4)_4NBr$: 0.2581 mol kg^{-1} (o), 0.5325 mol kg^{-1} (O), 0.8239 mol kg^{-1} (Δ), 1.1340 mol kg^{-1} (∇), 1.8386 mol kg^{-1} (◊) **(b)** H_2O (X), $(C_2H_5)_4NBr$: 0.1020 mol kg^{-1} (o), 0.4023 mol kg^{-1} (O), 0.5490 mol kg^{-1} (Δ), 1.2115 mol kg^{-1} (∇) **(c)** H_2O (X), $(C_4H_9)_4NBr$: 0.0509 mol kg^{-1} (o), 0.1034 mol kg^{-1} (O), 0.2709 mol kg^{-1} (Δ), 0.5890 mol kg^{-1} (∇), 0.7318 mol kg^{-1} (◊)

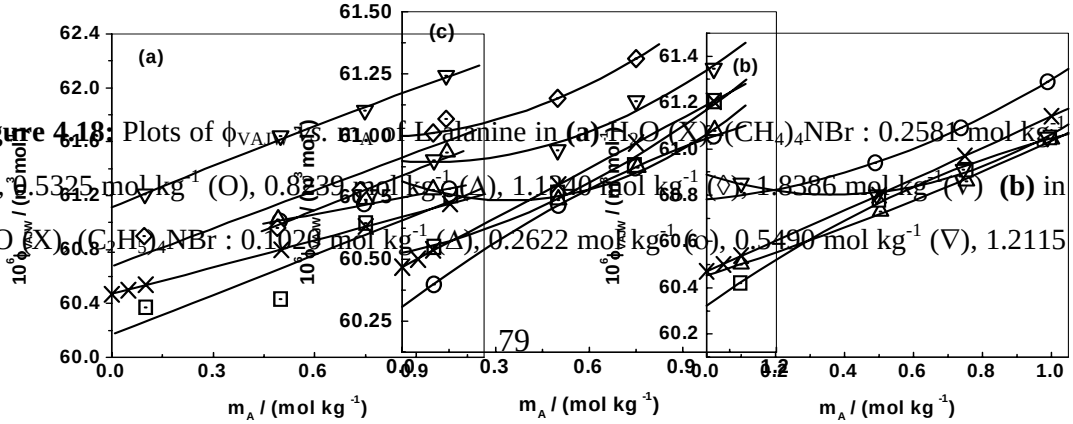


Figure 4.18: Plots of ϕ_{VAJW} *vs.* m_A of L-alanine in **(a)** H_2O (X), $(CH_4)_4NBr$: 0.2581 mol kg^{-1} (o), 0.5325 mol kg^{-1} (O), 0.8239 mol kg^{-1} (Δ), 1.1340 mol kg^{-1} (∇), 1.8386 mol kg^{-1} (◊) **(b)** in H_2O (X), $(C_2H_5)_4NBr$: 0.1020 mol kg^{-1} (Δ), 0.2622 mol kg^{-1} (o), 0.5490 mol kg^{-1} (∇), 1.2115

mol kg^{-1} (O) **(c)** H_2O (X), $(C_4H_9)_4NBr$: 0.0509 mol kg^{-1} (o), 0.1034 mol kg^{-1} (O), 0.2709 mol kg^{-1} (Δ), 0.5890 mol kg^{-1} (∇), 0.7318 mol kg^{-1} (◊)

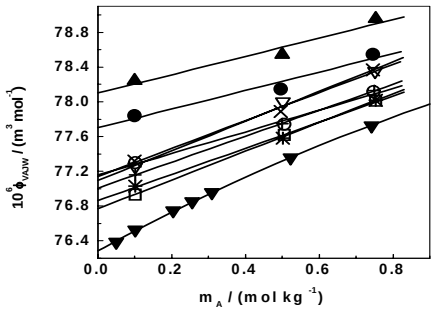


Figure 4.19: Plots of ϕ_{VAJW} *vs.* m_A of glycylglycine in H_2O (τ), in $(CH_3)_4NBr$: 0.2579 mol kg^{-1} (+), 0.8105 mol kg^{-1} (λ); $(C_2H_5)_4NBr$: 0.1020 mol kg^{-1} (o), 0.2623 mol kg^{-1} (O), 0.5491 mol kg^{-1} (X); $(C_4H_9)_4NBr$: 0.0509 mol kg^{-1} (T), 0.2710 mol kg^{-1} (∇). 0.5889 mol kg^{-1} (σ)

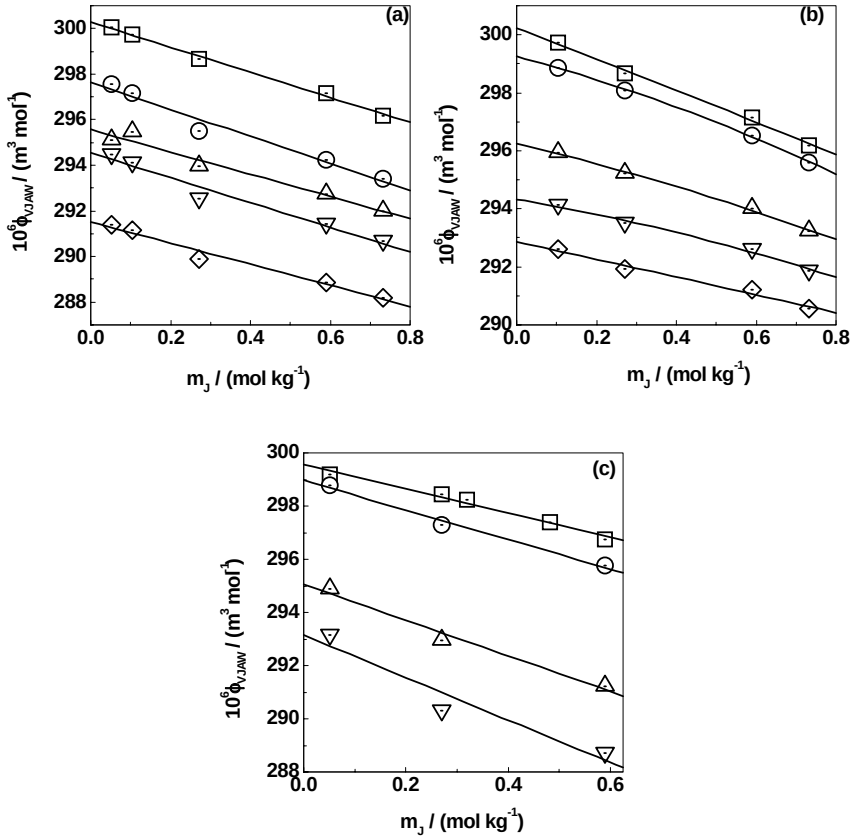


Figure 4.20: Plots of ϕ_{VJAW} vs. m_J of $(CH_3)_4NBr$ in **(a)** H_2O (o), glycine: 0.4949 mol kg^{-1} (O), 0.9948 mol kg^{-1} (Δ), 1.4940 mol kg^{-1} (∇), 1.9958 mol kg^{-1} (◊); **(b)** in H_2O (o), L-alanine: 0.0987 mol kg^{-1} (O), 0.4965 mol kg^{-1} (Δ), 0.7491 mol kg^{-1} (∇), 0.9941 mol kg^{-1} (◊); **(c)** in H_2O (o), glycylglycine: 0.0997 mol kg^{-1} (O), 0.4998 mol kg^{-1} (Δ), 0.7449 mol kg^{-1} (∇)

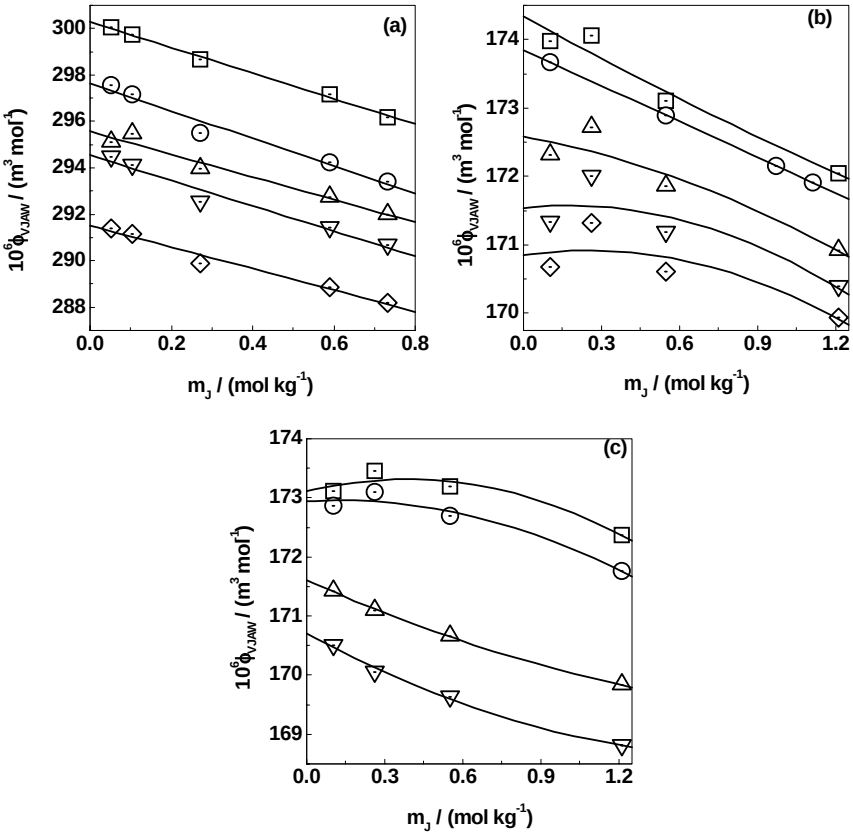


Figure 4.21: Plots of ϕ_{VJAW} *vs.* m_J of $(C_2H_5)_4NBr$ in **(a)** H_2O (o), glycine: 0.4957 mol kg^{-1} (O), 0.7477 mol kg^{-1} (Δ), 0.9968 mol kg^{-1} (∇), 1.5002 mol kg^{-1} (◊); **(b)** in H_2O (o), L-alanine: 0.0997 mol kg^{-1} (O), 0.4973 mol kg^{-1} (Δ), 0.7480 mol kg^{-1} (∇), 0.9949 mol kg^{-1} (◊); **(c)** in H_2O (o), glycylglycine: 0.1003 mol kg^{-1} (O), 0.5007 mol kg^{-1} (Δ), 0.7480 mol kg^{-1} (∇)

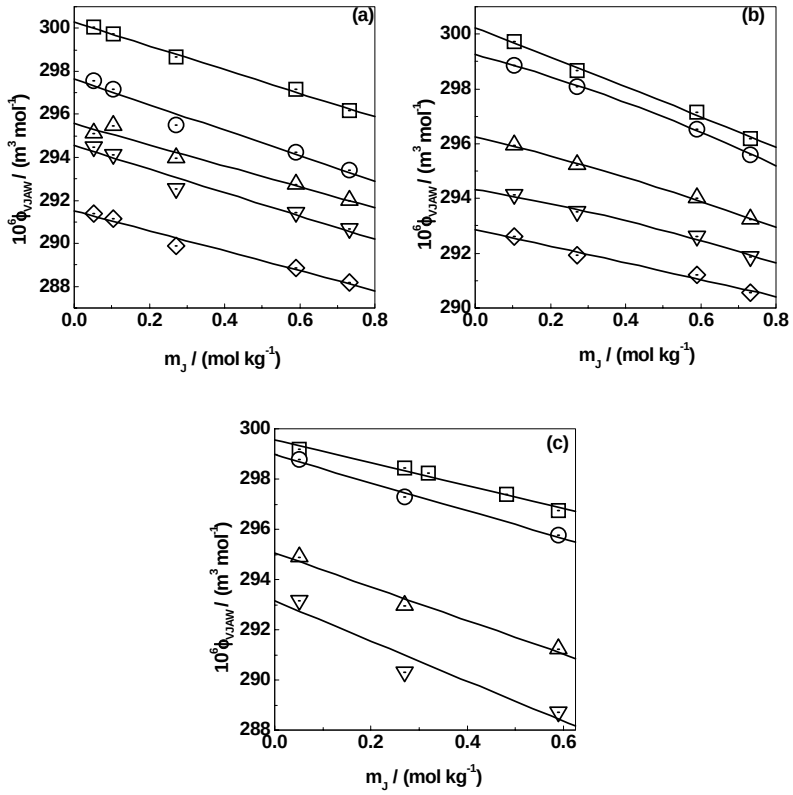


Figure 4.22: Plots of ϕ_{VJAW} vs. m_J of $(C_4H_9)_4NBr$ in **(a)** H_2O (o), glycine: 0.4991 mol kg^{-1} (O), 0.7503 mol kg^{-1} (Δ), 1.0025 mol kg^{-1} (∇), 1.5021 mol kg^{-1} (◊); **(b)** in H_2O (o), L-alanine: 0.1002 mol kg^{-1} (O), 0.4997 mol kg^{-1} (Δ), 0.7509 mol kg^{-1} (∇), 0.9994 mol kg^{-1} (◊); **(c)** in H_2O (o), glycylglycine: 0.1009 mol kg^{-1} (O), 0.5008 mol kg^{-1} (Δ), 0.7530 mol kg^{-1} (∇)

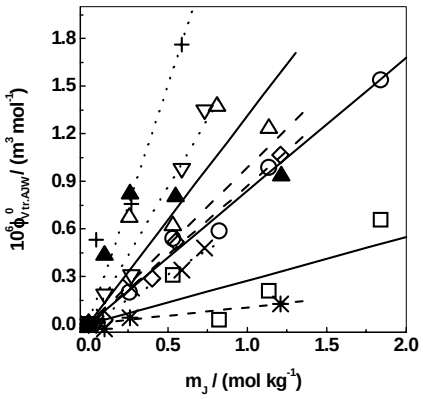


Figure 4.23: Plots of $\phi_V{}^0{}_{tr\ AJW}$ vs. m_J $(CH_3)_4NBr$ + (O), glycine; (o), L-alanine; (Δ), glycylglycine; $(C_2H_5)_4NBr$ + (◊), glycine; (T), L-alanine; (σ), glycylglycine; $(C_4H_9)_4NBr$ + (∇), glycine; (X), L-alanine; (+), glycylglycine

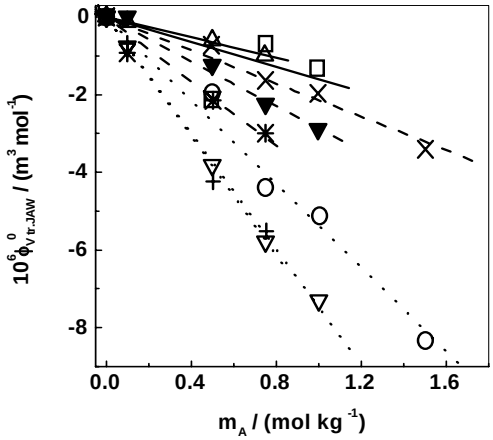


Figure 4.24: Plots of $\phi_V{}^0{}_{tr.JAW}$ vs. m_A glycine + (X), $(C_2H_5)_4NBr$; (O), $(C_4H_9)_4NBr$; L-alanine + (o), $(CH_3)_4NBr$; (τ), $(C_2H_5)_4NBr$; (∇), $(C_4H_9)_4NBr$; glycylglycine + (Δ), $(CH_3)_4NBr$; (T), $(C_2H_5)_4NBr$; (+), $(C_4H_9)_4NBr$

5.1 Preface:

The effect of pressure on the partial or apparent molar volume is given by partial or apparent molar compressibility defined by:

$$-\phi_K = (\partial\phi_V/\partial P)_T \quad (1)$$

It is however not easy to measure the apparent molar volume accurately as a function of pressure. It is easier to calculate ϕ_K. To obtain the equation for ϕ_K, equation for ϕ_V must be differentiated with respect to pressure. Apparent molar compressibilities, ϕ_K of amino acids or peptide, ϕ_{KAJW} or of electrolytes ϕ_{KJAW} may be calculated by:

$$-\phi_K = (-V\,\kappa_s + n_1\,V_1\,\kappa_s^0) / n_2 \quad (2a)$$

$$\phi_K = (\rho^0\,\kappa_s - \rho\,\kappa_s^0) / m\,\rho^0\,\rho + \kappa_s\,M / \rho \quad (2b)$$

where isentropic compressibility of solution, κ_s is given by:

$$\kappa_s = (-1/V)\,(\partial V/\partial P)_T = (-1/\rho)\,(\partial\rho/\partial P)_T \quad (3)$$

The superscript 'o' represents the solvent properties. m and M are the molality of component in question and its molar mass, respectively. In order to obtain accurate ϕ_K, κ_s should be measured accurately. κ_s is calculated from the speed of sound through the solution, u using the Laplace equation **(equation 4)** with analogous definition for κ_s^0.

$$\kappa_s = 1 / u^2 \rho \qquad (4)$$

The hydration numbers of amino acids or peptide and of electrolytes in the A–J–W system can be obtained using the apparent molar compressibility at infinite dilution. The hydration number of amino acids or peptide in different electrolytes can be calculated as:

$$n_H = - \phi_K{}^0{}_{AJW} / \overline{V}^0 \kappa_s{}^0{}_{JW} \qquad (5)$$

where, $\overline{V}^0$ is the molar volume of aqueous electrolytes and is calculated as $\overline{V}^0 = m_J M_J / \rho_{J\text{-}H2O}$. Analogous equation to **equation (5)** is used to calculate hydration number of electrolytes in aqueous amino acids.

In this chapter the apparent molar compressibility of amino acids in aqueous electrolytes, ϕ_{KAJW} and of electrolytes in aqueous amino acids, ϕ_{KJAW} are discussed in detail. The effect of temperature on ϕ_{KAJW} and ϕ_{KJAW} are also described.

5.2 Apparent molar compressibilty of glycine - electrolytes - water system:

The measured speed of sound, u and κ_s values calculated therefrom at different concentrations of glycine in NaBr, KCl, KBr and $MgCl_2$ systems are listed in **Table 5.1**. The ϕ_{KAJW} and ϕ_{KJAW} are calculated using **equation (2b)**. The variation of ϕ_{KAJW} with m_A is shown in **Figures 5.1 (a-d)**. The ϕ_{KAJW} of glycine changes from -25×10^{-15} to 5×10^{-15} m^3 mol^{-1} Pa^{-1} in the presence of different electrolytes. The

ϕ_{KAJW} values of glycine increase with the increase in m_A as well as m_J. The isentropic compressibility values, κ_s for glycine in aqueous electrolytes system are plotted as a function m_A in **Figure 5.2**.

Table 5.1: Experimental speed of sound and isentropic compressibilities, κs of aqueous glycine in different electrolytes at 298.15 K.

m_J / (mol kg^{-1})	u / (m s^{-1})	$10^{10}\kappa_s$ / (Pa^{-1})	m_J / (mol kg^{-1})	u / (m s^{-1})	$10^{10}\kappa_s$ / (Pa^{-1})
	NaBr				
	m_A / (mol kg^{-1}) = 0.5006			m_A / (mol kg^{-1})= 1.0006	
0.5010	1536.1	4.0381	0.5010	1557.2	3.8819
0.9991	1549.2	3.8405	0.9999	1568.2	3.7073
1.9986	1572.1	3.5093	2.0006	1592.3	3.3925
3.0020	1592.2	3.2419	2.9993	1612.1	3.1411
4.0008	1616.4	2.9987	4.0001	1640.0	2.8982
	m_A / (mol kg^{-1}) = 2.0004			m_A / (mol kg^{-1})= 3.0012	
0.4986	1600.4	3.5971	0.5015	1640.1	3.3575
1.0010	1608.1	3.4575	0.9996	1648.0	3.2367
1.9991	1632.3	3.1844	2.0011	1664.1	3.0194
2.9990	1648.2	2.9743	3.0001	1680.2	3.8315
4.0003	1672.1	2.7659	4.0010	1684.1	2.7060
	KCl				
	m_A / (mol kg^{-1}) = 0.5002			m_A / (mol kg^{-1}) = 0.9985	
1.0004	1568.2	4.0230	1.0001	1592.0	3.6971
2.0002	1608.1	3.6446	1.9995	1632.3	3.4009
3.0008	1648.3	3.3557	3.0011	1664.2	3.1739
4.0007	1680.2	3.1324	4.0004	1696.2	2.9754
	m_A / (mol kg^{-1}) = 2.0004			m_A / (mol kg^{-1}) = 3.0002	
0.9993	1632.1	3.4456	0.5004	1652.2	3.3511
2.0001	1664.1	3.2135	1.0003	1664.1	3.2534
3.0005	1696.4	3.0092	2.0002	1696.2	3.0453

4.0006	1712.2	2.8810	3.0003	1720.0	2.8868

KBr

m_A / (mol kg^{-1}) = 0.4998			m_A / (mol kg^{-1}) = 1.0010		
0.5017	1528.3	4.0704	0.5018	1552.2	3.8973
1.0009	1536.1	3.8819	2.0002	1572.2	3.4579
1.9995	1552.2	3.5787	3.0010	1584.1	3.2367
2.9979	1562.2	3.3429	4.0008	1592.4	3.0549
4.0117	1576.4	3.1301	5.0013	1596.3	2.9159
m_A / (mol kg^{-1}) = 2.0001			m_A / (mol kg^{-1}) = 3.0004		
0.5013	1596.1	3.6078	0.5017	1636.2	3.3675
1.0004	1599.3	3.4833	1.0015	1640.1	3.2565
2.0015	1608.0	3.2595	2.0013	1648.4	3.0614
3.0006	1616.3	3.0701	3.0006	1656.3	2.8969
4.0008	1624.2	2.9107	4.0027	1664.3	2.7528

$MgCl_2$

m_A / (mol kg^{-1}) = 0.5004			m_A / (mol kg^{-1}) = 1.0005		
0.1005	1531.1	4.1837	0.0995	1555.2	4.0003
0.5006	1568.4	3.8817	0.5002	1592.3	3.7213
1.0008	1616.0	3.5427	0.9996	1636.3	3.4212
1.5007	1664.3	3.2463	1.5013	1680.1	3.1561
m_A / (mol kg^{-1}) = 2.0006			m_A / (mol kg^{-1}) = 3.0002		
0.1005	1600.1	3.6886	0.1005	1640.4	3.4373
0.5002	1632.1	3.4651	0.4974	1672.1	3.2394
0.9995	1672.4	3.2136	0.9999	1704.3	3.0427
1.4992	1712.0	2.9901			

Water is having tetrahedrally arranged, hydrogen bonded H…O…H molecules forming a network. If an ion is present in water it breaks down the water structure by orienting water molecules around the ion. The water molecules around the ion are compressed and compactly arranged, making it uncompressible. Thus

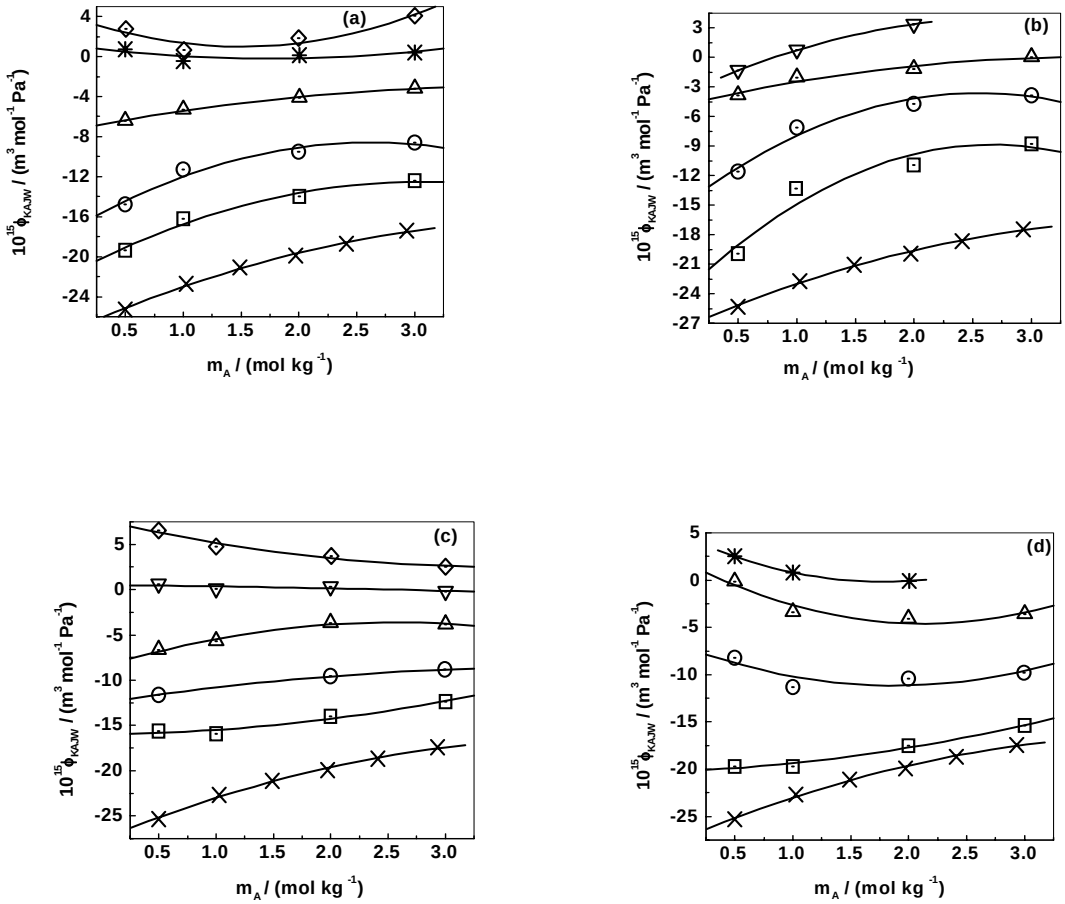


Figure 5.1: Plots of ϕ_{KAJW} of glycine *vs.* m_A in H_2O (X) **(a)** in NaBr: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (Σ), 4 mol kg^{-1} (◊) **(b)** KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (∇) **(c)** KBr: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (∇), 4 mol kg^{-1} (◊) **(d)** $MgCl_2$: 0.1 mol kg^{-1} (o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (Σ)

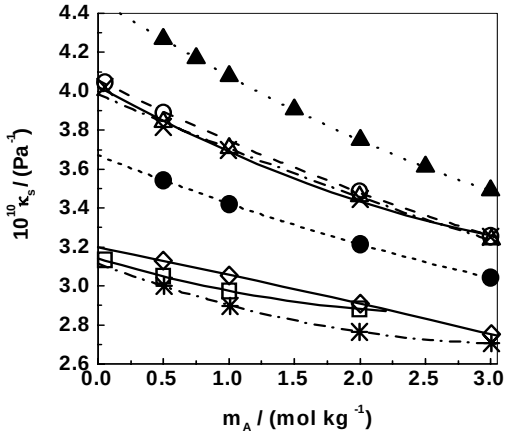


Figure 5.2: Plots of κ_s *vs.* m_A of glycine in (σ) H_2O, KCl: 1 mol kg^{-1} (X), 4 mol kg^{-1} (o); KBr: 1 mol kg^{-1} (O), 4 mol kg^{-1} (◊); NaBr 1 mol kg^{-1} (Δ), 4 mol kg^{-1} (T), $MgCl_2$: 1 mol kg^{-1} (●)

compressibility of water decreases as compared to bulk water and with the increase in concentration of ions isentropic compressibility of aqueous ionic solutions further decreases. The κ_s values of glycine - electrolyte aqueous solutions also decrease with increase in m_A at constant m_J, as discussed above. With the enhancement in m_J the κ_s value of the system further decreases. The κ_s value of glycine in 1 mol kg^{-1} of KCl, KBr and NaBr is almost constant, but addition of $MgCl_2$ lowers its compressibility as compared to 1:1 electrolytes. These results also support the conclusions drawn from the study of apparent molar volume of this system studied in **chapter 4**.

The transfer compressibilities, $\phi_K{}^o{}_{tr.AJW}$ of glycine are calculated using **equation (6)** as:

$$\phi_K{}^{o}{}_{tr.AJW} = \phi_K{}^{o}{}_{AJW} - \phi_K{}^{o}{}_{AW} \quad (6)$$

The effect of different electrolytes and their concentrations on $\phi_K{}^{o}{}_{tr.AJW}$ is shown in **Figure 5.3**. The transfer compressibilities are positive in the presence of all the studied electrolytes. The $\phi_K{}^{o}{}_{tr.AJW}$ values vary with m_J nonlinearly. The $\partial\phi_K{}^{o}{}_{tr.AJW}/\partial m_J$ values at 1 mol kg^{-1} of NaBr, KCl, KBr and $MgCl_2$ are 10.52 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, 5.51 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, 12.53 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} and 30.05 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, respectively. The values in presence of 1 mol kg^{-1} of $MgCl_2$ is 3-times higher than average value noted in presence of identical molality of 1:1 electrolytes. The $\partial\phi_K{}^{o}{}_{tr.AJW} / \partial m_J$ of glycine in the presence of NaBr and KBr is twice than in KCl.

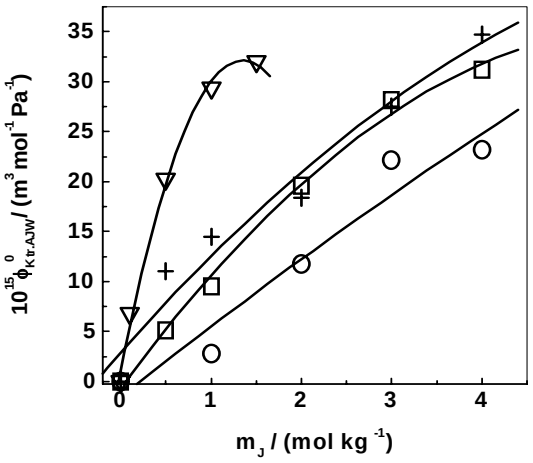


Figure 5.3: Plots of $\phi_K{}^{o}{}_{tr.AJW}$ of glycine *vs.* m_J in NaBr (o), KCl (O), KBr (+), $MgCl_2$ (∇)

Thus, it can be concluded that the transfer compressibilities of glycine are dependent on the nature of cation as well as anion.

The hydration number of glycine in water is 3 as reported[48]. The hydration number of glycine in the presence of electrolytes can be calculated using **equation (5)**. Due to the presence of ions in the solution hydration number of glycine decreases. NaBr, KCl and KBr reduce the hydration number of glycine from 3 to 1 at 1 mol kg^{-1} m_J while in the presence of 1 mol kg^{-1} $MgCl_2$ n_H of glycine shows negative values due to higher electrostriction effect of Mg^{2+} cation.

The apparent molar compressibilties of electrolytes are also affected due to the presence of glycine. The ϕ_{KJAW} of electrolytes are plotted as a function of m_J in **Figures 5.4 (a-d)**. The ϕ_{KJAW} values of NaBr increase from –35 to –10 x 10^{-15} m^3 mol^{-1} Pa^{-1}, that of KCl increases from –42 to –10 x 10^{-15} m^3 mol^{-1} Pa^{-1}, while that of KBr and $MgCl_2$ increase from –36 to -4 x 10^{-15} m^3 mol^{-1} $Pa^{-1}$and –100 to –30 x 10^{-15} m^3 mol^{-1} Pa^{-1}, respectively. As in case of apparent volumes the ϕ_{KJAW} of electrolytes increase with m_J as well as m_A. The transfer compressibilities of electrolytes, $\phi_K{}^o{}_{tr.JAW}$ are calculated using equation analogous to **equation (6)**. The change in $\phi_K{}^o{}_{tr.JAW}$ of NaBr, KCl, KBr and $MgCl_2$ in the presence of glycine is plotted in **Figure 5.5**. The $\partial\phi_K{}^o{}_{tr.JAW} / \partial m_A$ values of NaBr, KCl, KBr and $MgCl_2$ in glycine are 14.76 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, 14.17 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, 16.19 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} and 35.36 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, respectively. The 1:1 electrolytes have almost same slope value while in case of $MgCl_2$ the slope value is almost double than that of 1:1 electrolytes. Thus, ϕ_{KJAW} values of electrolytes are affected by glycine depending on the charge of cation and anion of electrolytes.

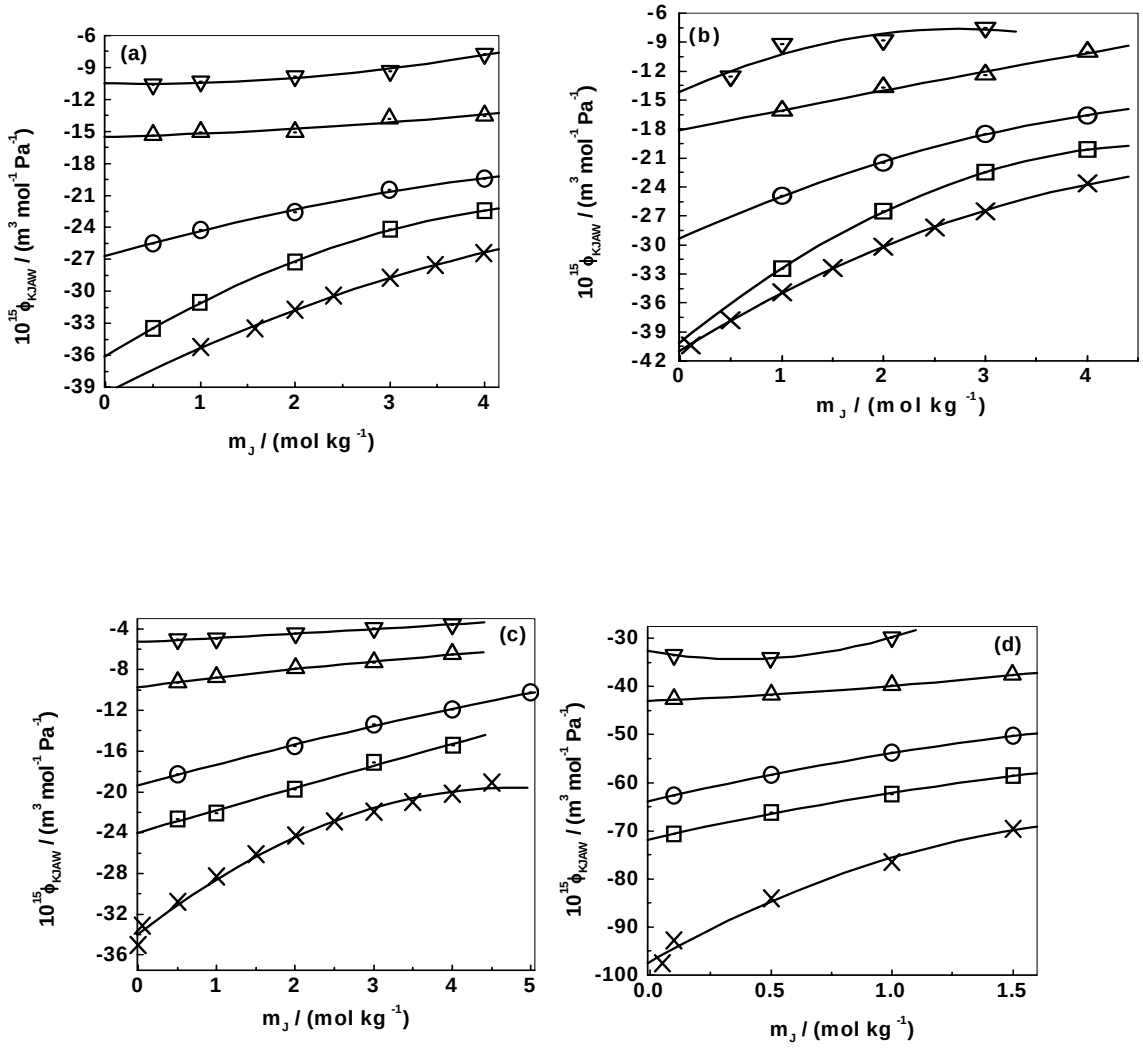


Figure 5.4: Variation of ϕ_{KJAW} with m_J of electrolytes **(a)** NaBr; **(b)** KCl; **(c)** KBr, **(d)** $MgCl_2$ in H_2O (X) and in glycine: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (∇)

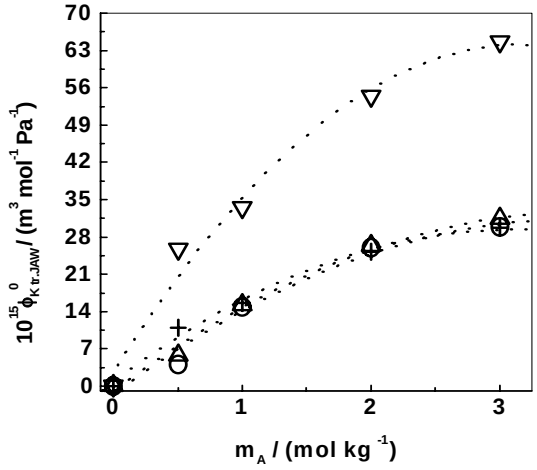


Figure 5.5: Plots of ${}^{o}\phi_{K\,tr.JAW}$ of electrolytes *vs.* m_J in glycine + NaBr (Δ), KCl (O), KBr (+), $MgCl_2$ (∇)

The hydration number of electrolytes also change in glycine. The hydration numbers of electrolytes in the presence of glycine, calculated using analogous equation to **equation (5)** are listed in **Table 5.2**.

Table 5.2: Hydration numbers of NaBr, KCl, KBr and $MgCl_2$ in the presence of glycine at 298.15 K.

m_A / (mol kg^{-1})	n_H of NaBr	n_H of KCl	n_H of KBr	n_H of $MgCl_2$
0	4.9	5.5	4.3	12.1
0.5	2.3	2.5	1.5	4.5
1	0.9	1.0	0.6	2.1
2	0.3	0.3	0.2	0.8
3	0.1	0.2	0.1	0.4

5.3: Apparent molar compressibilty of L-alanine - electrolytes - water system:

The measured u values for L-alanine in different electrolyte solutions are listed in **Table 5.3** at different concentrations of m_A and m_J. The κ_s values of L-alanine are also reported in **Table 5.3**. The calculated ϕ_{KAJW} and ϕ_{KJAW} are plotted as a function of m_A in **Figures 5.6 (a-c)**. The ϕ_{KAJW} of L-alanine increases from -25 to 15 x 10^{-15} m^3 mol^{-1} Pa^{-1} in the presence of KCl and $MgCl_2$. The variation of ϕ_{KAJW} of L-alanine in the presence of KBr and NaBr as a function of m_J is demonstrated in **Figure 5.6 (c).** The change in the isentropic compressibility, κ_s of L-alanine - KCl or - $MgCl_2$ system with m_A is shown in **Figure 5.7**. The κ_s values of L-alanine - eletcrolytes also decrease with increase in m_A and increase with increase in m_J as in glycine. The transfer compressibilities of L-alanine in the presence of different electrolytes are plotted in **Figure 5.8**. L-alanine shows positive transfer compressibilities in the presence of KCl and $MgCl_2$. The $\partial\phi_K{}^0{}_{tr.AJW}/\partial m_J$ for 1 mol kg^{-1} KCl and $MgCl_2$ are 16.50 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} and 27.22 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, respectively. The hydration number of L-alanine changes from 3 in water to 0.1 and –0.02 due to presence of 1 mol kg^{-1} of KCl and $MgCl_2$, respectively.

