EFFECT OF ELECTROLYTES ON THERMODYNAMICS OF AMINO ACIDS IN AQUEOUS AND NON-AQUEOUS MEDIA

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(RESEARCH GUIDE)

MAY 2008

Dedicated to

Father, Mother

&

Memory of Grand mother

CERTIFICATE

It is certified that the work incorporated in this thesis **"Effect of electrolytes on thermodynamics of amino acids in aqueous and non-aqueous media"** submitted by **Mr. Satpute Dilip Balbhim**, 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.

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DECLARATION

I hereby declare that the work incorporated in the present thesis **"Effect of electrolytes on thermodynamics of amino acids in aqueous and non-aqueous media."** Submitted for the Degree of Doctor of Philosophy to the University of Pune 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.

Date:

Place:

(D.B. Satpute)

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Chapter 1

INTRODUCTION

Physical, chemical and biological behavior of biological macromolecules like proteins, nucleic acids, etc is governed by the water content and ionic species present in the systems. To explain the behavior of these biological macromolecules it is important to understand the ionic solutions in terms of ion-ion and ion–water interactions along with the biomolecules– water interactions and how these interactions are altered in the presence of proteins and other bio-molecules. In spite of research carried over several years, these two aspects remain mystery for the physical and biological chemists and have been studied by investigating the physico-chemical behavior of ionic species in biological systems. Understanding of physicochemical studies of biological macromolecules in mixed aqueous solution helps in better knowledge of the interactions between them.

1. 1: Effect of electrolytes on biological macromolecules:

The structure of biomolecules is made up 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 depends upon several parameters like residue composition, sequence and solvent environment, etc. The number of different conformations can be divided into two types.

1. **Native conformation*:*** These are the conformations in which chain – chain contacts are thermodynamically favored over chain - solvent contacts.

and

2. **Random coil conformation*:*** These are the conformations in which chain – solvent contacts are thermodynamically favored over chain – chain contacts.

The energetic balance between native and random coil conformations depends upon many factors like chemical restrictions built into the covalent bonding of the back bone chains as well as hydrogen bonding, electrostatic interactions, hydrophobic bonding, etc.

The temperature, pH, ionic strength or concentration of specific small molecular interactions can be employed to stabilize the native conformation against transition process.

Neutral electrolytes influence conformational properties and stability of these biomolecules. The electrolytes that are significantly soluble in water do not alter the solution pH and hence do not 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.

Electrolytes and carbohydrates located at cell surfaces are important as receptor for the bioactive structures of harmones, enzymes, viruses, antibodies etc. The studies of electrolyte-protein and carbohydrate-protein interactions are also important for immunology, biosynthesis, pharmacology and medicine.

The classical work on effect of electrolytes on proteins was carried out by von Hippel[1]. It was concluded that the ions such as Na^+, K^+, NH_4^+, SO_4^{2-} etc. stabilize the native conformation of proteins. On the other hand, 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.

The effect of electrolytes on proteins has been rationalized in terms of melting temperature of proteins T_m with salt concentrations, c_S:

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

T_m^0 is the melting temperature of the same protein at zero concentration of electrolyte and K is molar effectiveness of the electrolyte. If a salt has a positive K value, it indicates stabilizer, otherwise destabilizer. In case K = 0, a salt has no effect on the protein stability. The T_m values for many proteins depend linearly on the salt concentration[2]. It may be noted that the value of K varied according to type of salt used for the investigation of the thermal stability of proteins. From an examination of the K values it is seen that GnCl is weaker destabilizer than GuSCN[3]. On the other hand Gn_2SO_4 is observed to be protein

stabilizer[3]. The tetraalkylammonium salts bear significant effect on T_m [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, while the increasing chain length influences the thermal stability of proteins to greater extent. 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 to

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

Where the subscript i indicates ionic species.

1.2 Thermodynamics of aqueous amino acids:

Thermodynamics of aqueous amino acid systems is required for designing separation techniques, purification processes and drying processes in food engineering. Amino acids and peptides are non-electrolytic in nature. They upon dissolved in water may have the dipolar, zwitterionic structural forms. The important interactions in aqueous amino acids include charged centers (COO^- and NH_3^+) and water molecules. The separation of COO^- and NH_3^+ groups by $-CH_2-$ groups increases the intermolecular interactions involving cospheres of charged centers and suppressed hydrophobic interactions due to steric effects. A large number of reports are available on equilibrium free energy, entropy, enthalpy of mixing, activity, osmotic coefficients[5-24] and heat capacities[25-31] of aqueous α-amino acids, ω-amino acids or oligopeptides. The hydration number of various amino acids and oligopeptides in aqueous solution as a function of temperature and pressure are studied[32-81]Few reports are also available on surface properties [82]. Below are outlines some relevant investigations made with respect to aqueous amino acids:

The solubility of amino acids varies with temperature and pH of aqueous amino acids. The solubilities of amino acids in water have been estimated and correlated in

terms of activity and osmotic coefficients [7, 8,10,13,19] .The activity and vapour pressure data of aqueous amino acids have been employed to model thermodynamics[89-99] of these systems using correlation based on UNIFAC[89], UNIQUAC[24, 90,] perturbation theory [91-94] and Monte Carlo method[95]. Leyendekkers developed a thermodynamic model for partial molar volume and partial molar compressibility of amino acids in water based on Kirkwood – Fuoss theory [59].

The problem of calculating number of water molecules bound to the charged centers of amino acids has been addressed by Millero et al. The information has been obtained by a thorough examination of apparent molar volumes, ϕ_{VAW} and compressibilities, ϕ_{KAW} derived from density and speed of sound data of few aqueous amino acids at 298.15 K[35]. Further, the poor additivity of standard partial molar quantities of aqueous amino acids at 298.15K has been attributed to ionization of COOH and NH_2 groups[26, 44, 45.] 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 combined effects of hydrophilic and hydrophobic solute–solute interactions mediated through typical water structure have been employed to explain the apparent molar volume of amino acid with concentration in water.

The speeds of sound for aqueous amino acids were measured in the temperature range of 288.15–343.15 K and the adiabatic compressibilities calculated there from [39-42]. 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 concluded that atomic groups of different chemical nature could exert different actions on relaxation part of water compressibility as:

1. 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.

2. 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 [50-53]

On the basis of the volumes, compressibilities, expansibilities and heat capacities of α-amino acids, ω-amino acids and polypeptides[27, 47,48] the volume change in the formation of zwitterionic structures were estimated and correlated with distance between the NH_3^+ and COO^- groups and with the nature of the chain separating them. The partial molar volumes of amino acids were less than those of neutral molecules. Other significant investigations in this area are made by Chalikian et.al [42, 43] and Shahidi and Farrell[38]. Chalikian et.al. Calculated contribution of $–CH_2$ group for explaining apparent molal volumes and compressibility[42, 43]. Shahidi and Farrell correlated partial molar volumes ofα, ω-amino acids with their van der Waals volumes[38]. The volume decrease was ascribed to the hydrophobic hydration of a $–CH_2$ group α to a COO^- group and to an NH_3^+ group.

The contribution from amino acid side chains $–CH_3$ and $–CH_2OH$ and end group hydration effects have been described by Jolicoeur and Boileau by measuring apparent molar volumes and heat capacities of glycine, alanine, serine and their oligopeptides at 298.15 K[37].

Interactions of some amino acids in aqueous solution of dodecyl sulphate and cetyltrimethylammonium bromide were studied by Singh et al.[100] The volumes of transfer data suggested that ion-ion or ion-hydrophilic group interactions of the amino acids and peptides were stronger with SDS as compared to those with CTAB. The interpretation was supported by the hydration number.

The changes in volumes of aqueous amino acids at 298.15K and at 1000 atm. pressure were also reported and it was observed that apparent molar volume of dipolar amino acids increased with pressure. Electrostriction decreases with increasing pressure and appeared to be dependent on the dipole moment of amino acids. Singh et. al. on the basis of the apparent molar volumes of various amino acids at 310.15 K concluded that the magnitude of change in apparent molar volume decreased from leucine>glycine>alanine, indicating the build up of hydrophilic-hydrophobic group interactions with increase of the chain side length of amino acids[101].

Important contribution on partial molar volume, isentropic compressibility, isentropic pressure coefficients at infinite dilution and isobaric expansion coefficients for peptides were added by Hedwig[15, 60-69]. Various thermodynamic properties of aqueous oligopeptides have been investigated by many workers including Hedwig[15, 60-69], Verrall[57], Iqbal [58], Makhatadze[28-30] and Privalov, etc.[22, 28-29, 70]. A detailed account of heat capacities of amino acids is presented by Makhatadze in a review[30]. It has been found the partial molar volume and compressibility of a glycyl unit in a peptide hypothetical infinite length contributes 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. Pioneering work on entropy and free energy of aqueous peptides along with the heat capacities and partial molar volumes was carried out by Privalov[22, 28, 29, 70].

A knowledge of viscosity B-coefficients is essential for understanding the structure-making and –breaking abilities of solutes in water. The viscosities B-coefficients for aqueous amino acids have been calculated at 278.15 and 298.15 K[83]. 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[84-88]. A review by Lark and coworkers compiles the viscosity and B coefficients for different amino acids [86].

Zhao thoroughly reviewed viscosity B-coefficients and standard partial molar volumes at different temperature and found that these data are important for interpretation of the hydration and other properties of proteins and peptides. The viscometric and volumetric properties of amino acids can help to interpret the behavior of peptides and proteins in aqueous solutions[102].

Interactions of few α-amino acids with tetra-n-alkylammonium bromides at different temperature were studied recently by Ali et. al. They noted that glycine alanine and valine behaved as structure breakers in the aqueous tetra-n-alkylammonium bromide solutions[103] .

Anwar Ali, et.al. have also studied effect of temperature on the apparent molar volumes, coefficients of viscosity and refractive indices of these systems. It was noted that glycine behaved as a structure maker while serine and valine as structure breakers in aqueous d-glucose solutions.[104] This observation was based upon the coefficients of viscosity i.e. A and B.