Table 5.3: Speeds of sound, u and isentropic compressibilities, κ_s at different molality of L-alanine, $m_{A,}$ and electrolytes, $m_{J,}$ at 298.15 K.

m_J / (mol kg^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})	m_J / (mol kg^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})
NaBr					
m_A = 0.5001 mol kg^{-1}			m_A = 1.0001 mol kg^{-1}		
0.0501	1530.0	4.2104	0.0500	1560.0	4.0008

0.5001	1540.0	4.0248	0.5001	1573.0	3.8170
1.0004	1552.0	3.8330	1.0001	1584.0	3.6467
2.0004	1576.0	3.4991	2.0004	1608.0	3.3403
2.9998	1592.0	3.2502	3.0002	1624.0	3.1106
4.0000	1616.0	3.0065	4.0004	1640.0	2.9130

KCl

m_A = 0.0505 mol kg^{-1}			m_A = 0.5004 mol kg^{-1}		
1.0017	1549.4	4.0229	1.0021	1566.0	3.8627
2.0037	1592.1	3.6441	2.0029	1609.0	3.5442
3.0022	1630.0	3.3543	3.0039	1648.0	3.2683
4.0036	1663.0	3.1316	4.0008	1672.0	3.0863
m_A = 0.1001 mol kg^{-1}			m_A = 0.9999 mol kg^{-1}		
1.0068	1551.0	3.9764	1.0008	1592.0	3.6727
2.0073	1594.0	3.6406	1.9997	1632.0	3.3799
3.0035	1632.0	3.3519	3.0014	1664.0	3.1855
4.0021	1664.0	3.1150	4.0006	1672.0	3.0126

KBr

m_A = 0.5001 mol kg^{-1}			m_A = 1.0003 mol kg^{-1}		
0.0500	1530.0	4.2094	0.0504	1559.0	4.0048
0.5001	1538.0	4.0256	0.5000	1566.0	3.8423
1.0001	1544.0	3.8564	1.0002	1572.0	3.6877
2.0004	1554.0	3.5753	2.0002	1580.0	3.4383
3.0003	1568.0	3.3253	3.0006	1592.0	3.2142

4.0000	1584.0	3.1060	4.0004	1600.0	3.0376
			$MgCl_2$		
	m_A = 0.1007 mol kg^{-1}			m_A = 0.7503 mol kg^{-1}	
0.0511	1509.0	4.3752	0.0505	1549.0	4.0828
0.4984	1556.0	3.9853	0.4984	1592.0	3.7532
0.9954	1608.0	3.6151	1.0018	1640.0	3.4298
1.5112	1656.0	3.3009	1.5017	1680.0	3.1789
	m_A = 0.5007 mol kg^{-1}			m_A = 1.0005 mol kg^{-1}	
0.1011	1539.0	4.1474	0.0516	1563.0	3.9858
0.5023	1576.0	3.8487	0.4995	1608.0	3.6598
0.9989	1624.0	3.5131	0.9997	1648.0	3.3824
1.4961	1664.0	3.2501	1.5006	1688.0	3.1382

In **Figure 5.9 (a-c)** the effect of L-alanine on the compressibilities of NaBr, KCl, KBr and $MgCl_2$ is depicted. The apparent molar compressibility of KCl and $MgCl_2$ increases from –42 x 10^{-15} to –12 x 10^{-15} m^3 mol^{-1} Pa^{-1} and –100 x 10^{-15} to –60 x 10^{-15} m^3 mol^{-1} Pa^{-1}, respectively. As shown in **Figure 5.9 (c)** the ϕ_{KJAW} values of NaBr change from –42 to –33 x 10^{-15} m^3 mol^{-1} Pa^{-1}, while the ϕ_{KJAW} values of KBr increase from –32 to –12 x 10^{-15} m^3 mol^{-1} Pa^{-1}. The transfer compressibilities of KCl and $MgCl_2$ in the presence of L-alanine are plotted in **Figure 5.10**. The $\partial\phi_K{}^0{}_{tr.JAW}$ / ∂m_A of KCl (20.5 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} in 1 mol kg^{-1} L-alanine) increases 1.5 times in $MgCl_2$ (32.4 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} in 1 mol kg^{-1} L-alanine). The effect of L-alnine is also more on 2:1 electrolyte ($MgCl_2$) than on 1:1 electrolyte (KCl). The n_H

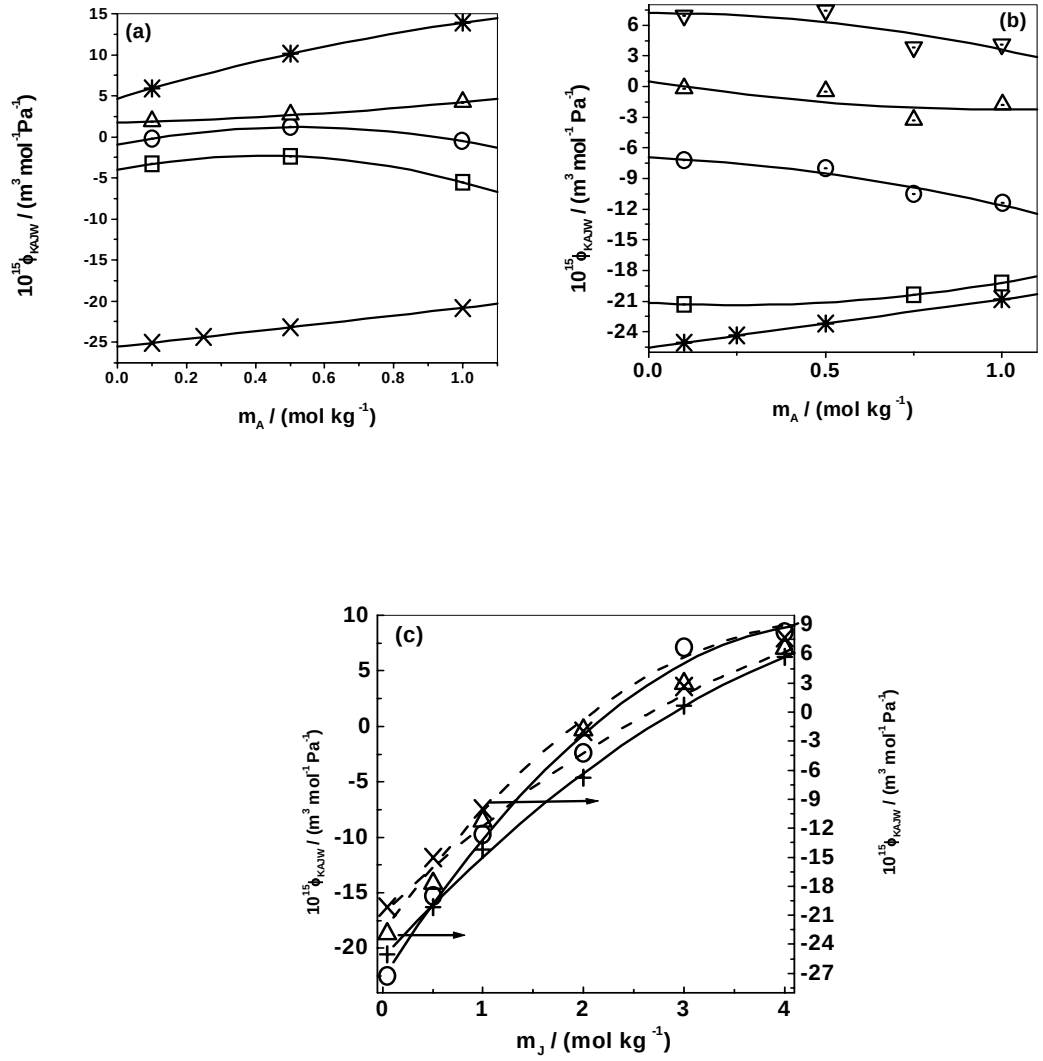


Figure 5.6: Variation of ϕ_{KAJW} of L-alanine as function of m_A in (a) H_2O (X), KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (T); (b) H_2O (T), $MgCl_2$ 0.05 mol kg^{-1} (o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (∇); (c) plots of ϕ_{KAJW} of L-alanine *vs.* m_J in NaBr: 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (+); in KBr 0.5 mol kg^{-1} (Δ), 1 mol kg^{-1} (X)

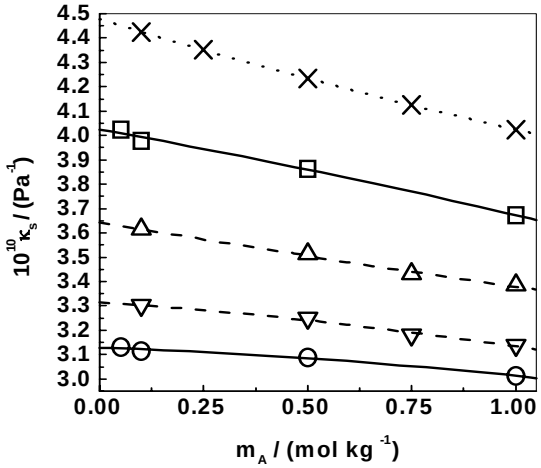


Figure 5.7: Dependence of isentropic compressibilities, κ_s on concentration, m_A of L-alanine in H_2O (X), in KCl: 1 mol kg^{-1} (o), 4 mol kg^{-1} (O); in $MgCl_2$: 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (∇)

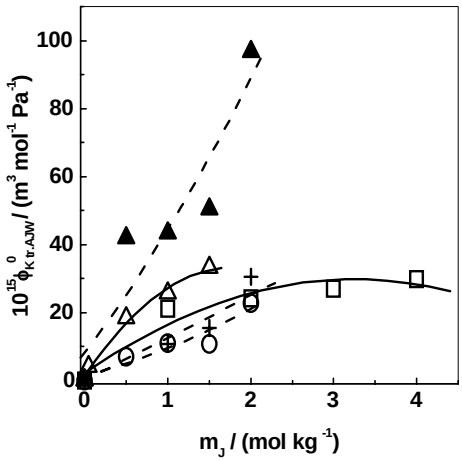


Figure 5.8: Change in $\phi_K{}^0{}_{tr.AJW}$ of L-alanine *vs.* m_J in KCl (o), $MgCl_2$ (Δ); of glycylglycine in KCl (+), KBr (O), Na_2SO_4 (σ)

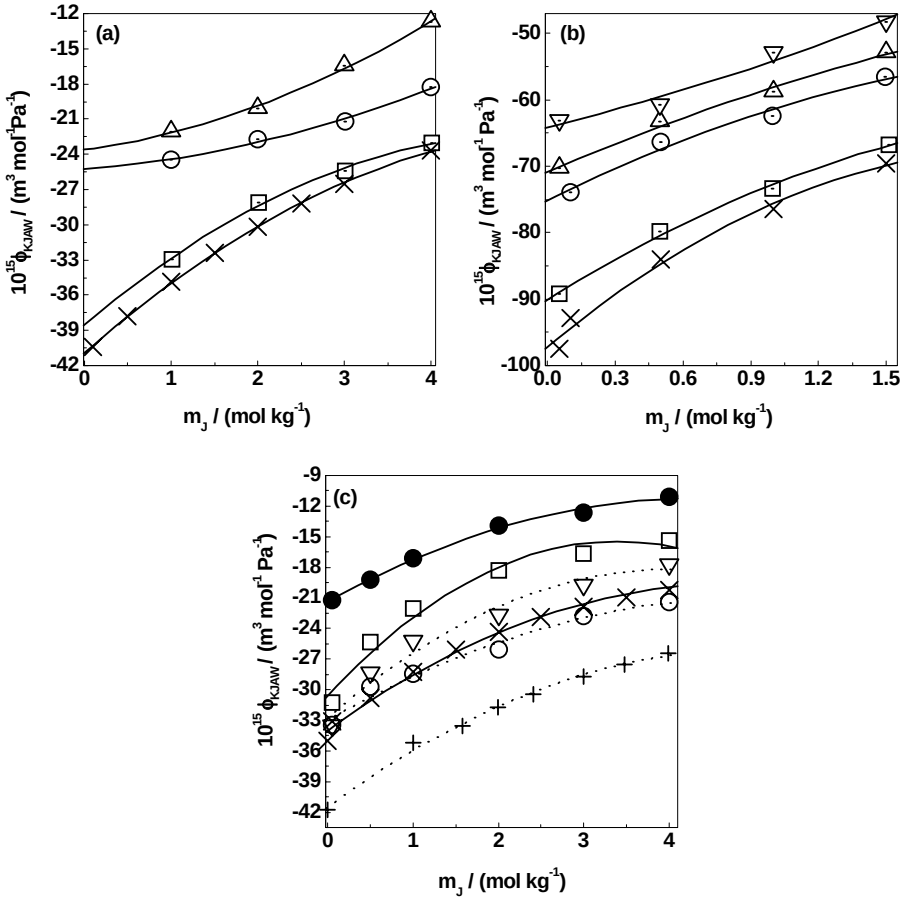


Figure 5.9: Variation of ϕ_{KJAW} of electrolytes as function of m_J **(a)** of KCl in H_2O (X), in L-alanine: 0.1 mol kg^{-1} (o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ); **(b)** $MgCl_2$; in L-alanine 0.1 mol kg^{-1} (o), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ), 1 mol kg^{-1} (∇); **(c)** of NaBr: in H2O (+), in L-alanine: 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (∇); of KBr in H_2O (X), in L-alanine: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (λ)

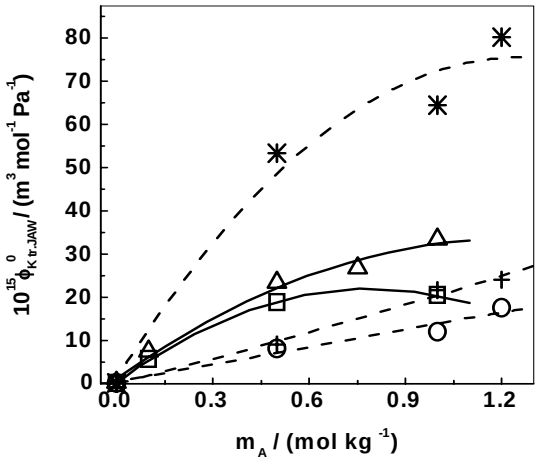


Figure 5.10: The change in transfer compressibilities, $\phi_K{}^0{}_{tr.JAW}$ of KCl (o), $MgCl_2$ (Δ) with respect to m_A, L-alanine; and of KCl (+), KBr (O) amd Na_2SO_4 (Σ) with respect to m_A, glycylglycine

of KCl in water is 5.5 which decreases to 0.7 in 1 mol kg^{-1} L-alanine, while that of $MgCl_2$ decreases from 12 in water to 1.8 in same concentration of L-alanine.

5.3 Apparent molar compressibilty of glycylglycine - electrolytes - water system:

The experimentally measured sound speeds, u at different concentrations of glycylglycine and electrolytes along with the calculated κ_S values are listed in the **Table 5.4**. Apparent molal compressibilities of glycylglycine, ϕ_{KAJW} calculated using **equation (2b)** are plotted as a function of m_A at different electrolyte concentrations in **Figures 5.11 (a-c)**. The ϕ_{KAJW} value of glycylglycine increases from –33.0 to +7.5 x 10^{-15} m^3 mol^{-1} Pa^{-1} in the presence of KCl, KBr and Na_2SO_4. The calculated κ_S values of glycylglycine as a function of m_A in different electrolytes are plotted in **Figure**

5.12. The peptide also shows decrease in κ_S values with increase in m_A and increase in κ_S values with increase in m_J as observed in case of amino acids.

Table 5.4: Speeds of sound, u and isentropic compressibilities, κs at different molality of glycylglycine $m_{A,}$ and electrolytes, $m_{J,}$ at 298.15 K.

m_J / (mol kg^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})	m_J / (mol kg^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})	m_J / (mol kg^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})
				KCl				
m_A = 0.5 mol kg^{-1}			m_A = 1.0 mol kg^{-1}			m_A = 1.2 mol kg^{-1}		
0.5007	1560.0	3.9342	0.5001	1592.2	3.6985	0.5001	1607.9	3.5995
0.9999	1582.5	3.7520	1.0008	1616.0	3.5282	1.0002	1630.1	3.4431
1.5001	1601.5	3.599	1.5002	1631.9	3.4034	1.5007	1648.1	3.3157
2.0001	1621.1	3.4546	1.9997	1652.0	3.2714	2.0010	1660.0	3.2198
				KBr				
0.5005	1544.0	3.9500	0.4996	1581.2	3.6927	0.4997	1596.9	3.5979
0.9995	1552.1	3.7780	1.0001	1586.9	3.5498	1.0006	1601.0	3.4654
1.5007	1560.0	3.6231	1.4995	1592.0	3.4259	1.5002	1606.5	3.3452
2.0002	1568.2	3.4826	2.0010	1600.0	3.2999	2.0001	1608.0	3.2523
				Na_2SO_4				
0.5001	1600.2	3.6184	0.5002	1640.0	3.3808	0.4993	1648.0	3.3262
0.9994	1668.1	3.1778	1.0004	1768.0	2.9993	1.0002	1776.1	2.9553
1.5014	1731.5	2.8285	1.5004	1768.1	2.6797	1.5001	1775.9	2.6437
2.0040	1795.1	2.5347	2.0001	1824.1	2.4313	2.0007	1832.0	2.4020

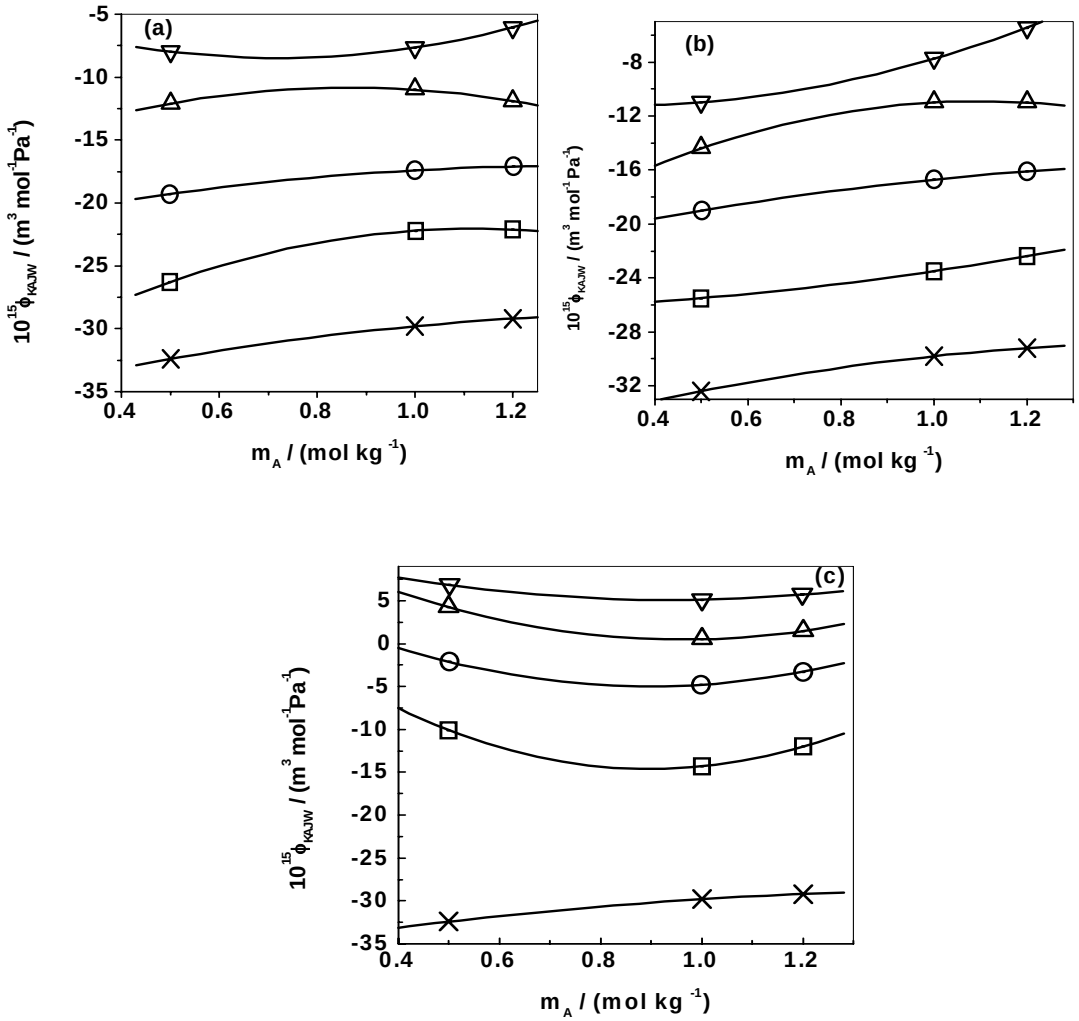


Figure 5.11: Plots of ϕ_{KAJW} *vs.* m_A of glycylglycine in H_2O (X), in 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (∇) of m_J, J = **(a)** KCl, **(b)** KBr and **(c)** Na_2SO_4

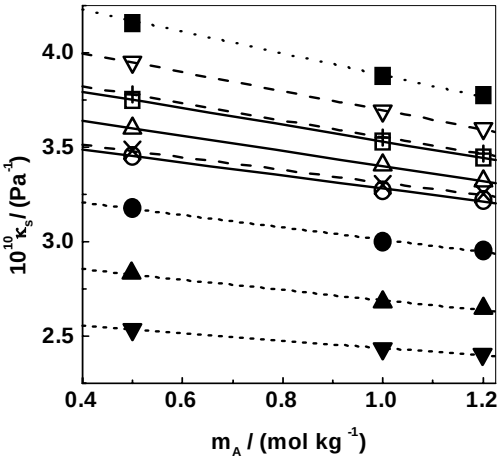


Figure 5.12: The variation of κ_s with m_A of glycylglycine in H_2O (ν), in KCl: 1 mol kg^{-1} (ο), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (O); in KBr: 0.5 mol kg^{-1} (∇), 1 mol kg^{-1} (+), 2 mol kg^{-1} (X); Na_2SO_4: 1 mol kg^{-1} (λ), 1.5 mol kg^{-1} (σ), 2 mol kg^{-1} (τ)

The apparent molar compressibilty of glycylglycine at infinite dilution, $\phi_K{}^0{}_{AJW}$ is significantly affected by addition of electrolytes. This effect can be accounted by calculating the transfer properties. The transfer compressiblities of glycylglycine in the presence of electrolytes are positive as shown in **Figure 5.5**. The dominance of 1:2 electrolytes on transfer compressibility of glycylglycine reflects in the $\partial\phi_K{}^0{}_{tr.AJW}$ / ∂m_J values. ($\partial\phi_K{}^0{}_{tr.AJW}$ / ∂m_J of glycylglycine in 1 mol kg^{-1} KCl = 7.1 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, in 1 mol kg^{-1} KBr = 9.5 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} and in 1 mol kg^{-1} Na_2SO_4 = 44 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}) From the slope values it can be also concluded that the compressibility of peptide is dependent on the nature and charge of cation as well as anion.

Glycylglycine exists in a zwitterionic state at neutral pH. The electrolytes like KCl, KBr, Na_2SO_4, etc. interact with the charged centers (NH^+, COO^-) of glycylglycine and show a decrease in the electrostriction effect. The ${\phi_K}^0_{tr.AJW}$ values for glycine – Na_2SO_4 are lower than ${\phi_K}^0_{tr.AJW}$ for glycylglycine – Na_2SO_4, which is in accordance with the observations of Chung and Vera[150]. Absence of hydrophobic hydration in glycylglycine due to absence of any methyl group (hydrophobic) and presence of peptide bond (hydrophilic) increase electrostriction effect than present in glycine, L-alanine or other amino acids. Na_2SO_4 shows higher electrostriction effect on water molecules than KCl and KBr.

In **Figure 5.13 (a-c)** the effect of glycylglycine on electrolyte compressibility is shown. The transfer compressibilities of electrolytes are plotted as a function of m_A in **Figure 5.8**. All the three electrolytes show positive transfer compressibilities. The $\partial {\phi_K}^0_{tr.JAW} / \partial m_A$ of KCl, KBr and Na_2SO_4 are observed to be 20.4 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, 13.8 x 10^{-15} m^3 kg mol^{-2} Pa^{-1} and 71.34 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}, respectively. Significant increase in the ϕ_{KJAW} due to glycylglycine is seen in Na_2SO_4 as compared to KCl and KBr.

Hydration number of glycylglycine in water is ≈ 5. Addition of KCl or KBr to glycylglycine decrease hydration number from 5 to 0 while Na_2SO_4 drastically decrease it to negative hydration numbers indicating removal of water molecules from zwitterionic groups and peptide bond. The reduction in hydration of electrolytes due to presence of peptide is more as compared to amino acids. The n_H of KCl in water changes from 5.5 in water to 1, 0.7 and 0.5 due to 1 mol kg^{-1} glycine, alanine and glycylglycine, respectively.

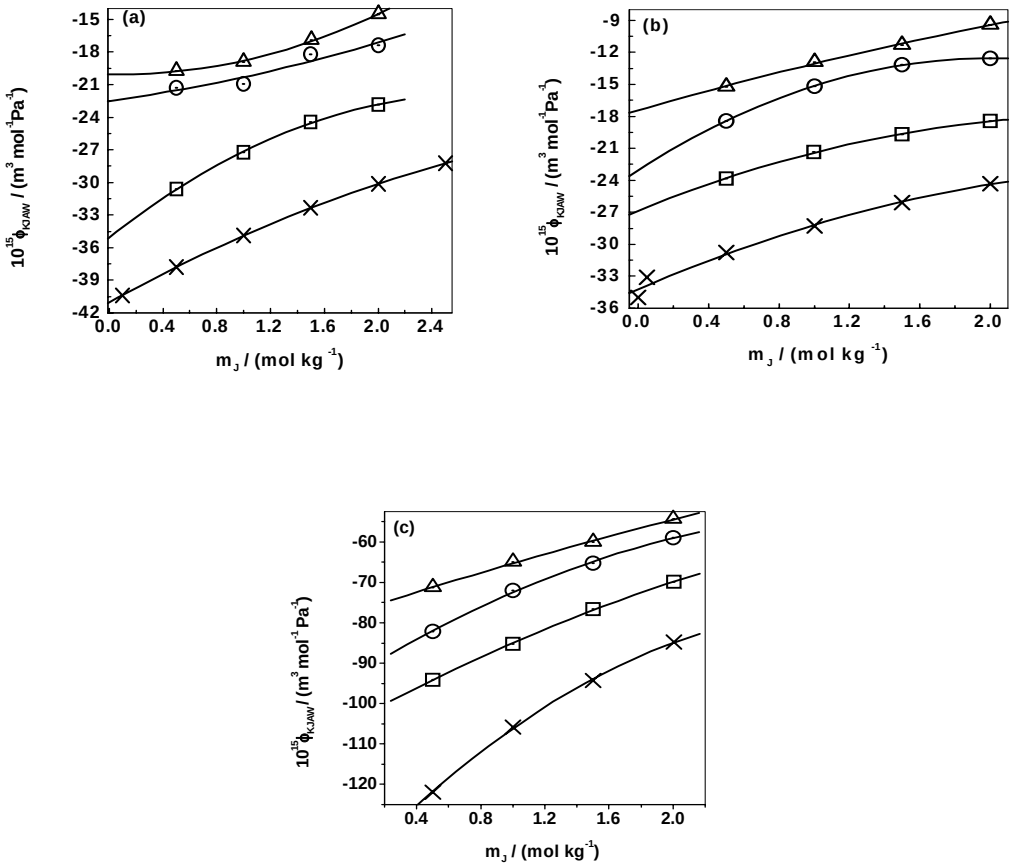


Figure 5.13: Plots of ϕ_{KJAW} of **(a)** KCl, **(b)** KBr and **(c)** Na_2SO_4 *vs.* m_J in H_2O (X), in glycylglycine: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ)

5.5: Effect of temperature on the apparent molar compressibilty of L-alanine - KCl - water system:

The experimental speed of sound of L-alanine - KCl - water system and isentropic compressibilities calculated therefrom are listed in **Table 5.5**. The ϕ_{KAJW} of L-alanine is plotted as a function of temperature and m_J in **Figures 5.14 (a and b)**. The change in the isentropic compressibility, κ_s with respect to temperature is shown in **Figure 5.15**. The adiabatic compressibility of L-alanine increases with the temperature rise. The rise in temperature favors the relaxation of water molecules than binding them to charged end groups which is seen in the form of the positive slopes of ϕ_{KAJW} *versus* temperature and ϕ_{KAJW} versus molality of KCl.

The change in hydration spheres of amino acids in the presence of ions can also be analyzed by comparing the hydration numbers of L-alanine at different temperatures and in different concentrations of KCl.

The hydration numbers of 1 mol kg^{-1} amino acid decreases from ≈ 5 to 3 with the increase in KCl concentration from (0 to 4) mol kg^{-1} at 313.15 K. The hydration number of L-alanine in KCl also decreases with the increase in temperature. This decrease in n_H supports the assumption that due to interaction of charged end groups and ions water is relaxed in bulk state.

Since the temperature effect on ϕ_{KAJW} in the presence of KCl is studied it would be of interest to check the thermal expansion of KCl as modified by L-alanine. The variation of apparent molar compressibility, ϕ_{KJAW} of KCl with the temperature is shown in **Figures 5.16 (a) and (b)**, respectively.

Hydration numbers are also calculated for KCl in the presence of amino acid. The effect of concentration of amino acid and temperature on the hydration number of

KCl is similar to that observed for L-alanine in aqueous KCl. The hydration number of KCl in 1 mol kg^{-1} aqueous L-alanine decreases from ≈ 5 to 3 when KCl concentration increases from 1 to 4 mol·kg^{-1} at 313.15 K.

Table 5.5: The speeds of sound, u and isentropic compressibilities, κ_s of the L-alanine - KCl - water system at different temperatures

T / K	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})	u / (m s^{-1})	10^{10} κ_s / (Pa^{-1})
	m_A = 0.5 mol·kg^{-1}							
	m_J = 1 mol kg^{-1}		m_J = 2 mol kg^{-1}		m_J = 3 mol kg^{-1}		m_J = 4 mol kg^{-1}	
283.15	1528.5	4.0495	1569.1	3.6591	1623.1	3.3542	1654.1	3.1386
288.15	1544.5	3.9731	1592.5	3.6025	1634.2	3.3144	1664.1	3.1065
308.15	1594.2	3.7513	1624.9	3.4838	1667.9	3.2118	1681.0	3.0668
313.15	1598.1	3.7405	1636.1	3.4442	1666.2	3.2184	1686.2	3.0550
	m_A =1 mol·kg^{-1}							
	m_J =1 mol kg^{-1}		m_J =2 mol kg^{-1}		m_J = 3 mol kg^{-1}		m_J = 4 mol kg^{-1}	
283.15	1557.1	3.8626	1605.0	3.4999	1645.1	3.2439	1674.0	3.0483
288.15	1574.2	3.7844	1616.0	3.4530	1656.5	3.2041	1684.1	3.0182
308.15	1626.1	3.5694	1648.2	3.3625	1688.0	3.1084	1700.5	2.9813
313.15	1629.9	3.5588	1656.1	3.3185	1684.1	3.1294	1703.9	2.9753

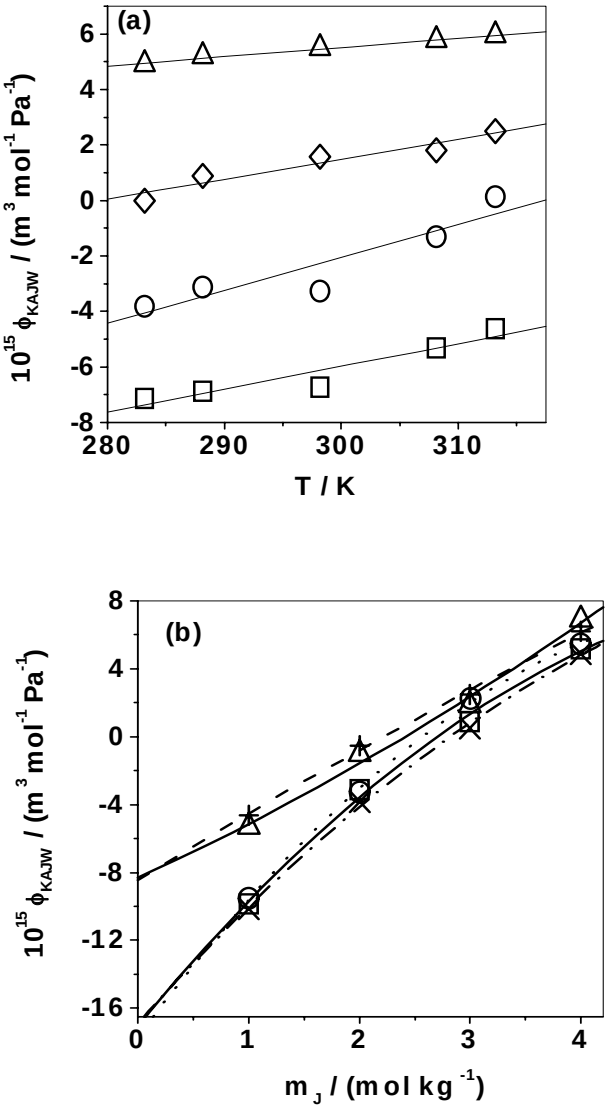


Figure 5.14: (a) ϕ_{KAJW} *vs.* temperature, T in 0.5 mol kg^{-1} L- alanine + 1 mol kg^{-1} KCl (o), + 3 mol kg^{-1} KCl (Γ); 1 mol kg^{-1} L- alanine + 2 mol kg^{-1} KCl (O), + 4 mol kg^{-1} KCl (Δ); (b) ϕ_{KAJW} *vs.* m_J in 0.5mol·kg^{-1} L- alanine at 308.15 K (Δ), 313.15 K (+) (- - - - -); 1 mol·kg^{-1} L-alanine at 283.15 K (X) (- . - . - . - .), 288.15 K (o), 298.15 K (O) (. . . . .)

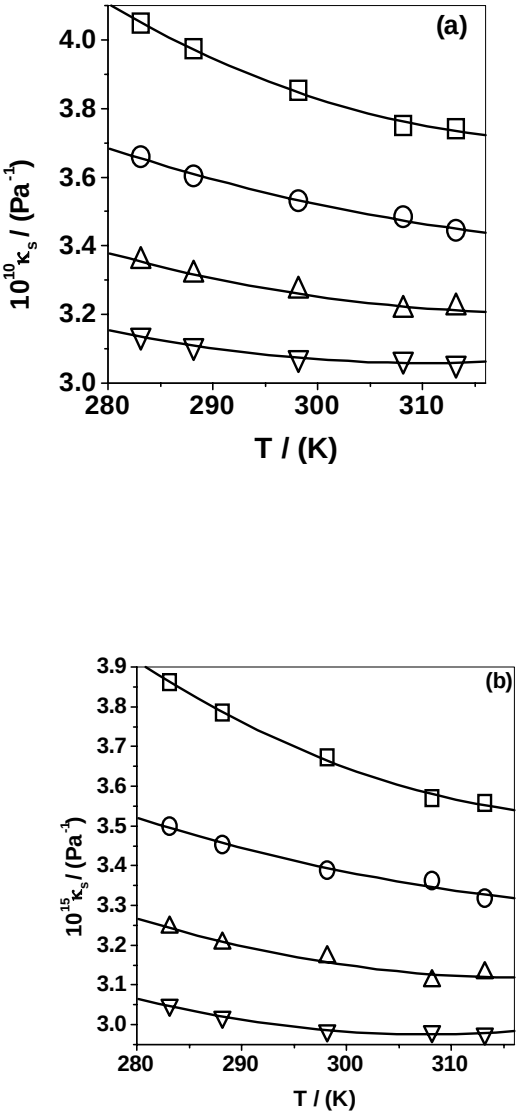


Figure 5.15: Variation of κ_s with temperature of L-alnine - KCl - water system of **(a)** 0.5 mol kg^{-1} L-alanine; **(b)** 1 mol kg^{-1} L-alanine in KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (∇)

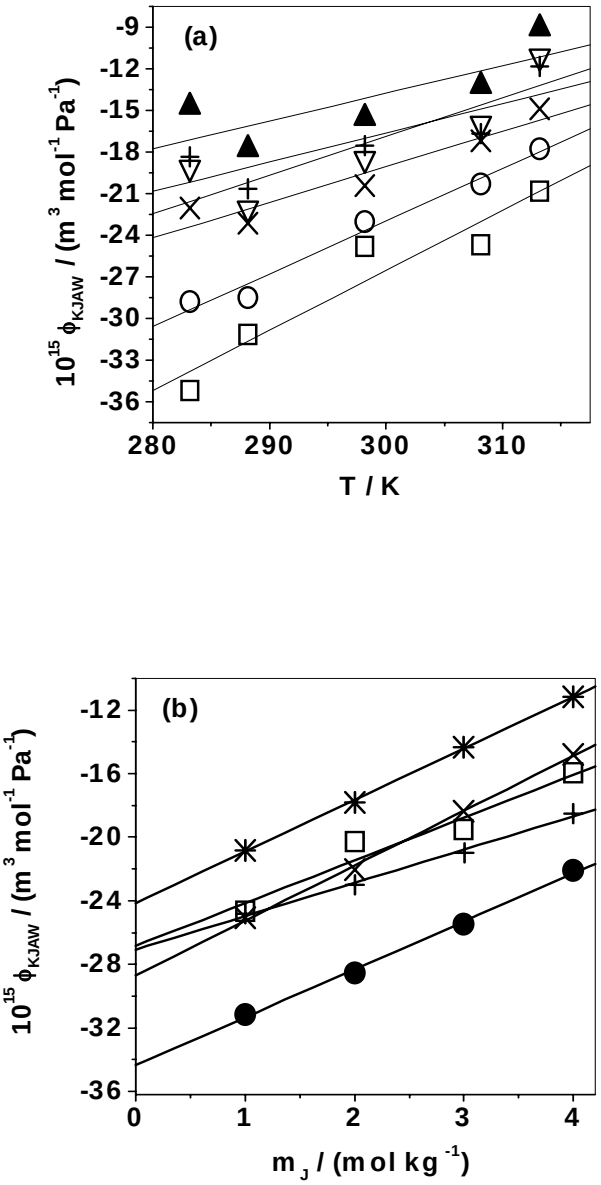


Figure 5.16 (a): Variation of ϕ_{KJAW} *vs.* temperature, T in 0.5 mol kg^{-1} L- alanine + 2 mol kg^{-1} KCl (O), + 4 mol kg^{-1} KCl (∇);1 mol kg^{-1} L- alanine + 1 mol kg^{-1} KCl (o), + 2 mol kg^{-1} KCl (X), + 3 mol kg^{-1} KCl (+), + 4 mol kg^{-1} KCl (σ) **(b)** ϕ_{KJAW} *vs.* m_J in 0.5 mol kg^{-1} L- alanine at 288.15 K (λ), 298.15 K (+), 308.15 K (o), 313.15 K (T); 1 mol kg^{-1} L- alanine at 283.15 K (X)

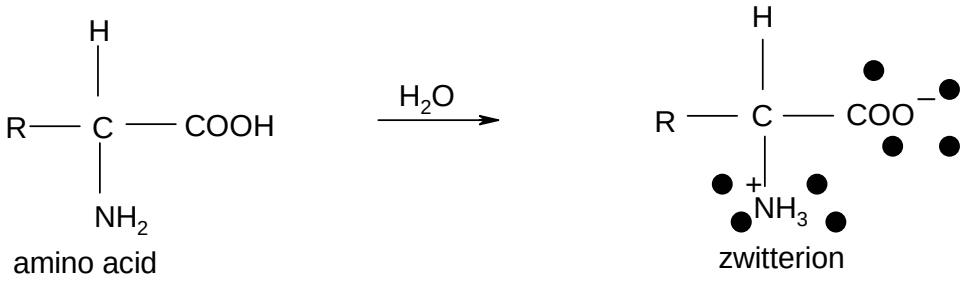
This chapter includes the development of equations and a model for correlating various thermodynamic properties of aqueous amino acids/peptide in the presence of electrolytes and vice versa. The derived properties, obtained from the experimental data are correlated using a simple set of equations.