1.3: Thermodynamics of aqueous electrolytes

Electrolytes play a significant role in 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.

In 1923, Debye and Hückel presented their theory of interionic attraction[105] 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. Later, several modifications of Debye-Huckel equations were proposed. Some important developments in this direction are given below:

Guggenheim and Turgeon presented a modified version of Debye– Hückel equation on the scale of mole fraction[106] according to which the activity coefficient of 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.

Later, Bromley suggested that the specific ion–solvent interactions could be taken into account in concentrated solutions[107, 108]. These interactions were calculated taking into account by ionic strength dependent constant B and proposed the following equation for the correlation of $\gamma_{\pm}$:

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

The Bromely method has been found to be applicable to strong electrolytes up to an ionic strength of 6 mol kg^{-1}. An attempt was also made to compensate strong ion association while dealing with salts like sulphates.

Meissner demonstrated that a family of curves could be obtained by plottingΓ, reduced activity coefficient ($\Gamma = \gamma_{\pm}^{1/z+z-}$) versus ionic strength[109-111]. If one value of $\gamma_{\pm}$ above the Debye–Hückel concentration range is obtained, then $\gamma_{\pm}$ for any concentration (from low to saturate) 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 more important in solutions of weak electrolytes, were ignored.

Chen et.al. developed 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[112]. 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[113]. The short–range interactions are function of mole fractions of ions and molecules, (locally and overall) NRTL interaction parameter and Chen interaction parameters.

Later, K. S. Pitzer from University of California at Berkeley developed a specific ion interaction theory to deal with concentrated electrolyte solutions.[114]. 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 short–range forces are accounted by virial coefficients. These coefficients are dependent 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 isν, $\nu = \nu_+ + \nu_-$ 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.

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[115] and Zemitis et.al.[116] Similarly for other thermodynamic properties the Horvath's[117] hand book can be referred.

1.4: Thermodynamics of aqueous amino acids in electrolytes

Literature survey shows that electrolytes can influence volumetric, 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. However there exist a very few studies on the effect of electrolytes on the volumetric properties of amino acids in the concentrated electrolyte solutions.

The non-idealities (activity, γ and osmotic coefficients,ϕ) in terms of in aqueous amino acids in electrolytes have been largely investigated in the past. A study of free energy relationships in some amino acids–NaCl–H_2O was studied by Schrier and Robinson by isopiestic vapour pressure method[118, 119]. 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.

Merida et.al. modified the Pitzer equations for amino acid–electrolyte–H_2O system[120]. The dependence of binary interaction parameter (amino acid–electrolyte) on both ionic strength and neutral species concentration were taken in to consideration. He measured the activity coefficients, γ_A of glycine, β-alanine and DL-α-aminobutyric acid

in aqueous NaCl[120-123]. 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. 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. It was also noted that amino acid concentration did 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 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[124]. The free energy, enthalpy and entropy of amino acid transfer from H_2O to aqueous electrolytic solutions were also calculated. The activity coefficients of DL-alanine in aqueous KCl or RbCl were measured at 308 K[125]. The results indicated net attractive interactions between electrolytes and DL–alanine.

Amino acids show variable solubility in NaCl[126, 127]. 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 conclude 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[128-137]. They examined 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 electrolytes of NaCl, NaBr, KCl, KBr, $NaNO_3$, KNO_3, HCl, HNO_3, NaOH and KOH. They also studied the effect of cations, anions and pH on activity coefficients. They concluded that solubility of amino acids depends on the nature of anion as well as cation. 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[138, 139]. The enthalpy data for the 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 have been reported for the enthalpies of mixing amino acids with electrolytes[140-144]. 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 enthalpy interaction parameters were found dependent on the ionic strength 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[145]. The enthalpy or entropy of interaction between L-cystein and NaCl is negative, while between L-cystein and $MgCl_2$ is positive. 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, and KCl to study the effect of cation[146].

The enthalpies of interaction of amino acids in aqueous electrolytes were studied in a series of papers[147-157]. 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 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 different temperatures[158]. 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 [159,160] apparent molar volumes and viscosities for amino acids at 288.15, 298.15 and 308.15 K in KSCN[159] solution and NH_4Cl [161]. 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[162, 163]. 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. 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 [164,165]. Positive transfer compressibilities were also obtained in presence of NaCl and glucose solution by Banipal and Sehgal[166]. The positive transfer properties obtained indicate glycine has larger size in aqueous electrolytes than in H_2O. This effect was attributed 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 amino acids in organic salts like sodium acetate and sodium butyrate[167-169]. 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 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[170, 171]. Ogawa et.al. have reported apparent molar volumes, compressibilities and relative viscosities of amino acids in LiCl, NaCl and KCl[172]. 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.

Surface tensions of amino acids in 0.1 M NaCl were measured by Bull et. al. at 303.15 K[173]. 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.

Viscosity and apparent molar volumes of glycine have been reported in transition metal chloride solutions[174]. All the electrolytes were observed to behave as structure makers or promoters in order of Ni^{2+}> Co^{2+}>Zn^{2+}>Cu^{2+}. Very few data 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[175, 176], and in alkali metal halides[172].

Recently Yan et.al. have measured viscosity of amino acids in aqueous urea and GnCl[177]. The B-coefficients and activation parameters for the viscous flow have been 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.

Urea and guanidinium salts are well known as 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. Lapanje et.al.

have studied the interaction of some oligoglycines and oligoleucines in aqueous urea and GnCl[178]. 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[179].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. Similarly Tanford also observed this conclusion[180-182]. Same 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[183].

Kresheck and Bejamin reported calorimetric study of amino acids in aqueous urea[184]. 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. 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[185]. 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[186].

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[187, 188]. 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[189]. The transfer properties were modelled using Helgeson, Kirkham and Flowers theory (HKF) theory[190].

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[191]. Bhat et.al measured densities

and heat capacities of some amino acids and peptides in aqueous glucose[192]. 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.

With regard to theoretical models, attempts have been made in the past for correlation of activity or osmotic coefficients of amino acids in aqueous electrolytes. Vera and coworkers attempted to correlate the results using Wilson equation, with satisfactory correlation obtained in high concentration region[128-137]. 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. 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. [193]. 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 $NaNO_3$[194]. Kuramochi and workers used the UNIFAC model for correlation of activity coefficients of amino acids[195].

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. Yet no equations are available to describe the thermodynamic behaviour of these systems.

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Chapter 2

OBJECTIVES

As discussed in the first chapter for sake of simplicity 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, different thermodynamic properties of amino acids in aqueous electrolyte solutions are studied. Also the effect of amino acids on electrolyte solutions has been examined. The thesis is aimed to measure the volumetric properties of amino acids and peptide in several aqueous electrolytic solutions and to study the effects of electrolytes on the properties of amino acids. The volumetric properties include apparent molal volumes and compressibilities of both amino acids/peptides in their aqueous solutions. The thesis also aims at proposing a thermodynamic model for excess Gibbs free energy of mixing amino acids and peptide with different electrolytes in water in terms of the ion – amino acid interaction parameter. The model is proposed to predict the properties of electrolytes in amino acids with the help of ion – amino acid – water interaction parameter derived above.

In order to achieve the above mentioned objectives the systems containing simple amino acids and electrolytes have been considered.

Chapter 3

EXPERIMENTAL SECTION

Experimental

The chemicals used in the experimentation and the few experimental techniques are discussed in this chapter.

A) Chemicals

Summary of chemicals used for 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.	DL-alanine	89.09	Biochemistry grade (>99%)	Heavy metals (as Pb) = 0.001%, TLC passes test	LOBA Chemie
4.	L-serine	105.09	Biochemistry grade (>99%)	Sulphated ash =0.1%, Iron =0.01%, Heavy metals (as Pb) = 0.001%,	LOBA Chemie
5.	DL-valine	117.15	Biochemistry grade (>99%)	Heavy metals (as Pb) = 0.001%, TLC passes test	LOBA Chemie

6.	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
7.	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 = 0.0005%	S. D. Fine Chem. Ltd.
8.	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
9.	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
10.	KBr	119.01	Pure 99%	Cl = 0.5%, I = 0.05%, SO_4 = 0.01%, BrO_3 = 0.002%, heavy metals (as Pb) =	Merck

				0.001%, Fe = 0.002%	
11.	$MgCl_2$	95.21	Synthesis grade >98%		Merck – Schuchardt
12.	Tetramethyl-ammonium bromide, $(CH_3)_4NBr$	154.06	Synthesis grade		Lancaster
13.	Tetraethyl-ammonium bromide, $(C_2H_5)_4NBr$	210.16	Pure >98%		SRL
14.	Tetra-n butylammonium bromide $(C_4H_9)_4NBr$	322.37	Extra pure A. R. > 99%	Sulphated ash = 0.1%	SRL
15.	glucose	180.16	Anhydrous G.R.	Substances Insoluble in water=0.003%,Substances Insoluble in alcohol =0.003 %, Cl =0.025, SO_4 =0.025 %, SO_{36} =0.005 % As =0.00002 % Cu =0.0001%, Fe =0.0001%, Pb= 0.0001% And sulphated ash = 0.003 %.	Merck

B) Composition of solutions

The chemicals were weighed on a CONTECH CB – series electronic balance. The accuracy of the balance is ± 0.001 g. All the salts were dried at 523 K (except tetra-n-alkylammonium bromide salts) for 2 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[1]. 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. All the solutions were prepared on the molality basis.

C) Measurement of density

Densities of the solutions of glycine, L-alanine and glycylglycine in aqueous NaBr, KCl, KBr, $MgCl_2$ and tetra-alkylsalts were measured using a DMA 60 vibrating tube digital density meter supplied by, ANTON PAAR. Its determination is based on measuring the period of oscillation of a vibrating U shaped sample tube, which is completely 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 various 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[2]. 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[3], methanol[4], and aqueous NaCl[5] solution at different concentrations. The accuracy of density meter was found to be ± 0.005 kg m^{-3}, while the precision was estimated as 0.002 kg $m.^{-3}$ A comparison of these values is given in Table 1.