6.1: Preface

As described in the "Introduction" chapter accurate models are available for predicting the thermodynamics of pure amino acids and of electrolytes in aqueous medium. Primarily these models are semiempirical in nature. Aqueous amino acid solutions have been described using the concept applicable to non-electrolyte solutions. It is however important that speciation (different species available in aqueous medium) be explicitly considered in the calculational procedure. At around pH 6.8 –7.1 amino acids exist in zwitterionic form and the different species of an amino acid in water depend on the pH of solution. The zwitterionic structure of amino acids and peptide and its interaction with aqueous ions is shown in **Scheme 1**.

An electrolyte when dissolved in water is dissociated into cation and anion. On the other hand, an amino acid forms different species when dissolved in aqueous media. Amino acid in water can loose a proton there by forming a negatively charged molecule. It can also gain a proton and become a positively charged molecule. When a positively charged NH_3^+ group and a negatively charged COO^- group are present in an amino acid, it is termed as a zwitterion. In the absence of a strong proton donor or (acid) or proton acceptor (base), more than 99% of amino acid molecules stay in zwitterionic form in the pH range of 6.8-7.2.

Scheme 1: (Schematic presentation of amino acid/peptide/electrolyte system)

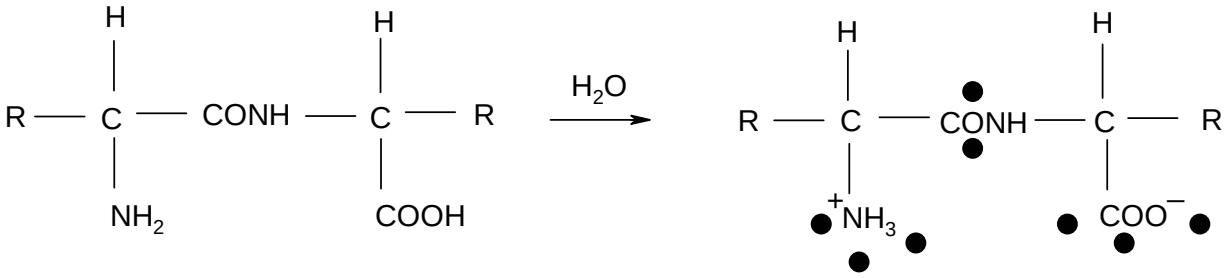


amino acid

zwitterion

(1)

● = H_2O, R = H = glycine
= CH_3 = alanine etc.



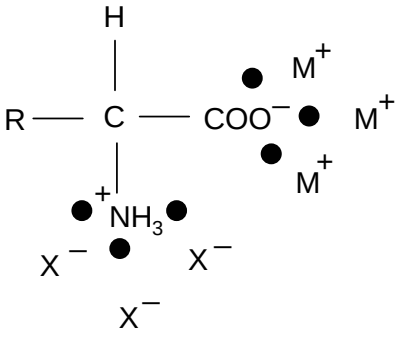
dipeptide

zwitterion

$$MX \xrightarrow{H_2O} M^+ + X^-$$

(2)

(1) + (2) →



The thermodynamics of strong electrolytes in water is relatively straightforward as compared to that of amino acids. This thermodynamics nevertheless becomes complex in the case of weak electrolytes exhibiting substantial ion pairing. One of the most effective formalisms to account for the thermodynamics of electrolyte solutions was put forward by Pitzer[123], who combined contribution due to long-range and short-range interactions. The Debye Hückel term is used to describe the long – range interaction term, while virial coefficients are employed for deciphering the short-range interactions.

In view of complete lack of equations that could be applied to the thermodynamics of aqueous amino acids - electrolyte solutions a suitable framework of equations was developed. The thermodynamic properties covered are activity coefficients, volumes and compressibilities, while developing such equations attention has been given to the fact that interaction parameters derived from the property of one component are used to deduce the property of another component.

6.2: Derivation of equations

The dimensionless excess free energy upon dissolving an amino acid in water, (G^{E}_{AW} / n_W) RT is written in the form of a molality – based polynomial expression to account for the short – range interaction forces as:

$$(G^{E}_{AW} / n_W)\, RT = RT \sum q_n\, m_A{}^n \qquad (1)$$

where, m_A is the molality of amino acid and q_n are the adjustable parameters. Similarly, the excess Gibbs free energy upon dissolving an electrolyte, MX (or J) in water, (G^E_{JW} / n_W) RT can be written in the form of the Pitzer theory considering the long-range and short-range interaction forces as:

$$(G^E_J / n_W)\, RT = f(I) + \sum_i \sum_j \lambda_{ij}(I)\, m_i\, m_j + \sum_i \sum_j \sum_k \mu_{ijk}\, m_i\, m_j\, m_k \qquad (2)$$

where an electrolyte J or MX dissociates into cation $M^{\nu+}$ and $X^{\nu-}$. ν^+ and ν^- are the number of particles dissociated from an electrolyte as $\nu = \nu^+ + \nu^-$. I is ionic strength given by $I = 0.5 \sum mi\, zi^2$ with z being the ionic charge. The subscripts i, j and k represent solutes.

The function f (I) denotes the effect of long – range electrostatic forces between ions. This effect is described in term of Debye – Hückel theory as

$$f(I) = -\left| z_M z_X \right| A_\varphi (4I / b) \ln (1 + b I^{0.5}) \qquad (3)$$

where A_φ is the Pitzer – Debye – Hückel limiting slope and b = 1.2. The effect of short – range forces between i and j is expressed in the form of second – virial coefficients indicated by λ_{ij}. The corresponding third virial coefficients, μ_{ijk} account for the interactions of i, j and k. In the Pitzer theory, λ_{ij} is a function of ionic strength, while μ_{ijk} is treated independent of ionic strength. The λ and μ matrices are taken to be symmetric i.e. $\lambda_{ij} = \lambda_{ji}$, etc. **equation (2)** can be simplified to give a parametric for an electrolyte MX with M^+ and X^- ions as.

$$(G^E_J / n_W)\, RT = f(I) + 2\, m_J^2\, \nu_M\, \nu_X\, [\beta^{(0)}_{MX} - (\beta^{(1)}_{MX} / \alpha^2\, I)$$
$$[1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] + m_J^3\, (\nu_M\, \nu_X)^{1.5}\, C^{\varphi}_{MX}] \qquad (4)$$

where $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$ are the second C^{φ}_{MX} is the third virial coefficient, respectively. $\alpha = 2.0$ (kg mol^{-1})$^{0.5}$. Additional term $\beta^{(2)}_{MX}$ may be necessary in some ion – pair forming (calcium sulphate) electrolytes.

The mixing of an amino acid with an electrolyte is accompanied with interaction between the amino acid and ions. Thus, the $\Delta_m G^E$ values on mixing of an amino acid with an electrolyte is the sum of **equations (1) and (4)** together with the term accounting for the mixing parameter, called as amino acid – electrolyte interaction parameter, λ_{AJW} as :

$$(\Delta_m G^E / n_W)\, RT = \sum q_n\, m_A^n + f(I) + 2\, m_J^2\, \nu_M\, \nu_X\, [\beta^{(0)}_{MXA} - (\beta^{(1)}_{MXA} / \alpha^2\, I)$$
$$[1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] + m_J^3\, (\nu_M\, \nu_X)^{1.5}\, C^{\varphi}_{MXA}] + 2\, \lambda_{AJW}\, m_A\, m_J \qquad (5)$$

where λ_{AJW} is amino acid – electrolyte interaction parameter to be defined as

$$\lambda_{AJW} = (\lambda_{AM^+W}\, \nu_M / \nu) + (\lambda_{AX^-W}\, \nu_X / \nu) \qquad (6)$$

with λ_{AM^+} and λ_{AX^-} being the amino acid – cation and amino acid – anion interaction parameter, respectively. It may be noted that λ_{AJW} and λ_{JAW} are symmetric in nature, hence:

$$\lambda_{AJW} = \lambda_{JAW} \qquad (7)$$

The Pitzer coefficients, $\beta^{(0)}_{MXA}$, $\beta^{(1)}_{MXA}$ and C^{φ}_{MXA} are now defined in amino acid – water system rather than in water alone as shown in **equation (4)**. This is due to the fact that now an electrolyte is dissolved in amino acid - water and not in water alone. Hence, amino acid – water is a solvent and not water alone.

Appropriate differentiation of **equation (5)** with respect to m_A and m_J yields expression for the activity coefficient of A, γ_A and of J, $\gamma_{\pm J}$ as:

$$\ln \gamma_{AJW} = \ln \gamma^{0}_{AJW} + 2\, s_{\phi}\, m_A + 3\, s_{\phi}^{'}\, m_A^{2} + 2\, \lambda_{AJW}\, m_J \qquad (8)$$

The value of n in q_n in **equations (1) and (5)** depends upon the nature of amino acid. But a m_A^3 term (n=3) should suffice most of the amino acids. The resultant expression describes the activity coefficient behavior of amino acid in water. Thus, $q_1 = \ln \gamma^{0}_{AJW}$; a value of $\ln \gamma_{AJW}$ in electrolyte water at infinite dilution of amino acid and is known from the experimental data, $q_2 = 2\, s_{\phi}$ and $q_3 = 3\, s_{\phi}^{'}$ are the empirical fitting parameters. It may be noted that the parameters s_{ϕ} and $s_{\phi}^{'}$ are obtained keeping in mind that the solvent is not water but an electrolyte – water system and

$$\ln\gamma_{\pm JAW} = \ln\gamma_{\pm}{}^{0}_{JAW} + f\,'(I) + 4\, \nu_M\, \nu_X\, m_J\, [\beta^{(0)}_{MXA} - (2\, \beta^{(1)}_{MXA} / \alpha^2\, I)$$
$$[1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] + 3\, m_J^{2}\, (\nu_M\, \nu_X)^{1.5}\, C^{\varphi}_{MXA}] + 2\, \lambda_{AJW}\, m_A \qquad (9)$$

where f'(I) is defined as:

$$f'(I) = - \left| Z_M Z_X \right| A_\phi (I^{0.5} / (1 + b I^{0.5}) + (2 / b) \ln (1 + b I^{0.5}) \quad (10)$$

$\ln \gamma_{\pm}^{0}{}_{JAW}$ is the activity coefficient of electrolyte at infinite dilution in amino acid – water. A_ϕ is the Pitzer – Debye – Hückel slope for activity coefficient having value 0.39145 $kg^{0.5}$ $mol^{-0.5}$ at 298.15 K[233]. The expression for correlating apparent molar volume of an amino acid in electrolyte – water system, ϕ_{VAJW} and of an electrolyte in amino acid – water system can be obtained from the above equations. These expressions are:

$$\phi_{VAJW} = \phi_V^{0}{}_{AJW} + 2 s_V m_A + 3 s_V' m_A^2 + 2 R T \lambda^V{}_{AJW} m_J \quad (11)$$

with the following definitions:

$$\lambda^V{}_{AJW} = (\partial \lambda_{AJW} / \partial P),\ s_V = (\partial s_\varphi / \partial P) \text{ and } s_V' = (\partial s_\varphi' / \partial P)$$

$\phi_V^{0}{}_{AJW}$ is the apparent molar volume of amino acid at infinite dilution of amino acid in electrolyte solution. The expression for apparent molar volume of an electrolyte in amino acid solution, ϕ_{VJAW} is given by:

$$\phi_{VJAW} = \phi_V{}^0{}_{JAW} + \nu \left|Z_M Z_X\right| (A_V / 2\,b) \ln (1 + b\, I^{0.5}) + \nu_M \nu_X R\, T\, m_J$$
$$[\beta^{(0)V}{}_{MXA} + 2\, \beta^{(1)V}{}_{MXA} [\,[1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] / (\alpha^2\, I)\,]$$
$$+ m_J{}^2 [(\nu_M Z_M) / 2 \left|Z_M Z_X\right|^{0.5} C^{\varphi V}{}_{MXA}] + 2\, R\, T\, \lambda^V{}_{AJW}\, m_A \qquad (12)$$

where $\beta^{(0)V}{}_{MXA} = (\partial\beta^{(0)}{}_{MXA} / \partial P)$, $\beta^{(1)V}{}_{MXA} = (\partial\beta^{(1)}{}_{MXA} / \partial P)$ and $C^{\varphi V}{}_{MXA} = (\partial C^{\varphi}{}_{MXA} / \partial P)$. Av is the Pitzer - Debye – Hückel limiting slope for volume having value 1.8743 x 10^{-6} m^3 $kg^{0.5}$ $mol^{-1.5}$ at 298.15 K[233].

Similar equations can be obtained for apparent molar compressibility of amino acid and electrolyte in amino acid – electrolyte – water mixture. The apparent molar compressibility of amino acid in electrolyte – water mixture can be given by:

$$\phi_{KAJW} = \phi_K{}^0{}_{AJW} + 2\, s_K\, m_A + 3\, s_K{}'\, m_A{}^2 + 2\, R\, T\, \lambda^K{}_{AJW}\, m_J \qquad (13)$$

where:

$$\lambda^K{}_{AJW} = (\partial^2\lambda_{AJW} / \partial P^2),\ s_K = (\partial^2 s_\varphi / \partial P^2) \text{ and } s_K{}' = (\partial^2 s_\varphi{}' / \partial P^2)$$

$\phi_K{}^0{}_{AJW}$ is the apparent molar compressibility of amino acid at infinite dilution of amino acid in electrolyte solution. The equation for apparent molar compressibility of an electrolyte in amino acid solution, ϕ_{KJAW} is given by:

$$\phi_{KJAW} = \phi_K{}^0{}_{JAW} + \nu \left| Z_M Z_X \right| (A_K / 2\,b) \ln (1 + b\, I^{0.5}) + \nu_M \nu_X R\, T\, m_J$$
$$[\beta^{(0)K}{}_{MXA} + 2\,\beta^{(1)K}{}_{MXA} [\,[1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] / (\alpha^2\, I)]$$
$$+ m_J{}^2 [(\nu_M Z_M) / 2 \left| Z_M Z_X \right|^{0.5} C^{\varphi K}{}_{MXA}] + 2\, R\, T\, \lambda^K{}_{AJW}\, m_A \qquad (14)$$

The Pitzer coefficients are defined as $\beta^{(0)K}{}_{MXA} = (\partial \beta^{(0)\ 2}{}_{MXA} / \partial P^2)$, $\beta^{(1)K}{}_{MXA} = (\partial\ \beta^{(1)\ 2}{}_{MXA} / \partial\ P^2)$ and $C^{\varphi K}{}_{MXA} = (\partial^2 C^{\varphi}{}_{MXA} / \partial P^2)$. A_K is Debye – Hückel limiting slope for compressibility having value -3.7784×10^{-15} $m^3\ kg^{0.5}\ mol^{-1.5}\ Pa^{-1}$ at 298.15 K[233]. In a typical calculation the derived property y_A was fitted with m_A to extract λ_{AJW} at constant m_J. The λ_{AJW} was input in the equation to represent y_J, for evaluating the Pitzer coefficients ($\beta^{(0)}{}_{MXA}$, $\beta^{(1)}{}_{MXA}$ and $C^{\varphi}{}_{MXA}$). The fitting procedure was a Least Squares Fitting program with the minimization of objective function given by:

$$\text{Objective function} = (\sum (y_{exp.} - y_{cal.})^2 / N)^{0.5} \qquad (15)$$

6.3: Data analysis and discussions

In this work **equations (8), (9) and (11-14)** were the operational equations for testing the experimental data on activity coefficients and volumetric properties of both amino acid and electrolyte in the aqueous mixtures of amino acid and electrolyte. A large number of experimental data on activity coefficient, volume and compressibility of the amino acid – electrolyte – water solutions were subjected to these equations. A summary of the experimental data and literature data together with their sources is described in **Table 6.1**.

Table 6.1: List of systems analyzed for testing **equations (8), (9) and (11-14)**. (Wherever the reference showing the data source is not mentioned in the last column of the table means that the data are collected in this laboratory)

No.	System	m_A	m_J	Property	Reference
1.	Glycine – NaCl - H_2O	0.5 – 3	0.2 – 1	V, K, γ	180, 135
2.	Glycine – $NaNO_3$ – H_2O	0.5 – 3	0.2 – 1	V, K	180
3.	Glycine – NaBr – H_2O	0.5 – 3	0.5 – 4	V, K	
4.	Glycine – KCl – H_2O	0.5 – 3	0.2-1	V, K	180
5.	Glycine – KCl – H_2O	0.5 – 3	0.5 – 4	V, K	
6.	Glycine – KNO_3 – H_2O	0.5 – 3	0.2 – 1	V, K	180
7.	Glycine – KBr – H_2O	0.5 – 3	0.5 – 4	V, K	
8.	Glycine – $MgCl_2$ – H_2O	0.5 – 3	0.1 – 1.5	V, K	
9.	Alanine – KCl – H_2O	0.1 – 1	1 – 4	V, K	
10.	Alanine – $MgCl_2$ – H_2O	0.1 – 1	0.05 – 1.5	V, K	
11.	Glycylglycine – KCl – H_2O	0.5 –1.2	0.5 – 2	V, K	
12.	Glycylglycine – KBr- H_2O	0.5 – 1.2	0.5 – 2	V, K	
13.	Glycylglycine – $MgCl_2$ – H_2O	0.5 - 1	0.5 - 1.5	V, K	
14.	Glycylglycine – Na_2SO_4 – H_2O	0.5 - 1	0.5 – 2	V, K	
15.	Glycine – $(CH_3)_4NBr$ - H_2O	0.5 - 2	0.25 –1.8	V	
16.	Glycine – $(C_2H_5)_4NBr$ - H_2O	0.5 – 1.5	0.5 – 1.5	V	
17.	Glycine – $(C_4H_9)_4NBr$ – H_2O	0.5 –1.5	0.05 – 0.73	V	
18.	Alanine – $(CH_3)_4NBr$ – H_2O	0.5 –1	0.25 – 1.8	V	
19.	Alanine – $(C_2H_5)_4NBr$ -	0.1 – 1	0.1 –1.2	V	

	H_2O				
20.	Alanine – $(C_4H_9)_4NBr$ – H_2O	0.1 – 1	0.05 – 0.73	V	
21.	Glycylglycine – $(CH_3)_4NBr$ - H_2O	0.1 – 0.75	0.25 – 0.8	V	
22.	Glycylglycine – $(C_2H_5)_4NBr$ - H_2O	0.1 – 0.75	0.1 – 1.2	V	
23.	Glycylglycine – $(C_4H_9)_4NBr$ – H_2O	0.1 – 0.75	0.05 - 0.5	V	
24.	Glycine – KSCN – H_2O	0.1 – 0.3	1 – 5	V	173
25.	Alanine – KSCN – H_2O	0.075 – 0.25	1 – 5	V	173
26.	Proline – KSCN – H_2O	0.05 – 0.3	1 – 5	V	173
27	Threonine – KSCN – H_2O	0.05 – 0.25	1 – 5	V	173
28.	β-Alanine – KSCN – H_2O	0.1 – 0.35	1 – 5	V	173
29.	γ-amino-n-butyric acid – KSCN – H_2O	0.1 – 0.3	1 – 5	V	173
30.	ε-aminocaproic acid – KSCN – H_2O	0.05 – 0.25	1 – 5	V	173
31.	Glycine – sodium butyrate – H_2O	0.1 – 0.35	0.5 – 2	V	183
32.	DL α-Alanine – sodium butyrate – H_2O	0.1- 0.35	0.5 – 2	V	183
33.	DL α-amino-n-butyric acid – sodium butyrate – H_2O	0.1- 0.35	0.5 – 2	V	183
34.	Leucine – sodium butyrate – H_2O	0.02 - 0.05	0.5 - 2	V	183
35.	Valine – sodium butyrate – H_2O	0.1 – 0.35	0.5 - 2	V	183

36.	β-Alanine – NaCl – H_2O	0 -4	0 – 4	γ	136
37.	DL-α-amino-n-butyric acid – NaCl – H_2O	0 –1.5	0 – 4	γ	137

6.31: Activity coefficient:

A stringent test was first performed on the ln γ_{AJW} in electrolyte solution. An exhaustive data array is available for activity coefficients of amino acids in NaCl only. The amino acids investigated were glycine, β-alanine and DL-α-amino butyric acid. The ln γ_{AJW} data of amino acids in NaCl were first analysed using **equation (8)**. In **Table 6.2** are given the values of the s_ϕ, s_ϕ' and λ_{AJW} parameters for different amino acids in aqueous NaCl together with rmsd of their fits. The maximum concentration of amino acids and electrolytes was 2 mol kg^{-1} and 4 mol kg^{-1}, respectively. **Figure 6.1** shows the applicability of **equation (8)** in duplicating the experimental γ_{AJW} data for some representative situations. The ln γ_{AJW} of glycine from dilute (0.01 mol kg^{-1}) to the concentrated (4 mol kg^{-1}) NaCl solution can be correlated with m_A with rmsd of 0.001 to 0.002, which is an excellent agreement. As evident from **Figure 6.1**, an addition of glycine at constant NaCl concentration decreases the activity of glycine in NaCl showing the association of amino acid. **Equation (8)** is capable to reproduce the ln γ_{AJW} data with high accuracy. In the case of DL-α- amino butyric acid, the changes in its activity coefficients with enhanced concentration of the amino acid can be accounted for by the use of **equation (8)** in NaCl up to 4 mol kg^{-1}. The average rmsd value in ln γ_{AJW} in the solutions of NaCl from 0.01 to 4 mol kg^{-1} is estimated as 0.001. The changes in the activity coefficient of β-alanine in NaCl are different from those observed in glycine. In this case, an increase in the activity

coefficients with the enhanced concentration of amino acid indicates anti-association effect. The use of **equation (8)** to these data shows good fits of the ln γ_{AJW} vs. m_A in NaCl up to 4 mol kg^{-1}. The ln γ_{AJW} values of β-alanine can be correlated with an average rmsd of 0.014. As seen from the above three examples, **equation (8)** can correlate the activity coefficients of different types of amino acids in NaCl with excellent accuracy. The data described herein can be fitted with an average rmsd (in $\ln\gamma_{AJW}$) of 0.003 obtained from the analysis of the activity coefficient data of three amino acids in NaCl.

Table 6.2: The coefficients of **equation (8)** for the activity coefficients of amino acids in aqueous NaCl solution at 298.15 K standard errors in the parameters are given in the parenthesis.

m_J / (mol kg^{-1})	ln γ^0_{AJW}	s_ϕ / (kg mol^{-1})	s'_ϕ / (kg $mol^{-1})^{-2}$	λ_{AJW} / (kg mol^{-1})	rmsd ($\ln\gamma_{AJW}$)
		Glycine - NaCl – H_2O			
0.01	-0.0045	-0.0895	0.0102	0.0022	0.001
	(0.0006)	(0.0106)	(0.0012)	(0.0003)	
0.05	-0.0170	-0.0876	0.0102	9.0×10^{-5}	0.001
	(0.0008)	(0.0023)	(0.0003)	(0.23×10^{-5})	
0.1	-0.0312	-0.0844	0.0098	-0.0001	0.002
	(0.0020)	(0.0084)	(0.0010)	(0.00001))	
0.5	-0.1042	-0.0806	0.0123	3.00×10^{-5}	0.001
	(0.0001)	(0.0025)	(0.0004)	(0.095×10^{-5})	
1	-0.1668	-0.0696	0.01003	-1.00×10^{-5}	0.001
	(0.0011)	(0.0028)	(0.0004)	(0.04×10^{-5})	
1.5	-0.2149	-0.0655	0.0098	9.8×10^{-6}	0.001
	(0.0007)	(0.0040)	(0.0006)	(0.59×10^{-6})	

2	-0.2564	-0.0625	0.0096	4.58 x 10^{-6}	0.002
	(0.0010)	(0.0011)	(0.0002)	(0.084 x 10^{-6})	
2.5	-0.2936	-0.0616	0.0099	6.42 x 10^{-8}	0.001
	(0.0009)	(0.0019)	(0.0003)	(0.203 x 10^{-9})	
3	-0.3278	-0.0592	0.0095	-7.74 x 10^{-6}	0.001
	(0.0006)	(0.0022)	(0.0003)	(0.28 x 10^{-6})	
4	-0.3924	-0.0599	0.0103	3.59 x 10^{-8}	0.001
	(0.0009)	(0.0019)	(0.0003)	(0.11 x 10^{-8})	
		DL-α-amino-n-butyric acid – NaCl - H_2O			
0.01	-0.0027	0.0266	0.0027	-7 x 10^{-5} (0.92	0.001
	(0.0006)	(0.0035)	(0.0003)	x 10^{-5})	
0.05	-0.0095	0.0286	0.0027	3 x 10^{-4} (0.27	0.001
	(0.0005)	(0.0026)	(0.0002)	x 10^{-4})	
0.1	-0.0146	0.0306	0.0026	-1.4 x 10^{-4}	0.001
	(0.0005)	(0.0035)	(0.0003)	(0.161 x 10^{-4})	
0.5	-0.0236	0.0382	0.0025	-4 x 10^{-5}	0.001
	(0.0006)	(0.0009)	(0.0001)	(0.092 x 10^{-5})	
1	-4.36 x 10^{-5}	0.0394	0.0027	4.193 x 10^{-11}	0.001
	(0.35x10^{-5})	(0.0028)	(0.0002)	(0.3 x 10^{-11})	
1.5	0.0378	0.0383	0.0025	-6.68 x 10^{-6}	0.001
	(0.0004)	(0.0014)	(0.0001)	(0.25 x 10^{-6})	
2	0.0831	0.0346	0.0029	1.43 x 10^{-6}	0.001
	(0.0003)	(0.0014)	(0.0001)	(0.05 x 10^{-6})	
3	0.1842	0.0268	0.0026	-2.13 x 10^{-6}	0.001
	(0.0006)	(0.0001)	(0.0001)	(0.01 x 10^{-6})	
4	0.2931	0.0170	0.0025	6.22 x 10^{-6}	0.001
	(0.0003)	(0.0005)	(0.0001)	(0.2 x 10^{-6})	
		β-alanine - NaCl - H_2O			
0.01	-0.0084	-0.0499	0.0136	0.0019	0.004
	(0.0027)	(0.0048)	(0.0013)	(0.0002)	

0.05	-0.0211	-0.0481	0.0139	5 x 10^{-5} (0.38	0.004
	(0.0030)	(0.0037)	(0.0011)	x 10^{-5})	
0.1	-0.0338	-0.0458	0.0139	0.0002	0.004
	(0.0029)	(0.0035)	(0.0011)	(0.0001)	
0.5	-0.0927	-0.0332	0.0137	2 x 10^{-5} (0.05	0.004
	(0.0026)	(0.0008)	(0.0003)	x 10^{-5})	
1	-0.1247	-0.0256	0.0138	1 x 10^{-5} (0.06	0.004
	(0.0025)	(0.0017)	(0.0009)	x 10^{-5})	
1.5	-0.1384	-0.0246	0.0159	-3.8305 x 10^{-7}	0.003
	(0.0016)	(0.0010)	(0.0006)	(0.1563x10^{-7})	
2	-0.1549	-0.0064	0.0094	0.0015	0.010
	(0.0107)	(0.0001)	(0.0002)	(0.0001)	
2.5	-0.1470	-0.0037	0.0076	-3.9489 x 10^{-6}	0.030
	(0.0236)	(0.0002)	(0.0004)	(0.2280x10^{-6})	
3	-0.1529	-0.0026	0.0094	9.7 x 10^{-4}	0.010
	(0.0108)	(0.0001)	(0.0005)	(0.531 x 10^{-4})	
4	-0.1709	0.0149	0.0068	0.0012	0.003
	(0.0088)	(0.0003)	(0.0001)	(0.0001)	

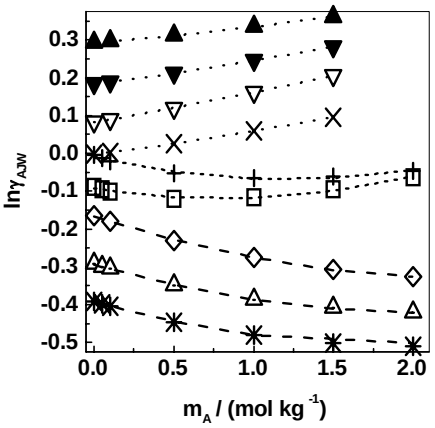


Figure 6.1: Plots of $\ln\gamma_{AJW}$ vs. m_A for glycine + NaCl 1 mol kg^{-1} (◊), 2.5 mol kg^{-1} (Δ), 4 mol kg^{-1} (T); + DLα-amino-n-butyric acid + NaCl 0.01 mol kg^{-1} (X), 2 mol kg^{-1} (∇), 3 mol kg^{-1} (τ), 4 mol kg^{-1} (σ); β-alanine + NaCl 3 mol kg^{-1} (+), 4 mol kg^{-1} (ο) (points-experimental data and lines-correlated data)

Variation of λ_{AJW} of three amino acids as a function of NaCl concentration is shown in **Figure 6.2**. λ_{AJW} for glycine and β-alanine decrease with m_J in dilute

solutions, while in concentrated solution it remains almost constant. The decrease in the λ_{AJW} values in dilute solution shows the dominance of zwitterionic head group – ion (COO^- - Na^+ and NH_3^+ - Cl^-) interaction than the ion – ion and amino acid – amino acid interactions. DL-α-amino butyric acid being bulkier does not favor the ion – zwitterion head group interactions, which is seen from the increase in the λ_{AJW} values with increase in NaCl concentration, m_J.

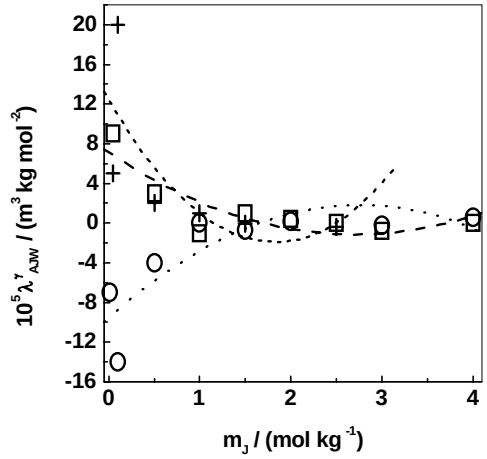


Figure 6.2: Plots of λ_{AJW} versus m_J for NaCl + glycine (o), DL-α amino butyric acid (O), β-alanine (+)

The values of λ_{AJW} obtained from **equation (8)** were treated as input data in **equation (9)** for the fitting of activity coefficients of electrolyte, J in amino acid solutions by evaluating the Pitzer coefficients. The resulting Pitzer coefficients of **equation (9)** are listed in **Table 6.3. Figure 6.3** shows the experimental γ_{JAW} values when plotted against the correlated ones. The plots are shown for the activity coefficients of NaCl in three different amino acids showing the success of **equation**

(9). The plots shows linear variation of experimental γ_{JAW} with correlated ones with some data points deviating from the linear relationship by about 5% in worst case. In dilute NaCl solution, where long-range interaction interactions are predominant over short-range interactions, **equation (9)** reproduces the activity coefficients of NaCl in all the amino acids. This is due to the fact that **equation (9)** contains a Debye - Hückel term sufficing the duplication of long-range interactions in dilute NaCl solutions. In the higher NaCl solutions, the role of the Pitzer coefficients becomes dominant. The rmsd value of fits varies from 0.003 to 0.055 for the activity coefficients of NaCl in amino acids. The effect of presence of amino acids on the Pitzer coefficients of aqueous NaCl can be clearly seen in **Figure 6.4 (a, b, c)**. The Pitzer coefficients of NaCl in water are altered in the presence of amino acids. The $\beta^{(0)}_{MXA}$ value decreases from –0.010 to –0.035 x 10^{-6} showing influence of the nature of NaCl as a strong electrolyte. This shows that NaCl, which is a strong electrolyte in pure water displays noticeable inhibition in its role as a strong electrolyte with the enhanced NaCl concentration. The $\beta^{(1)}_{MXA}$ parameter, essentially to account for the changes in the dilute NaCl solution is not expected to changes in the range studied herein. The change in the $\beta^{(1)}_{MXA}$ parameter is in between –3.0 to –2.5 x 10^{-6}. It was further noticeable that the ternary ionic interactions in a pure electrolyte like NaCl are not affected by the increasing concentrations of amino acids. In general, it has been observed that the C^{φ}_{MXA} term, which is small in aqueous concentrated electrolyte solution and shows that ternary interactions in water are insensitive to amino acids. These observations are clearly depicted in **Figure 6.4 (a, b, c)**.

Table 6.3: Pitzer coefficients of **equation (9)** for correlating $\ln\gamma_{JAW}$ at 298.15 K.

m_A / (mol kg^{-1})	$\ln\gamma^0_{JAW}$	$\beta^{(0)}_{MXA}$ / (kg mol^{-1})	$\beta^{(1)}_{MXA}$ / (kg mol^{-1})	C^{φ}_{MXA} / (kg^2 mol^{-2})	rmsd ($\ln\gamma_{JAW}$)
		Glycine – NaCl – H_2O			
0.05	-0.3038	-0.0085	-2.913	-0.0068	0.055
	(0.0446)	(0.0001)	(0.053)	(0.0001)	
0.1	-0.2791	-0.0327	-2.855	-0.0008	0.039
	(0.0326)	(0.0006)	(0.052)	(0.0001)	
0.5	-0.3595	-0.0146	-2.806	-0.0050	0.046
	(0.0352)	(0.0003)	(0.051)	(0.0001)	
1	-0.4285	-0.0209	-2.673	-0.0039	0.049
	(0.0384)	(0.0004)	(0.049)	(0.0001)	
1.5	-0.5334	-0.0665	-2.271	0.0067	0.009
	(0.0126)	(0.0012)	(0.041)	(0.0001)	
2.0	-0.5211	-0.0198	-2.559	-0.0039	0.040
	(0.0314)	(0.0004)	(0.046)	(0.0001)	
		DL-α-amino-n-butyric acid - NaCl – H_2O			
0.1	-0.2853	0.0203	-3.044	-0.0136	0.055
	(0.0423)	(0.0004)	(0.056)	(0.0002)	
0.5	-0.3196	-0.0097	-2.823	-0.0063	0.045
	(0.0400)	(0.0002)	(0.051)	(0.0001)	
1	-0.3511	-0.0194	-2.667	-0.0041	0.045
	(0.0333)	(0.0003)	(0.049)	(0.0001)	
1.5	-0.3618	-0.0151	-2.622	-0.0054	0.045
	(0.0330)	(0.0003)	(0.048)	(0.0001)	
		β-alanine - NaCl – H_2O			
0.05	-0.2288	0.6293	-4.799	-0.3243	0.047
	(0.0484)	(0.0257)	(0.196)	(0.0132)	
0.1	-0.2387	0.6067	-4.716	-0.3135	0.045
	(0.0455)	(0.0248)	(0.192)	(0.0128)	

0.5	-0.3585	-0.0133	-2.789	-0.0054	0.052
	(0.0406)	(0.0004)	(0.088)	(0.0002)	
1	-0.4196	-0.0139	-2.647	-0.0056	0.044
	(0.0399)	(0.0004)	(0.084)	(0.0002)	
1.5	-0.4726	-0.0270	-2.478	-0.0025	0.032
	(0.0294)	(0.0008)	(0.078)	(0.0001)	
2	-0.5010	-0.0325	-2.397	-0.0009	0.037
	(0.0294)	(0.0008)	(0.062)	(0.0001)	

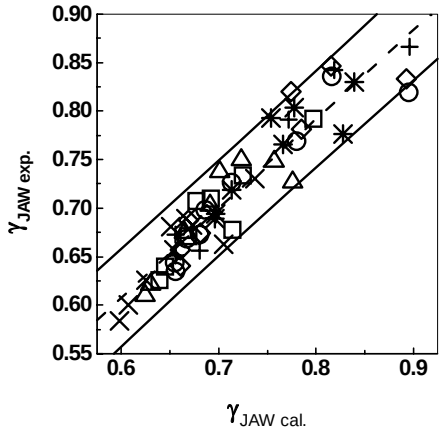


Figure 6.3: Variation of $\gamma_{JAWexp.}$ vs. $\gamma_{JAWcor.}$ in NaCl + glycine 0.05 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 2 mol kg^{-1} (X); + 2 amino-n-butyric acid 0.1 mol kg^{-1} (◊), 1.5 mol kg^{-1} (T); β-alanine 0.05 mol kg^{-1} (+), 2 mol kg^{-1} (o)

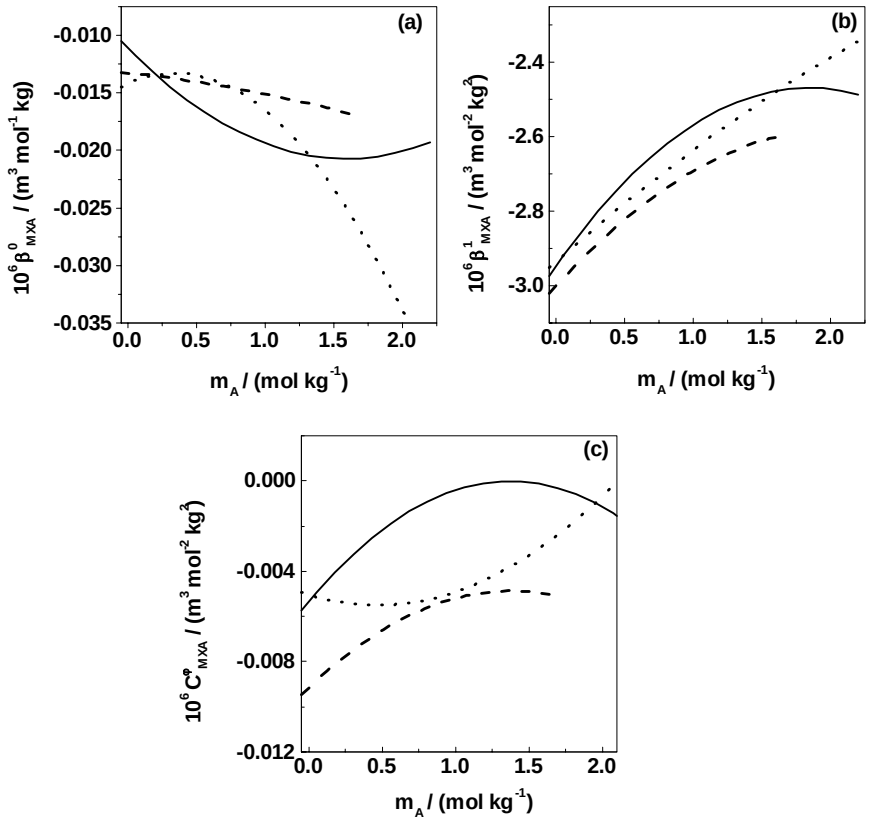


Figure 6.4: Pitzer coefficients depicted as a function of m_A in NaCl + glycine (—), DL-α-amino-n-butyric acid (- - -), β-alanine (…….) **(a)** β^0_{MXA}, **(b)** β^1_{MXA} and **(c)** C^φ_{MXA}

6.32: Apparent molar volume:

6.32 (a): Apparent molar volume experimental data obtained in this laboratory:

After a successful demonstration of **equations (8) and (9)** in correlating activity coefficients of electrolytes and of amino acids in their mixtures, the next quantity, apparent molar volume was considered. Apparent molar volumes of amino acids and peptide are successfully correlated using **equation (11)**. The term s_V is used

in Masson's equation ($\phi_{VAW} = \phi_V^0{}_{AW} + s_V m_A + s_V' m_A^2$)[48] to signify the amino acid – amino acid (solute – solute) interactions in aqueous amino acid solutions. The fitting of the concentrated amino acid solutions requires s_V' term. Both these coefficients are adjustable parameters. The $\phi_V^0{}_{AW}$, apparent molar volume of amino acids or peptide in water at infinite dilution for glycine, L-alanine and glycylglycine obtained in this study are 43.26 x 10^{-6} m^3 mol^{-1}, 60.47 x 10^{-6} m^3 mol^{-1} and 76.30 x 10^{-6} m^3 mol^{-1}, respectively. These values are in close agreement with the literature values of glycine (43.19 x 10^{-6} m^3 mol^{-1} [48], 43.23 x 10^{-6} m^3 mol^{-1} [179], 43.14 x 10^{-6} m^3 mol^{-1} [176] and 43.23 x 10^{-6} m^3 mol^{-1} [186]). For L-alanine, the $\phi_V^0{}_{AW}$ values from the literature are 60.47 x 10^{-6} m^3 mol^{-1} [48] and 60.50 x 10^{-6} m^3 mol^{-1} [186], while for glycylglycine the $\phi_V^0{}_{AW}$ values as 76.63 x 10^{-6} m^3 mol^{-1} [176], 76.34 x 10^{-6} m^3 mol^{-1} [22], 76.76 x 10^{-6} m^3 mol^{-1} [70] are reported. The $\phi_V^0{}_{AJW}$ data in concentrated electrolyte solutions are not available in literature for comparison except that in KCl. The $\phi_V^0{}_{AJW}$ of glycine in 1 mol kg^{-1} KCl was found to be 46.96 x 10^{-6} m^3 mol^{-1} in this study and the value observed by Soto et al. is 46.78 x 10^{-6} m^3 mol^{-1} in 1 mol kg^{-1} KCl[180], while the same values obtained by Ogawa et. al. in 1 and 2 mol kg^{-1} KCl are 44.89 and 46.12 x 10^{-6} m^3 mol^{-1} [186]. The coefficients of **equation (11)** obtained for the experimental systems are listed in **Table 6.4**. Several electrolytes dissolved in amino acids and peptide, mentioned in **Table 6.1** were regressed for their apparent molar volumes. The results of such a regression are displayed in **Figure 6.5 (a -c)** for a few chosen systems for the sake of clarity and convenience. **Figure 6.5 (a, b)** depicts the $\Delta\phi_{VAJW}$ ($\Delta\phi_{VAJW} = \phi_{VAJWexp.} - \phi_{VAJWcor.}$) as a function of m_A in the glycine with solutions of KCl, KBr, NaBr and $MgCl_2$ at different concentrations. One sees a random distribution of the difference

quantity in this depiction. The minimum and maximum differences are in the range of -0.20 and 0.15 x 10^{-6} m^3 mol^{-1}, respectively. This range of $\Delta\phi_{VAJW}$ in these systems shows that **equation (11)** is a useful and effective expression for the correlation of apparent molar volumes of amino acids in electrolytes. **Figure 6.5 (c)** displays random distribution of $\Delta\phi_{VAJW}$ for the mixing of L-alanine and glycylglycine with KCl, $MgCl_2$ and Na_2SO_4 at different concentration profiles. The range of the $\Delta\phi_{VAJW}$ values in this Figure varies from –0.16 to 0.04 x 10^{-6} m^3 mol^{-1} indicating excellent agreement between the two quantities. The average rmsd in ϕ_{VAJW} observed are 0.01 x 10^{-6} m^3 mol^{-1}, 0.02 x 10^{-6} m^3 mol^{-1} and 0.02 x 10^{-6} m^3 mol^{-1} for glycine, L-alanine and glycylglycine, respectively in the presence of electrolytes NaBr, KCl, KBr, $MgCl_2$ and Na_2SO_4 at different concentrations. If the correlated values of ϕ_{VAJW} are introduced to compute densities of the solutions, the calculated densities are in good agreement with those obtained experimentally. **Table 6.5** depicts the differences between experimental and calculated densities, $\Delta\rho$ for all the systems studied. The $\Delta\rho$ values vary between 4 to 254 x 10^{-3} kg m^{-3}.