Table 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

D) Measurement speed of sound

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[6]. 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[2] and aqueous NaCl[7] data at 298.15 K. A cell with 4 MHz. frequency was used to measure the speed of sound. The cell was filled by 6 to 8 ml of the solution and was allowed to equilibrate for 20 minutes 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)[2]. 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}.[7]

E) Measurement of viscosity of solution:

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[8], aqueous KCl[9] and Na_2SO_4[8]. 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:

$$\eta / \rho = C\,t - K / t \qquad (3)$$

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 [2,8].

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 20 minutes before taking reading.

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Chapter 4

VOLUMES

The partial molar volume of an electrolyte, V_2 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.

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

where n_2 is number of moles at constant temperature, T and pressure, P. It is not possible to determine the partial molar volume using the above form of expression. This is however done by using apparent molar volume, ϕ_V defined as:

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

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

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

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

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

The 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:

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

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)[1] 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:

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

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

Glycine in aqueous electrolyte solutions

The experimental densities of glycine in aqueous NaBr, KCl, KBr and $MgCl_2$ are listed in **Table 1**. The effect of different electrolytes on ϕ_{VAJW} of glycine in different electrolytes is shown in Figs. 1 – 4. The ϕ_{VAJW} of glycine increases from 42 to 55 x 10^{-6} m^3 mol^{-1} in the presence of different electrolytes. The solution of amino acid in water

shows an overall decrease in the volume of water. This is due to the electrostriction phenomena by charged end groups of amino acids. An addition of electrolyte will affect the hydration spheres of the charged end groups. As result of cation-COO^- and anion-NH_3^+ interactions, the hydrated water molecules are permitted 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 (m_J > 2 mol kg^{-1}) the slopes become negative. In dilute electrolytic solution with the increase in the concentration of amino acid, 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 increase, less number of water molecules becomes 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 1: The 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 = 0.5016 mol		m_A = 1.0036 mol		m_A = 2.0024 mol		m_A = 3.1112 mol	
kg^{-1}		kg^{-1}		kg^{-1}		kg^{-1}	
0.5011	1049.6	0.5110	1062.6	0.4985	1085.9	0.5055	1107.3
0.9921	1085.2	0.9929	1097.1	1.0310	1118.5	0.9946	1137.6
1.9936	1153.1	2.0036	1163.0	1.9491	1179.0	2.0331	1196.1
3.0040	1217.0	2.9943	1225.1	2.9590	1237.9	3.0561	1251.3
4.0028	1276.9	4.0051	1282.8	4.0603	1293.2	4.0010	1303.1

KCl

m_A = 0.5012 mol		m_A = 0.9905 mol		m_A = 2.0014 mol		m_A = 3.0022 mol	
kg^{-1}		kg^{-1}		kg^{-1}		kg^{-1}	
1.0204	1054.7	1.0021	1067.2	0.9923	1089.7	0.5014	1093.4
2.0302	1093.1	1.9925	1103.9	2.0031	1123.9	1.0023	1110.1
3.0408	1128.5	3.0031	1137.9	3.0045	1155.3	2.0032	1141.2
4.0607	1161.8	4.0044	1168.4	4.0056	1184.2	3.4003	1170.3

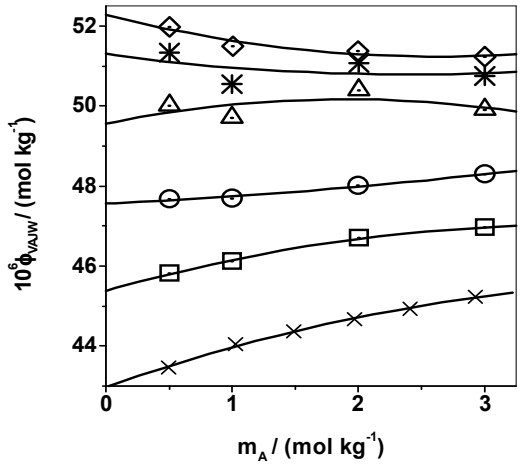
KBr

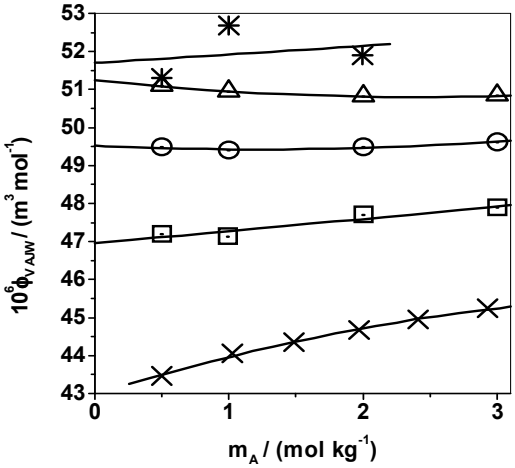
m_A = 0.4908 mol		m_A = 1.0010 mol		m_A = 2.0001 mol		m_A = 3.0004 mol	
kg^{-1}		kg^{-1}		kg^{-1}		kg^{-1}	
0.5217	1052.2	0.5011	1065.2	0.5113	1088.1	0.5117	1109.5
1.0309	1089.8	2.0022	1170.7	1.0204	1122.8	1.0215	1141.7
1.9495	1160.1	3.0030	1231.3	2.0315	1186.5	2.0313	1202.7

2.9579	1226.1	4.0058	1291.7	3.0406	1247.2	3.0406	1258.7
4.0017	1286.7	5.0613	1346.3	4.0558	1302.6	4.0627	1311.8

$MgCl_2$

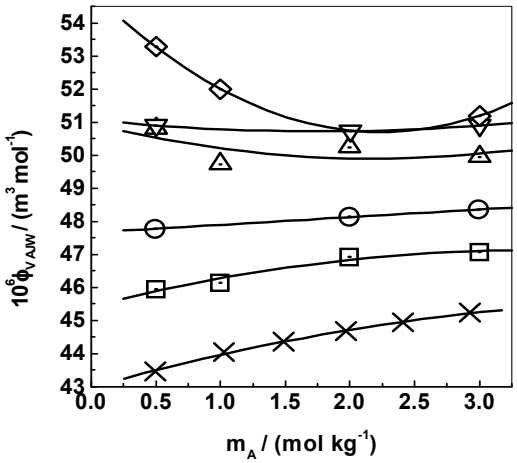
m_A = 0.5014 mol kg^{-1}		m_A = 1.0022 mol kg^{-1}		m_A = 2.0201 mol kg^{-1}		m_A = 3.0112 mol kg^{-1}	

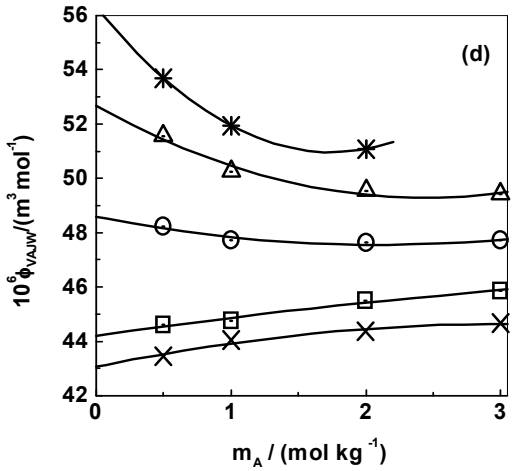




0.1015	1019.7	0.0945	1033.8	0.1015	1058.9	0.1105	1081.6
0.5026	1047.8	0.5052	1060.3	0.5022	1083.5	0.4944	1104.2
1.0038	1080.9	0.9990	1092.0	0.9945	1113.1	0.9949	1131.9
1.5037	1112.5	1.5011	1122.6	1.4952	1141.0		

The apparent molar volume of electrolytes, ϕ_{VJAW} are also affected due to glycine. The changes in ϕ_{VJAW} of different electrolytes as a function of m_J are depicted in Figs. 5 – 8. 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

Fig. 1 Fig. 2

Fig. 1: Plots of ϕ_{VAJW} *vs.* m_A of glycine in H_2O (X), NaBr: 0.5 mol kg^{-1} (o), 1 mol kg^{-1} (O), 2 mol kg^{-1} (Δ), 3 mol kg^{-1} (✱), 4 mol kg^{-1} (◇); **Fig. 2** KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (✱)

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.

Fig. 3 Fig. 4

Fig 3: Plots of ϕ_{VAJW} *vs.* m_A of glycine in H_2O (X) 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); **Fig. 4** $MgCl_2$: 0.1 mol kg^{-1}(o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (◇)

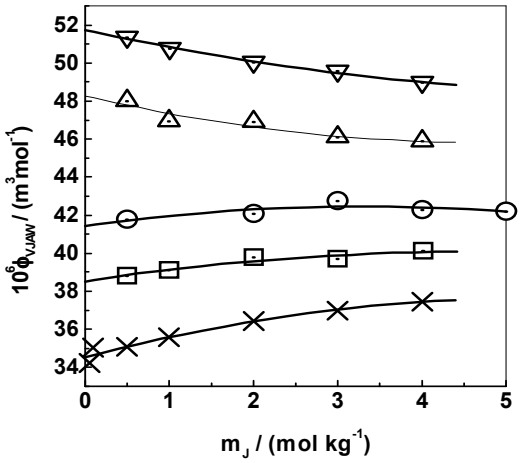


Fig. 5: Plots of ϕ_{VJAW} *vs.* m_J of NaBr in H_2O (X), 0.5 mol kg^{-1} glycine (o), 1 mol kg^{-1} glycine (O), 2 mol kg^{-1} glycine (Δ), 3 mol kg^{-1} glycine (∇)