Table 6.4: Coefficients for the apparent molar volume of amino acids/peptide, ϕ_{VAJW} in the presence of electrolytes at 298.15 K for the experimentally studied systems.

m_J / (mol kg^{-1})	10^6 ${\phi_V}^0_{AJW}$ / (m^3 mol^{-1})	10^6 s_V / (m^3 kg mol^{-2})	10^6 s_V' / (m^3 kg^2 mol^{-3})	10^6 ${\lambda^V}_{VAJW}$ RT / (kg m^3 mol^{-2})	10^6 rmsd / (m^3 mol^{-1})
		Glycine - NaBr - H_2O			
0.5005	45.38 (0.02)	0.4456 (0.0257)	-0.0404 (0.0023)	0.0017 (0.0001)	0.02

0.9999	47.56 (0.13)	0.0718 (0.0058)	0.0112 (0.0009)	-0.0002 (0.0004)	0.03
1.9998	49.55 (0.23)	0.3233 (0.0457)	-0.0567 (0.0080)	0.0012 (0.0002)	0.25
3.0001	51.30 (0.37)	-0.2173 (0.0355)	0.0307 (0.0050)	-0.0002 (0.0001)	0.31
4.0005	52.28 (0.32)	-0.3986 (0.0399)	0.0508 (0.0225)	-0.0002 (0.0001)	0.10
		Glycine - KCl - H_2O			
0.9999	46.96 (0.39)	0.1576 (0.0158)	0.0004 (0.0001)	-0.0009 (0.0001)	0.20
2.0001	49.52 (0.10)	-0.0772 (0.0044)	0.0211 (0.0012)	-6.6993×10^{-6} (0.3868×10^{-6})	0.05
3.0007	51.25 (0.02)	-0.1875 (0.0108)	0.0262 (0.0015)	-5×10^{-5} (0.29×10^{-5})	0.01
4.0006	51.69 (0.42)	1.6295 (0.3120)	-0.4056 (0.0778)	-0.1955 (0.0374)	0.33
		Glycine - KBr - H_2O			
0.5016	45.43 (0.14)	0.4970 (0.0406)	-0.0483 (0.0039)	-0.0029 (0.0002)	0.08
1.0009	47.66 (0.01)	0.1163 (0.0067)	-0.5×10^{-4} (0.03×10^{-4})	0.0025 (0.0001)	0.01
2.0006	48.72 (0.69)	0.6304 (0.0364)	-0.0943 (0.0054)	-9.036×10^{-8} (0.52×10^{-8})	0.09
3.0001	51.01 (0.11)	-0.1286 (0.0074)	0.0241 (0.0014)	0.0007 (0.0001)	0.06
4.0040	52.86 (0.90)	-1.083 (0.140)	0.1348 (0.0174)	0.1554 (0.0201)	0.03

		Glycine - $MgCl_2$ - H_2O			
0.1001	44.21 (0.26)	0.3510	-0.0156	-0.0197	0.08
		(0.0286)	(0.0013)	(0.0016)	
0.4995	48.59 (0.30)	-0.4955	0.0783	0.0042	0.09
		(0.0404)	(0.006)	(0.0003)	
0.9999	52.67 (0.55)	-1.390	0.1903	0.0017	0.16
		(0.160)	(0.0220)	(0.0002)	
1.5004	56.32 (0.12)	-3.065	0.5851	-0.0012	0.01
		(0.177)	(0.0338)	(0.0001)	
		L-alanine – KCl – H_2O			
1.0032	65.59 (0.25)	-2.135	0.8900	-0.0012	0.14
		(0.276)	(0.1149)	(0.0001)	
2.0033	68.15 (0.33)	-2.967	1.154	0.0012	0.17
		(0.343)	(0.133)	(0.0001)	
3.0029	70.01 (0.53)	-4.368	1.859	0.0002	0.30
		(0.756)	(0.322)	(0.0001)	
4.0012	70.86 (0.49)	-4.217	1.710	0.0002	0.26
		(0.243)	(0.099)	(0.0001)	
		L-alanine – $MgCl_2$ – H_2O			
0.0511	62.68 (0.10)	-0.9887	0.2735	-0.0216	0.09
		(0.0989)	(0.0273)	(0.0022)	
0.4966	65.49 (0.03)	-0.6345	0.0504	0.0025	0.03
		(0.0366)	(0.0029)	(0.0001)	
0.9989	68.16 (0.01)	-0.9406	0.0058	0.0027	0.01
		(0.0543)	(0.0003)	(0.0001)	
1.5024	67.63 (0.34)	1.095	-0.5564	0.0007	0.29
		(0.167)	(0.0850)	(0.0001)	
		Glycylglycine – KCl – H_2O			
0.5003	82.34 (0.69)	-2.956	1.450	0.0057	0.01
		(0.171)	(0.084)	(0.0003)	

1.0003	83.80 (0.20)	-0.8823	0.3364	0.0015	0.01
		(0.051)	(0.019)	(0.0001)	
1.5003	86.49 (0.34)	-1.852	0.6471	0.0015	0.01
		(0.107)	(0.037)	(0.0001)	
2.0003	87.18 (0.14)	-0.7194	0.1932	0.0013	0.01
		(0.041)	(0.007)	(0.0001)	
		Glycylglycine – KBr – H_2O			
0.4999	79.64 (0.48)	-6.911	3.219	6.270	0.01
		(0.399)	(0.186)	(0.362)	
1.0001	84.11 (0.12)	-0.2444	0.1513	0.0015	0.01
		(0.0141)	(0.0087)	(0.0001)	
1.5001	86.54 (0.14)	-0.5206	0.1887	-0.0007	0.01
		(0.0300)	(0.0109)	(0.0001)	
2.0004	89.52 (0.43)	2.149	0.8550	0.0014	0.01
		(0.122)	(0.0494)	(0.0001)	
		Glycylglycine – Na_2SO_4 - H_2O			
0.4998	83.66 (0.35)	-0.3104	0.2387	0.0006	0.05
		(0.0179)	(0.0138)	(0.0001)	
1.0001	87.79 (0.32)	-0.6246	0.2193	-0.0016	0.05
		(0.0510)	(0.0179)	(0.0001)	
1.5006	90.52 (0.34)	-1.050	0.2280	-0.0004	0.05
		(0.061)	(0.0132)	(0.0001)	
2.0016	88.65 (0.25)	0.1038	0.1667	0.0015	0.04
		(0.0060)	(0.0096)	(0.0001)	
		Glycine - $(CH_3)_4NBr$ – H_2O			
0.2580	43.50 (0.04)	0.3329	0.0077	-3×10^{-5}	0.01
		(0.0192)	(0.0004)	(0.2×10^{-5})	
0.5320	43.84 (0.17)	0.2819	0.0137	-0.0024	0.03
		(0.0163)	(0.0008)	(0.0001)	
0.8239	44.14 (0.12)	0.0044	0.0826	-0.0018	0.05
		(0.0002)	(0.0048)	(0.0001)	

1.134	44.22 (0.12)	0.3302	-0.0092	0.0017	0.03
		(0.0191)	(0.0005)	(0.0001)	
1.8386	44.71 (0.03)	0.4727	-0.0333	0.0006	0.01
		(0.0273)	(0.0.0019)	(0.0001)	
		Glycine - $(C_2H_5)_4NBr - H_2O$			
0.1020	43.15 (0.10)	0.5571	-0.0517	-0.0152	0.02
		(0.0322)	(0.0030)	(0.0009)	
0.4023	43.55 (0.02)	0.3289	0.0175	0.0577	0.01
		(0.019)	(0.0010)	(0.0033)	
0.5490	43.78 (0.02)	0.4797	-0.0373	-0.0878	0.01
		(0.0277)	(0.0021)	(0.0051)	
1.2115	44.05 (0.13)	0.6534	-0.1054	0.0012	0.02
		(0.0377)	(0.0061)	(0.0001)	
		Glycine - $(C_4H_9)_4NBr - H_2O$			
0.0509	43.18 (0.22)	0.4850	-0.0289	0.0285	0.03
		(0.0280)	(0.0017)	(0.0016)	
0.1034	43.33 (0.08)	0.4965	-0.0436	0.0162	0.01
		(0.0287)	(0.0025)	(0.0009)	
0.2709	43.44 (0.01)	0.5430	-0.0466	-0.0003	0.01
		(0.0313)	(0.0027)	(0.0001)	
0.5890	44.27 (0.13)	0.3006	0.0124	0.0011	0.02
		(0.0173)	(0.0007)	(0.0001)	
0.7318	44.60 (0.01)	0.3113	-0.0009	0.0014	0.01
		(0.0180)	(0.0001)	(0.0001)	
		L-alanine - $(CH_3)_4NBr - H_2O$			
0.2581	60.34 (0.29)	-0.0277	0.3230	-0.0014	0.10
		(0.0028)	(0.032)	(0.0001)	
0.5325	60.77 (0.02)	0.3385	-0.0440	-0.0604	0.01
		(0.0195)	(0.0025)	(0.0035)	
0.8239	60.49 (0.19)	-0.5768	0.4844	0.4565	0.03
		(0.0333)	(0.0280)	(0.0263)	

1.1340	60.97 (0.02)	-0.4270	0.5615	-0.0008	0.01
		(0.0246)	(0.0324)	(0.0001)	
1.8386	61.11 (0.05)	0.5251	-0.0243	0.0008	0.02
		(0.0303)	(0.0014)	(0.0001)	
		L-alanine - $(C_2H_5)_4NBr - H_2O$			
0.1020	60.45 (0.02)	0.2375	0.0355	0.0157	0.01
		(0.0137)	(0.0020)	(0.0009)	
0.2622	60.32 (0.03)	0.5254	-0.1097	0.0053	0.02
		(0.0303)	(0.0063)	(0.0003)	
0.5490	60.55 (0.03)	0.2257	0.0138	0.0082	0.01
		(0.0130)	(0.0008)	(0.0005)	
1.2115	60.59 (0.04)	0.1492	0.0905	0.0575	0.01
		(0.0086)	(0.0052)	(0.0033)	
		L-alanine - $(C_4H_9)_4NBr - H_2O$			
0.0509	60.52 (0.06)	0.1403	0.1073	0.0417	0.01
		(0.0081)	(0.0062)	(0.0024)	
0.1034	60.31 (0.01)	0.4732	-0.0851	-0.0115	0.01
		(0.0273)	(0.0049)	(0.0007)	
0.2709	60.46 (0.02)	0.2619	0.0092	0.0097	0.01
		(0.0151)	(0.0005)	(0.006)	
0.5890	60.90 (0.08)	-0.0418	0.1573	-0.0029	0.04
		(0.0024)	(0.0001)	(0.0002)	
0.7318	60.95 (0.04)	0.1108	0.0909	0.0259	0.01
		(0.0064)	(0.0052)	(0.0015)	
		Glycylglycine - $(CH_3)_4NBr - H_2O$			
0.2579	77.01 (0.01)	0.7272	0.0162	0.0051	0.01
		(0.0420)	(0.0009)	(0.0003)	
0.5322	77.06 (0.01)	0.8051	-0.00001	0.0011	0.01
		(0.0465)	(0.5×10^{-6})	(0.0001)	
0.8105	77.70 (0.11)	0.1547	0.3022	0.0692	0.04
		(0.0089)	(0.0174)	(0.0040)	

		Glycylglycine – $(C_2H_5)_4NBr$ – H_2O			
0.1020	76.77 (0.02)	0.8842	-0.0423	-0.0924	0.01
		(0.0510)	(0.0024)	(0.0053)	
0.2623	77.15 (0.07)	0.4325	0.1520	0.1189	0.02
		(0.0250)	(0.0088)	(0.0069)	
0.5491	77.14 (0.07)	0.6094	0.1549	0.0529	0.02
		(0.0352)	(0.0089)	(0.0030)	
1.2122	77.28 (0.01)	1.065	-0.00001	0.0016	0.01
		(0.061)	(0.5×10^{-6})	(0.0001)	
		Glycylglycine – $(C_4H_9)_4Br$ – H_2O			
0.0509	76.86 (0.05)	0.5991	0.1201	0.4753	0.02
		(0.0346)	(0.0069)	(0.0274)	
0.2709	77.09 (0.07)	1.0468	-0.1518	-0.0952	0.02
		(0.0604)	(0.0088)	(0.0055)	
0.5889	78.10 (0.12)	0.1813	0.2731	0.0875	0.05
		(0.0105)	(0.0158)	(0.0050)	

Table 6.5: The deviations of experimental properties from the correlated properties, ϕ_{AJW}

Electrolyte	Glycine		L-alanine		Glycylglycine	
	10^{-3} $\Delta\rho$ / (kg m^{-3})	Δu / (m s^{-1})	10^{-3} $\Delta\rho$ / (kg m^{-3})	Δu / (m s^{-1})	10^{-3} $\Delta\rho$ / (kg m^{-3})	Δu / (m s^{-1})
NaBr	254	1.3	—	—	—	—
KCl	94	1.7	75	1.1	4	0.5
KBr	158	2.0	—	—	4	0.3
$MgCl_2$	118	1.1	87	0.9	—	—
Na_2SO_4	—	—	—	—	36	0.1
$(CH_3)_4NBr$	53	—	44	—	12	—
$(C_2H_5)_4NBr$	10	—	7	—	53	—
$(C_4H_9)_4NBr$	10	—	36	—	48	—

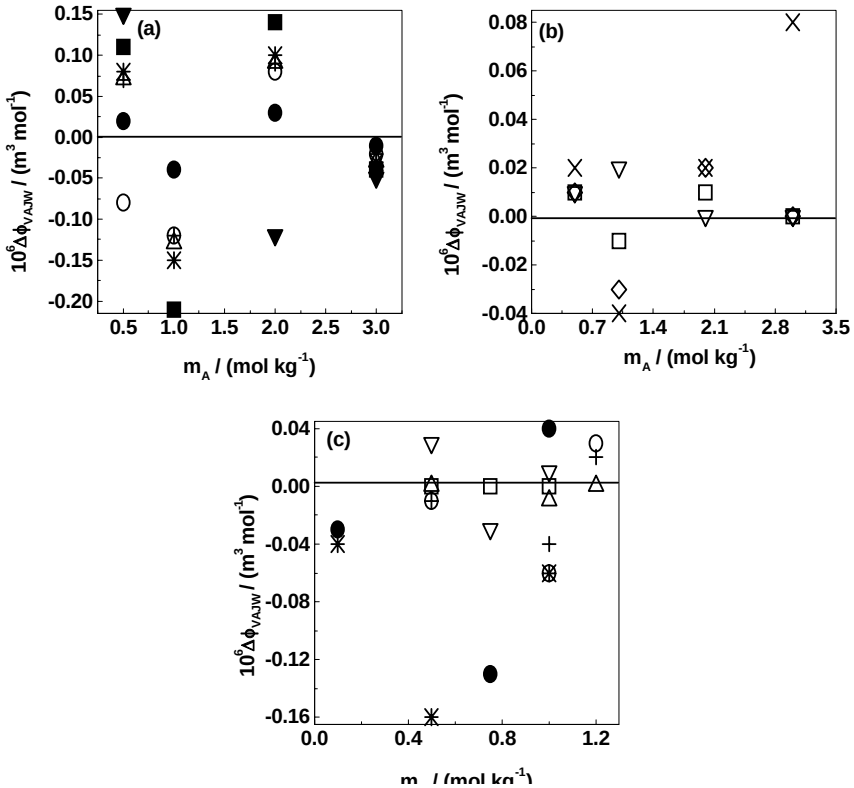


Figure 6.5: Plots of $\Delta\phi_{VAJW}$ as a function m_A for **(a)** glycine + KCl 1 mol kg^{-1} (T), 2 mol kg^{-1} (λ); + KBr 0.5 mol kg^{-1} (+), 4 mol kg^{-1} (τ); + NaBr 4 mol kg^{-1} (Δ); + $MgCl_2$ 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (ν); **(b)** glycine + KCl 3 mol kg^{-1} (ο), + KBr 1 mol kg^{-1} (∇), + NaBr 0.5 mol kg^{-1} (◊), 1 mol kg^{-1} (X); **(c)** L-alanine + KCl 2 mol kg^{-1} (T) + $MgCl_2$ 0.05 mol kg^{-1} (λ), 0.5 mol kg^{-1} (∇), 1 mol kg^{-1} (ο); glycylglycine + KCl 2 mol kg^{-1} (Δ); + Na_2SO_4 1.5 mol kg^{-1} (O), 2 mol kg^{-1} (+)

The interaction coefficient between amino acid and electrolytes, λ^V_{AJW} deduced from the apparent molar volume for systems listed in **Table 6.4** are plotted in **Figure 6.6 (a, b)** as a function of m_J. In general, λ_{AJW} decreases in a majority of cases showing the dominance of zwitterionic head group – ion (COO^- - Na^+ and NH_3^+ - Cl^-) interaction than the ion – ion and amino acid – amino acid interactions, an

observation consistent with the trend of λ_{AJW} obtained during the analysis of activity coefficient data. The λ^{V}_{AJW} obtained using **equation (11)** are transferred to **equation (12)** in order to fit the ϕ_{VJAW} - m_J data. The Pitzer coefficients $\beta^{(0)V}_{MXA}$, $\beta^{(1)V}_{MXA}$ and $C^{\varphi V}_{MXA}$ along with the apparent molar volume of electrolyte at infinite dilution in presence of amino acid, $\phi_V{}^0_{JAW}$ are tabulated in **Table 6.6**. In **Figure 6.7 (a)** are plotted the experimental ϕ_{VJAW} as a function of m_J for some representative systems glycine – NaBr, glycine – KCl, glycine – KBr, L-alanine – $MgCl_2$ and glycylglycine – Na_2SO_4 having 1 mol kg^{-1} amino acid. Also shown are the calculated values in the form of lines in contrast to the experimental data points. An excellent agreement between the two values can be seen upon the examination of **Figure 6.7 (a)**. Accurate densities of the aqueous amino acid – electrolyte solutions can be calculated from the ϕ_{VJAW} values obtained from the use of **equation (12).** The deviation in densities, $\Delta\rho$ are shown in **Figure 6.7 (b and c)** as a function of m_J for glycine, L-alanine and glycylglycine in different electrolytes. A random scatter in $\Delta\rho$ values is noted throughout. The overall scatter ranges in between –100 to 60 x 10^{-3} kg m^3. **Table 6.5** shows a list of $\Delta\rho$ values obtained from such an exercise. The $\phi_V{}^0_{JAW}$ data of electrolytes are not reported in literature. The only data that can be compared are the $\phi_V{}^0_{JW}$. The $\phi_V{}^0_{JW}$ values obtained here for NaBr = 23.48 x 10^{-6} m^3 mol^{-1}(23.48 x 10^{-6} m^3 mol^{-1} [234,235], 23.45 x 10^{-6} m^3 mol^{-1} [236]), KCl = 26.85 x 10^{-6} m^3 mol^{-1}(26.90 x 10^{-6} m^3 mol^{-1} [237], 26.89 x 10^{-6} m^3 mol^{-1} [238]), KBr = 33.73 x 10^{-6} m^3 mol^{-1}(33.73 x 10^{-6} m^3 mol^{-1} [234] 33.75 x 10^{-6} m^3 mol^{-1} [239]), $MgCl_2$ = 14.52 x 10^{-6} m^3 mol^{-1} (14.49 x 10^{-6} m^3 mol^{-1} [240], 14.6 x 10^{-6} m^3 mol^{-1} [241],) and that for Na_2SO_4 = 11.56 x 10^{-6} m^3 mol^{-1} (11.62

x 10^{-6} m^3 mol^{-1} [240], 11.64 x 10^{-6} m^3 mol^{-1} [235], are in close agreement with the literature values.

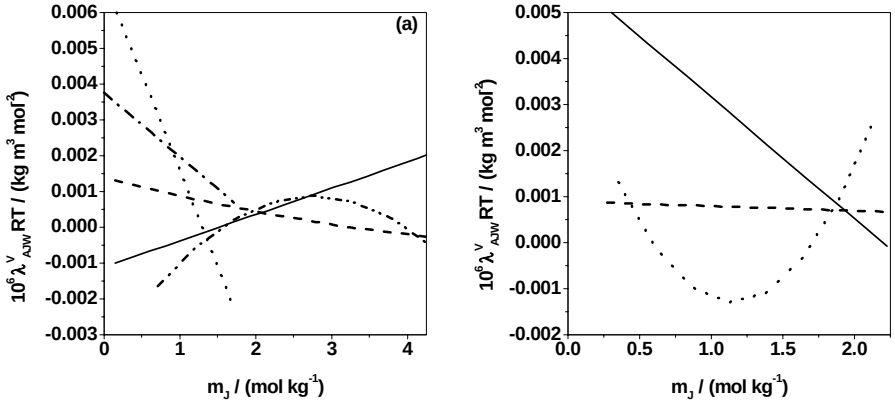


Figure 6.6: Variation of λ^V_{AJW} as a function of m_J in **(a)** glycine + KBr (———), NaBr (— — —), $MgCl_2$ (……); L-alanine + KCl (. . — . . — . .), $MgCl_2$ (. — . — .) **(b)** glycylglycine KCl (——), KBr (— —) and Na_2SO_4 (…….)

Table 6.6: Pitzer coefficients for apparent molar volume of electrolytes obtained in experimentally studied systems

m_A / (mol kg^{-1})	10^6 $\phi_V{}^0_{JAW}$ / (m^3 mol^{-1})	10^{16} $\beta^{(0)V}_{MXA}$ / (kg mol^{-1} Pa^{-1})	10^{16} $\beta^{(1)V}_{MXA}$ / (kg mol^{-1} Pa^{-1})	10^{17} $C^{\varphi V}_{MXA}$ / (kg^2 mol^{-2} Pa^{-1})	10^6 rmsd / (m^3 mol^{-1})
		Glycine – NaBr – H_2O			
0.5006	28.08 (0.01)	-0.3876 (0.0224)	-2.004 (0.115)	0.6954 (0.0401)	0.02
1.0006	31.43 (0.09)	-2.002 (0.115)	-2.003 (0.100)	2.253 (0.130)	0.04
2.0004	36.87 (0.40)	-2.003 (0.150)	-2.002 (0.200)	1.257 (0.131)	0.36
3.0012	40.87 (0.22)	-3.001 (0.173)	-2.002 (0.114)	3.071 (0.177)	0.03

		Glycine – KCl – H_2O			
0.5002	30.28 (0.01)	0.6086	-3.001	-0.7465	0.03
		(0.0351)	(0.173)	(0.0431)	
0.9985	32.23 (0.08)	0.1912	-3.003	0.2100	0.03
		(0.0110)	(0.173)	(0.0121)	
2.0001	36.49 (0.03)	2.002	-3.002	2.087	0.03
		(0.115)	(0.200)	(0.120)	
3.0002	38.49 (0.04)	1.001	-2.001	1.242	0.02
		(0.058)	(0.115)	(0.072)	
		Glycine – KBr – H_2O			
0.4998	38.53 (0.29)	-0.1518	2.001	0.2909	0.18
		(0.0124)	(0.163)	(0.0237)	
1.0010	41.45 (0.43)	-0.1488	2.002	-0.5246	0.33
		(0.0121)	(0.200)	(0.0428)	
2.0001	48.28 (0.56)	-4.001	-2.002	4.064	0.42
		(0.327)	(0.160)	(0.3318)	
3.0004	51.75 (0.16)	-4.002	-2.003	3.265	0.16
		(0.516)	(0.258)	(0.421)	
		Glycine – $MgCl_2$ – H_2O			
0.5004	22.74 (0.15)	-8.002	-4.020	30.1 (17.3)	0.22
		(0.462)	(0.231)		
1.0004	26.09 (0.43)	-6.001	-4.010	20.1 (4.5)	0.10
		(1.342)	(0.894)		
2.0005	36.33 (0.48)	-27.0 (4.9)	-4.010	80.2 (14.6)	0.47
			(0.730)		
3.0002	39.66 (0.19)	-27.1 (4.9)	-3.010	100.1	0.24
			(0.548)	(18.26)	
		L-alanine – KCl – H_2O			
0.0505	28.04 (0.07)	1.050	-3.001	-0.6730	0.01
		(0.002)	(0.101)	(0.0438)	

0.1001	28.40 (0.05)	0.9170	-3.002	-0.5951	0.01
		(0.0005)	(0.005)	(0.0125)	
0.5004	30.57 (0.15)	0.3250	-3.002	-0.0407	0.02
		(0.2654)	(0.245)	(0.0033)	
0.9999	32.76 (0.01)	-0.0841	-3.003	0.2863	0.02
		(0.0048)	(0.173)	(0.0165)	
		L-alanine – $MgCl_2$ – H_2O			
0.1007	19.90 (0.29)	-10.01	-2.010	40.0 (6.53)	0.48
		(1.63)	(0.327)		
0.5007	24.45 (0.31)	-16.00	-4.002	50.1 (9.57)	0.41
		(3.06)	(0.766)		
0.7503	26.78 (0.11)	-18.03	-2.003	59.9 (6.00)	0.40
		(1.80)	(0.200)		
1.0005	27.54 (0.25)	-14.01	-2.001	40.1 (7.30)	0.22
		(2.56)	(0.365)		
		Glycylglycine – KCl – H_2O			
0.4998	31.59 (0.13)	0.4667	-2.001	-1.340	0.01
		(0.0269)	(0.115)	(0.077)	
1.0001	34.55 (0.45)	-0.6045	-2.004	1.561	0.01
		(0.0349)	(0.120)	(0.090)	
1.2002	35.92 (0.50)	-6.001	5.002	20.02 (2.00)	0.22
		(0.600)	(0.499)		
		Glycylglycine – KBr – H_2O			
0.5001	41.42 (0.21)	24.0 (2.7)	-45.1 (5.2)	-90.0 (10.3)	0.14
1.0001	46.51 (0.35)	49.1 (7.5)	-88.0 (13.4)	-190. (29.0)	0.26
1.2001	47.08 (0.08)	46.2 (15.0)	-82.2 (26.8)	-170. (55.5)	0.96
		Glycylglycine – Na_2SO_4 – H_2O			
0.4998	27.10 (0.22)	2.005	-14.0 (0.8)	3.001	0.04
		(0.115)		(0.173)	
1.0001	36.00 (0.33)	-1.999	-14.1 (0.1)	7.801	0.02
		(0.001)		(0.001)	

1.1999	39.96 (0.45)	-6.002 (0.346)	-14.1 (0.8)	10.2 (0.58)	0.03
		Glycine – $(CH_3)_4NBr$ – H_2O			
0.4949	116.45 (0.97)	-1.402 (0.200)	-2.002 (0.400)	90.01 (18.00)	0.57
0.9948	114.31 (0.01)	-4.002 (0.402)	-2.002 (0.210)	50.02 (5.01)	0.03
1.4904	115.28 (0.77)	-13.01 (2.25)	-2.003 (0.346)	90.01 (15.59)	0.45
1.9958	114.85 (0.01)	-12.02 (0.69)	-1.005 (0.058)	100.2 (5.8)	0.02
		Glycine – $(C_2H_5)_4NBr$ – H_2O			
0.5001	173.23 (0.05)	-9.002 (0.520)	-0.8683 (0.0501)	20.01 (1.15)	0.03
0.7502	172.36 (0.01)	-8.001 (0.462)	-0.8020 (0.0463)	20.01 (1.09)	0.03
1.0003	172.07 (0.01)	10.02 (0.58)	-0.7318 (0.0422)	30.02 (1.73)	0.03
1.5002	170.73 (0.02)	-8.001 (0.653)	-0.6212 (0.0507)	20.03 (1.63)	0.03
		Glycine – $(C_4H_9)_4NBr$ – H_2O			
0.5001	298.04 (0.30)	-25.01 (2.50)	-0.7768 (0.0778)	130.1 (13.0)	0.28
0.7502	295.64 (0.40)	-16.00 (2.06)	-0.8464 (0.0109)	50.01 (6.45)	0.35
1.0002	294.93 (0.29)	-23.10 (1.88)	-0.8353 (0.0682)	130.1 (10.6)	0.28
1.5003	291.77 (0.21)	-19.01 (1.10)	-0.9308 (0.0537)	90.02 (5.20)	0.20

		L-alanine – $(CH_3)_4NBr$ – H_2O			
0.5001	113.29	2.005	-2.002	30.0 (3.46)	0.39
	(0.61)	(0.231)	(0.231)		
0.7503	114.84	-6.001	-2.003	60.1 (3.50)	0.14
	(0.26)	(0.346)	(0.115)		
1.0010	114.33	-3.002	-1.999	39.9 (3.27)	0.05
	(0.06)	(0.245)	(0.163)		
		L-alanine – $(C_2H_5)_4NBr$ – H_2O			
0.1003	173.85	-7.002	-0.0957	10.02 (0.58)	0.02
	(0.01)	(0.404)	(0.0552)		
0.4999	172.58	-5.005	-1.001	-0.7970	0.20
	(0.27)	(0.289)	(0.058)	(0.0460)	
0.7503	174.54	-7.003	-9.002	7.895	0.22
	(0.32)	(0.571)	(0.735)	(0.645)	
1.0005	170.85	-2.005	-1.003	-10.02	0.22
	(0.30)	(0.115)	(0.058)	(0.01)	
		L-alanine – $(C_4H_9)_4NBr$ – H_2O			
0.1001	299.24	-11.10	-0.8779	-10.05	0.04
	(0.06)	(1.27)	(0.1014)	(1.15)	
0.5002	296.25	-11.10	-0.9455	-1.578	0.06
	(0.08)	(1.25)	(0.1072)	(0.182)	
0.7503	294.33	-8.002	-0.9926	-8.334	0.09
	(0.13)	(1.131)	(0.1404)	(1.179)	
1.0005	292.85	-10.02	-10.05	10.02 (1.53)	0.11
	(0.16)	(1.53)	(1.50)		
		Glycylglycine – $(CH_3)_4NBr$ – H_2O			
0.0997	115.00	-2.003	-1.002	10.03 (0.58)	0.02
	(0.05)	(0.115)	(0.058)		
0.4988	114.53	-4.005	-1.005	20.05 (0.19)	0.10
	(0.44)	(0.401)	(0.101)		

0.7449	114.14 (0.39)	-4.005 (0.399)	-0.9999 (0.100)	20.08 (0.21)	0.10
		Glycylglycine – $(C_2H_5)_4NBr$ – H_2O			
0.1003	172.94 (0.12)	-3.002 (0.387)	-0.9814 (0.0127)	-6.061 (0.782)	0.08
0.5007	171.61 (0.01)	-8.005 (0.462)	-0.7789 (0.0450)	30.02 (1.73)	0.04
0.7480	170.70 (0.05)	-10.02 (0.82)	-0.6352 (0.0519)	40.05 (3.27)	0.06
		Glycylglycine – $(C_4H_9)_4NBr$ – H_2O			
0.1009	299.18 (0.01)	-21.1 (1.21)	-0.8287 (0.0478)	120.0 (6.9)	0.02
0.5008	295.41 (0.01)	-27.2 (1.56)	-1.002 (0.058)	170.1 (9.8)	0.03
0.7530	294.00 (0.01)	-39.9 (2.31)	-2.005 (0.115)	350.0 (20.2)	0.03

Applicability of **equations (11) and (12)** is not only restricted for amino acids and peptides in electrolytes like NaBr, KCl, KBr, $MgCl_2$ and Na_2SO_4. The apparent molar volumes of amino acids and peptide in tetra-n-alkylammonium bromides are also successfully correlated using these equations. The interest in these electrolytes stems from the fact that they undergo hydrophobic hydration, hence their behavior is different from those shown by NaBr, KCl, KBr, $MgCl_2$ and Na_2SO_4. Some representative plots showing the variation of ϕ_{VAJW} of glycine, L-alanine and glycylglycine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ are depicted in **Figure 6.8 (a-c)** where, the experimental data are shown by points and lines represent correlated values. The lines showing the correlated values fall very close to the experimental

quantities showing an excellent agreement between the two. The close correlation between $\phi_{VAJWexp.}$ and $\phi_{VAJWcor.}$ is also reflected in **Table 6.5**, where the $\Delta\rho$ values are listed. The densities can be correlated with average $\Delta\rho < 55 \times 10^{-3}$ kg m^{-3} for these systems.

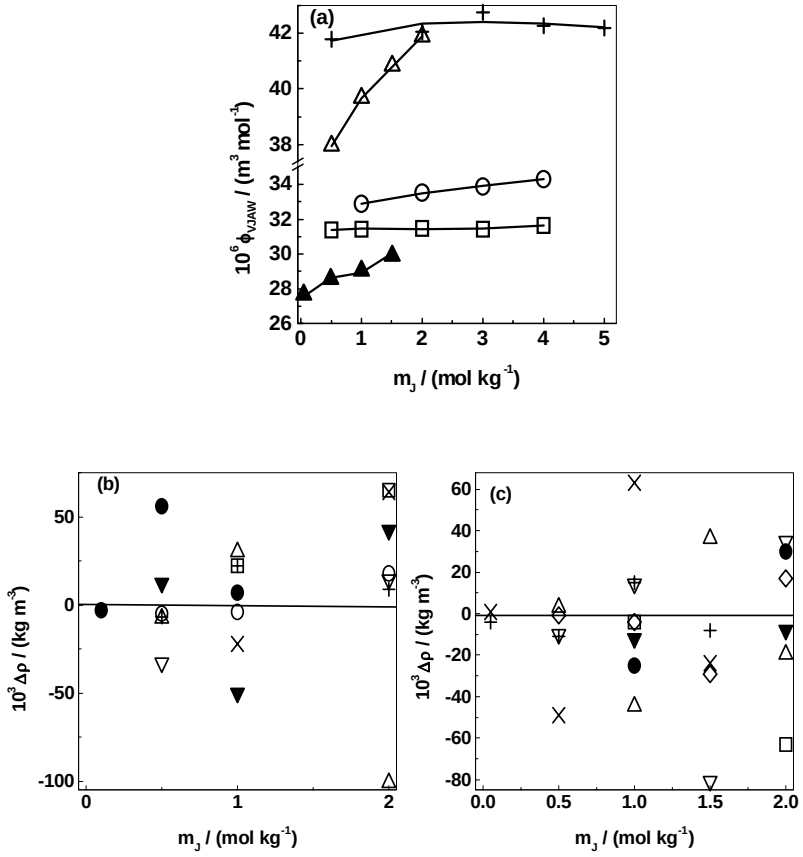


Figure 6.7: Plots of ϕ_{VJAW} vs. m_J for glycine + NaBr (o), glycine + KCl (O), glycine + KBr (+), L-alanine + $MgCl_2$ (σ), glycylglycine + Na_2SO_4 (Δ); Plots of $\Delta\rho$ versus m_J for **(b)** KCl + glycine 0.5 mol kg^{-1} (o), 2 mol kg^{-1} (X), 3 mol kg^{-1} (O); KBr + 1 mol kg^{-1} glycine (∇); NaBr + glycine 0.5 mol kg^{-1} (+), 1 mol kg^{-1} (Δ), 3 mol kg^{-1} (τ); $MgCl_2$ + 0.5 mol kg^{-1} glycine (λ) **(c)** KCl + L-alanine 0.1 mol kg^{-1} (τ), 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (λ); KCl + glycylglycine 0.5 mol kg^{-1} (+), 1 mol kg^{-1} (X); Na_2SO_4 0.5 mol kg^{-1} (∇), 1 mol kg^{-1} ($\Diamond$), 1.2 mol kg^{-1} (Δ)

The correlated values of ϕ_{VJAW} as calculated from λ^{V}_{AJW} and the Pitzer coefficients, listed in **Table 6.6** show deviation of –0.26 to 0.56 x 10^{-6} m^3 mol^{-1}, -0.20

to 0.38 x 10^{-6} m^3 mol^{-1} and –0.22 to 0.38 x 10^{-6} m^3 mol^{-1} in the presence of $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$, respectively. The $\Delta\rho$ values from ϕ_{VJAW} are shown for some representative examples in **Figure 6.9 (a, b and c)**. From the data reported in **Table 6.7,** a range of $\Delta\rho$ from –100 to 100 x 10^{-3} kg m^{-3} is seen in random fashion insisting that the equation described above is a precise expression for the estimation of volumes and densities of the amino acids and peptides as influenced by R_4NBr in aqueous medium.

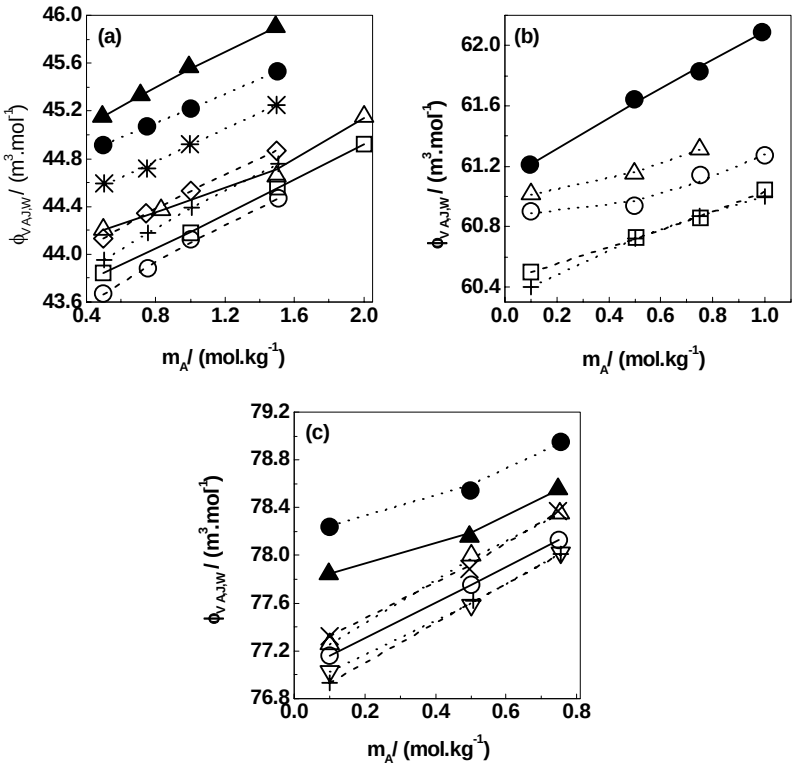


Figure 6.8: Plots of ϕ_{VAJW} vs. m_A a) glycine + $(CH_3)_4NBr$: (o), 0.258 mol kg^{-1}; (Δ), 0.824 mol kg^{-1}; (σ), 1.839 mol kg^{-1}; + $(C_2H_5)_4NBr$: (μ), 0.102 mol kg^{-1}; (◊), 0.549 mol kg^{-1}; + $(C_4H_9)_4NBr$: (+), 0.270 mol kg^{-1}; (T), 0.589 mol kg^{-1}; (λ), 0.730 mol kg^{-1}; b) L-alanine + $(CH_3)_4NBr$: (λ), 1.8386 mol kg^{-1}; + $(C_2H_5)_4NBr$: (o), 0.102 mol kg^{-1}; + $(C_4H_9)_4NBr$: (+), 0.103 mol kg^{-1}; (μ), 0.589 mol kg^{-1}; (Δ), 0.732 mol kg^{-1} c) glycylglycine + $(CH_3)_4NBr$: (μ), 0.258 mol kg^{-1}; (σ), 0.810 mol kg^{-1}; + $(C_2H_5)_4NBr$: (+), 0.102 mol kg^{-1}; (X), 0.549 mol kg^{-1}; + $(C_4H_9)_4NBr$: (∇), 0.05 mol kg^{-1}; (Δ), 0.270 mol kg^{-1}; (λ), 0.589 mol kg^{-1}

Table 6.7: The deviations of experimental properties from the correlated properties, ϕ_{JAW}

Electrolyte	Glycine		L-alanine		Glycylglycine	
	10^{-3} $\Delta\rho$ / (kg m^{-3})	Δu / (m s^{-1})	10^{-3} $\Delta\rho$ / (kg m^{-3})	Δu / (m s^{-1})	10^{-3} $\Delta\rho$ / (kg m^{-3})	Δu / (m s^{-1})
NaBr	114.	0.9	—	—	—	—
KCl	59	1.4	35	1.3	90	0.5
KBr	329	1.3	—	—	259	0.2
$MgCl_2$	238	1.3	269	1.7	—	—
Na_2SO_4	—	—	—	—	31	2.0
$(CH_3)_4NBr$	211	—	166	—	45	—
$(C_2H_5)_4NBr$	13	—	65	—	23	—
$(C_4H_9)_4NBr$	69	—	38	—	5	—

The apparent molar volume of R_4NBr at infinite dilution calculated from the plot of ϕ_{VJW} vs. $m_J^{0.5}$ of this study yielded excellent agreement with the values reported in the literature. In the case of aqueous $(CH_3)_4NBr$, a value of $\phi_V^0{}_{JW}$ 114.9 x 10^{-6} m^3 mol^{-1} agrees with 114.40 x 10^{-6} m^3 mol^{-1} [237], 114.8 x 10^{-6} m^3 mol^{-1} [230] and 114.25 x 10^{-6} m^3 mol^{-1} [232]. A value of 174.1 x 10^{-6} m^3 mol^{-1} for aqueous $(C_2H_5)_4NBr$ is in agreement with those 173.65 x 10^{-6} m^3 mol^{-1}, 174.3 x 10^{-6} m^3 mol^{-1}, 175.0 x 10^{-6} m^3 mol^{-1} reported elsewhere [242-244]. An excellent agreement is noticed between the $\phi_V^0{}_{JW}$ value of $(C_4H_9)_4NBr$ obtained in the current work 300.50 x 10^{-6} m^3 mol^{-1} and that 300.4 x 10^{-6} m^3 mol^{-1} reported earlier [239].

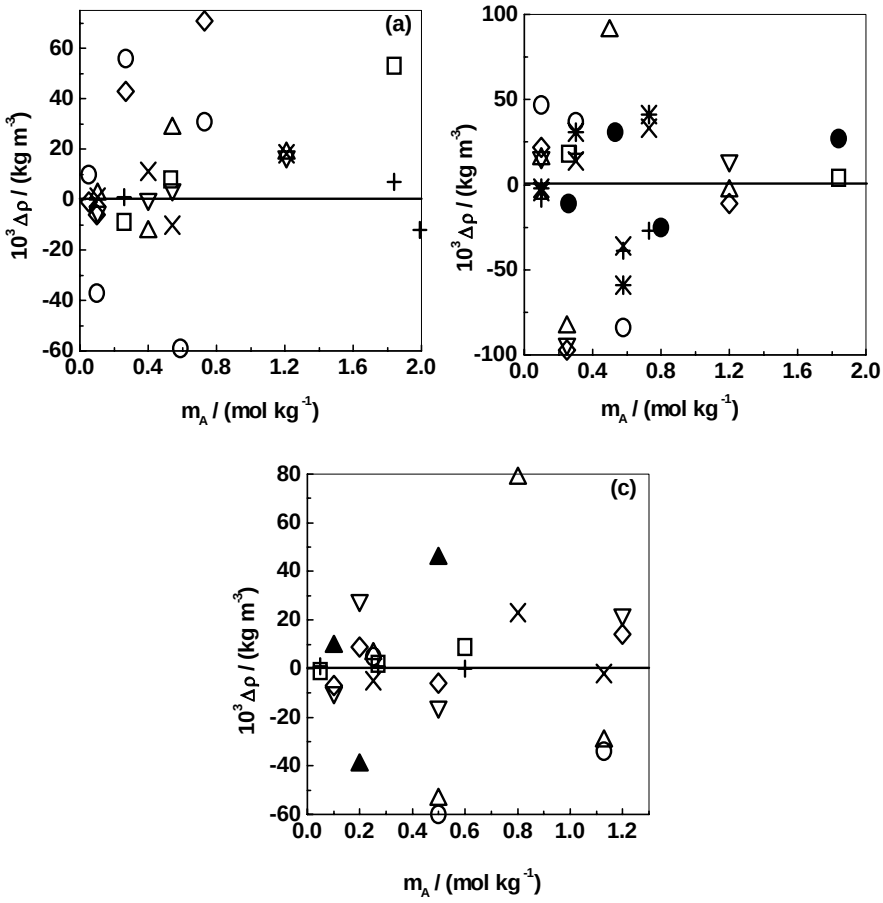


Figure 6.9: Deviations of densities, $\Delta\rho$ as a function of mJ in **(a)** $(CH_3)_4NBr$ + glycine (o) 1 mol kg^{-1}, (+) 2 mol kg^{-1}, $(C_2H_5)_4NBr$ + glycine (Δ) 0.5 mol kg^{-1}, (∇) 0.75 mol kg^{-1}, (X) 1.5 mol kg^{-1}, $(C_4H_9)_4$ + glycine (O) 0.75 mol kg^{-1}, ($\Diamond$) 1.5 mol kg^{-1}; **(b)** $(CH_3)_4NBr$ + L-alanine (o) 0.75 mol kg^{-1}, (λ) 1 mol kg^{-1}, $(C_2H_5)_4NBr$ + L-alanine (Δ) 0.5 mol kg^{-1}, (∇) 0.75 mol kg^{-1}, ($\Diamond$) 1 mol kg^{-1}, $(C_4H_9)_4$ + L-alanine (+) 0.1 mol kg^{-1}, (X) 0.5 mol kg^{-1}, (T) 0.75 mol kg^{-1}, (O) 1 mol kg^{-1}; **(c)** $(CH_3)_4NBr$ + glycylglycine (X) 0.1 mol kg^{-1}, (O) 0.5 mol kg^{-1}, (Δ) 0.75 mol kg^{-1}, $(C_2H_5)_4NBr$ + glycine (σ) 0.1 mol kg^{-1}, ($\Diamond$) 0.5 mol kg^{-1}, (∇) 0.75 mol kg^{-1}, $(C_4H_9)_4$ + glycylglycine (o) 0.1 mol kg^{-1}, (+) 0.5mol kg^{-1}

6.32 (b): Apparent molar volume from the literature:

The strength of **equations (11) and (12)** can be seen from the fact that these equations can be applied to the available literature data producing precise experimental densities. The coefficients of **equation (11)** for glycine, alanine, β-alanine, γ-amino-n-butyric acid, ε-aminocaproic acid, proline, leucine, valine and threonine in NaCl, $NaNO_3$, KCl, KNO_3, KSCN and sodium butyrate are enumerated in **Table 6.8**. NaCl, $NaNO_3$ and KNO_3 enlarge the apparent molar volumes of glycine due to the doubly charged behavior of glycine than to the formation of physically bonded ion-pairs between the charged groups of glycine and the cation and the anion of the electrolyte. This increase in volume approximately by 3×10^{-6} m^3 mol^{-1} can be accurately accounted for by **equation (11)**. **Figure 6.10 (a)** shows the experimental ϕ_{VAJW} as contrasted by the correlated ϕ_{VAJW} for the glycine – 1 mol kg^{-1} aqueous NaCl, KCl, $NaNO_3$ and KNO_3 systems. An examination of the plots given in **Figure 6.10 (a)** confirms that the effect of several electrolytes can be accurately described by **equation (11)**. Average difference in experimental and correlated densities calculated using coefficients from **Table 6.8** are summarized in **Table 6.9**. In **Figure 6.10 (b)** are shown the deviations in densities, $\Delta\rho$ as a function of m_A for glycine, alanine, β-alanine, 6-aminocaproic acid and threonine in KSCN solutions. The $\Delta\rho$ values for some representative systems comprising DL-alanine, glycine and α-amino butyric acid in sodium butyrate, NaCl, KCl, $NaNO_3$ and KNO_3 are depicted in **Figure 6.10 (c).** Both the figures contain the random scattering of $\Delta\rho$ values ($\pm 30 \times 10^{-3}$ kg m^{-3}) throughout the concentration profiles.

Table 6.8: the coefficients for correlation of ϕ_{VAJW} of amino acids in different electrolytes at 298.15 K for literature data

m_J / (mol kg^{-1})	10^6 ${\phi_V}^0_{AJW}$ / (m^3 mol^{-1})	10^6 s_V / (kg m^3 mol^{-2})	10^6 s_V' / (kg^2 m^3 mol^{-3})	10^6 ${\lambda^V}_{AJW}$ RT / (kg m^3 mol^{-2})	10^6 rmsd / (m^3 mol^{-1})
		Glycine – NaCl – H_2O			
0.2	44.00 (0.05)	0.3840 (0.0222)	-0.0154 (0.0009)	-0.0013 (0.0001)	0.01
0.4	44.94 (0.01)	0.2699 (0.0156)	-0.0081 (0.0005)	0.0070 (0.0004)	0.09
0.6	45.46 (0.02)	0.2588 (0.0149)	-0.0063 (0.0004)	0.0010 (0.0001)	0.01
0.8	45.86 (0.03)	0.3163 (0.0183)	-0.0200 (0.0011)	0.0024 (0.0001)	0.02
1	46.24 (0.03)	0.3800 (0.0219)	-0.0327 (0.0019)	-0.0019 (0.0001)	0.01
		Glycine – $NaNO_3$ – H_2O			
0.2	44.21 (0.01)	0.4161 (0.0240)	-0.0227 (0.0013)	-0.3998 (0.0231)	0.04
0.4	45.02 (0.01)	0.3314 (0.0191)	-0.0142 (0.0008)	-0.1199 (0.0069)	0.01
0.6	45.78 (0.01)	0.2927 (0.0169)	-0.0153 (0.0009)	-0.0896 (0.0052)	0.02
0.8	46.46 (0.01)	0.1823 (0.0105)	-0.0013 (0.0001)	-0.0087 (0.0005)	0.02
1	46.88 (0.01)	0.2408 (0.0139)	-0.0106 (0.0006)	-0.0358 (0.0021)	0.01
		Glycine - KCl - H_2O			
0.2	44.36 (0.01)	0.2928 (0.0169)	-0.0065 (0.0004)	-0.1095 (0.0063)	0.01

0.4	45.02 (0.01)	0.3270	-0.0167	-0.1330	0.03
		(0.0189)	(0.0010)	(0.0077)	
0.6	45.59 (0.01)	0.3586	-0.0243	-0.1214	0.05
		(0.0207)	(0.0014)	(0.0070)	
0.8	46.25 (0.01)	0.3128	-0.0209	-0.0933	0.01
		(0.0180)	(0.0012)	(0.0054)	
1.0	46.78 (0.01)	0.2445	-0.0107	-0.0399	0.04
		(0.0141)	(0.0006)	(0.0023)	
		Glycine - KNO_3 - H_2O			
0.2	44.31 (0.01)	0.4139	0.0233	-0.4233	0.01
		(0.0239)	(0.0013)	(0.0244)	
0.4	45.14 (0.01)	0.3578	-0.0204	-0.1671	0.02
		(0.0206)	(0.0012)	(0.0096)	
0.6	46.01 (0.01)	0.2658	-0.0118	-0.0655	0.03
		(0.0153)	(0.0007)	(0.0038)	
0.8	46.73 (0.01)	0.1804	-0.0035	-0.0178	0.01
		(0.0104)	(0.0002)	(0.0010)	
1	47.25 (0.01)	0.2002	-0.0082	-0.0320	0.02
		(0.0115)	(0.0005)	(0.0018)	
		Glycine – $CH_3(CH_2)_2COONa$ – H_2O			
0.5	44.67 (0.05)	0.1399	0.3108	0.0002	0.04
		(0.0081)	(0.0179)	(0.0001)	
1	45.91 (0.04)	0.3933	-0.3231	-4×10^{-5}	0.03
		(0.0227)	(0.0186)	(0.23×10^{-5})	
1.5	46.78 (0.07)	0.6225	-0.7438	-6.7×10^{-4}	0.06
		(0.0359)	(0.0429)	(0.39×10^{-5})	
2	48.23 (0.02)	-0.6124	0.2915	-1.3×10^{-4}	0.02
		(0.0353)	(0.0168)	(0.07×10^{-4})	
		DL-alanine - $CH_3(CH_2)_2COONa$ – H_2O			
0.5	61.52 (0.02)	-0.1272	0.2526	0.0021	0.02
		(0.0073)	(0.0146)	(0.0001)	

1	62.36 (0.03)	0.5063	-0.3855	0.0020	0.03
		(0.0292)	(0.0222)	(0.0001)	
1.5	62.91 (0.03)	0.1199	0.0734	-0.0003	0.03
		(0.0069)	(0.0042)	(0.0001)	
2	63.68 (0.03)	0.4518	-0.6693	-0.0004	0.03
		(0.0261)	(0.0386)	(0.0001)	
	DL-amino butyric acid - $CH_3(CH_2)_2COONa$ – H_2O				
0.5	76.31 (0.03)	0.0377	0.0845	-0.0037	0.02
		(0.0022)	(0.0049)	(0.0002)	
1	76.80 (0.02)	0.2616	0.0232	0.0006	0.02
		(0.0151)	(0.0013)	(0.0003)	
1.5	77.17 (0.03)	0.4753	0.0608	-3.0×10^{-5}	0.03
		(0.0274)	(0.0035)	(0.17×10^{-5})	
2	77.88 (0.04)	0.9719	-0.8582	0.0004	0.04
		(0.0561)	(0.0495)	(0.0002)	
	Valine - $CH_3(CH_2)_2COONa$ – H_2O				
0.5	91.32 (0.05)	0.2523	-0.6524	0.0030	0.04
		(0.0146)	(0.0378)	(0.0002)	
1	91.52 (0.05)	0.7117	-0.8462	0.0007	0.06
		(0.0411)	(0.0488)	(0.0001)	
1.5	91.92 (0.05)	0.0216	0.6323	0.0003	0.04
		(0.0012)	(0.0365)	(0.0001)	
2	92.48 (0.03)	0.9435	-0.5170	-0.0004	0.03
		(0.0545)	(0.0298)	(0.0001)	
	Leucine - $CH_3(CH_2)_2COONa$ – H_2O				
0.5	107.50 (0.12)	2.969	-20.16	-0.0020	0.04
		(0.1714)	(1.16)	(0.0001)	
1	107.78 (0.12)	2.618	-16.62	0.0014	0.05
		(0.1512)	(0.96)	(0.0001)	
1.5	108.03 (0.06)	6.605	-49.24	0.0008	0.03
		(0.3813)	(2.84)	(0.0001)	

2	108.32 (0.06)	6.168	-41.30	0.0004	0.03
		(0.356)	(2.38)	(0.0001)	
		Glycine – KSCN – H_2O			
1	44.72 (0.04)	-0.1625	0.3962	0.0021	0.03
		(0.0094)	(0.0229)	(0.0001)	
3	46.68 (0.08)	0.4167	-1.192	-0.0005	0.04
		(0.0240)	(0.069)	(0.0001)	
5	46.99 (0.04)	-0.1879	-0.9631	-0.0003	0.03
		(0.0108)	(0.0556)	(0.0001)	
		Alanine – KSCN – H_2O			
1	61.85 (0.05)	0.2306	-0.0118	-0.0017	0.05
		(0.0133)	(0.0007)	(0.0001)	
3	62.87 (0.03)	0.1158	-0.1309	0.0005	0.03
		(0.0067)	(0.0075)	(0.0001)	
5	64.19 (0.05)	0.3038	-0.3286	0.0002	0.03
		(0.0175)	(0.0190)	(0.0001)	
		Proline – KSCN – H_2O			
1	84.43 (0.04)	-0.1995	0.2232	0.0022	0.03
		(0.0115)	(0.0129)	(0.0001)	
3	86.32 (0.06)	-0.5978	0.4284	-0.0006	0.06
		(0.0345)	(0.0247)	(0.0001)	
5	86.70 (0.12)	0.8776	-1.448	-0.0002	0.05
		(0.0507)	(0.084)	(0.0001)	
		Threonine – KSCN – H_2O			
1	78.35 (0.04)	0.8125	-0.3442	0.0029	0.04
		(0.0469)	(0.0199)	(0.0001)	
3	80.47 (0.23)	0.4322	-0.3021	-0.0003	0.08
		(0.0249)	(0.0174)	(0.0001)	
5	82.63 (0.09)	-3.827	5.637	0.0002	0.06
		(0.221)	(0.325)	(0.0001)	

		β-alanine – KSCN – H_2O			
1	60.27 (0.06)	-1.167	1.659	-0.0007	0.04
		(0.095)	(0.135)	(0.0001)	
3	61.45 (0.11)	0.6040	-1.031	0.0006	0.08
		(0.0349)	(0.059)	(0.0001)	
5	62.03 (0.08)	1.136	-1.398	0.0003	0.05
		(0.066)	(0.081)	(0.0001)	
		ε-aminocaproic acid – KSCN - H_2O			
1	106.31 (0.05)	-0.3514	0.4566	0.0001	0.05
		(0.0203)	(0.0264)	(0.000_5)	
3	109.07 (0.10)	-2.247	3.223	0.0001	0.05
		(0.129)	(0.186)	(0.000_3)	
5	110.22 (0.07)	-2.106	3.315	-0.0001	0.05
		(0.122)	(0.191)	(0.000_2)	
		γ-aminobutyric acid – KSCN – H_2O			
1	75.10 (0.05)	-0.7083	0.9332	0.0021	0.04
		(0.0409)	(0.0539)	(0.0001)	
3	76.43 (0.06)	0.2769	-0.0530	0.0005	0.05
		(0.0160)	(0.0030)	(0.0001)	
5	77.66 (0.11)	-1.198	2.305	0.0005	0.06
		(0.069)	(0.133)	(0.0001)	

Table 6.9: Average differences in the experimental and correlated densities and sound speeds for the data form literature at 298.15 K.

System	10^{-3} Δρ / kg m^{-3}	Δu / m s^{-1}	10^{-3} Δρ / kg m^{-3}	10^{-3} Δu
	Back calculated from ϕ_{AJW}		Back calculated from ϕ_{JAW}	
Glycine – NaCl – H_2O	25	0.8	41	0.2
Glycine – $NaNO_3$ – H_2O	23	0.3	64	1.0
Glycine – KCl – H_2O	25	0.3	76	1.0
Glycine – KNO_3 – H_2O	22	0.4	67	1.2

Alanine – KSCN – H_2O	6	121
Proline – KSCN – H_2O	12	134
Glycine – KSCN – H_2O	6	140
Threonine – KSCN – H_2O	10	144
6-aminocaproic acid – KSCN – H_2O	8	176
γ-amino butyric acid – KSCN – H_2O	11	111
β - alanine	46	91
Glycine – sodium butyrate – H_2O	6	55
DL-alanine – sodium butyrate – H_2O	10	27
Leucine – sodium butyrate – H_2O	12	69
Valine – sodium butyrate – H_2O	8	53
α-amino butyric acid – sodium butyrate – H_2O	6	257

The amino acid – electrolyte – water coefficients, λ^{V}_{AJW} obtained from apparent molar volumes are plotted as a function of m_J in **Figures 6.11, 6.12 and 6.13** for different systems taken from the literature. The Pitzer coefficients for these systems are tabulated in **Table 6.10**. The difference between the experimental $\phi_{VJAWexp.}$ and the $\phi_{VJAWcor.}$ obtained using the coefficients listed in **Table 6.10** are plotted in **Figure 6.14** for the KSCN-containing mixtures of glycine, β-alanine and threonine. The deviations, scattered in their distribution are less than $\pm$ 0.15 x 10^{-6} m^3 mol^{-1}.

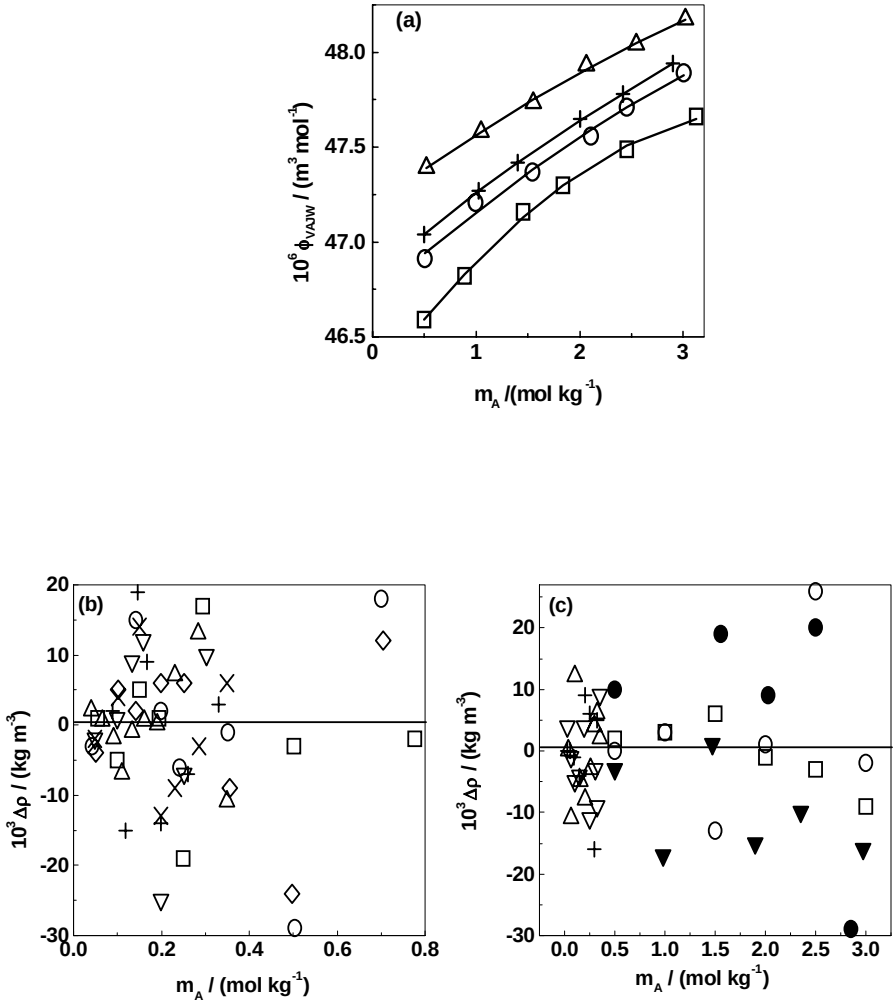


Figure 6.10: (a) Variation of ϕ_{VAJW} with m_A for glycine + 1 mol kg^{-1} of NaCl (o), $NaNO_3$ (+), KCl (O), KNO_3 (Δ); Plots of Δρ versus m_A for literature data systems **(b)** glycine + 5 mol kg^{-1} KSCN (Δ), alanine + 1 mol kg^{-1} KSCN (o), Proline + 3 mol kg^{-1} KSCN (O), β-alanine + 5 mol kg^{-1} KSCN (X); γ-amino butyric acid + 5 mol kg^{-1} KSCN (∇), 6-aminocaproic acid + 1 mol kg^{-1} KSCN (◊), threonine + 3 mol kg-1 KSCN (+) **(c)** DL-alanine + 0.5 mol kg^{-1} sodium butyrate, (+), glycine + 1.5 mol kg^{-1} sodium butyrate (Δ), α-amino butyric acid + 1 mol kg^{-1} sodium butyrate (∇), glycine + 0.2 mol kg^{-1} NaCl (o), glycine + 0.4 mol kg^{-1} $NaNO_3$ (O), glycine + 0.8 mol kg^{-1} KCl (τ), glycine + 0.6 mol kg^{-1} KNO_3 (λ)

Table 6.10: Pitzer coefficients for apparent molar volume of systems from literature.

m_A / (mol kg^{-1})	10^6 $\phi_V{}^0_{JAW}$ / (m^3 mol^{-1})	10^{11} $\beta^{(0)V}_{MXA}$ / (kg mol^{-1} Pa^{-1})	10^{11} $\beta^{(1)V}_{MXA}$ / (kg mol^{-1} Pa^{-1})	10^{11} $C^{\varphi V}_{MXA}$ / (kg^2 mol^{-2} Pa^{-1})	10^6 rmsd / (m^3 mol^{-1})
		Glycine - NaCl - H_2O			
0.4967	19.64 (0.10)	0.2656 (0.0153)	-1.005 (0.058)	-4.003 (0.231)	0.04
0.9788	21.13 (0.36)	4.001 (0.231)	-1.002 (0.060)	-40.01 (2.30)	0.17
1.4665	23.12 (0.26)	-0.1889 (0.0154)	-1.002 (0.049)	-0.9020 (0.0520)	0.12
1.9255	25.17 (0.11)	-2.002 (0.115)	-1.001 (0.050)	-5.457 (0.315)	0.04
2.4678	26.02 (0.10)	-0.2310 (0.0133)	-1.006 (0.055)	-5.887 (0.340)	0.05
2.9973	27.58 (0.19)	-5.003 (0.289)	-0.9999 (0.052)	30.02 (1.73)	0.10
		Glycine – $NaNO_3$ - H_2O			
0.5	32.11 (0.07)	-4.005 (0.2309)	0.5824 (0.0336)	30.02 (1.73)	0.04
1	34.47 (0.11)	-6.003 (0.4899)	2.005 (0.1633)	40.04 (3.27)	0.0
2	38.76 (0.29)	14.02 (1.61)	6.004 (0.693)	90.05 (10.39)	0.13
2.5	40.66 (0.35)	-18.10 (2.08)	8.002 (0.924)	12.01 (13.86)	0.14
		Glycine – KCl - H_2O			
0.5	30.33 (0.15)	-1.005 (0.058)	-0.9853 (0.0567)	9.898 (0.571)	0.07

1	32.62 (0.21)	-1.006 (0.060)	-0.8049 (0.0465)	3.954 (0.228)	0.09
2	36.04 (0.25)	-0.7452 (0.0740)	-0.4407 (0.0441)	-7.576 (0.437)	0.13
2.5	37.35 (0.62)	-1.005 (0.058)	-0.2364 (0.0136)	-4.080 (0.236)	0.29
		Glycine - KNO_3 - H_2O			
0.5	42.02 (0.11)	-3.002 (0.173)	0.7456 (0.0430)	20.02 (1.15)	0.06
1	44.69 (0.21)	-5.002 (0.289)	3.002 (0.173)	30.05 (1.73)	0.09
2	49.70 (0.02)	16.02 (0.92)	6.005 (0.346)	100.1 (5.8)	0.01
2.5	51.55 (0.28)	-20.03 (1.15)	8.004 (0.462)	120.1 (6.9)	0.12
		Glycine – $CH_3(CH_2)_2COONa$ – H_2O			
0.1	70.05 (0.12)	0.8445 (0.0844)	-2.002 (0.201)	0.0609 (0.0061)	0.05
0.2	70.35 (0.11)	0.7375 (0.0738)	-2.001 (0.200)	0.2030 (0.2000)	0.05
0.3	70.62 (0.10)	0.8544 (0.0698)	-1.005 (0.082)	-0.1218 (0.0009)	0.05
0.35	70.79 (0.10)	0.4377 (0.0440)	-2.005 (0.199)	0.8786 (0.088)	0.05
		DL-alanine - $CH_3(CH_2)_2COONa$ – H_2O			
0.1	69.86 (0.20)	1.005 (0.082)	-2.002 (0.163)	-1.612 (0.132)	0.05
0.2	69.83 (0.07)	2.002 (0.163)	-2.004 (0.160)	-4.063 (0.332)	0.02

0.3	69.63 (0.08)	3.002	-2.004	-7.970	0.01
		(0.173)	(0.115)	(0.460)	
0.35	69.47 (0.17)	4.002	-2.001	-10.02 (5.77)	0.03
		(0.231)	(0.105)		
		DL-amino butyric acid - $CH_3(CH_2)_2COONa$ – H_2O			
0.1	70.31 (0.28)	0.3270	-2.002	1.570	0.07
		(0.0327)	(0.201)	(0.160)	
0.2	70.89 (0.29)	-0.3448	-2.002	3.499	0.07
		(0.0340)	(0.199)	(0.400)	
0.3	71.48 (0.32)	-1.001	-2.003	5.350	0.08
		(0.101)	(0.200)	(0.530)	
0.35	71.75 (0.35)	-1.005	-2.001	6.290	0.08
		(0.011)	(0.231)	(0.726)	
		Valine - $CH_3(CH_2)_2COONa$ – H_2O			
0.1	70.01 (0.29)	0.8239	-2.002	0.4772	0.07
		(0.0673)	(0.163)	(0.0389)	
0.2	71.10 (0.34)	-0.8004	-2.002	5.119	0.08
		(0.0653)	(0.160)	(0.418)	
0.3	72.68 (0.04)	-0.9453	-3.001	2.246	0.01
		(0.0772)	(0.245)	(0.183)	
0.35	74.24 (0.12)	-3.001	-2.005	5.358	0.03
		(0.245)	(0.159)	(0.437)	
		Leucine - $CH_3(CH_2)_2COONa$ – H_2O			
0.02	69.83 (0.18)	0.9083	-2.001	-0.0562	0.07
		(0.0908)	(0.200)	(0.0060)	
0.03	69.86 (0.18)	0.8996	-2.003	-0.0038	0.07
		(0.0900)	(0.199)	(0.0004)	
0.04	69.86 (0.17)	0.9611	-2.001	-0.1513	0.07
		(0.0960)	(0.205)	(0.0150)	
0.05	69.85 (0.17)	1.002	-2.001	-0.4222	0.07
		(0.100)	(0.210)	(0.0400)	

		Glycine – KSCN – H_2O			
0.1	50.96 (0.07)	-0.0777	-3.002	0.6165	0.05
		(0.0045)	(0.173)	(0.0356)	
0.15	51.07 (0.08)	-0.0866	-3.001	0.5964	0.05
		(0.0005)	(0.170)	(0.0344)	
0.2	51.18 (0.08)	-0.0955	-3.001	0.5762	0.05
		(0.0055)	(0.169)	(0.0333)	
0.25	51.26 (0.08)	-0.1015	-3.001	0.5629	0.05
		(0.0059)	(0.171)	(0.0325)	
0.3	51.36 (0.08)	-0.1217	-3.002	0.5630	0.05
		(0.0070)	(0.160)	(0.0320)	
		Alanine – KSCN – H_2O			
0.075	50.98 (0.07)	-0.0777	-3.001	0.6164	0.05
		(0.0045)	(0.173)	(0.0356)	
0.1	51.06 (0.07)	-0.1031	-3.002	0.6501	0.04
		(0.0059)	(0.170)	(0.0375)	
0.2	51.36 (0.06)	-0.1645	-3.001	0.7086	0.04
		(0.0095)	(0.170)	(0.0409)	
0.25	51.50 (0.05)	-0.1995	-3.001	0.7513	0.04
		(0.0115)	(0.165)	(0.0434)	
		Proline – KSCN – H_2O			
0.05	50.93 (0.08)	-0.0445	-3.002	0.5850	0.05
		(0.0026)	(0.173)	(0.0338)	
0.1	51.13 (0.08)	-0.0664	-3.002	0.5963	0.05
		(0.0038)	(0.170)	(0.0344)	
0.2	51.51 (0.07)	-0.1102	-3.004	0.6189	0.05
		(0.0064)	(0.160)	(0.0357)	
0.3	51.85 (0.08)	-0.1190	-3.006	0.5989	0.05
		(0.0069)	(0.175)	(0.0346)	

		Threonine – KSCN – H_2O			
0.05	50.89 (0.08)	-0.0191	-3.002	0.5513	0.06
		(0.0011)	(0.173)	(0.0318)	
0.1	51.06 (0.08)	-0.0410	-3.004	0.5627	0.05
		(0.0024)	(0.170)	(0.0325)	
0.2	51.38 (0.08)	-0.0848	-3.001	0.5853	0.05
		(0.0049)	(0.170)	(0.0338)	
0.25	51.53 (0.08)	-0.0954	-3.004	0.5764	0.05
		(0.0055)	(0.165)	(0.0333)	
		β-alanine – KSCN – H_2O			
0.1	51.18 (0.05)	-0.1977	-3.002	0.7396	0.04
		(0.0114)	(0.173)	(0.0427)	
0.2	51.46 (0.04)	-0.2434	-3.001	0.7732	0.03
		(0.0140)	(0.170)	(0.0446)	
0.3	51.70 (0.04)	-0.2636	-3.004	0.7730	0.03
		(0.0152)	(0.165)	(0.0446)	
0.35	51.80 (0.05)	-0.2618	-3.001	0.7619	0.03
		(0.0151)	(0.160)	(0.0440)	
		ε-aminocaproic acid – KSCN - H_2O			
0.05	50.96 (0.10)	0.0738	-3.001	0.4727	0.06
		(0.0043)	(0.170)	(0.0273)	
0.1	51.22 (0.10)	0.0597	-3.002	0.4862	0.06
		(0.0034)	(0.160)	(0.0281)	
0.2	51.71 (0.10)	0.0554	-3.001	0.4615	0.06
		(0.0032)	(0.165)	(0.0266)	
0.25	51.96 (0.10)	0.0430	-3.001	0.4638	0.06
		(0.0025)	(0.150)	(0.0268)	
		γ-aminobutyric acid – KSCN – H_2O			
0.1	51.27 (0.06)	-0.1847	-3.001	0.7082	0.04
		(0.0107)	(0.165)	(0.0409)	

0.2	51.63 (0.05)	-0.2286	-3.004	0.7306	0.04
		(0.0132)	(0.177)	(0.0422)	
0.3	51.96 (0.05)	-0.2583	-3.004	0.7395	0.04
		(0.0149)	(0.170)	(0.0427)	

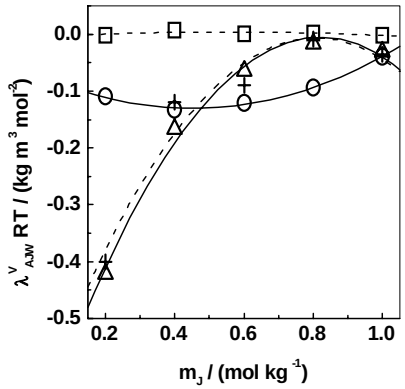


Figure 6.11: Variation of λ^{V}_{AJW} as a function of m_J for glycine + NaCl (o), $NaNO_3$ (+), KCl (O), KNO_3 (Δ)

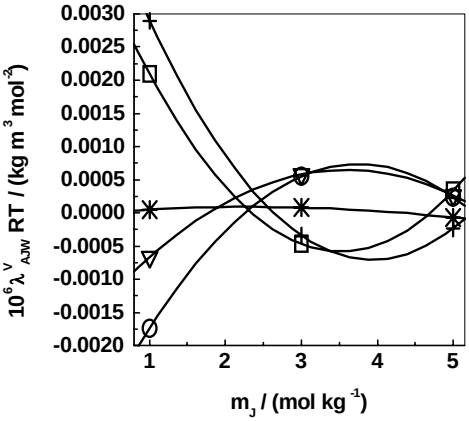


Figure 6.12: Plots of λ^{V}_{AJW} as a function of m_J in KSCN + glycine (o), alanine (O), threonine (+), β-alanine (∇), ε-amino caproic acid (T) systems

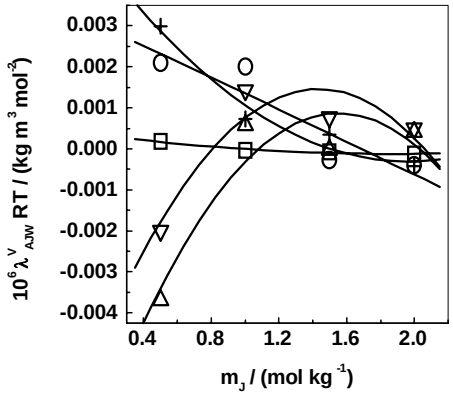


Figure 6.13: Variation of λ^{V}_{AJW} as a function of m_J for sodium butyrate + glycine (o), DL-alanine (O), DL-amino butyric acid (Δ), leucine (∇), valine (+)

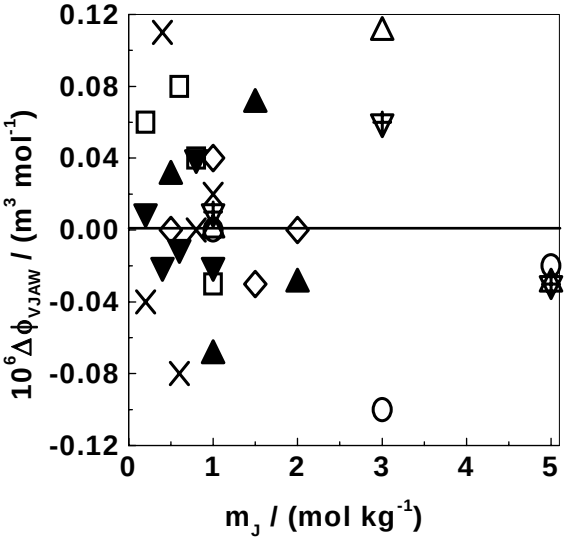


Figure 6.14: Plots of $\Delta\phi_{VJAW}$ versus m_J for 0.1 mol kg^{-1} β-alanine + KSCN (+), 0.3 mol kg^{-1} glycine + KSCN (Δ), 0.25 mol kg^{-1} threonine + KSCN (O), 0.25 mol kg^{-1} alanine + KSCN (∇), 0.35 mol kg^{-1} alanine + sodium butyrate (◊), 0.1 mol kg^{-1} glycine + sodium butyrate (σ), 0.5 mol kg^{-1} glycine + $NaNO_3$ (τ), 2.0 mol kg^{-1} glycine + KCl (ο), 1 mol kg^{-1} glycine + KNO_3 (X)

6.33: Apparent molar compressibility

6.33 (a) Apparent molar compressibility experimental data obtained in this laboratory:

In section **6.32** the pressure derivative of **equations (8) and (9)** (volume) were elaborated. It is also important to study the second pressure derivatives of **equations (8) and (9)** for delineating the compressibility of the mixtures. The apparent molar compressibility of amino acids, ϕ_{KAJW} and that of electrolytes, ϕ_{KJAW} in the aqueous mixtures were correlated using **equations (13) and (14)**, respectively. The

coefficients obtained from **equation (13)** $\phi_K^0{}_{AJW}$, S_K, S_K' and $\lambda^K{}_{AJW}$ for different experimental systems are listed in **Table 6.11**. The $\phi_K^0{}_{AJW}$ of amino acids are not available in literature for comparison. The $\phi_K^0{}_{AJW}$ of glycine in 2 mol kg^{-1} of KCl obtained experimentally is –15.29 x 10^{-15} m^3 mol^{-1} Pa^{-1} while the value in literature is –11.03 x 10^{-15} m^3 mol^{-1} Pa^{-1} [186]. The $\phi_K^0{}_{AW}$ of amino acids (glycine = -27.00 x 10^{-15} m^3 mol^{-1} Pa^{-1}, L-alanine = -25.16 x 10^{-15} m^3 mol^{-1} Pa^{-1} and glycylglycine = -33.5 x 10^{-15} m^3 mol^{-1} Pa^{-1}) are in good agreement with those reported earlier [48,70].