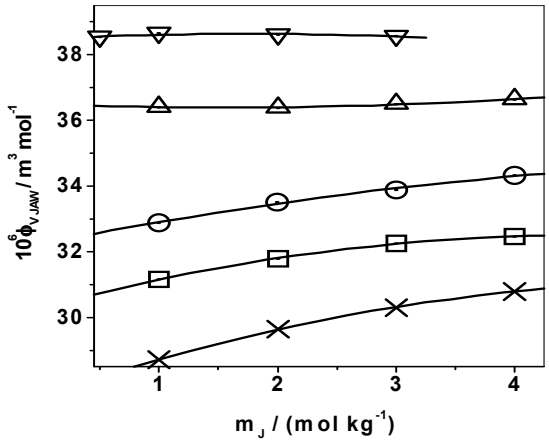


Fig. 6: Plots of ϕ_{VJAW} *vs.* m_J of KCl in H_2O (X), 0.5 mol kg^{-1} glycine (o), 1 mol kg^{-1} glycine (O), 2 mol kg^{-1} glycine (Δ), 3 mol kg^{-1} glycine (∇)

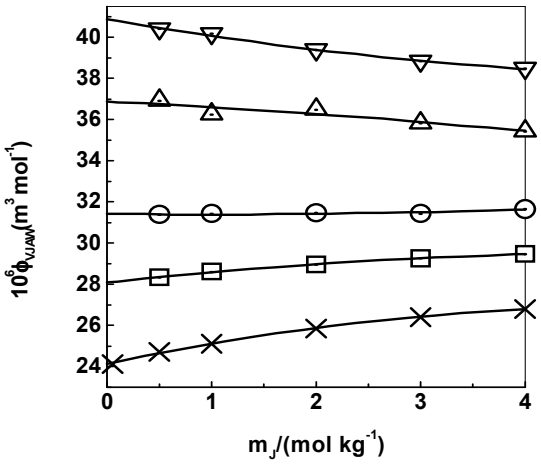


Fig. 7: Plots of ϕ_{VJAW} *vs.* m_J of KBr in H_2O (X), 0.5 mol kg^{-1} glycine (o), 1 mol kg^{-1} glycine (O), 2 mol kg^{-1} glycine (Δ), 3 mol kg^{-1} glycine (∇)

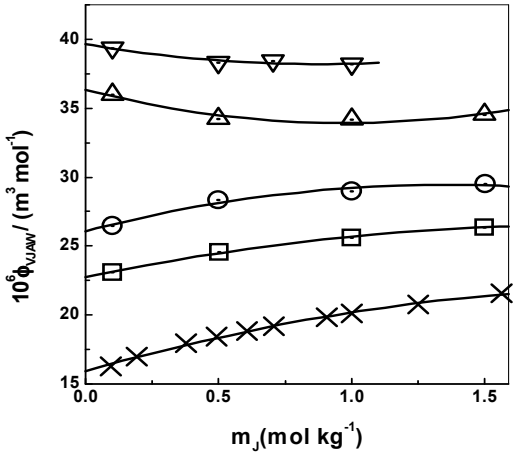


Fig. 8: Plots of ϕ_{VJAW} *vs.* m_J of $MgCl_2$: in H_2O (X), 0.5 mol kg^{-1} glycine (o), 1 mol kg^{-1} glycine (O), 2 mol kg^{-1} glycine (Δ), 3 mol kg^{-1} glycine (∇)

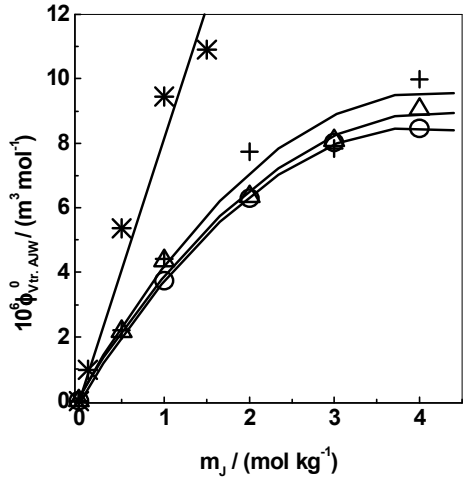


Fig. 9: Plots of $\phi_V{}^0{}_{tr.AJW}$ of glycine *vs.* m_J in NaBr (Δ), KCl (O), KBr (+) and $MgCl_2$ (✱)

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 Fig. 9. The $\phi_V^0{}_{tr.AJW}$ are positive in the presence of all the electrolytes. The $\phi_V^0{}_{tr.JAW}$ values are plotted as a function of m_A in Fig. 10. The $\phi_V^0{}_{tr.JAW}$ values are positive for all the electrolytes.

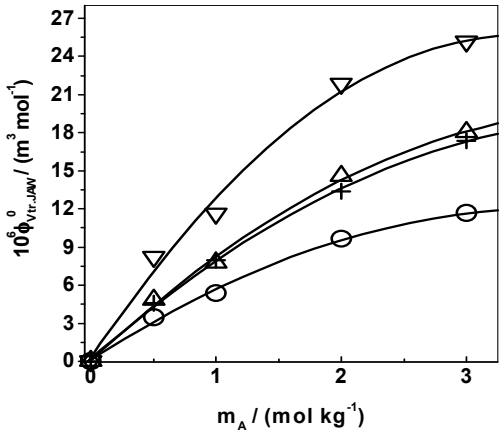


Fig. 10 Plots of $\phi_V^0{}_{tr.JAW}$ of glycine *vs.* m_A in NaBr (+), KCl (O), KBr (Δ) and $MgCl_2$ (∇)

L-alanine in aqueous electrolyte solutions

In Table 2 are listed the densities of L-alanine in aqueous KCl 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 Figs. 11 and 12.. 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 Figs. 13 and 14. 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.

Table 2: The densities of aqueous L-alanine in electrolytes at 298.15 K.

m_J / (mol kg^{-1})	ρ / (kg m^{-3})	m_J / (mol kg^{-1})	ρ / (kg m^{-3})
KCl			
m_A = 0.0535 mol kg^{-1}		m_A = 0.5004 mol kg^{-1}	
1.0072	1042.7	1.0221	1053.8
2.0037	1082.6	2.0329	1091.2
3.0422	1119.3	3.0439	1126.0
4.0236	1153.2	4.0508	1159.1
m_A = 0.1011 mol kg^{-1}		m_A = 0.9996 mol kg^{-1}	
1.0368	1044.0	1.0208	1063.67
2.0473	1083.4	1.9937	1100.3
3.0038	1120.6	3.0044	1133.7

4.0065	1153.8	4.0008	1164.6

$MgCl_2$

m_A = 0.0992 mol kg^{-1}		m_A = 0.7299 mol kg^{-1}	
0.0511	1003.4	0.0505	1020.9
0.4984	1036.9	0.4984	1051.7
0.9954	1070.3	1.0018	1084.4
1.5112	1104.7	1.5017	1114.5
m_A = 0.5017 mol kg^{-1}		m_A = 1.0035 mol kg^{-1}	
0.1014	1017.9	0.0546	1026.9
0.5033	1046.1	0.4955	1056.7
0.9988	1079.2	0.9990	1088.6
1.4976	1111.2	1.5026	1118.3

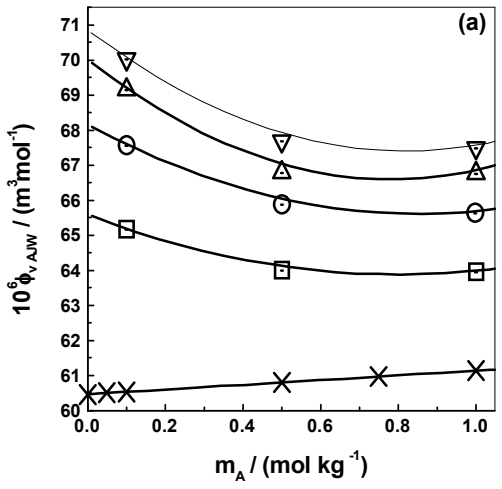


Fig. 11: Plots of ϕ_{VAJW} of L-alanine *vs.* m_A in H_2O (X), KCl: 1 mol kg^{-1} (o), 2 mol kg^{-1} (O), 3 mol kg^{-1} (Δ), 4 mol kg^{-1} (∇)

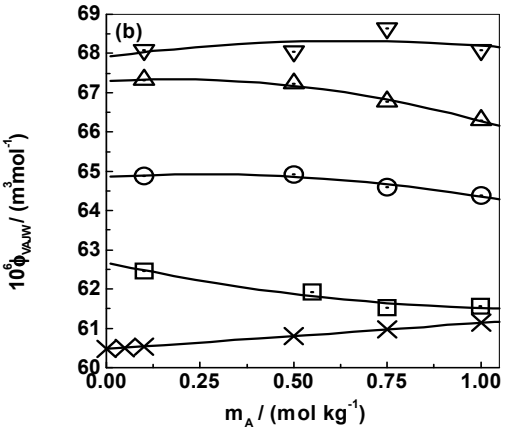


Fig. 12: Plots of ϕ_{VAJW} of L-alanine *vs.* m_A in H_2O (X), $MgCl_2$: 0.05 mol kg^{-1} (o), 0.5 mol kg^{-1} (O), 1 mol kg^{-1} (Δ), 1.5 mol kg^{-1} (∇)

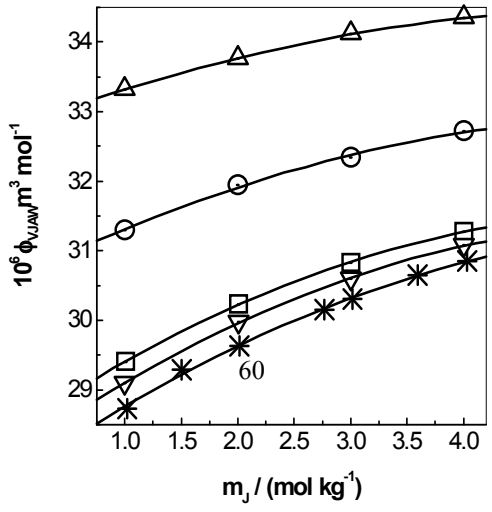


Fig. 13: Plots of ϕ_{VJAW} vs. m_J in KCl: + H_2O (T), 0.05 mol kg^{-1} + L- alanine (∇), 0.1 mol kg^{-1} L-alanine (o), 0.5 mol kg^{-1} L- alanine (O), 1 mol kg^{-1} L- alanine (Δ)

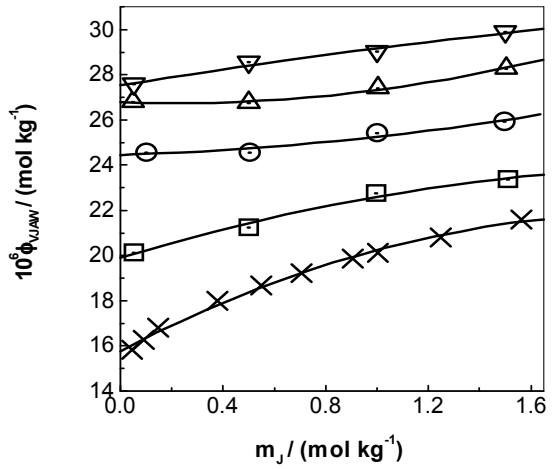


Fig. 14: Plots of ϕ_{VJAW} vs. m_J in H_2O (X), 0.1 mol kg^{-1} $MgCl_2$ (o), 0.5 mol kg^{-1} $MgCl_2$ (O), 0.75 mol kg^{-1} $MgCl_2$ (Δ), 1 mol kg^{-1} $MgCl_2$ (∇)

The transfer volumes of L-alanine in electrolytes are plotted in **Fig. 15** as a function of m_J. L-alanine shows positive transfer volumes in all electrolytes studied. The $(\partial\phi_V{}^0{}_{tr.AJW}/\partial m_J)$ values of L-alanine in 1 mol kg^{-1} $MgCl_2$ (6.83 x 10^{-6} m^3 kg mol^{-2}) is almost 1.5 times more than that in KCl (4.45 x 10^{-6} m^3 kg mol^{-2}). The dominance of $MgCl_2$ on $\phi_V{}^0{}_{tr.AJW}$ can be clearly seen in **Fig. 15**. The transfer volumes of electrolytes from water to aqueous L-alanine are shown in **Fig. 16**. The effect of L-alanine on $\phi_V{}^0{}_{JAW}$

of $MgCl_2$ is almost twice than that on KCl, which is reflected in $(\partial\phi_V{}^0{}_{tr.JAW}/\partial m_A)$ values. The $(\partial\phi_V{}^0{}_{tr.JAW}/\partial m_J)$ values for $MgCl_2$ and KCl in 1 mol kg^{-1} L-alanine are 12.81 x 10^{-6} m^3 kg mol^{-2} and 5.88 x 10^{-6} m^3 kg mol^{-2}, respectively.

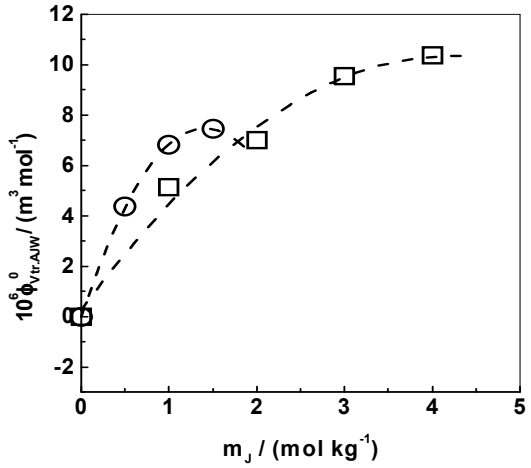


Fig. 15: Plots of $\phi_V{}^0{}_{tr.AJW}$ *vs.* m_J of L-alanine in KCl (o), $MgCl_2$ (O)

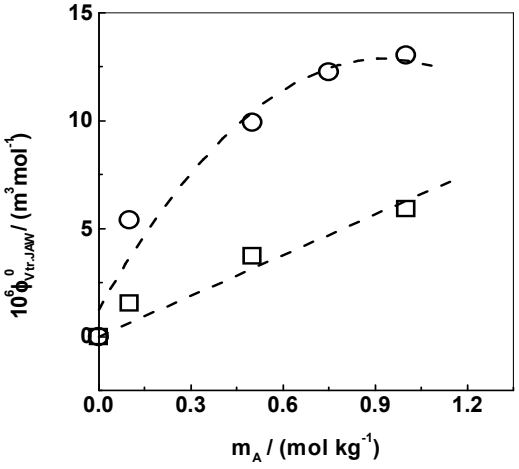


Fig. 16: Plots of ϕV^{0}_{trJAW} *vs.* m_A of L-alanine in KCl (o), $MgCl_2$ (O)

The amino acids in tetra-n-alkylammonium bromide solutions

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[2]. 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[2]. The aqueous solutions of these salts have been found to be highly viscous[3] and bear high apparent molal heat capacities[4,5] apparent molar volumes[6] and peculiar activity coefficients[7,8]. It will be therefore important to study the effect of these tetra-n-alkylammonium salts on the volumetric properties of aqueous amino acids.

The densities of amino acids and peptide in tetra-n-alkylammonium bromides are reported in Tables 3, 4 and 5**.** The ϕ_{VAJW} values for glycine are plotted as a function of their respective molalities, m_A in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ in Figs. 17, 18 and 19, respectively. Figs. 20, 21 and 22 display the ϕ_{VAJW} values for alanine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$, respectively, while for glycylglycine in Figs. 23, 24 and 25. 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 3: Densities, ρ of 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 = 0.2510 mol kg^{-1}		m_J = 0.5220 mol kg^{-1}		m_J = 0.8229 mol kg^{-1}	
0	1006.8	0	1016.9	0	1025.9
0.4978	1022.0	0.4982	1031.5	0.4956	1026.2
1.0001	1036.3	0.7446	1038.3	1.4981	1067.9
1.5012	1049.6	0.9923	1045.4	1.9990	1079.6

1.9993	1061.9	1.4966	1058.9
m_J = 1.1332 mol kg^{-1}		m_J = 1.8336 mol kg^{-1}	
0	1036.1	0	1046.0
0.4923	1050.6	0.4908	1060.6
1.4852	1076.3	0.9921	1074.0
1.9891	1087.2	1.4891	1086.2
2.1861	1091.8		

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	1006.9	0	1016.5	0.4927	1039.3
0.1005	1009.7	0.4967	1029.5	0.7507	1045.6
0.4955	1020.6	0.7467	1036.3	0.9905	1050.8
0.7511	1026.9	0.9967	1042.1		
1.0010	1032.9				
m_J = 1.1329 mol kg^{-1}		m_J = 1.8366 mol kg^{-1}			
0.0935	1038.3	0.0975	1049.3		
0.4884	1048.4	0.4381	1059.1		
0.7338	1054.3	0.7479	1065.9		
0.9873	1060.2	0.9883	1070.1		

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	1006.5	0	1016.4	0	1025.5

0.1014	1012.6	0.5023	1042.4	0.0965	1031.1
0.5031	1032.3	0.7445	1053.8	0.4972	1052.3
0.7425	1044.9			0.7464	1062.9

m_J = 1.1342 mol kg^{-1}

0	1035.7
0.0991	1040.8
0.4963	1060.9
0.7493	1072.4

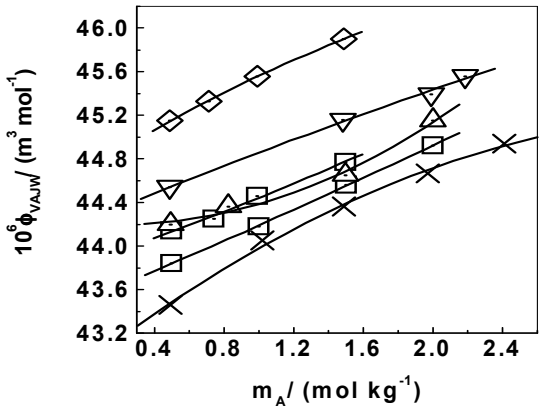


Fig. 17: Plots of ϕ_{VAJW} *vs.* m_A of glycine in H_2O (X), $(CH_3)_4NBr$: 0.2581 mol kg^{-1} (o), 0.5325 mol kg^{-1} (O), 0.8239 mol kg^{-1} (Δ), 1.1340 mol kg^{-1} (∇), 1.8386 mol kg^{-1} (◊)

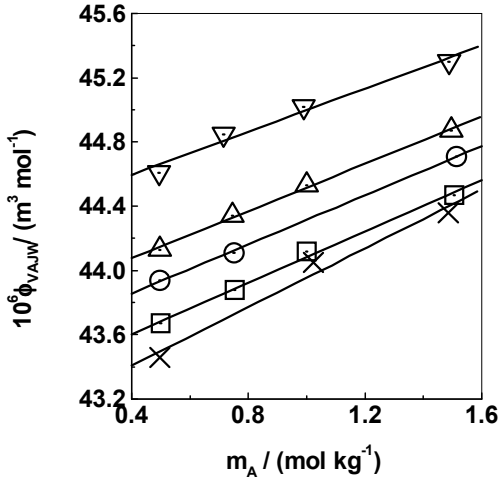


Fig. 18: Plots of ϕ_{VAJW} *vs.* m_A of glycine in H_2O (X), $(C_2H_5)_4NBr$: 0.1020 mol kg^{-1} (o), 0.4023 mol kg^{-1} (O), 0.5490 mol kg^{-1} (Δ), 1.2115 mol kg^{-1} (∇)