Table 6.11: Coefficients for the apparent molar compressibility of amino acids and peptide in the presence of electrolytes at 298.15 K for the experimentally studied systems.

m_J / (mol kg^{-1})	10^{15} $\phi_K^0{}_{AJW}$ / (m^3 mol^{-1} Pa^{-1})	10^{15} s_K / (kg m^3 mol^{-2} Pa^{-1})	10^{15} s_K' / (kg^2 m^3 mol^{-3} Pa^{-1})	10^{15} $\lambda^K{}_{AJW}$ RT / (kg m^3 mol^{-2} Pa^{-1})	10^{15} rmsd / (m^3 mol^{-1} Pa^{-1})
		Glycine - NaBr - H_2O			
0.5005	-21.9 (1.40)	3.002 (0.005)	-0.3001 (0.0005)	0.0485 (0.0001)	0.48
0.9999	-17.5 (1.80)	3.401 (0.009)	-0.4001 (0.0010)	-0.0034 (0.0001)	0.53
1.9998	-7.41 (0.35)	1.102 (0.001)	-0.0967 (0.0001)	-0.0006 (0.0001)	0.10
3.0001	1.16 (1.27)	-0.8002 (0.0009)	0.2004 (0.0002)	0.0006 (0.0001)	0.38
4.0005	4.15 (1.79)	-2.101 (0.005)	0.5002 (0.0013)	0.0001 (0.0000_5)	0.53
		Glycine - KCl - H_2O			
0.9999	-24.25 (0.02)	5.801 (0.032)	-0.7005 (0.0038)	-0.0025 (0.0001)	2.16

2.0001	-15.29 (0.11)	4.600	-0.6004	0.0001	1.08
		(0.017)	(0.0022)	(0.0000_3)	
3.0007	-4.89 (0.05)	1.402	-0.1001	-0.0004	0.62
		(0.004)	(0.0002)	(0.0001)	
4.0006	-3.83 (0.06)	2.101	-0.2001	0.0067	0.16
		(0.002)	(0.0002)	(0.0001)	
		Glycine - KBr - H_2O			
0.5016	-16.0 (0.25)	0.0266	0.1001	0.0614	0.32
		(0.0001)	(0.0003)	(0.0002)	
1.0009	-12.5 (0.59)	1.001	-0.0810	-0.0047	0.01
		(0.003)	(0.0002)	(0.0001)	
2.0006	-8.58 (0.04)	1.902	-0.3004	-0.0006	0.19
		(0.006)	(0.0009)	(0.0001)	
3.0001	0.531 (0.008)	-0.0732	-0.0081	0.0001	0.18
		(0.0008)	(0.0001)	(0.0000_4)	
4.0040	7.67 (0.12)	-1.502	0.1005	0.0003	0.30
		(0.002)	(0.0002)	(0.0001)	
		Glycine - $MgCl_2$ - H_2O			
0.1001	-20.22 (0.85)	0.3001	0.1004	-0.0594	0.26
		(0.0005)	(0.0002)	(0.0001)	
0.4995	-6.75 (0.10)	-2.301	0.4002	-0.0130	0.85
		(0.006)	(0.0011)	(0.0004)	
0.9999	2.32 (0.09)	-3.300	0.5001	0.0003	0.58
		(0.012)	(0.0018)	(0.0001)	
1.5004	5.01 (0.08)	-2.902	0.6002	0.0008	0.35
		(0.001)	(0.0001)	(0.0001)	
		L-alanine – KCl – H_2O			
1.0032	-4.04 (0.02)	4.001	-3.200	-0.0017	0.01
		(0.037)	(0.029)	(0.0001)	
2.0033	-0.924 (0.08)	4.001	-2.602	-0.0001	1.0
		(0.013)	(0.007)	(0.0000_5)	

3.0029	1.77 (0.05)	5.002 (0.040)	5.001 (0.004)	-0.0006 (0.0001)	0.01
4.0012	4.70 (0.21)	6.201 (0.087)	-1.101 (0.015)	0.0001 (0.0000_3)	0.01
		L-alanine – $MgCl_2$ – H_2O			
0.0511	-21.1 (0.91)	-1.001 (0.001)	1.300 (0.001)	-0.5001 (0.0003)	0.01
0.4966	-6.92 (1.20)	-0.8002 (0.0132)	-1.002 (0.002)	0.0005 (0.0001)	0.60
0.9989	0.53 (2.41)	-2.701 (0.007)	0.9001 (0.0024)	-0.0001 (0.0000_1)	1.21
1.5024	7.20 (2.63)	0.0159 (0.0001)	-1.200 (0.003)	-0.0008 (0.0001)	1.31
		Glycylglycine – KCl – H_2O			
0.5003	-29.3 (1.61)	7.701 (0.014)	-1.801 (0.003)	-3.501 (0.006)	0.45
1.0003	-20.9 (0.48)	3.100 (0.002)	-0.6001 (0.0001)	-0.5002 (0.0003)	0.12
1.5003	-12.3 (1.41)	4.502 (0.008)	-1.601 (0.003)	-1.102 (0.002)	0.36
2.0003	-9.3 (1.55)	-3.301 (0.007)	1.702 (0.004)	0.9001 (0.0019)	0.42
		Glycylglycine – KBr – H_2O			
0.4999	-27.7 (0.31)	1.201 (0.001)	0.4002 (0.0002)	0.7001 (0.0004)	0.08
1.0001	-21.1 (0.34)	2.902 (0.002)	-0.3001 (0.0002)	-0.3002 (0.0316)	1.09
1.5001	-16.8 (1.43)	6.801 (0.004)	-1.702 (0.001)	-1.101 (0.001)	0.37
2.0004	-15.0 (1.06)	0.801 (0.001)	1.201 (0.001)	0.6001 (0.0003)	0.29

Glycylglycine – Na_2SO_4 – H_2O

0.4998	-8.701 (1.18)	-25.6 (0.1)	9.501 (0.005)	17.1 (0.1)	0.03
1.0001	8.32 (0.95	-16.5 (0.2)	6.100 (0.003)	0.7001 (0.0004)	0.01
1.5006	9.80 (0.56)	-16.9 (0.1)	5.901 (0.003)	2.301 (0.001)	0.01
2.0016	16.70 (0.08)	-8.40 (0.1)	3.002 (0.002)	-0.9001 (0.0005)	0.01

The accuracy of estimation of ϕ_{KAJW} can be seen from **Figure 6.15** where, experimental data are shown as points and correlated data as lines as a function of m_A for glycine, L-alanine and glycylglycine in NaBr, KCl, KBr, $MgCl_2$ and Na_2SO_4 systems. It is interesting to find that the equations that are based on the second derivative of excess Gibbs free energy of mixing are quite accurate in correlating the positive and negative concentration dependence of ϕ_{KAJW} of amino acids when dissolved in ionic solutions of variety. Further, the correlated ϕ_{KAJW} when converted to speed of sound agree well with those measured in this laboratory. This can be seen from a glance at **Table 6.5,** where a summary of Δu is recorded for all the systems. The average Δu values for glycine, L-alanine and glycylglycine are observed to be less than 1.5, 1.0 and 0.3 m s^{-1}, respectively.

Variation of λ^K_{AJW} as a function of m_J is shown in **Figure 6.16**. The glycine – electrolyte and L-alanine – electrolyte systems show positive slopes for λ^K_{AJW} versus m_J plots, while glycylglycine shows strong negative slope for glycylglycine – KCl –

water system. The plot indicates stronger association of ions with glycylglycine as compared to glycine and L-alanine.

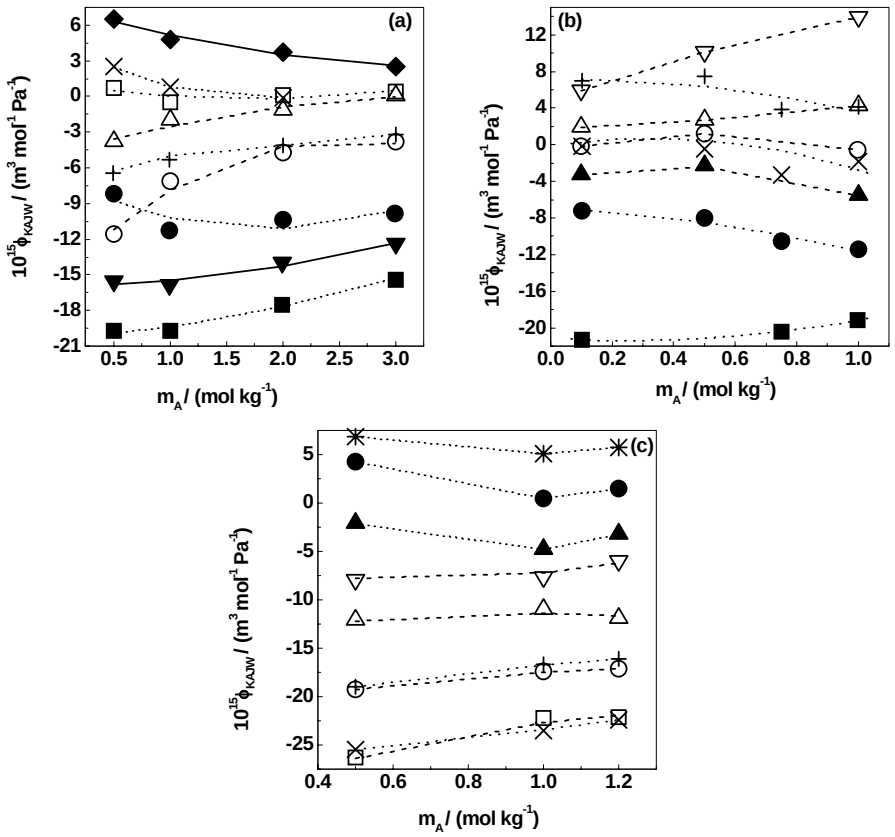


Figure 6.15: Plots of ϕ_{KAJW} versus m_A for **(a)** glycine + KCl 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), + KBr 0.5 mol kg^{-1} (τ), 4 mol kg^{-1} (υ), + NaBr 2 mol kg^{-1} (+), 3 mol kg^{-1} (ο), + $MgCl_2$ 0.1 mol kg^{-1} (ν), 0.5 mol kg^{-1} (λ), 1.5 mol kg^{-1} (X), **(b)** L-alanine + KCl 1 mol kg^{-1} (σ), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (∇); $MgCl_2$ 0.05 mol kg^{-1} (ν), 0.5 mol kg^{-1} (λ), 1 mol kg^{-1} (X), 1.5 mol kg^{-1} (+), (c) glycylglycine + KCl 0.5 mol kg^{-1} (ο), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (∇), + KBr 0.5 mol kg^{-1} (X), 1 mol kg^{-1} (+), Na_2SO_4 1 mol kg^{-1} (σ), 1.5 mol kg^{-1} (λ), 2 mol kg^{-1} (T)

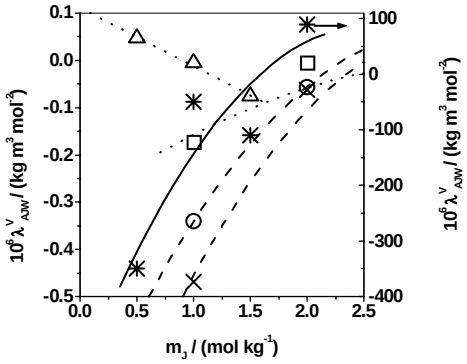


Figure 6.16: Plot of λ^K_{AJW} versus m_J for glycine + KBr (X), glycine + NaBr (O), L-alanine + KCl (o), L-alanine + $MgCl_2$ (Δ), glycylglycine + KCl (T)

The Pitzer coefficients for the electrolytes in amino acids were obtained by regressing ϕ_{KJAW} using **equation (14)**. The Pitzer coefficients for the electrolytes are tabulated in **Table 6.12**. A difficult test of testing **equation (14)** is given in **Figure 6.17**, where the Δu are plotted as a function of m_J. In **Figure 6.17 (a)** Δu obtained from correlated ϕ_{KJAW} of NaBr, KCl, KBr and $MgCl_2$ and **Figure 6.17 (b)** presents ϕ_{KJAW} of KCl, KBr, $MgCl_2$ and Na_2SO_4 in L-alanine, glycylglycine. The tabulation of Δu values obtained from ϕ_{KJAW} are listed in **Table 6.7**. The average rmsd in ϕ_{KJAW} observed for glycine, L-alanine and glycylglycine are 0.38 x 10^{-15} m^3 mol^{-1} Pa^{-1}, 0.79 x 10^{-15} m^3 mol^{-1} Pa^{-1} and 0.46 x 10^{-15} m^3 mol^{-1} Pa^{-1}, respectively.

Table 6.12: Pitzer coefficients for apparent molar compressibility of electrolytes obtained in experimentally studied systems

m_A / (mol kg^{-1})	10^{15} ${\phi_K}^0_{JAW}$ / (m^3 mol^{-1} Pa^{-1})	10^{19} $\beta^{(0)K}_{MXA}$ / (kg mol^{-1} Pa^{-2})	10^{20} $\beta^{(1)K}_{MXA}$ / (kg mol^{-1} Pa^{-2})	10^{20} $C^{\varphi K}_{MXA}$ / (kg^2 mol^{-2} Pa^{-2})	10^{15} rmsd / (m^3 mol^{-1} Pa^{-1})
		Glycine – KCl – H_2O			
0.5002	-40.06 (0.12)	1.981 (0.004)	6.147 (0.011)	-2.051 (0.004)	0.07
0.9985	-29.32 (0.11)	1.221 (0.002)	6.210 (0.011)	-1.052 (0.002)	0.07
2.0001	-18.15 (0.08)	0.7155 (0.0131)	7.295 (0.013)	-0.3635 (0.0066)	0.56
3.0002	-14.18 (0.71)	1.336 (0.002)	4.077 (0.007)	-2.339 (0.0043)	1.48
		Glycine – KBr – H_2O			
0.4998	-24.0 (0.02)	0.0750 (0.0014)	4.823 (0.009)	-0.3708 (0.0007)	0.24
1.0010	-19.4 (0.01)	0.7005 (0.0013)	4.721 (0.009)	-0.3648 (0.0007)	0.20
2.0001	-9.74 (0.03)	0.5371 (0.0003)	3.879 (0.002)	-0.5218 (0.0003)	0.26
3.0004	-5.31 (0.01)	0.4303 (0.0008)	3.452 (0.006)	-0.4302 (0.0008)	0.11
		Glycine – NaBr – H_2O			
0.5006	-36.04 (0.09)	1.414 (0.001)	4.671 (0.0027)	-1.407 (0.001)	0.14
1.0006	26.66 (0.12)	0.8190 (0.0005)	4.487 (0.002)	-0.7160 (0.0001)	0.26
2.0004	-15.51 (0.86)	0.3714 (0.0002)	4.157 (0.002)	-0.2474 (0.0001)	0.10

3.0012	-10.49 (0.55)	0.3092 (0.0007)	3.657 (0.008)	-0.0162 (0.0001)	0.41
		Glycine – $MgCl_2$ – H_2O			
0.5004	-71.68 (1.12)	5.606 (0.101)	7.956 (0.016)	-11.07 (0.02)	0.76
1.0004	-63.80 (1.50)	5.717 (0.010)	8.198 (0.014)	-11.32 (0.02)	0.56
2.0005	-42.95 (0.88)	3.722 (0.009)	8.575 (0.024)	-70.96 (0.02)	0.52
3.0002	-32.71 (0.95)	2.400 (0.001)	7.928 (0.005)	1.125 (0.001)	0.43
		L-alanine – KCl – H_2O			
0.1001	-38.5 (1.14)	1.530 (0.001)	6.145 (0.003)	-1.496 (0.001)	0.27
0.5004	-25.3 (1.09)	0.3808 (0.0010)	6.351 (0.002)	0.0308 (0.0001)	0.26
0.9999	-23.6 (1.05)	0.4660 (0.0003)	6.274 (0.004)	0.0600 (0.0003)	0.19
		L-alanine – $MgCl_2$ – H_2O			
0.1007	-90.1 (1.02)	7.797 (0.014)	4.463 (0.008)	-14.80 (0.03)	1.45
0.5007	-75.10 (1.98)	6.683 (0.024)	8.367 (0.030)	-12.77 (0.05)	1.80
0.7503	-70.80 (1.13)	6.358 (0.016)	5.383 (0.014)	-11.53 (0.03)	1.60
1.0005	-64.10 (2.06)	5.039 (0.003)	6.631 (0.004)	-6.27 (1.08)	0.50
		Glycylglycine – KCl – H_2O			
0.4998	-35.1 (0.38)	1.848 (0.003)	20.56 (0.04)	-3.491 (0.006)	0.07

1.0001	-22.5 (2.67)	-0.3101 (0.0008)	37.13 (0.10)	2.127 (0.005)	0.59
1.2002	-20.0 (0.42)	-0.9003 (0.0016)	43.50 (0.08)	4.489 (0.008)	0.10
		Glycylglycine – KBr – H_2O			
0.5001	-26.8 (0.29)	2.844 (0.002)	-7.318 (0.001)	-8.077 (0.005)	0.07
1.0001	-23.0 (0.07)	4.715 (0.003)	-18.32 (0.01)	-15.70 (0.01)	0.43
1.2001	-17.4 (0.68)	3.962 (0.002)	-22.66 (0.01)	-12.92 (0.01)	0.14
		Glycylglycine – Na_2SO_4 – H_2O			
0.4998	-104.4 (0.86)	9.316 (0.024)	-131.6 (0.3)	-14.20 (0.04)	0.70
1.0001	-88.70 (1.7)	11.76 (0.03)	-310.6 (0.8)	-22.05 (0.06)	0.94
1.1999	-77.50 (1.1)	11.62 (0.04)	-356.9 (1.1)	-23.29 (0.07)	1.11

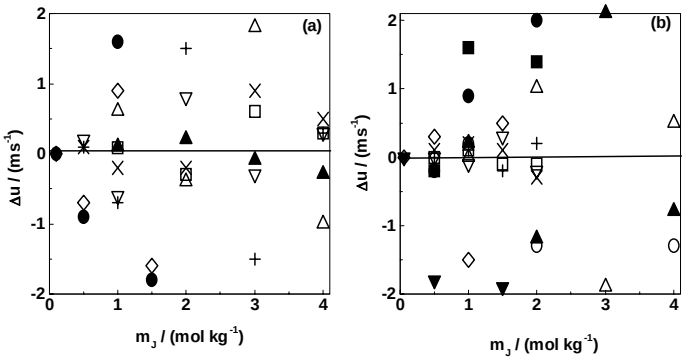


Figure 6.17: Plots of Δu vs. m_J obtained from experimental data for (a) KCl + glycine 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (σ), KBr + glycine 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (X), NaBr + glycine 1 mol kg^{-1} (∇), 2 mol kg^{-1} (+), $MgCl_2$ + glycine 0.5 mol kg^{-1} (λ), 1 mol kg^{-1} (◊); (b) KCl + L-alanine 0.1 mol kg^{-1} (σ), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ); $MgCl_2$ + L-alanine 0.75 mol kg^{-1} (τ), 1 mol kg^{-1} (◊); KCl + glycylglycine 0.5 mol kg^{-1} (+), 1.2 mol kg^{-1} (X); KBr + glycylglycine 0.5 mol kg^{-1} (∇), 1 mol kg^{-1} (o), 1.2 mol kg^{-1} (ν), Na_2SO_4 + 1 mol kg^{-1} (λ)

Equations (13) and (14) can be successfully applied to literature data. In literature data on measurement of speed of sound of amino acid – electrolyte – water system are scarce. The only detail study available is by Soto et. al.[180]. The coefficients obtained for correlation of ϕ_{KAJW} and ϕ_{KJAW} using **equations (13) and (14)** are listed in **Table 6.13 and 6.14**, respectively. The coefficients in **Table 6.13** can correlate ϕ_{KAJW} accurately as can be seen from **Figure 6.18 (a)**, where ϕ_{KAJW} of glycine in 1 mol kg^{-1} of NaCl, KCl and $NaNO_3$ are shown as points and correlated values are depicted by lines. The deviation in speed of sound, Δu ($u_{exp.} - u_{cor.}$) for glycine in NaCl, $NaNO_3$, KCl and KNO_3 are plotted as a function of m_A in **Figure 6.18 (b)**. The average rmsd in ϕ_{KAJW} of glycine in NaCl, $NaNO_3$, KCl and KNO_3 is found to be 0.28 x 10^{-15} m^3 mol^{-1} Pa^{-1}, 0.23 x 10^{-15} m^3 mol^{-1} Pa^{-1}, 0.12 x 10^{-15} m^3 mol^{-1} Pa^{-1} and 0.17 x 10^{-15} m^3 mol^{-1} Pa^{-1}, respectively.

Table 6.13: the coefficients for correlation of apparent molar compressibilities of amino acids in different electrolytes at 298.15 K for data from literature

m_J / (mol kg^{-1})	10^{15} $\phi_K{}^0{}_{AJW}$ / (m^3 mol^{-1} Pa^{-1})	10^{15} s_K / (kg m^3 mol^{-2} Pa^{-1})	10^{15} s_K' / (kg^2 m^3 mol^{-3} Pa^{-1})	10^{15} $\lambda^K{}_{AJW}$ / RT / (kg m^3 mol^{-2} Pa^{-1})	10^{15} rmsd / (m^3 mol^{-1} Pa^{-1})
		Glycine – NaCl – H_2O			
0.2	-23.3 (0.14)	1.801 (0.001)	-0.1001 (0.0001)	0.1001 (0.0001)	0.08
0.4	-21.0 (0.25)	1.802 (0.001)	-0.1001 (0.0001)	0.0525 (0.0030)	0.14
0.6	-18.3 (0.53)	1.200 (0.001)	-0.0419 (0.0002)	0.0050 (0.0001)	0.29
0.8	-16.6 (0.20)	1.200 (0.001)	-0.0480 (0.0003)	-0.0129 (0.0007)	0.12

1	-14.6 (0.27)	1.101	-0.0455	-0.0032	0.16
		(0.001)	(0.0003)	(0.0002)	
		Glycine – $NaNO_3$ – H_2O			
0.2	-23.15 (0.04)	2.001	-0.1001	-2.301	0.14
		(0.002)	(0.0001)	(0.003)	
0.4	-20.46 (0.10)	1.901	-0.1000	-1.200	0.21
		(0.002)	(0.0001)	(0.001)	
0.6	-18.82 (0.05)	2.003	-0.2001	-0.9001	0.20
		(0.002)	(0.0002)	(0.0073)	
0.8	-16.74 (0.02)	0.1204	-0.0047	-0.2002	0.10
		(0.0007)	(0.0003)	(0.0003)	
1	-15.28 (0.06)	1.502	-0.0986	-0.3001	0.05
		(0.001)	(0.0006)	(0.0002)	
		Glycine + KCl + H_2O			
0.2	-22.96 (0.05)	1.901	-0.1001	-1.801	0.11
		(0.011)	(0.0001)	(0.001)	
0.4	-20.05 (0.02)	1.502	-0.0883	-0.701	0.04
		(0.001)	(0.0002)	(0.006)	
0.6	-18.28 (0.09)	1.601	-0.1001	-0.501	0.15
		(0.001)	(0.0001)	(0.0011)	
0.8	-16.21 (0.10)	1.501	-0.0946	0.401	0.11
		(0.001)	(0.0010)	(0.002)	
1.0	-13.96 (0.01)	1.301	-0.1001	-0.401	0.20
		(0.001)	(0.0001)	(0.005)	
		Glycine + KNO_3 + H_2O			
0.2	-23.38 (0.14)	2.301	-0.2001	-3.001	0.20
		(0.003)	(0.0003)	(0.004)	
0.4	-20.45 (0.55)	1.800	0.1001	0.2010	0.01
		(0.002)	(0.0001)	(0.0010)	
0.6	-18.66 (0.20)	1.901	-0.2003	-0.9010	0.28
		(0.031)	(0.0033)	(0.0015)	

0.8	-15.81 (0.72)	0.9001	-0.0063	-0.0234	0.13
		(0.0009)	(0.0001)	(0.0002)	
1	-14.11 (0.44)	0.8002	-0.0003	0.0005	0.15
		(0.0006)	(0.0001)	(0.0001)	

Table 6.14: Pitzer coefficients for apparent molar compressibility, ϕ_{KJAW} of systems from literature at 298.15 K.

m_A / (mol kg^{-1})	$10^{15}\ \phi_K{}^0{}_{JAW}$ / ($m^3\ mol^{-1}\ Pa^{-1}$)	$10^{19}\ \beta^{(0)K}$ / ($kg\ mol^{-1}\ Pa^{-2}$)	$10^{19}\ \beta^{(1)K}$ / ($kg\ mol^{-1}\ Pa^{-2}$)	$10^{19} C^{\varphi K}$ / ($kg^2\ mol^{-2}\ Pa^{-2}$)	10^{15} rmsd / ($m^3\ mol^{-1}\ Pa^{-1}$)
		Glycine – NaCl - H_2O			
0.4967	-42.01 (0.67)	2.364	0.1909	-0.7271	0.29
		(0.001)	(0.0001)	(0.0004)	
0.9788	-37.70 (1.20)	3.667	0.1413	-1.989	0.56
		(0.007)	(0.0003)	(0.004)	
1.4665	-31.70 (0.64)	2.384	0.1019	-0.8727	0.28
		(0.001)	(0.0001)	(0.0005)	
1.9255	-29.30 (0.24)	3.968	0.0603	-2.347	0.12
		(0.002)	(0.0001)	(0.001)	
2.4678	-22.60 (0.75)	2.041	-0.0056	-0.8436	0.34
		(0.002)	(0.0001)	(0.0005)	
2.9973	-20.10 (0.24)	1.855	-0.0626	-0.5262	0.11
		(0.001)	(0.0001)	(0.0004)	
		Glycine - $NaNO_3$ - H_2O			
0.5	-30.3 (0.07)	0.3570	1.1583	0.2521	0.03
		(0.0004)	(0.0012)	(0.0002)	
1	-26.2 (0.58)	-0.4967	2.0748	0.8101	0.23
		(0.0003)	(0.0012)	(0.0005)	
2	-17.4 (0.17)	-2.3283	3.9143	1.662	0.10
		(0.0013)	(0.0023)	(0.0010)	

2.5	-10.3 (1.30)	-6.0659	4.8457	4.282	0.45
		(0.0049)	(0.0039)	(0.0035)	
		Glycine - KCl – H_2O			
0.5	-33.6 (0.06)	1.200	0.9883	0.0660	0.59
		(0.002)	(0.0014)	(0.0093)	
1	-30.6 (0.09)	1.996	1.716	-0.650	0.67
		(0.003)	(0.0030)	(0.1126)	
2	-18.0 (0.02)	-2.396	3.229	2.317	0.14
		(0.002)	(0.0026)	(0.189)	
2.5	-15.9 (0.11)	-2.668	3.996	2.516	0.28
		(0.003)	(0.0040)	(0.252)	
		Glycine – KNO_3 - H_2O			
0.5	-21.8 (1.40)	-1.949	1.461	2.509	0.63
		(0.225)	(0.169)	(0.299)	
1	-17.5 (0.85)	-3.394	2.701	3.604	0.49
		(0.650)	(0.517)	(0.690)	
2	-6.78 (2.55)	-8.624	5.146	7.320	1.34
		(2.170)	(1.295)	(0.184)	
2.5	-6.43 (0.62)	-7.680	6.395	5.706	0.47
		(1.173)	(0.977)	(0.872)	

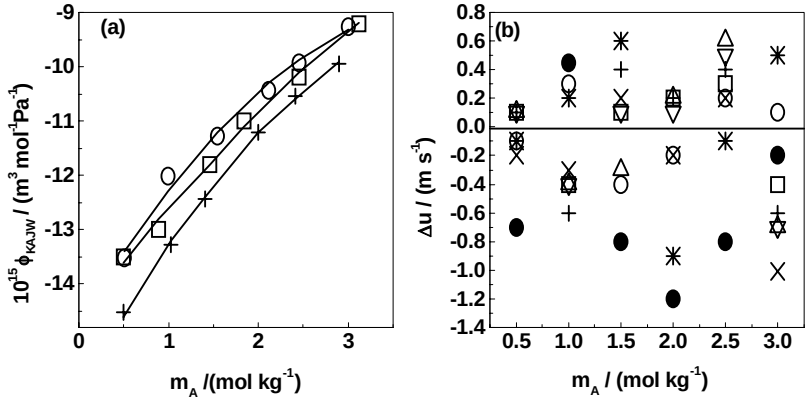


Figure 6.18 : Plots of **(a)** ϕ_{KAJW} vs. m_J for glycine in 1 mol kg^{-1} of NaCl (o), $NaNO_3$ (+), KCl (O); **(b)** Δ ρ vs. m_A in Glycine + NaCl 0.4 mol kg^{-1} (X), 0.6 mol kg^{-1} (λ), + $NaNO_3$ 0.2 mol kg^{-1} (o), 0.4 mol kg^{-1} (+), + KCl 0.6 mol kg^{-1} (∇), 0.8 mol kg^{-1} (O), + KNO_3 0.2 mol kg^{-1} (Δ), 1 mol kg^{-1} (T)

Variation of λ^K_{AJW} coefficient of glycine – electrolyte water systems with m_J is depicted in **Figure 6.19**. The λ^K_{AJW} of glycine – NaCl – water system remains almost constant in 0 to 1 mol kg^{-1} of NaCl, while glycine – $NaNO_3$ – water, glycine – KCl – water and glycine – KNO_3 – water shows increase in λ^K_{AJW} from –3.2 to 0.4 x 10^{-15} m^3 kg mol^{-2} Pa^{-1}. The Pitzer coefficients listed in **Table 6.14** can precisely correlate the ϕ_{KJAW} as shown in **Figure 6.20 (a) and (b)**. In **Figure 6.20 (a)** ϕ_{KJAW} is plotted as a function of m_J with experimental data depicted as points and correlated data as lines for NaCl, $NaNO_3$ and KCl in aqueous glycine. The accuracy in correlation of ϕ_{KJAW} can also be seen from **Figure 6.20 (b)** where deviations of experimental and correlated u, Δu are plotted as a function of m_J. The difference in

speed of sound back calculated from correlated ϕ_{KAJW} and ϕ_{KJAW} are listed in **Table 6.9**.

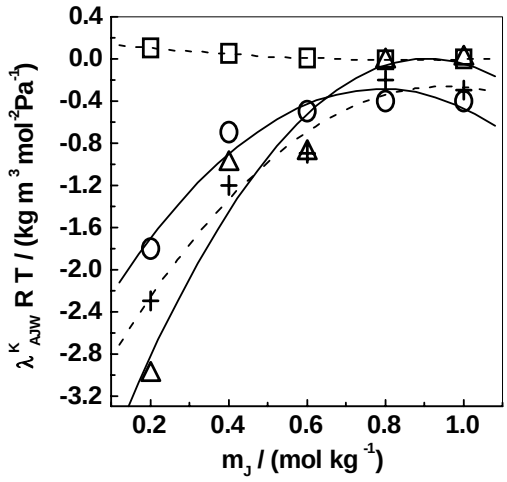


Figure 6.19: λ^{K}_{AJW} versus m_J for glycine + NaCl (o), $NaNO_3$ (+), KCl (O), KNO_3 (Δ)

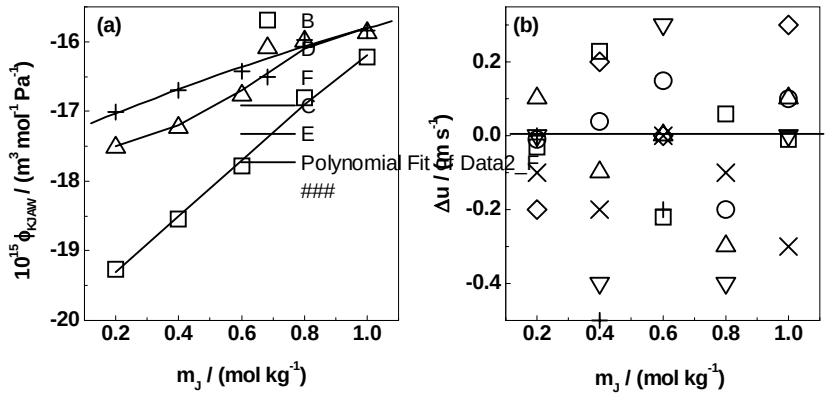


Figure 6.20 : Plots of **(a)** ϕ_{KJAW} vs. m_J for NaCl + 3 mol kg^{-1} glycine (o), KCl + 3 mol kg^{-1} glycine (Δ), $NaNO_3$ + glycine 2 mol kg^{-1} (+); **(b)** Δ ρ versus m_J in NaCl + glycine 0.5 mol kg^{-1} (o), 3 mol kg^{-1} (O); $NaNO_3$ + glycine 2 mol kg^{-1} (X), 2.5 mol kg^{-1} (◊), KCl + glycine 2 mol kg^{-1} (Δ), 2.5 mol kg^{-1} (∇), KNO_3 + glycine 2.5 mol kg^{-1} (+)

The Pitzer coefficients for electrolytes β^0, $\beta^{(1)}$ and C^{φ} are altered in the presence of amino acids and peptide. The effect of peptide on the Pitzer coefficients is greater as compared to amino acids. The effect of amino acids and peptides on the Pitzer coefficients of different electrolytes for volumetric properties of a few representative systems is shown in **Figure 6.21, 6.22 and 6.23**. The Pitzer coefficient, β^0 is an important binary interaction term that accounts for the interaction between a pair of ions. In general, it is seen that the β^0 volume parameter of 1:1 strong electrolyte is not greatly affected upon the addition of glycylglycine. The variation is quite small. However, the β^0 coefficient of Na_2SO_4 reduces sharply with the concentration of glycylglycine indicating the association of Na^+ and SO_4^{2-} species. Na_2SO_4 is considered a strong electrolyte, as no ion pairing has been noted in its solution in water at room temperature. Addition of an amino acid or a peptide can decrease the relative permittivity of water. When an electrolyte is added to such a solution, the coulombic forces of attraction increase. As thermal energy of solution given by ½ kT (k=Boltzamann constant) does not exceed the coulombic energy, the phenomenon of association sets in, thereby resulting into a decrease of the value of β^0 with the concentration of amino acid or peptide. $\beta^{(1)}$ is normally required while the data in very dilute range. In the current situation, $\beta^{(1)}$ has less importance, as the objective of the work was centered around concentrated solutions. With respect to the volume C^{φ} parameter, the ternary interactions in 1:1 electrolytes do not vary appreciably with the concentrations of amino acids. However, this was also true in the case of $Na_2SO_{4,\ which}$ is not expected, but might be possible due to the restricted concentration of electrolyte used in the investigation. Both the nitrates and $MgCl_2$

have enriched solutions in ternary interactions that enhance with the amino acid concentrations. The nitrates undergo further association in amino acids and peptides. The β^0 volume parameter is also supported by β^0 parameter obtained from the regression of compressibility data. The decreasing β^0 parameter for compressibility of $MgCl_2$, Na_2SO_4 and nitrates again indicates towards association in amino acids and peptides with their increasing concentrations. The 1:1 electrolytes like KCl, KBr, NaBr tend to exhibit less influence on their nature of strong electrolytes. The structure of amino acids and peptides will play important roles in determining whether the Pitzer coefficients of electrolytes should increase or decrease with their concentrations present in the solutions. The C^{φ} parameter for compressibility can also be explained on the similar lines.

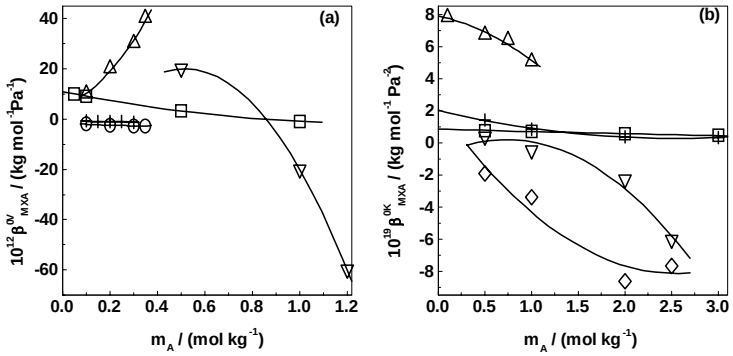


Figure 6.21: Effect of amino acids on Pitzer coefficient, β^0 in **(a)** volume L-alanine – KCl (o), glycylglycine – Na_2SO_4 (∇), DL-alanine – sodium butyrate (Δ), glycine – KSCN (+), β-alanine – KSCN (O), **(b)** compressibility glycine – KBr (o), glycine – NaBr (+), L-alanine – $MgCl_2$ (Δ), glycine – $NaNO_3$ (∇), glycine – KNO_3 (◊)

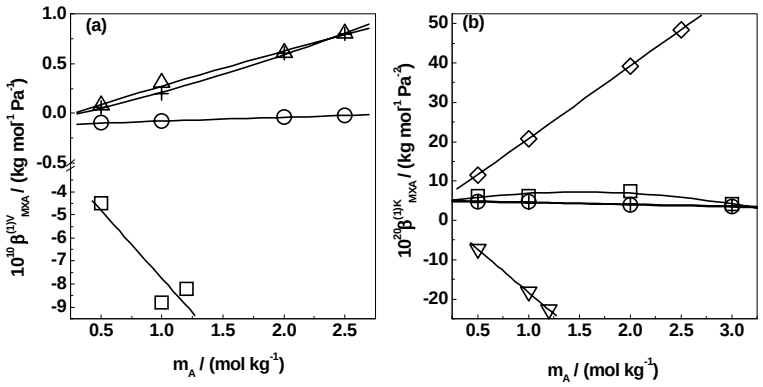


Figure 6.22: Plots of the Pitzer coefficient, β^1 in **(a)** volume glycylglycine – KBr (o), glycine – KCl (O), glycine – KNO_3 (Δ), glycine – $NaNO_3$ (+) **(b)** compressibility glycine – KCl (o), glycine – KBr (O), glycine – NaBr (+), glycine – $NaNO_3$ (◊), glycine – KBr (∇)

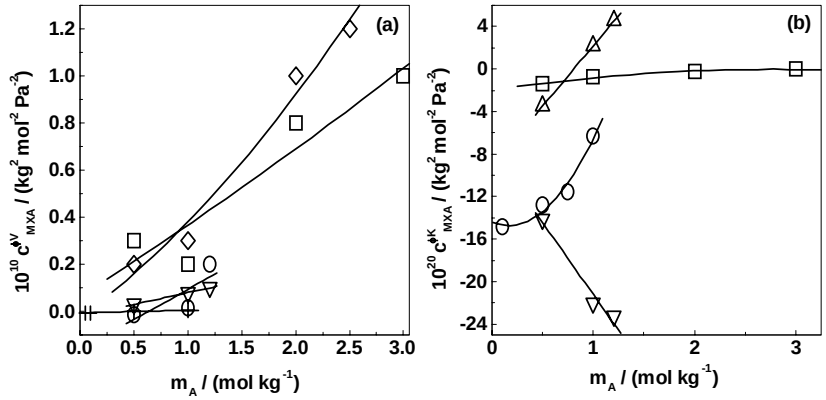


Figure 6.23: Plots of the Pitzer coefficient, c^{φ} in **(a)** volume glycine – $MgCl_2$ (o), alanine – KCl (+), glycylglycine – KCl (O), glycylglycine – Na_2SO_4 (∇), glycine – KNO_3 (◊) **(b)** compressibility glycine – NaBr (o), L-alanine – $MgCl_2$ (O), glycine – KCl (Δ), glycylglycine – Na_2SO_4 (∇)

In nutshell, thermodynamic properties of the amino acid/peptide in aqueous electrolyte solution and of electrolyte in aqueous amino acid/peptide solutions up to high concentrations have been described within a single framework of equations. The quantitative information extracted from the analysis of aqueous amino acid has been transferred for correlating the thermodynamic properties of aqueous electrolyte. Good level of accuracy is achieved for activity coefficients, volumes and compressibilities of both the amino acid/peptide and electrolyte.

Two points should be brought out at this juncture of the work. First, it was not possible to model thermal expansion coefficients in the form of apparent molar expansibility due to less number of data points collected. However, it is believed that if apparent molar volumes can be described by using the above given framework at 298 K, it will also be applicable to apparent molar volume data at other temperatures where data were collected. Second, the data collected in the mixed electrolytes were restricted in the number due to solubility problem and also in view of scope of the research problem investigated here. That has put constraints on regressing the mixture data by the equations developed in this chapter.

Aim of this thesis has been to understand the amino acid – ion interactions. In the previous chapters the ion – amino acid interactions were investigated using equilibrium thermodynamic properties like volume and compressibility. One of the most important tools to study the solute – solute interactions is by studying its transport property i.e. viscosity. In this chapter the detailed examination of viscosity of amino acids and peptide (glycine, L-alanine and glycylglycine) in various electrolytes is presented. The prime focus of the present work was to find an equation of simple form that could fit viscosities of mixtures of amino acids or peptides and broad range of electrolytes with a precision of better than 1% using the least number of adjustable parameters. Thus, a simple model is proposed for correlation of viscosities and the thermodynamic Gibbs free energy of activation for the viscous flow for the mixture of aqueous amino acids and electrolytes.

7.1: Preface

Thermodynamic and transport properties of very dilute electrolyte solutions can be interpreted with reasonable accuracy by original and modified Debye – Huckel theory. In the case of concentrated solutions, however, present understanding is still incomplete, mainly because of lack of suitable working hypotheses and precise data obtained from well-designed experimental systems. Most widely accepted method of representing viscosity data is by Jones –Dole equation[245]. The concentration dependence of viscosity, η can be given as **equation (1a)** for electrolytes and by **equation (1b)** for non-electrolytes using Jones – Dole equation ($c < 0.5$ mol l^{-1}).

$$\eta_r = 1 + A\, c^{0.5} + B\, c \qquad (1a)$$

$$\eta_r = 1 + B\, c \qquad (1b)$$

where η_r is the relative viscosity ($\eta_r = \eta_{solution} / \eta_{solvent}$) and c is the molarity. While A is calculated from the solvent properties (Falkenhagen constant), parameter B is an empirical coefficient. Though parameter B is empirical in nature, it gives vital information on how a given ion interacts with the water molecules. In the literature, there exist several proposals to compute the value of the B-coefficients of various ions in water. At moderate or higher concentration (c > 0.5 mol l^{-1}) **equation (1a)** can be modified to **equation (2)**, ignoring the contribution of ($A c^{0.5}$) but adding a c^2 term[246].

$$\eta_r = 1 + B c + D c^2 \qquad (2)$$

The solutes (ions) increase or decrease the viscosity of solvents depending on their structure-making or -breaking abilities. Considering the hydrophobic hydration abilities of tetra-n-alkyl ammonium salts (R_4NBr, R = ($(CH_3)_4$, $(C_2H_5)_4$,$(C_4H_9)_4$) in water, it will be of interest to study the effect of these bulky ions on the viscosity of amino acids. These cations are known to orient the water molecules around them depending on their alkyl chain. The R_4N^+ cations are strong structure-makers because of their large sizes, weak charges and inability to break down the tetrahedral structure of water. The B-coefficients for these cations are (+0.12, +0.38 and +1.28 dm^3 mol^{-1}) for $(CH_3)_4N^+$, $(C_2H_5)_4N^+$ and $(C_4H_9)_4N^+$ species, respectively[223]. The aqueous solutions of these electrolytes have been found to be highly viscous[227]. On the contrary, the ions that undergo hydrophilic hydration display entirely opposite picture with regard to the orientation of water molecules in terms of physical interaction.

The Gibbs free energy of activation for the viscous flow of mixture, $\Delta G^{\#}$ can be obtained using Eyring type equation[247,248] where $\Delta G^{\#}$ is correlated to viscosity, η as:

$$\Delta G^{\#} = R\ T \ln (V^* \eta / h N) \quad (3)$$

Where V* is molar volume of solution, h is Planck constant (6.62618×10^{-34} J s) and N is Avagadro's number (6.0220×10^{23} mol^{-1}).

7.2: Derivation of equations

The viscosity of concentrated aqueous amino acid, η_{AW} can be given as:

$$\eta_{AW} = \eta^0_W + q_{A1}\ m_A \quad q_{A2}\ m_A^2 \quad (4a)$$

where η^0_{AW} is the viscosity of water (0.8903 mPa s) and q_{A1} and q_{A2} are the empirical parameters referring to concentration dependence of viscosity of aqueous amino acid. Similar equation can be written for viscosity of aqueous concentrated electrolytic solution by **equation (4b)**[246].

$$\eta_{JW} = \eta^0_W + q_{J1}\ m_J\ + q_{J2}\ m_J^2 \quad (4b)$$

The viscosity of the mixture of aqueous amino acid and electrolyte can be given by the combination of **equation (4a)** and **(4b)**.

Let the viscosity of each component vary from its value in aqueous solution alone due to the non-ideality, δ_{AJW} upon mixing of electrolyte and non-electrolyte by:

$$\eta'_{AJW} = \eta_{AW} + \delta^0_{AJW}\ m_A\, m_J + \delta^1_{AJW}\ m_A^2\, m_J^2 \qquad (5)$$

Analogous equation can be written for η_{JAW}:

$$\eta'_{JAW} = \eta_{JW} + \delta^0_{JAW}\ m_A\, m_J + \delta^1_{JAW}\ m_A^2\, m_J^2 \qquad (6)$$

The mixing parameters being symmetric ($\delta^0_{AJW} = \delta^0_{JAW}$ and $\delta^1_{AJW} = \delta^1_{JAW}$) are called as the empirical amino acid – electrolyte viscous flow interaction parameters.

The bulk viscosity, η_{AJW} of such a mixture can be defined as:

$$\eta_{AJW} = (m_A\, \eta'_{AJW} + m_J\, \eta'_{JAW}) / (m_A + m_J) \qquad (7)$$

Substitution of **equations (5)** and **(6)** into **equation (7)** and on simplification, one gets:

$$\eta_{AJW} = \eta_{ideal} + m_A\, m_J\ [\ \delta^0_{JAW} + \delta^1_{JAW}\ m_A\, m_J\ ] \qquad (8)$$

where η_{ideal} is given by:

$$\eta_{ideal} = (m_A\, \eta_{AW} + m_J\, \eta_{JW}) / (m_A + m_J) \qquad (9)$$

Equation (8) is the working equation for correlating the mixture viscosity with the molalities of amino acid and of electrolyte.

The Gibbs free energy of activation for viscous flow of the mixtures, $\Delta G^{\#}_{AJW}$ can also be derived on the lines described above in order to yield:

$$\Delta G^{\#}_{AJW} = (\Delta G^{\#}_{AW}\, m_A + \Delta G^{\#}_{JW}\, m_J) / (m_A + m_J) + m_A\, m_J\, [g^0_{AJW} + g^1_{AJW}\, m_A\, m_J\,] \quad (10)$$

where $\Delta G^{\#}_{AW}$ and $\Delta G^{\#}_{JW}$ are the Gibbs free energies of activation for viscous flow of aqueous amino acid and aqueous electrolyte solutions, respectively.

7.3 : Viscosity of amino acids and peptide in aqueous electrolyte solutions

The method used for obtaining the experimental viscosities from measured flow time and density of solution is described in **Chapter 3**. The viscosities of glycine and L-alanine in KCl and $MgCl_2$ are listed in **Table 7.1 and 7.2**, respectively, while the viscosity of mixture of glycylglycine in KCl, KBr and Na_2SO_4 are Tabulated in **Table 7.3**. The effect of electrolytes on viscosities of amino acid – electrolyte mixture are shown in the **Figures 7.1, 7.2 and 7.3**. A cursory glance at **Figures 7.1 – 7.3** signifies higher effect of $MgCl_2$ and Na_2SO_4 on the viscosity of mixture of amino acid - electrolyte as compared to KCl and KBr (1:1). This effect of electrolytes on viscosity of mixtures can be very well understood by studying the slope values, $\partial\eta/\partial m_J$ for η versus m_J plots. The $\partial\eta/\partial m_J$ value for KCl in 1 mol kg^{-1} of glycine, L-alanine and glycylglycine are almost constant with values 0.018 mPa s kg mol^{-1}, 0.015 mPa s kg mol^{-1} and 0.02 mPa s

kg mol^{-1}, respectively. The slope value increases twice in the presence of $MgCl_2$ with values 0.26 mPa s kg mol^{-1} and 0.31 mPa s kg mol^{-1} in 1 mol kg^{-1} of glycine and L-alanine, while in 1 mol kg^{-1} glycylglycine and Na_2SO_4 it increases to 0.95 mPa s kg mol^{-1}.

Table 7.1: Experimental viscosity of aqueous glycine in KCl and $MgCl_2$ solutions at 298.15 K

m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})	m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})
Glycine – KCl – H_2O					
	m_A = 0.4991 mol kg^{-1}			m_A = 1.0004 mol kg^{-1}	
0	0.9561	12.84	0	1.1894	12.98
0.5003	0.9671	12.81	0.5002	1.0397	12.96
1.0006	0.9723	12.77	0.9994	1.0398	12.91
1.9999	0.9793	12.70	1.9999	1.0548	12.86
3.0006	0.9971	12.66	3.0006	1.0831	12.85
3.9981	1.0227	12.65	3.9985	1.0990	12.82
	m_A = 1.9993 mol kg^{-1}			m_A = 2.9999 mol kg^{-1}	
0	1.1894	13.28	0	1.3738	13.59
0.5002	1.2005	13.26	0.1001	1.3753	13.58
0.9979	1.2110	13.24	0.4999	1.3961	13.59
1.9993	1.2198	13.18	1.0002	1.3900	13.54
3.0009	1.2521	13.17	2.0004	1.4147	13.51
3.9995	1.2904	13.18	3.0001	1.4670	13.53

Glycine – $MgCl_2$– H_2O

m_A = 0.4999 mol kg^{-1}			m_A = 0.9998 mol kg^{-1}		
0.0987	0.9909	13.02	0.0998	1.0603	13.10
0.5010	1.0865	13.38	0.5001	1.1805	13.46
1.0001	1.1960	13.64	0.9988	1.2922	13.71
1.5001	1.3329	13.88	1.5007	1.4177	13.93
m_A = 1.9990 mol kg^{-1}			m_A = 3.0002 mol kg^{-1}		
0.0998	1.2304	13.39	0.0998	1.4237	13.68
0.4999	1.3343	13.63	0.4989	1.5395	13.90
0.9987	1.4664	13.88	0.9999	1.6964	14.15
1.4976	1.6206	14.12	1.4989	1.8813	14.40

Table 7.2: Experimental viscosity of aqueous L-alanine in KCl and $MgCl_2$ solutions at 298.15 K

m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})	m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})
L-alanine – KCl – H_2O					
m_A = 0.1003 mol kg^{-1}			m_A = 0.4995 mol kg^{-1}		
0	0.9179	13.19	0	1.0166	13.42
0.5003	0.9239	12.74	0.5003	1.0156	13.15
0.9992	0.9164	12.69	0.9992	1.0123	13.02
1.9984	0.9328	12.62	1.9995	1.0253	12.91
2.9999	0.9467	12.56	2.9989	1.0428	12.84

3.9999	0.9432	12.56	4.0016	1.0775	12.84
	m_A = 0.7497 mol kg^{-1}			m_A = 1.0002 mol kg^{-1}	
0	1.0793	13.55	0	1.1525	13.70
0.5002	1.0913	13.36	0.5003	1.1536	13.52
1.0005	1.0815	13.22	1.0006	1.1547	13.40
1.9995	1.1078	13.12	2.0001	1.1638	13.26
2.9995	1.1179	13.03	3.0002	1.1875	13.20
3.9999	1.1487	13.01	3.9999	1.2170	13.17

L-alanine – $MgCl_2$ – H_2O

	m_A = 0.1003 mol kg^{-1}			m_A = 0.4995 mol kg^{-1}	
0.0494	0.9423	13.31	0.0504	1.0355	13.47
0.5010	1.0435	13.56	0.4999	1.1537	13.73
0.9999	1.1612	13.76	1.0009	1.2871	13.95
1.4990	1.2897	13.95	1.4999	1.4188	14.14
	m_A = 0.7498 mol kg^{-1}			m_A = 1.0002 mol kg^{-1}	
0.0515	1.1042	13.61	0.0504	1.1711	13.74
0.4999	1.2236	13.85	0.5001	1.2997	13.97
0.9999	1.3609	14.07	0.9989	1.4529	14.20
1.5001	1.5118	14.27	1.4998	1.6263	14.42

Table 7.3: Experimental viscosity of aqueous glycylglycine in KCl, KBr and Na_2SO_4 solutions at 298.15 K

m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})	m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})
Glycylglycine – KCl – H_2O					
m_A = 0.2496 mol kg^{-1}			m_A = 0.5003 mol kg^{-1}		
0	0.9784	14.30	0	1.0617	14.47
0.5002	0.9752	13.39	0.5003	1.0562	13.80
1.0006	0.9751	13.13	1.0005	1.0534	13.51
1.9997	0.9869	12.92	1.9984	1.0684	13.25
3.0009	1.0045	12.82	3.0006	1.0940	13.13
m_A = 0.7501 mol kg^{-1}			m_A = 0.9999 mol kg^{-1}		
0	1.1450	14.63	0	1.2326	14.79
0.5003	1.1427	14.10	0.5002	1.2305	14.35
1.0005	1.1589	13.86	1.0005	1.2374	14.10
1.9995	1.1597	13.55	1.9984	1.2593	13.82
3.0001	1.2072	13.47	3.0003	1.2884	13.68
Glucylglycine – KBr – H_2O					
m_A = 0.5002 mol kg^{-1}			m_A = 0.9997 mol kg^{-1}		
0.5001	1.0423	14.21	0.5008	1.2215	14.60
1.0007	1.0526	14.11	1.0001	1.2227	14.48
1.5002	1.0558	14.01	1.4990	1.2093	14.35
2.0001	1.0486	13.91	1.9998	1.2271	14.30

m_A = 1.1999 mol kg^{-1}

0	1.3102	14.92
0.4999	1.3025	14.75
1.5975	1.2900	14.49
1.0001	1.2976	14.62
1.1997	1.2913	14.43

Glycylglycine – Na_2SO_4 – H_2O

m_A = 0.5001 mol kg^{-1}			m_A = 0.9999 mol kg^{-1}		
0.4998	1.3281	14.99	0.4998	1.5759	15.34
1.0004	1.6665	15.46	0.9990	1.9544	15.79
1.5001	2.1034	15.95	1.4996	2.4660	16.29
2.0001	2.1562	15.93	2.0006	3.1603	16.83

m_A = 1.1997 mol kg^{-1}

0.4998	1.6746	15.46
1.0004	2.0867	15.93
1.5003	2.6347	16.44
2.0001	3.3549	16.96

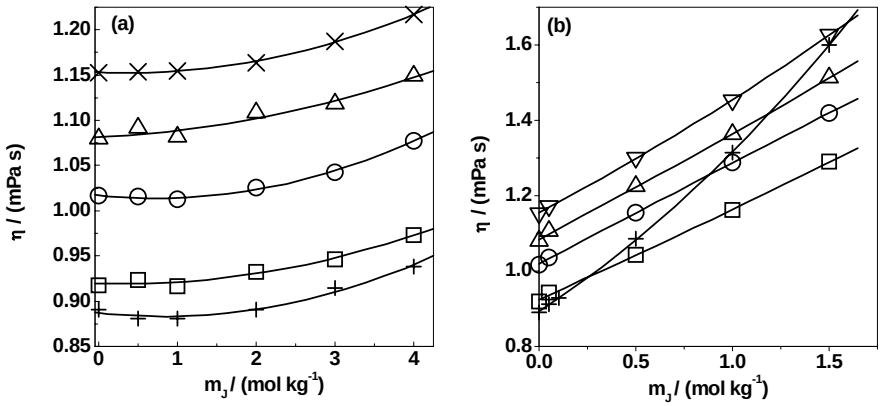


Figure 7.1: Plots of viscosity, η vs. m_J **(a)** in KCl + H_2O (+), + glycine 0.5 mol kg^{-1} (π), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (X); **(b)** in $MgCl_2$ + H_2O (+), + glycine 0.5 mol kg^{-1} (π), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (X)

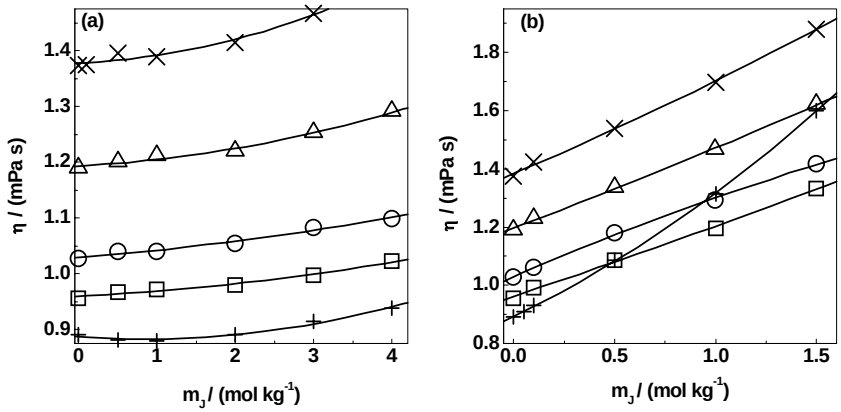


Figure 7.2: Plots of viscosity, η vs. m_J **(a)** in KCl + H_2O (+), + L-alanine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ), 1 mol kg^{-1} (X); **(b)** in $MgCl_2$ + H_2O (+), + L-alanine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ), 1 mol kg^{-1} (∇)

The experimental viscosities were correlated using **equation (8)**. The coefficients of regression, δ^0_{AJW} and δ^1_{AJW} along with rmsd of the fits are listed in **Table 7.4**. The correlation power of **equations (8)** can be seen from an examination of **Figure 7.4 (a)**, where variations of viscosities as a function of m_J are shown with experimental viscosity

values as points and correlated values as lines. The concentration dependence of coefficients δ^0_{AJW} and δ^1_{AJW} is shown in **Figure 7.5 (a)**. The $\delta^{0\eta}_{AJW}$ decreases with increase in concentration of J. This decline on mixing $MgCl_2$ (2:1) and Na_2SO_4 (1:2) electrolytes is higher as compared to 1:1 electrolytes. The rmsd for glycine – J (KCl and $MgCl_2$) is 0.0128 mPa s that for L-alanine – J (KCl and $MgCl_2$) and glycylglycine – J (KCl, KBr and Na_2SO_4) are 0.0149 and 0.0172 mPa s, respectively.

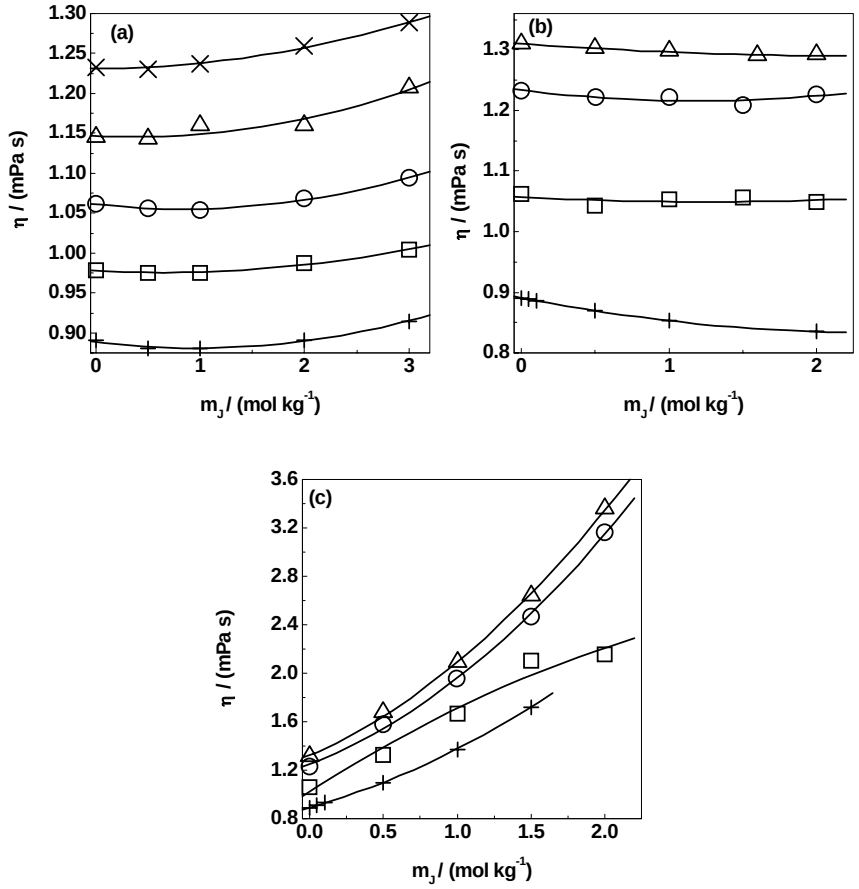


Figure 7.3: Plots of viscosity, η vs. m_J **(a)** in KCl + H_2O (+), + glycylglycine 0.25 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ), 1 mol kg^{-1} (X); **(b)** in KBr + H_2O (+), + glycylglycine 0.5 mol kg^{-1} (π), 1 mol kg^{-1} (O), 1.2 mol kg^{-1} (Δ); **(c)** in Na_2SO_4 + H_2O (+), + glycylglycine 0.5 mol kg^{-1} (π), 1 mol kg^{-1} (O), 1.2 mol kg^{-1} (Δ)

Table 7.4: Viscosity coefficients δ^0_{AJW} and δ^1_{AJW} for glycine, L-alanine and glycylglycine in the presence of different electrolytes at 298.15 K.

m_A / (mol kg^{-1})	δ^0_{AJW} / (mPa s kg^2 mol^{-2})	δ^1_{AJW} / (mPa s kg^4 mol^{-4})	rmsd / (mPa s)	m_A / (mol kg^{-1})	δ^0_{AJW} / (mPa s kg^2 mol^{-2})	δ^1_{AJW} / (mPa s kg^4 mol^{-4})	rmsd / (mPa s)
	Glycine – KCl – H_2O				Glycine – $MgCl_2$ – H_2O		
0.4991	0.1300 (0.0213)	-0.0466 (0.0125)	0.0141	0.4999	0.4059 (0.0756)	-0.7414 (0.1145)	0.0170
1.0004	0.0922 (0.0083)	-0.0144 (0.0024)	0.0114	0.9998	0.3515 (0.0266)	-0.2161 (0.0201)	0.0118
1.9993	00619 (0.0049)	-0.0037 (0.0007)	0.0138	1.9990	0.1995 (0.0119)	-0.0384 (0.0045)	0.0105
2.9990	0.0522 (0.0038)	-0.0019 (0.0005)	0.0114	3.0002	0.1558 (0.0090)	-0.0134 (0.0023)	0.0122
	L-alanine – KCl – H_2O				L-alanine – $MgCl_2$ – H_2O		
0.1003	0.3493 (0.0780)	-0.6689 (0.2140)	0.0100	0.1010	0.3686 (0.3474)	-14.28 (2.60)	0.0141
0.4995	0.1744 (0.0274)	-0.0574 (0.0160)	0.0200	0.4955	0.6014 (0.0512)	-0.8798 (0.0781)	0.0100
0.7497	0.1685 (0.0211)	-0.0367 (0.0082)	0.0224	0.7498	0.4945 (0.0412)	-0.3755 (0.0415)	0.0138

1.0002	0.1409	-0.0212	0.0200	1.0002	0.4184	-0.1891	0.0089
	(0.0146)	(0.0043)			(0.0202)	(0.0153)	
Glycylglycine – KCl – H_2O				Glycylglycine – KBr – H_2O			
0.2496	0.3877	-0.3761	0.0138	0.5002	0.3513	-0.1835	0.0005
	(0.0575)	(0.0878)			(0.0017)	(0.0020)	
0.5003	0.2780	-0.1179	0.0173	0.9997	0.2259	-0.0499	0.0100
	(0.0345)	(0.0262)			(0.0168)	(0.0098)	
0.7501	0.2459	-0.0626	0.0224	1.1999	0.2143	-0.0418	0.0077
	(0.0313)	(0.0159)			(0.0099)	(0.0048)	
0.9999	0.2147	-0.0396	0.0141				
	(0.0151)	(0.0058)					
Glycylglycine – Na_2SO_4 – H_2O							
0.5001	1.0257	-0.4030	0.0164				
	(0.0742)	(0.1121)					
0.9999	0.6750	0	0.0303				
	(0.0111)						
1.1997	0.6137	0	0.0387				
	(0.0551)						

Table 7.5: The coefficients, g^0_{AJW} and g^1_{AJW} for free energy of activation for viscous flow for glycine, L-alanine and glycylglycine in the presence of different electrolytes at 298.15 K.

m_A / (mol kg^{-1})	g^0_{AJW} / (kJ kg^2 mol^{-3})	g^1_{AJW} / (kJ kg^4 mol^{-5})	rmsd / (kJ mol^{-1})	m_A / (mol kg^{-1})	g^0_{AJW} / (kJ kg^2 mol^{-3})	g^1_{AJW} / (kJ kg^4 mol^{-5})	rmsd / (kJ mol^{-1})
	Glycine – KCl – H_2O				Glycine – $MgCl_2$ – H_2O		
0.4991	0.2392	-0.0852	0.0263	0.4999	0.6832	-1.287	0.0469
	(0.0380)	(0.0223)			(0.2105)	(0.319)	
1.0004	0.1567	-0.0234	0.0167	0.9998	0.6191	-0.4006	0.0332
	(0.0120)	(0.0035)			(0.0747)	(0.0566)	
1.9993	0.0981	-0.0054	0.0202	1.9990	0.3217	-0.0726	0.0263
	(0.0073)	(0.0011)			(0.0292)	(0.0111)	
2.9990	0.0764	-0.0023	0.0192	3.0002	0.2322	-0.0269	0.0245
	(0.0066)	(0.0008)			(0.0182)	(0.0046)	
	L-alanine – KCl – H_2O				L-alanine – $MgCl_2$ – H_2O		
0.1003	0.7712	-1.478	0.0158	0.1010	-0.1814	-19.40	0.0412
	(0.1140)	(0.332)			(0.9232)	(6.92)	
0.4995	0.3728	-0.1230	0.0412	0.4955	1.003	-1.526	0.0302
	(0.0594)	(0.0348)			(0.138)	(0.210)	
0.7497	0.3509	-0.0774	0.0458	0.7498	0.8304	-0.6724	0.0346
	(0.0437)	(0.0170)			(0.1046)	(0.1055)	

1.0002	0.2817	-0.0428	0.0387	1.0002	0.6931	-0.3559	0.0232
	(0.0282)	(0.0083)			(0.0523)	(0.0396)	
Glycylglycine – $KCl – H_2O$				Glycylglycine – $KBr – H_2O$			
0.2496	1.236	-1.307	0.0628	0.5002	0.6392	-0.2829	0.0077
	(0.259)	(0.396)			(0.0226)	(0.0263)	
0.5003	0.8057	-0.3807	0.0630	0.9997	0.3657	-0.0635	0.0170
	(0.1296)	(0.0987)			(0.0257)	(0.0150)	
0.7501	0.6365	-0.1760	0.0693	1.1999	0.3430	-0.0565	0.0105
	(0.0952)	(0.0484)			(0.0134)	(0.0064)	
0.9999	0.5214	-0.1055	0.0447				
	(0.0461)	(0.0176)					
Glycylglycine – $Na_2SO_4 – H_2O$							
0.5001	2.186	-1.839	0.0566				
	(0.172)	(0.200)					
0.9999	1.117	-0.2431	0.0721				
	(0.109)	(0.0632)					
1.1997	1.0082	-0.1774	0.0628				
	(0.0791)	(0.0384)					

From the experimental viscosities of mixtures Gibbs free energy of activation for viscous flow, $\Delta G^{\#}$ is calculated using **equation (10)** with the use of the molar volumes of the mixtures computed from the measured densities and molalities. The values of $\Delta G^{\#}$ for

glycine, L-alanine and glycylglycine in the presence of KCl, KBr, $MgCl_2$ and Na_2SO_4 are listed in **Tables 7.1, 7.2 and 7.3**, respectively. The coefficients of **equation (10),** g^0_{AJW} and g^1_{AJW} for the amino acids and peptide in KCl, KBr, $MgCl_2$ and Na_2SO_4 are listed in **Table 7.5**. The variation of g^0_{AJW} with m_A is depicted in **Figure 7.6 (a)**. The dependence of g^1_{AJW} on m_A is similar to that of δ^0_{AJW} shown in **Figure 7.5 (a)**.

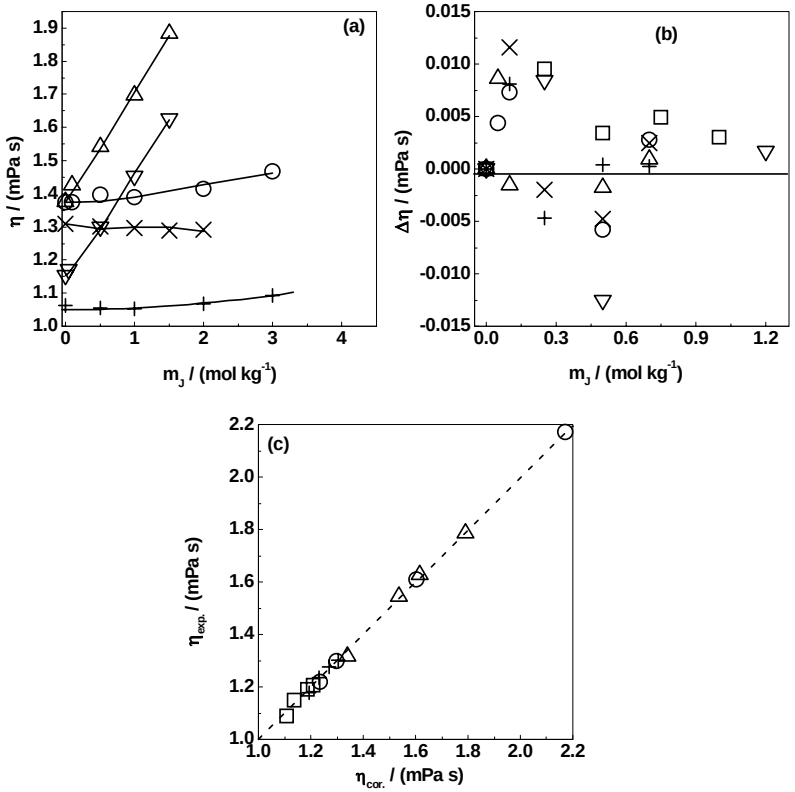


Figure 7.4: Plots of **(a)** η vs. m_J for 3 mol kg^{-1} glycine – KCl (O), for 3 mol kg^{-1} glycine – $MgCl_2$ (Δ), 1 mol kg^{-1} L-alanine – $MgCl_2$ (∇), 0.5 mol kg^{-1} glycylglycine – KCl (+), 0.5 mol kg^{-1} glycylglycine – KCl (X); **(b)** Δη vs. m_J for 0.5 mol kg^{-1} glycine – $(C_2H_5)_4NBr$ (o), 1mol kg^{-1} glycine – $(C_4H_9)_4NBr$ (O), 1.5 mol kg^{-1} glycine – $(C_4H_9)_4NBr$ (Δ), 0.5 mol kg^{-1} L-alanine – $(C_2H_5)_4NBr$ (∇), 0.5 mol kg^{-1} L-alanine – $(C_4H_9)_4NBr$ (X), 1 mol kg^{-1} L-alanine – $(C_4H_9)_4NBr$ (+); **(c)** $\eta_{exp.}$ vs. $\eta_{cor.}$ for 0.5 mol kg^{-1} glycylglycine + $(CH_3)_4NBr$ (o), 0.75 mol kg^{-1} glycylglycine + $(CH_3)_4NBr$ (+), 1 mol kg^{-1} glycylglycine + $(C_2H_5)_4NBr$ (Δ), 0.75 mol kg^{-1} glycylglycine + $(C_4H_9)_4NBr$ (O)

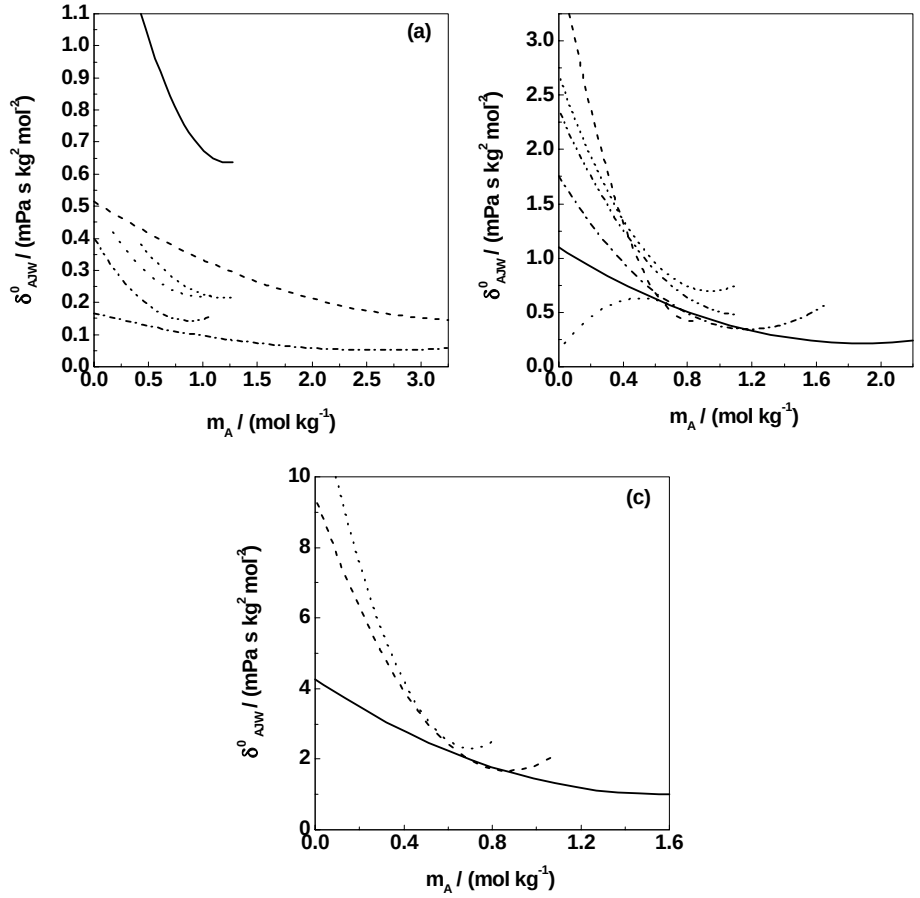


Figure 7.5: Dependence of δ^0_{AJW} on m_A for **(a)** glycine KCl (— • —), glycine $MgCl_2$ (— —), L-alanine – KCl (— • • —) glycylglycine – KCl (. . . . . .), glycylglycine – KBr (- - - - -), glycylglycine – Na_2SO_4 (———); **(b)** glycine – $(CH_3)_4NBr$ (———), L-alanine – $(CH_3)_4NBr$ (— —), glycylglycine – $(CH_3)_4NBr$ (. . . . . .), glycine – $(C_2H_5)_4NBr$ (— • —), L-alanine – $(C_2H_5)_4NBr$ (— • • —), glycylglycine – $(C_2H_5)_4NBr$ (- - - - -); **(c)** glycine – $(C_4H_9)_4NBr$ (———), L-alanine – $(C_4H_9)_4NBr$ (- - - - -), glycylglycine – $(C_4H_9)_4NBr$ (. . . . . .)