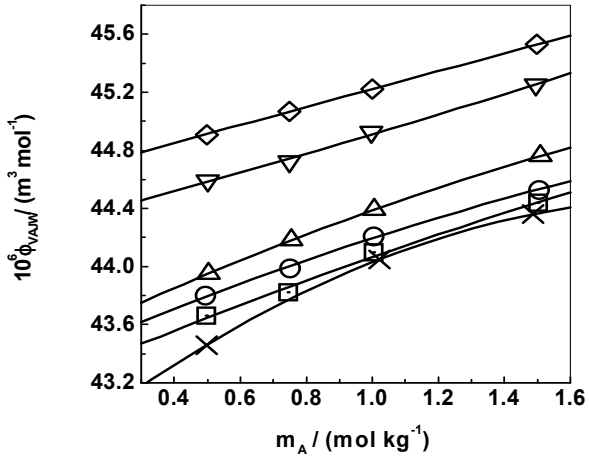


Fig. 19: Plots of ϕ_{VAJW} *vs.* m_A of glycine in H_2O (X), $(C_4H_9)_4NBr$: 0.0509 mol kg^{-1} (o), 0.1034 mol kg^{-1} (O), 0.2709 mol kg^{-1} (Δ), 0.5890 mol kg^{-1} (∇), 0.7318 mol kg^{-1} (◊)

Table 4: Densities, ρ of 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	1000.7	0	1006.2	0	1015.3	0	1035.7
0.4979	1016.0	0.4964	1026.0	0.4957	1030.7	0.4928	1050.8
0.7540	1023.4	0.7502	1033.3	0.7450	1037.2	0.7416	1056.9
1.0001	1303.7	0.9317	1040.5	1.0005	1044.4	0.9898	1063.5
1.5055	1043.8	1.5126	1053.0	1.4951	1057.7	1.4877	1076.2
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	1003.6	0.0984	1008.9	0.1003	1018.5	0.4902	1048.6
0.5053	1014.6	0.4999	1019.8	0.4939	1029.1	0.7383	1054.3
0.7539	1021.0	0.7534	1026.3	0.7463	1035.5	0.9900	1060.8
1.0013	1027.6	0.9974	1032.3	0.9907	1041.5		
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	1006.4	0.1011	1011.8	0.0997	1021.7	0	1035.5

0.5054	1027.9	0.5059	1032.7	0.4958	1041.7	0.4958	1060.5
0.7534	1039.8	0.7482	1044.4	0.7457	1053.4	0.7446	1072.2

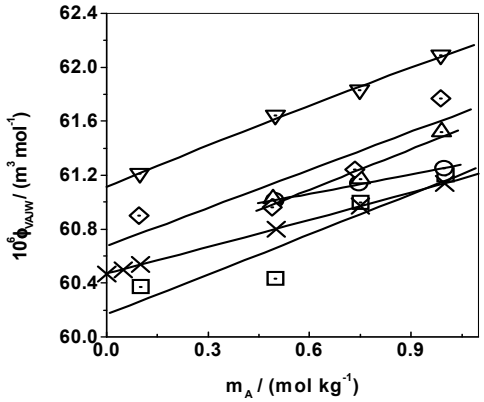


Fig. 20: Plots of ϕ_{VAJW} *vs.* m_A of L-alanine in H_2O (X), $(CH_4)_4NBr$: 0.2581 mol kg^{-1} (o), 0.5325 mol kg^{-1} (O), 0.8239 mol kg^{-1} (Δ), 1.1340 mol kg^{-1} (◊), 1.8386 mol kg^{-1}(∇)

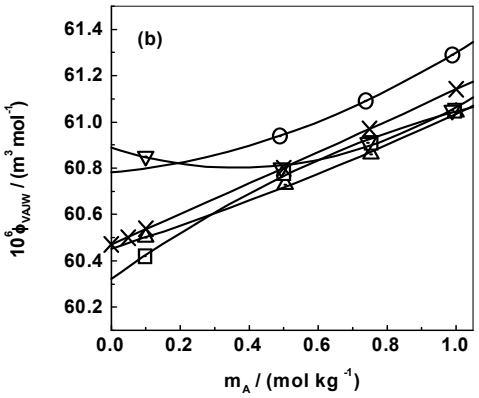


Fig. 21: Plots of ϕ_{VAJW} *vs.* m_A of L-alanine in H_2O (X), $(C_2H_5)_4NBr$: 0.1020 mol kg^{-1} (Δ), 0.2622 mol kg^{-1} (o), 0.5490 mol kg^{-1} (∇), 1.2115 mol kg^{-1} (O)

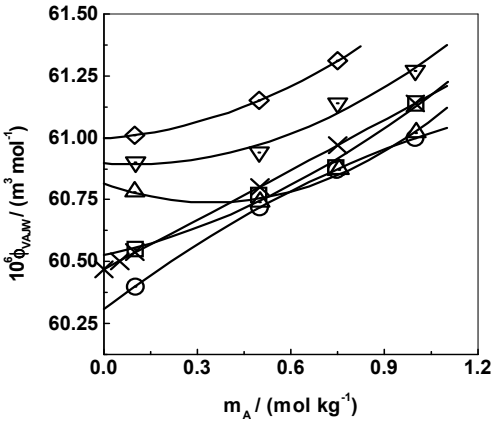


Fig. 22: Plots of ϕ_{VAJW} *vs.* m_A of L-alanine in H_2O (X), $(C_4H_9)_4NBr$: 0.0509 mol kg^{-1} (o), 0.1034 mol kg^{-1} (O), 0.2709 mol kg^{-1} (Δ), 0.5890 mol kg^{-1} (∇), 0.7318 mol kg^{-1} (◊)

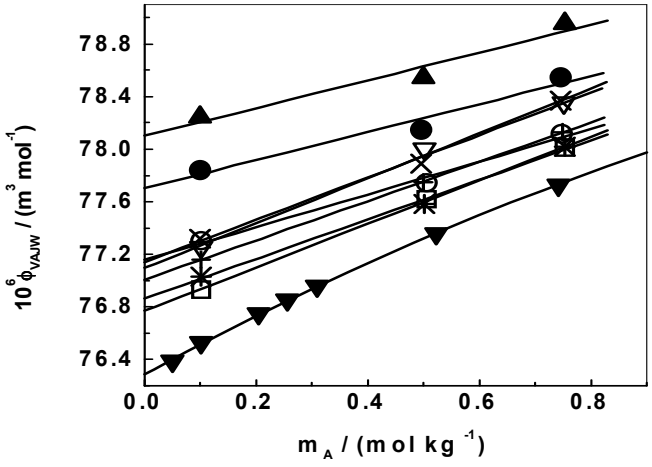


Table 5: Densities, ρ of the amino acid or peptide – $(C_4H_9)_4NBr$ – H_2O system at 298.15 K

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	998.2	0	999.3	0	1003.8		
0.4985	1013.5	0.4968	1014.0	0.5026	1018.7		
0.7473	1020.8	0.7508	1021.9	0.7537	1025.8		
1.0058	1028.0	1.0041	1029.8	1.0058	1032.7		
1.5035	1041.4	1.5055	1042.9	1.5083	1045.3		
m_J = 0.5890 mol kg^{-1}		m_J = 0.7318 mol kg^{-1}					
0	1010.9	0	1013.7				
0.5002	1024.3	0.4973	1027.8				
0.7499	1031.9	0.7496	1034.8				
0.9967	1038.9	0.9999	1041.6				
1.4941	1051.7	1.4993	1054.3				

Fig. 23: Plots of ϕ_{VAJW} *vs.* m_A of glycylglycine in H_2O (▼), in $(CH_3)_4NBr$: 0.2579 mol kg^{-1} (+), 0.8105 mol kg^{-1}(●); $(C_2H_5)_4NBr$: 0.1020 mol kg^{-1} (□), 0.2623 mol kg^{-1} (O), 0.5491 mol kg^{-1} (X); $(C_4H_9)_4NBr$: 0.0509 mol kg^{-1} (✱), 0.2710 mol kg^{-1} (∇). 0.5889 mol kg^{-1} (▲)

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	1002.7	0.1001	1005.9	0.1010	1012.8	0.0989	1015.9
0.5006	1013.9	0.5007	1016.9	0.4995	1023.5	0.4978	1026.5
0.7487	1019.6	0.7545	1023.6	0.7508	1029.0	0.7496	1032.8
		1.0017	1029.5	0.9996	1035.9		

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	1003.8	0.1013	1008.5	0.0999	1015.6
0.5022	1024.3	0.5013	1029.3	0.4988	1035.8
0.7538	1036.7	0.7516	1041.3	0.7538	1047.1

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 solutions, 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[6]. 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 **Figs. 24, 25** and **26.** In **Fig. 24**, the ϕ_{VJAW} values are plotted as a function of m_J in glycine, alanine and glycylglycine. 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.