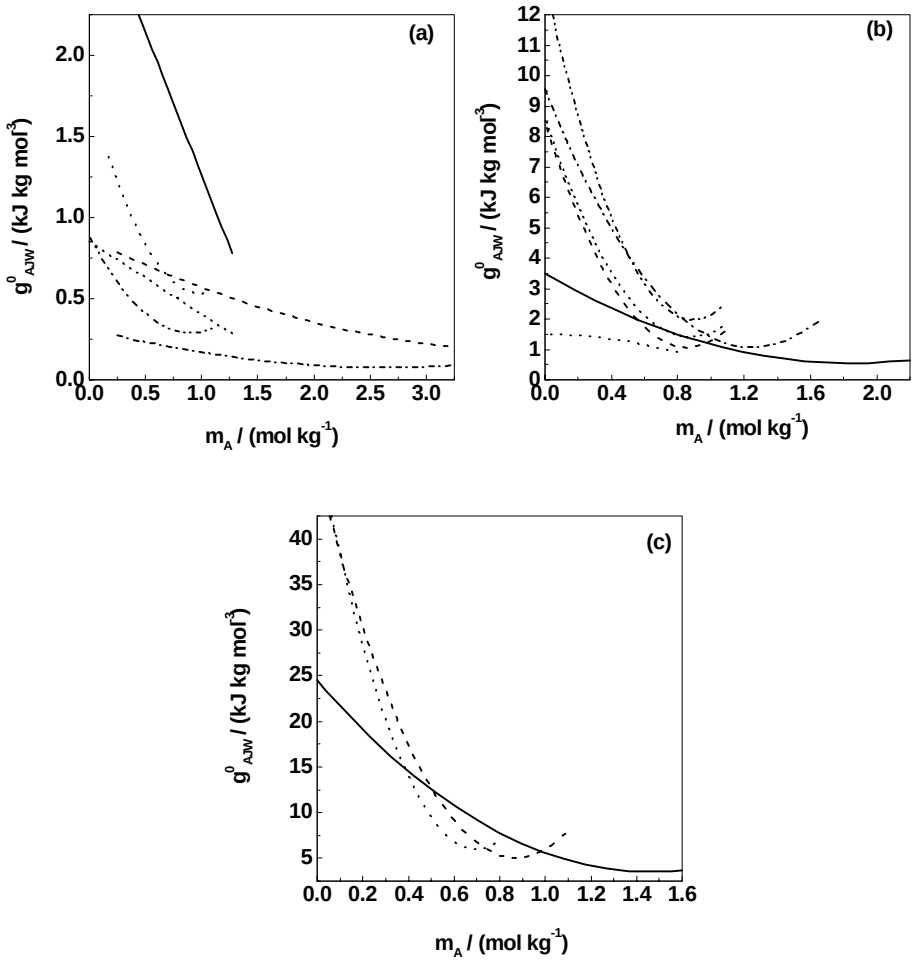


Figure 7.6: Dependence of g^0_{AJW} on m_A for **(a)** glycine KCl (— • —), glycine $MgCl_2$ (— —), L-alanine – KCl (— • • —) glycylglycine – KCl (. . . . . .), glycylglycine – KBr (- - - - -), glycylglycine – Na_2SO_4 (———); **(b)** glycine – $(CH_3)_4NBr$ (———), L-alanine – $(CH_3)_4NBr$ (— —), glycylglycine – $(CH_3)_4NBr$ (. . . . . .), glycine – $(C_2H_5)_4NBr$ (— • —), L-alanine – $(C_2H_5)_4NBr$ (— • • —), glycylglycine – $(C_2H_5)_4NBr$ (- - - - -); **(c)** glycine – $(C_4H_9)_4NBr$ (———), L-alanine – $(C_4H_9)_4NBr$ (- - - - -), glycylglycine – $(C_4H_9)_4NBr$ (. . . . . .)

7.4: Viscosity of amino acids and peptide in aqueous tetra-n-alkylammonium bromides solutions

The effect of hydrophilic cations and anions on viscosity of aqueous amino acid and peptide is discussed in **Section 7.2**. Here the influence of large hydrophobic tetraalkyl ammonium ions on viscosity is elaborated. In **Tables 7.6, 7.7 and 7.8** the experimental viscosities and Gibbs free energy of activation for viscous flow, $\Delta G^{\#}$ are listed for amino acids and peptides in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$, respectively. The change in viscosities of amino acid or peptide in the tetra-n-alkylammonium bromide solutions is plotted as a function of concentration of $(CH_3)_4NBr$ in **Figures 7.7**, $(C_2H_5)_4NBr$ in **Figure 7.8** and that of $(C_4H_9)_4NBr$ in **Figure 7.9**.

Table 7.6: Experimental Viscosities of glycine, L-alanine and glycylglycine in $(CH_3)_4NBr$ at 298.15 K

m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})	m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})
Glycine - $(CH_3)_4NBr - H_2O$					
m_A = 0.4993 mol kg^{-1}			m_A = 1.0003 mol kg^{-1}		
0.2505	1.0038	13.68	0.2499	1.0805	13.56
0.4992	1.0296	14.03	0.5004	1.1069	13.87
1.0009	1.0928	14.41	1.0002	1.1743	14.29
1.5007	1.1716	14.67	1.5007	1.2404	14.58
m_A = 1.4999 mol kg^{-1}			m_A = 1.9995 mol kg^{-1}		
0.2499	1.1608	13.58	0.2499	1.2462	13.73

0.4998	1.1988	13.87	0.5005	1.2846	13.91
1.0010	1.2639	14.26	1.0002	1.3696	14.30
1.5002	1.3683	14.61	1.5001	1.4599	14.62

L-alanine - $(CH_3)_4NBr - H_2O$

$m_A = 0.1002$ mol kg^{-1}			$m_A = 0.4992$ mol kg^{-1}		
0.2505	0.9607	14.32	0.2505	1.0563	14.03
0.4991	0.9884	14.51	0.4997	1.0840	14.31
1.0002	1.0460	14.69	0.9995	1.1565	14.64
1.4999	1.1107	14.85	1.4993	1.2403	14.88
$m_A = 0.7503$ mol kg^{-1}			$m_A = 0.9992$ mol kg^{-1}		
0.2499	1.1347	14.07	0.2505	1.2133	14.14
0.4998	1.1617	14.33	0.5004	1.2417	14.38
1.0003	1.2342	14.67	1.0002	1.3184	14.73
1.4993	1.3009	14.89	1.4481	1.3921	14.95

Glycylglycine – $(CH_3)_4NBr – H_2O$

$m_A = 0.0995$ mol kg^{-1}			$m_A = 0.5004$ mol kg^{-1}		
0	0.9265	14.19	0.2499	1.1081	14.69
0.2499	0.9622	14.55	0.4998	1.1364	14.80
0.4998	1.0030	14.66	0.7997	1.1882	14.93
0.7997	1.0372	14.74	1.0009	1.2110	14.98
0.9997	1.0654	14.80			

m_A = 0.7502 mol kg^{-1}

0.2493	1.1950	14.82
0.4998	1.2302	14.93
0.7492	1.2687	15.02
0.9997	1.3055	15.10

Table 7.7: Experimental Viscosities of $(C_2H_5)_4NBr$ in glycine, L-alanine and glycylglycine at 298.15 K

m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})	m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})
Glycine - $(C_2H_5)_4NBr - H_2O$					
m_A = 0.4999 mol kg^{-1}			m_A = 0.7501 mol kg^{-1}		
0.2498	1.0682	14.26	0	0.9910	12.91
0.4991	1.1710	14.89	0.2498	1.1103	14.09
0.7501	1.2765	15.31	0.5001	1.2079	14.71
0.9998	1.3889	15.64	0.7499	1.3129	15.14
			1.0008	1.4339	15.51
m_A = 0.9997 mol kg^{-1}			m_A = 1.4992 mol kg^{-1}		
0.2493	1.1505	14.00	0	1.1059	13.13
0.4996	1.2590	14.61	1.4992	1.2397	13.84
0.7494	1.3769	15.07	1.5004	1.3711	14.55
0.9996	1.4978	15.43	1.4992	1.4996	15.00
			1.4981	1.6307	15.37

L-alanine - $(C_2H_5)_4NBr - H_2O$

m_A = 0.0996 mol kg^{-1}			m_A = 0.4993 mol kg^{-1}		
0.0999	0.9815	14.64	0.0999	1.0725	14.05
0.2493	1.0291	15.13	0.2493	1.1286	14.58
0.5001	1.1172	15.52	0.5006	1.2326	15.14
1.1997	1.4183	16.20	1.1992	1.5675	16.07
m_A = 0.7501 mol kg^{-1}			m_A = 1.001 mol kg^{-1}		
0.0999	1.1424	14.05	0.1004	1.2108	14.10
0.2498	1.2053	14.53	0.2498	1.2762	14.53
0.5001	1.3044	15.06	0.5001	1.3933	15.06
1.1996	1.6550	16.03	1.2003	1.7575	16.03

Glycylglycine - $(C_2H_5)_4NBr - H_2O$

m_A = 0.0998 mol kg^{-1}			m_A = 0.5001 mol kg^{-1}		
0	0.9265	14.19	0.1832	1.1458	15.01
0.0999	0.9862	14.98	0.3663	1.2247	15.35
0.1837	1.0154	15.20	0.5862	1.3416	15.69
0.3669	1.0818	15.49	0.7333	1.3903	15.83
0.5863	1.1688	15.73	0.9997	1.5197	16.11
0.7332	1.2279	15.86			
0.9993	1.3532	16.12			
m_A = 1.0002 mol kg^{-1}					
0.1832	1.3381	15.21			
0.5863	1.5367	15.80			

0.7332	1.6146	15.97
1.0006	1.7910	16.28

Table 7.8: Experimental Viscosities of $(C_4H_9)_4NBr$ in glycine, L-alanine and glycylglycine at 298.15 K

m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})	m_J / (mol kg^{-1})	η / (mPa s)	$\Delta G^{\#}$ / (kJ mol^{-1})
Glycine - $(C_4H_9)_4NBr - H_2O$					
m_A = 0.4996 mol kg^{-1}			m_A = 0.7503 mol kg^{-1}		
0.0499	1.0312	13.67	0.0502	1.0710	13.57
0.0996	1.0918	15.25	0.0999	1.1376	14.06
0.4997	1.6643	16.60	0.4998	1.7300	16.35
0.6997	2.0068	17.30	0.7010	2.0894	17.08
m_A = 1.0001 mol kg^{-1}			m_A = 1.5001 mol kg^{-1}		
0.0502	1.0987	13.51	0.0499	1.1847	13.55
0.1002	1.1701	13.95	0.0999	1.2475	13.89
0.4998	1.7710	16.14	0.4998	1.8977	15.94
0.6997	2.1294	16.88	0.7002	2.2798	16.67
L-alanine - $(C_4H_9)_4NBr - H_2O$					
m_A = 0.1007 mol kg^{-1}			m_A = 0.4992 mol kg^{-1}		
0.0992	1.05603	14.64	0.1002	1.1635	14.05
0.2501	1.2468	15.13	0.2501	1.3767	14.58
0.5004	1.6169	15.52	0.5004	1.7852	15.14

0.6999	1.9527	16.20	0.6998	2.1324	16.07
	m_A = 0.7498 mol kg^{-1}			m_A = 0.9996 mol kg^{-1}	
0.1002	1.2468	14.05	0.0999	1.3164	14.10
0.2503	1.4605	14.53	0.2501	1.5495	14.53
0.5003	1.8671	15.06	0.5001	1.9916	15.06
0.7002	2.3332	16.03	0.6997	2.3607	16.0

Glycylglycine - $(C_4H_9)_4NBr – H_2O$

	m_A = 0.1001 mol kg^{-1}			m_A = 0.4997 mol kg^{-1}	
0.0499	1.0139	15.38	0.0502	1.1415	14.96
0.0999	1.0735	15.89	0.0999	1.2120	15.33
0.2999	1.3344	16.89	0.2997	1.4995	16.38
0.6003	1.8108	17.81	0.6002	2.0152	17.47
	m_A = 0.7506 mol kg^{-1}				
0					
0.0499	1.2339	15.03			
0.1002	1.2990	15.33			
0.2891	1.6041	16.29			
0.5996	2.1728	17.42			

Viscosity of amino acid or peptide in R_4NBr increases with increase in concentration of A and J. The enhancement in viscosity is in the order of glycine < L-alanine < glycylglycine and $(CH_3)_4NBr$ < $(C_2H_5)_4NBr$ < $(C_4H_9)_4NBr$. Thus, with the increase in bulky groups on amino acids or R_4NBr the viscosity increases. This sequence

is also reflected in the $\partial\eta / \partial m_J$ values. The $\partial\eta / \partial m_J$ values of 1 mol kg^{-1} glycine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ are 0.14, 0.47 and 1.56 mPa s kg mol^{-1}, respectively. The values increase to 0.16 mPa s kg mol^{-1} in $(CH_3)_4NBr$, 0.54 mPa s kg mol^{-1} in $(C_2H_5)_4NBr$ and 1.72 mPa s kg mol^{-1} in $(C_4H_9)_4NBr$ in 1 mol kg^{-1} L-alanine.

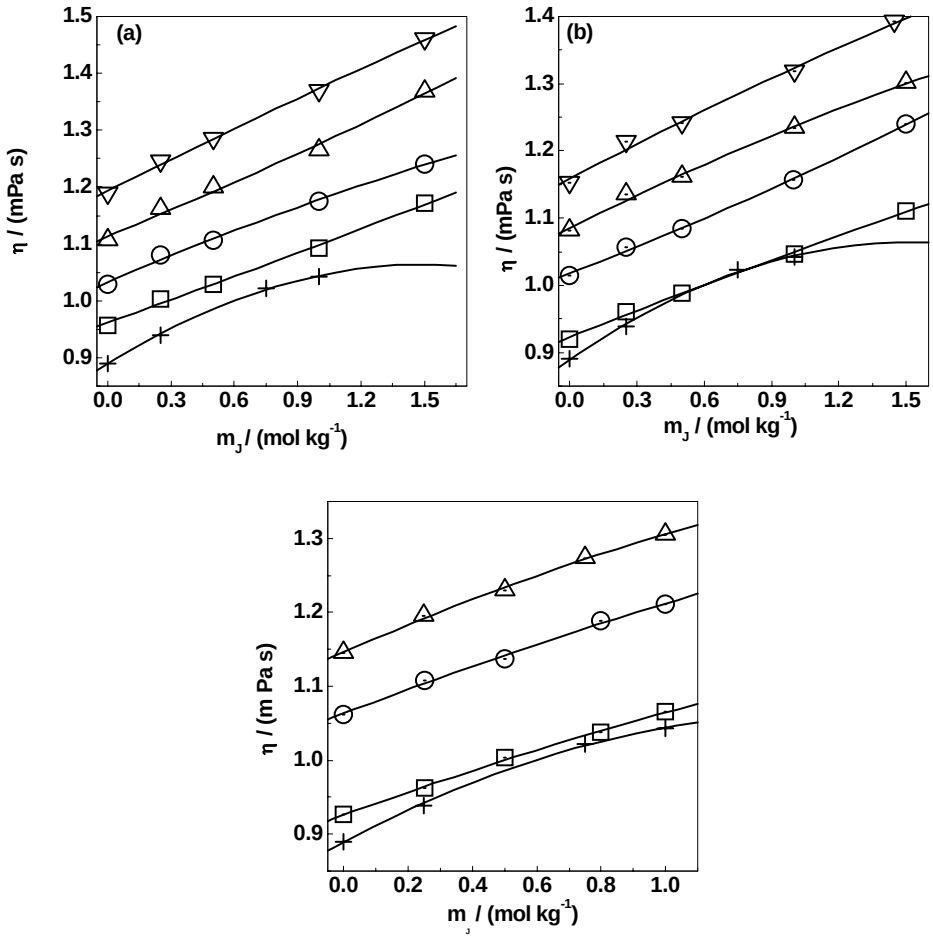


Figure 7.7: Variations of viscosity, η vs. m_J of $(CH_3)_4NBr$ **(a)** in H_2O (+), glycine 0.5 mol kg^{-1} (π), 1 mol kg^{-1} (O), 1.5 mol kg^{-1} (Δ), 2 mol kg^{-1} (∇); **(b)** in H_2O (+), L-alanine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ) 1 mol kg^{-1} (∇); **(c)** in H_2O (+), + glycylglycine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ)

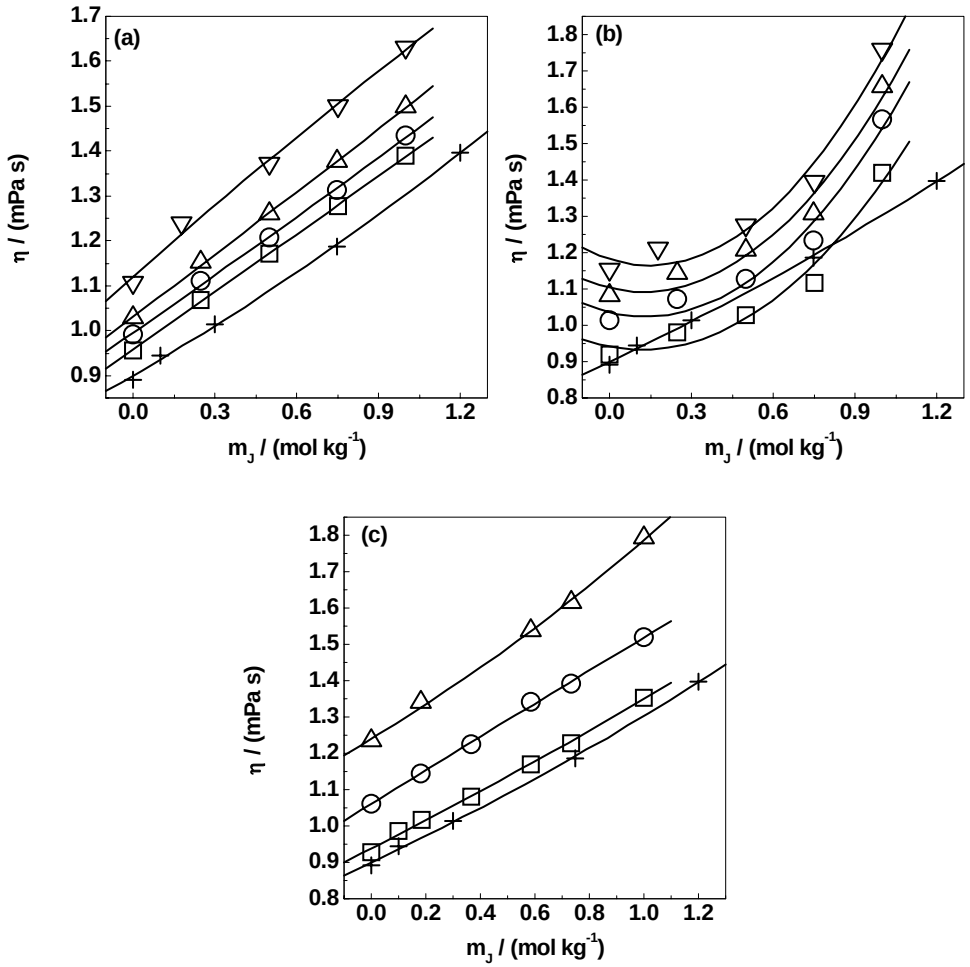


Figure 7.8: Plots of viscosity, η vs. m_J of $(C_2H_5)_4NBr$ **(a)** in H_2O (+), glycine 0.5 mol kg^{-1} (π), 0.75 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (∇); **(b)** in H_2O (+), L-alanine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ) 1 mol kg^{-1} (∇); **(c)** in H_2O (+), + glycylglycine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ)

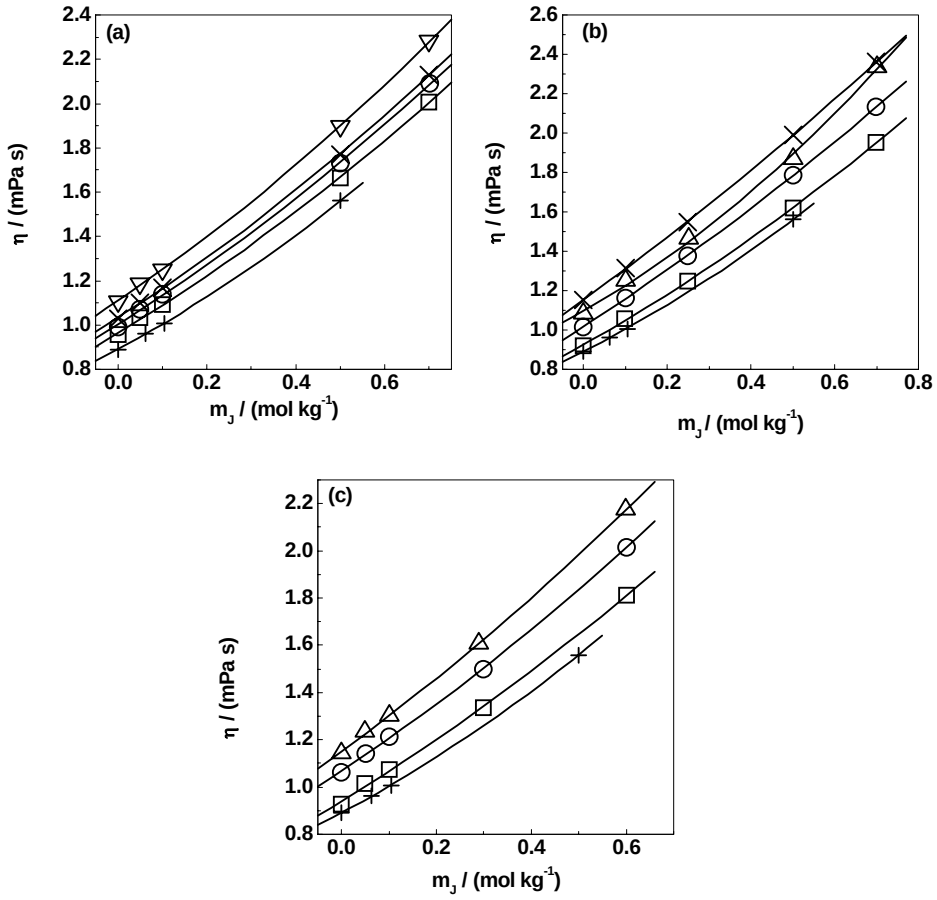


Figure 7.9: Plots of viscosity, η vs. m_J of $(C_4H_9)_4NBr$ **(a)** in H_2O (+), glycine 0.5 mol kg^{-1} (π), 0.75 mol kg^{-1} (O), 1 mol kg^{-1} (X), 1.5 mol kg^{-1} (∇); **(b)** in H_2O (+), L-alanine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ) 1 mol kg^{-1} (X); **(c)** in H_2O (+), + glycylglycine 0.1 mol kg^{-1} (π), 0.5 mol kg^{-1} (O), 0.75 mol kg^{-1} (Δ)

The viscosities listed in **Table 7.6 – 7.8** can be successfully correlated using **equations (8)**. The coefficients δ^0_{AJW} and δ^1_{AJW} obtained by regression along with rmsd of the fits are tabulated in **Table 7.9**. Accurate correlation of mixture viscosities using the coefficients listed in **Table 7.9** are presented in **Figures 7.4 (b) and (c).** In the **Figure 7.4 (b)** the $\Delta\eta$ ($\Delta\eta = \eta_{exp.} - \eta_{cor.}$) are plotted as a function of m_J for amino acids and peptides in $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$. The maximum deviation noted in $(CH_3)_4NBr$ is 0.0796 mPa s and minimum deviation is –0.0572 m Pa s, while that in $(C_2H_5)_4NBr$ is 0.0339 mPa s and –0.0387 m Pa s, respectively. The $\eta_{exp.}$ values are plotted as a function of $\eta_{cor.}$ in **Figure 7.4 (c)** for amino acids and peptide in $(C_4H_9)_4NBr$. The average rmsd for $(C_4H_9)_4NBr$ is observed to be 0.0127 mPa s in glycine, 0.0153 mPa s in L-alanine and 0.0162 mPa s in glycylglycine.

The δ^0_{AJW} coefficients listed in **Table 7.9** are plotted as a function of m_A in **Figure 7.5 (b)** for amino acids and peptide in $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$. In **Figure 7.5 (c)** δ^0_{AJW} for amino acids and peptides in $(C_4H_9)_4NBr$ is depicted. The δ^0_{AJW} for mixtures decrease with increase in m_A. The decrease in δ^0_{AJW} in presence of hydrophobic ions is more as compared to hydrophilic ions. The $\Delta G^{\#}$ listed in **Tables 7.6 – 7.8** of amino acids and peptide in R4NBr are regressed using **equation (7)**. The coefficients of regression g^0_{AJW} and g^1_{AJW} are tabulated in **Table 7.10**. The variation of g^0_{AJW} of amino acids and peptide as a function of m_A is shown in **Figures 7.6 (b)** in the presence of $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ and in $(C_4H_9)_4NBr$ in **Figure 7.6 (c).** g^0_{AJW} shows a decrease with increase in m_A as observed for δ^0_{AJW}.

Table 7.9: viscosity coefficients, δ^0_{AJW} and δ^1_{AJW} for glycine, L-alanine and glycylglycine in the presence of tetra-n-alkylammonium bromides at 298.15 K.

m_A / (mol kg^{-1})	δ^0_{AJW} / (mPa s kg^2 mol^{-2})	δ^1_{AJW} / (mPa s kg^4 mol^{-4})	rmsd / (mPa s)	m_A / (mol kg^{-1})	δ^0_{AJW} / (mPa s kg^2 mol^{-2})	δ^1_{AJW} / (mPa s kg^4 mol^{-4})	rmsd / (mPa s)
Glycine – $(CH_3)_4NBr$ – H_2O				L-alanine – $(CH_3)_4NBr$ – H_2O			
0.4993	0.6947 (0.1620)	-1.2726 (0.2472)	0.0387	0.1002	3.058 (0.985)	-36.38 (7.08)	0.0490
1.0003	0.3927 (0.0655)	-0.2936 (0.0499)	0.0010	0.4992	0.8038 (0.1639)	-1.3198 (0.2505)	0.0400
1.4999	0.2657 (0.0252)	-0.1060 (0.0128)	0.0173	0.7503	0.6378 (0.0936)	-0.6134 (0.0952)	0.0346
1.9995	0.2116 (0.0221)	-0.0554 (0.0084)	0.0214	0.9992	0.4798 (0.0498)	-0.2865 (0.0393)	0.0224
Glycylglycine – $(CH_3)_4NBr$ – H_2O				Glycine – $(C_2H_5)_4NBr$ – H_2O			
0.0995	0.3214 (0.0851)	0.0145 (0.9697)	0.0022	0.4999	0.7839 (0.0405)	-0.7146 (0.0943)	0.0063
0.5004	0.6319 (0.0802)	-0.6311 (0.1842)	0.0126	0.7500	0.6028 (0.0413)	-0.3206 (0.0641)	0.0104
0.7502	0.5163 (0.0446)	-0.3087 (0.0692)	0.0109	0.9997	0.3209 (0.0266)	-0.0765 (0.0135)	0.0192

				1.4992	0.4538	-0.1035	0.0221
					(0.0471)	(0.0363)	
L-alanine – $(C_2H_5)_4NBr$ – H_2O				Glycylglycine – $(C_2H_5)_4NBr$ – H_2O			
0.0999	2.059	-13.10	0.0217	0.0998	2.2889	-13.26	0.0182
	(0.604)	(5.49)			(0.4782)	(5.76)	
0.4993	0.9823	-0.8510	0.0155	0.5001	1.1344	-1.039	0.0095
	(0.0864)	(0.1585)			(0.0504)	(0.121)	
0.7500	0.7792	-0.3964	0.0179	1.0001	0.6993	-0.1725	0.0155
	(0.0667)	(0.0808)			(0.0509)	(0.0593)	
1.0001	0.4703	0.2603	0.0313				
	(0.1456)	(0.2371)					
Glycine – $(C_4H_9)_4NBr$ – H_2O				L-alanine – $(C_4H_9)_4NBr$ – H_2O			
0.4996	2.506	-3.395	0.0134	0.1007	7.788	-86.7	0.0179
	(0.165)	(0.521)			(0.827)	(13.3)	
0.7503	1.887	-1.346	0.0118	0.4992	2.953	-3.830	0.0077
	(0.098)	(0.206)			(0.070)	(0.230)	
1.0001	1.422	-0.5703	0.0200	0.7498	1.972	-0.8038	0.0300
	(0.039)	(0.0611)			(0.186)	(0.4033)	
1.5001	1.021	-0.1554	0.0055	0.9996	1.768	-0.7364	0.0055
	(0.0217)	(0.0228)			(0.0252)	(0.0410)	
Glycylglycine – $(C_4H_9)_4NBr$ – H_2O							
0.1001	9.840	-118.0	0.0264				
	(1.522)	(27.8)					

0.4997	3.162	-4.202	0.0126
	(0.145)	(0.532)	
0.7506	2.357	-1.513	0.0095
	(0.072)	(0.174)	

Table 7.10: The coefficients, g^0_{AJW} and g^1_{AJW} for free energy of activation for viscous flow for glycine, L-alanine and glycylglycine in the presence of tetra-n-alkylammonium bromides at 298.15 K.

m_A / (mol kg^{-1})	g^0_{AJW} / (kJ kg^2 mol^{-3})	g^1_{AJW} / (kJ kg^4 mol^{-5})	rmsd / (kJ mol^{-1})	m_A / (mol kg^{-1})	g^0_{AJW} / (kJ kg^2 mol^{-3})	g^1_{AJW} / (kJ kg^4 mol^{-5})	rmsd / (kJ mol^{-1})
Glycine – $(CH_3)_4NBr$ – H_2O				L-alanine – $(CH_3)_4NBr$ – H_2O			
0.4993	2.126	-3.362	0.0559	0.1002	6.895	-74.8	0.0933
	(0.2310)	(0.352)			(1.920)	(14.6)	
1.0003	1.109	-0.7474	0.0447	0.4992	2.029	-3.098	0.0608
	(0.092)	(0.0701)			(0.250)	(0.383)	
1.4999	0.7016	-0.2723	0.0239	0.7503	1.531	-1.414	0.0529
	(0.0328)	(0.0167)			(0.145)	(0.148)	
1.9995	0.5457	-0.1476	0.0520	0.9992	1.140	-0.697	0.041
	(0.0534)	(0.0203)			(0.089)	(0.071)	
Glycylglycine – $(CH_3)_4NBr$ – H_2O				Glycine – $(C_2H_5)_4NBr$ – H_2O			
0.0995	1.487	-9.703	0.0277	0.4999	3.985	-5.542	0.0808

	(0.873)	(10.1)			(0.488)	(1.138)	
0.5004	1.252	-1.355	0.0303	0.7500	2.728	-2.301	0.0706
	(0.189)	(0.435)			(0.284)	(0.441)	
0.7502	0.9709	-0.6339	0.0255	0.9997	1.162	-0.3466	0.1063
	(0.1024)	(0.1591)			(0.146)	(0.0744)	
				1.4992	1.449	-0.5065	0.0683
					(0.146)	(0.1124)	
L-alanine – $(C_2H_5)_4NBr$ – H_2O				Glycylglycine – $(C_2H_5)_4NBr$ – H_2O			
0.0999	10.80	-80.2	0.1640	0.0998	7.072	-52.88	0.0728
	(4.57)	(41.5)			(1.911)	(23.03)	
0.4993	3.800	-4.629	0.0943	0.5001	2.729	-3.241	0.0316
	(0.532)	(0.975)			(0.170)	(0.407)	
0.7500	2.624	-1.932	0.0789	1.0001	1.544	-0.7112	0.0400
	(0.293)	(0.355)			(0.131)	(0.1526)	
1.0001	2.010	-1.025	0.0538				
	(0.252)	(0.411)					
Glycine – $(C_4H_9)_4NBr$ – H_2O				L-alanine – $(C_4H_9)_4NBr$ – H_2O			
0.4996	12.629	-26.02	0.2119	0.1007	38.65	-488	0.2522
	(2.639)	(0.31)			(11.59)	(187)	
0.7503	8.216	-10.06	0.1466	0.4992	11.53	-22.99	0.1356
	(1.222)	(2.56)			(1.27)	(4.18)	
1.0001	5.744	-4.745	0.0975	0.7498	7.309	-8.171	0.1265
	(0.611)	(0.965)			(0.783)	(1.700)	

1.5001	3.503	-1.617	0.0557	0.9996	5.456	-4.401	0.0678
	(0.234)	(0.245)			(0.316)	(0.515)	
Glycylglycine – $(C_4H_9)_4NBr$ – H_2O							
0.1001	38.34	-541	0.2007				
	(11.57)	(212)					
0.4997	9.482	-19.62	0.0735				
	(0.845)	(3.10)					
0.7506	6.263	-7.507	0.0443				
	(0.340)	(0.826)					

7.5 Conclusion:

In this chapter the experimental viscosity data on the mixtures of amnio acids/peptide and electrolytes have been collected. The effect of hydrophilic and hydrophobic ions on viscosity of mixture of aqueous amino acid or peptide in electrolytic solution is discussed. As observed in volumetric studies, the effect of $MgCl_2$ and Na_2SO_4 on viscosity of mixtures is higher as compared to 1:1 electrolytes KCl and KBr. The hydrophobic ions show maximum influence on viscosity of mixtures. The increase in the slope of the η vs. m_J plots is almost 10-fold in the case of hydrophobic ions than in hydrophilic ions. A simple empirical set of equations is proposed to correlate viscosities of mixtures in concentrated solutions. The utility of equations is extended to the Gibbs free energy of activation for viscous flow of solution.

An examination of ionic interactions in aqueous amino acids is the sole objective of this thesis. Ionic interactions have been examined with the help of volumetric and viscous behavior the amino acid – electrolyte – water systems.

In view of a careful literature survey indicating absence of investigation in concentrated solutions, an attempt has been made in this thesis to measure density and speed of sound of glycine, L-alanine and glycylglycine (a peptide) in 1-1 and 2-1 hydrophilic electrolytes. Considering the hydrophobic hydration present in quaternary ammonium electrolytes, exhaustive studies were made involving these electrolytes and amino acids.

Since no equations are available to date for accounting the ionic interactions in amino acids, a semi-empirical model was developed. The property of amino acid in an electrolyte solution was represented with the help of a single ion – amino acid interaction parameter. This parameter was then used in the Pitzer equation to calculate the properties of electrolyte. The developed equations were noted to describe activity coefficients, apparent molar volume and apparent molar compressibility of both the amino acid and electrolyte in their aqueous mixtures.

The viscosity of aqueous amino acid – electrolyte solutions was measured and analysed in terms of binary and ternary interactions.

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List of Publications

1. **Rohini Badarayani,** Anil Kumar, Experimental sound velocities and derived compressibilities of the KCl (1) + $CaCl_2$ (2) + water (3) and KCl (1) + $MgCl_2$ (2) + water (3) systems up to ionic strength of 4 mol kg^{-1} at 298.15 K, *J. Chem. Eng. Data*, **1999**, 44, 1076.
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6. **Rohini Badarayani,** Anil Kumar, Effect of temperature on the volumetric properties of L-alanine (1) + KCl (2) + H_2O (3) system, *J. Chem. Eng. Data*, **2003**, 48, 664.
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8. **Rohini Badarayani,** Anil Kumar, Effect of tetra-n-alkylammonium bromides on the volumetric properties of glycine, L-alanine and glycylglycine at T = 298.15 K, *J. Chem. Thermodyn*. **2003** in Press

Manuscripts under Preparation:

1. **Rohini Badarayani**, Anil Kumar, Thermodynamics of amino acids in concentrated ionic solutions: correlations
2. **Rohini Badarayani**, Anil Kumar, The mixing effect of glycylglycine - KCl, KBr and Na_2SO_4 from volumetric and viscometric investigations at 298.15K
3. **Rohini Badarayani**, Anil Kumar, The ionic interactions of amino acids: viscometric investigations
4. **Rohini Badarayani**, Anil Kumar, Amino acid – tetra-n-alkylammonium bromide – water interactions: viscometric study
5. **Rohini Badarayani**, Anil Kumar, Volumetric investigations of amino acids in the mixture of ions at 298.15 K.