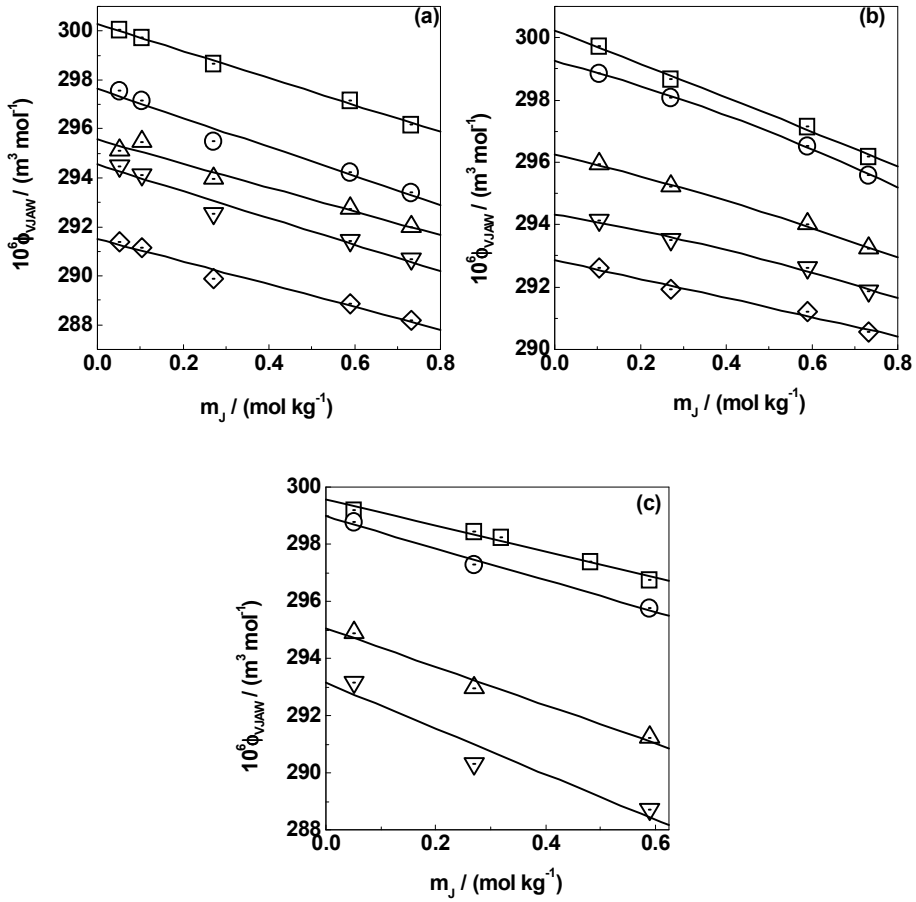


Fig. 24: Plots of ϕ_{VJAW} vs. m_J of $(CH_3)_4NBr$ in **(a)** H_2O (o), glycine: 0.4949 mol kg^{-1} (O), 0.9948 mol kg^{-1} (Δ), 1.4940 mol kg^{-1} (∇), 1.9958 mol kg^{-1} (◊); **(b)** in H_2O (o), L-alanine: 0.0987 mol kg^{-1} (O), 0.4965 mol kg^{-1} (Δ), 0.7491 mol kg^{-1} (∇), 0.9941 mol kg^{-1} (◊); **(c)** in H_2O (o), glycylglycine: 0.0997 mol kg^{-1} (O), 0.4998 mol kg^{-1} (Δ), 0.7449 mol kg^{-1} (∇)

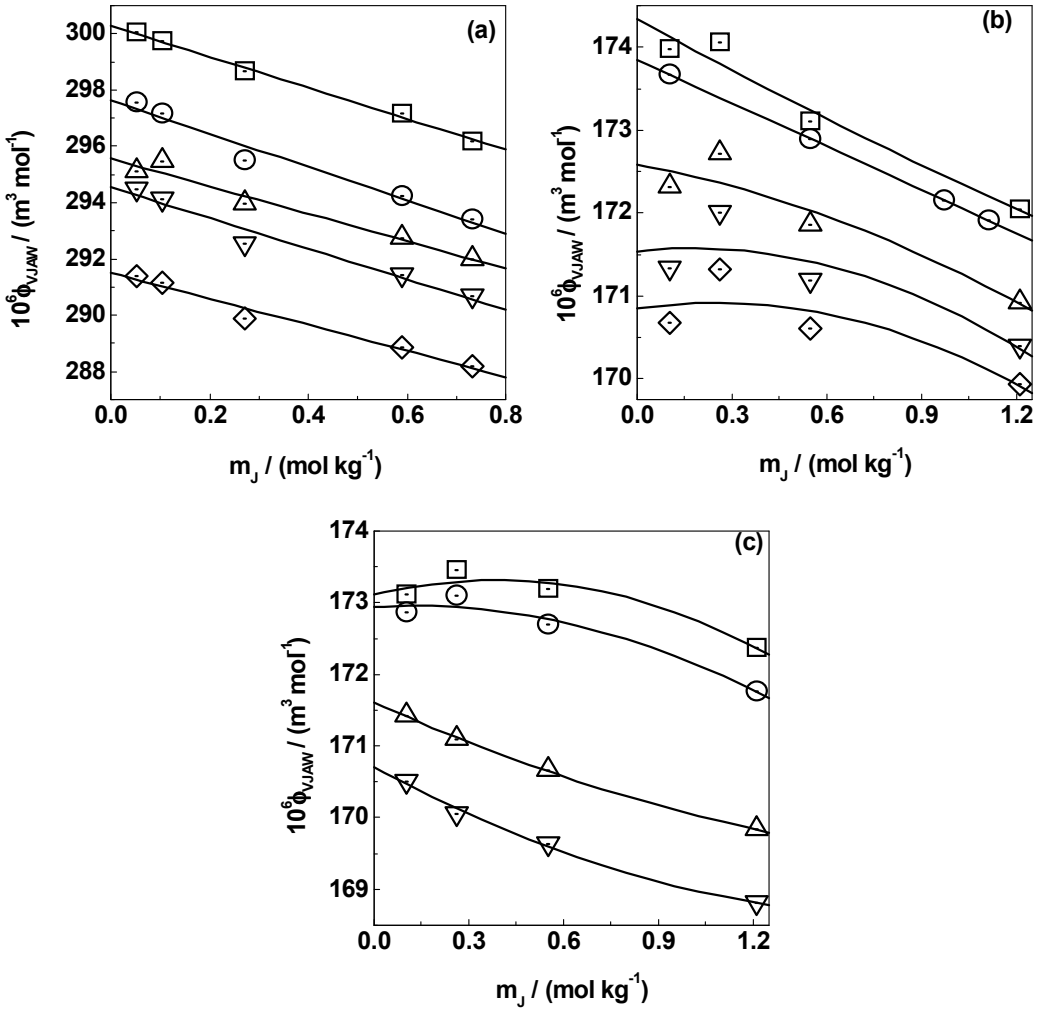


Fig. 25: Plots of ϕ_{VJAW} *vs.* m_J of $(C_2H_5)_4NBr$ in **(a)** H_2O (o), glycine: 0.4957 mol kg^{-1} (O), 0.7477 mol kg^{-1} (Δ), 0.9968 mol kg^{-1} (∇), 1.5002 mol kg^{-1} (◊); **(b)** in H_2O (o), L-alanine: 0.0997 mol kg^{-1} (O), 0.4973 mol kg^{-1} (Δ), 0.7480 mol kg^{-1} (∇), 0.9949 mol kg^{-1} (◊); **(c)** in H_2O (o), glycylglycine: 0.1003 mol kg^{-1} (O), 0.5007 mol kg^{-1} (Δ), 0.7480 mol kg^{-1} (∇)

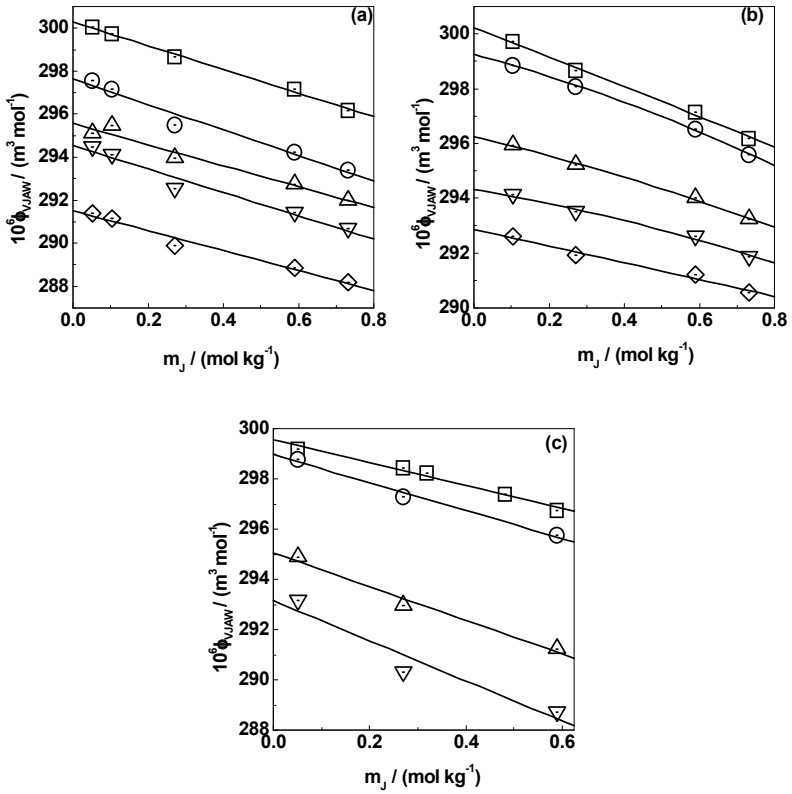


Fig. 26: Plots of ϕ_{VJAW} vs. m_J of $(C_4H_9)_4NBr$ in **(a)** H_2O (o), glycine: 0.4991 mol kg^{-1} (O), 0.7503 mol kg^{-1} (Δ), 1.0025 mol kg^{-1} (∇), 1.5021 mol kg^{-1} (◊); **(b)** in H_2O (o), L-alanine: 0.1002 mol kg^{-1} (O), 0.4997 mol kg^{-1} (Δ), 0.7509 mol kg^{-1} (∇), 0.9994 mol kg^{-1} (◊); **(c)** in H_2O (o), glycylglycine: 0.1009 mol kg^{-1} (O), 0.5008 mol kg^{-1} (Δ), 0.7530 mol kg^{-1} (∇)

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 **Fig. 27**. 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 **Fig. 28**. All the systems show negative slopes. 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.

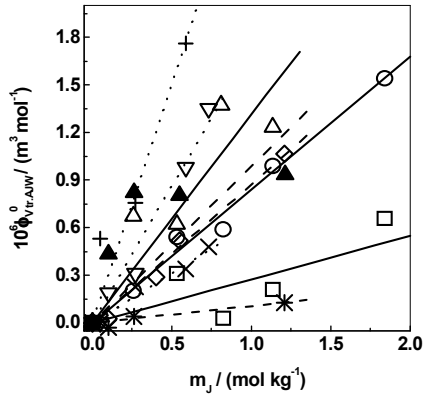


Fig. 27: Plots of $\phi_V{}^0{}_{tr\,AJW}$ vs. m_J $(CH_3)_4NBr$ + (O), glycine; (o), L-alanine; (Δ), glycylglycine; $(C_2H_5)_4NBr$ + (◊), glycine; (T), L-alanine; (σ), glycylglycine; $(C_4H_9)_4NBr$ + (∇), glycine; (X), L-alanine; (+), glycylglycine

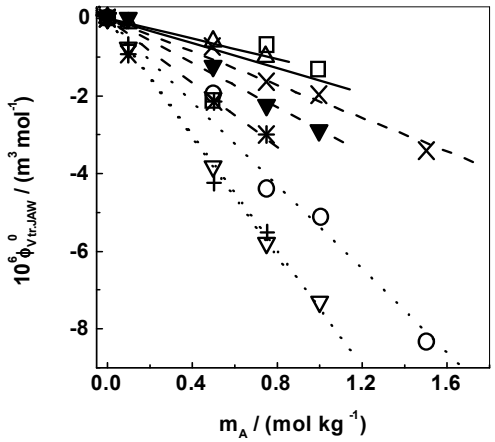


Fig. 28: Plots of $\phi_V^0{}_{tr.JAW}$ vs. m_A glycine + (X), $(C_2H_5)_4NBr$; (O), $(C_4H_9)_4NBr$; L-alanine + (o), $(CH_3)_4NBr$; (▼), $(C_2H_5)_4NBr$; (∇), $(C_4H_9)_4NBr$; glycylglycine + (Δ), $(CH_3)_4NBr$; (T), $(C_2H_5)_4NBr$; (+), $(C_4H_9)_4NBr$

Attempts were also made to investigate the ϕ_{VAJW} of several amino acids in glucose at its fixed concentration of 0.2 mol kg^{-1} . The experimental data are listed in Table 6. The ϕ_{VAJW} values of glycine in glucose is significantly influenced by an in increase in temperature (Fig. 29). Also, these values decrease with an increase in the concentrations of glycine itself. The behaviour is different from the one observed in the case of strong electrolytes.

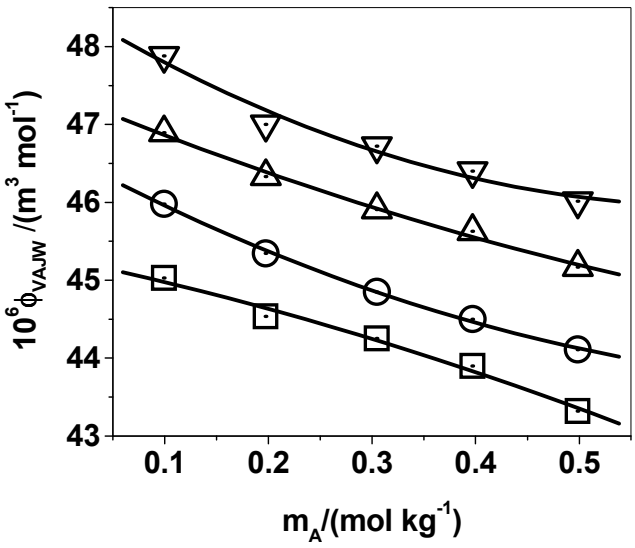


Fig. 29: Plots of ϕ_{VAJW} (of glycine) *versus* m_A at m_J= 0.2 mol kg^{-1} in glucose system and different temperatures (□) 298.15, (○) 303.15, (Δ) 308.15 and (∇) 313.15K

However, an investigation of the ϕ_{VAJW} values for DL-alanine in glucose shows a completely different picture. An increase in the ϕ_{VAJW} values for DL-alanine is seen in 0.2 mol kg^{-1} of glucose (Fig. 30). The range in which the ϕ_{VAJW} values increase includes 58 to 66 x 10^{-6} m^3 mol^{-1}. This reversal in the trend may be due to the presence of a methyl group in DL-alanine and can be explained in terms of structure-making and –breaking effects. However, both the amino acids are non-polar in nature. On the other hand, DL-valine also displays a decrease in ϕ_{VAJW} in the presence of 0.2 mol kg^{-1} of glucose (Fig. 31). The ϕ_{VAJW} values for L-serine, a polar amino acid do not change with its concentration. The temperature dependence is also not prominent in the system (Fig. 32).

Table 6: Experimental densities, ρ and speed of sound, u at different temperature with molality of amino acids m_A in glucose solution.

T/K	ρ (kg m^{-3})	T/K	ρ (kg m^{-3})
Glycine			
m_A= 0.1 mol kg^{-1}		m_A= 0.2 mol kg^{-1}	
298.15	1013.5	298.15	1016.5
303.15	1011.8	303.15	1015.0
308.15	1010.2	308.15	1013.3
313.15	1008.3	313.15	1011.4

m_A= 0.3 mol kg^{-1}		m_A= 0.4 mol kg^{-1}	
298.15	1019.1	298.15	1023.1
303.15	1018.0	303.15	1020.7
308.15	1016.2	308.15	1019.2
313.15	1014.3	313.15	1017.2

m_A= 0.5 mol kg^{-1}	
298.15	1026.5
303.15	1024.1
308.15	1022.2
313.15	1020.3

DL-Alanine

m_A= 0.1 mol kg^{-1}		m_A= 0.2 mol kg^{-1}	
298.15	1013.8	298.15	1016.6
303.15	1012.1	303.15	1014.8
308.15	1010.4	308.15	1013.0
313.15	1008.5	313.15	1011.1

m_A= 0.3 mol kg^{-1}		m_A= 0.4 mol kg^{-1}	
298.15	1018.9	298.15	1021.1
303.15	1017.1	303.15	1019.2
308.15	1015.3	308.15	1017.3
313.15	1013.3	313.15	1015.3

m_A= 0.5 mol kg^{-1}

298.15	1022.9
303.15	1021.1
308.15	1019.2
313.15	1017.1

L-Serine

m_A= 0.1 mol kg^{-1}		m_A= 0.2 mol kg^{-1}	
298.15	1015.1	298.15	1019.6
303.15	1013.4	303.15	1017.8
308.15	1011.7	308.15	1016.3
313.15	1009.8	313.15	1014.0

m_A= 0.3 mol kg^{-1}		m_A= 0.4 mol kg^{-1}	
298.15	1023.9	298.15	1028.1
303.15	1022.1	303.15	1026.3
308.15	1020.2	308.15	1024.3
313.15	1018.1	313.15	1022.2

m_A= 0.5 mol kg^{-1}

298.15	1032.3
303.15	1030.4
308.15	1028.4
313.15	1026.2

DL-Valine

m_A= 0.1 mol kg^{-1}		m_A= 0.2 mol kg^{-1}	
298.15	1013.0	298.15	1015.5
303.15	1011.3	303.15	1013.8
308.15	1009.6	308.15	1012.0
313.15	1007.8	313.15	1010.1
m_A= 0.3 mol kg^{-1}		m_A= 0.4 mol kg^{-1}	
298.15	1018.0	298.15	1020.4
303.15	1016.2	303.15	1018.6
308.15	1014.3	308.15	1016.6
313.15	1012.4	313.15	1014.7

m_A= 0.5 mol kg^{-1}	
298.15	1022.8
303.15	1021.0
308.15	1018.9
313.15	1017.0

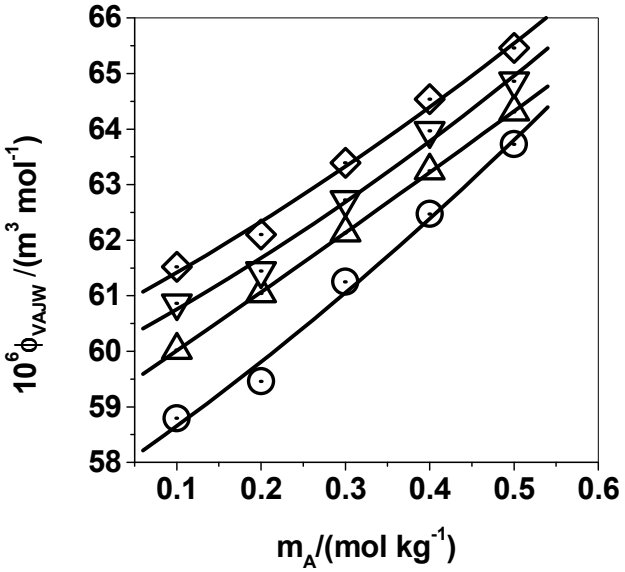


Fig. 30: Plots of ϕ_{VAJW} (of DL-alanine) *versus* m_A at m_J= 0.2 mol kg^{-1} in glucose system and different temperatures (□) 298.15, (○) 303.15, (Δ) 308.15 and (∇) 313.15K

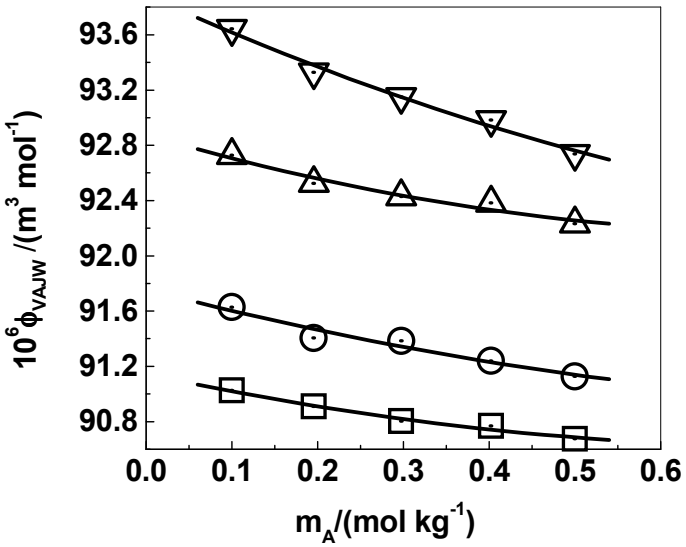


Fig. 31: Plots of ϕ_{VAJW} (of DL-valine) *versus* m_A at m_J= 0.2 mol kg^{-1} in glucose system and different temperatures (□) 298.15, (○) 303.15, (Δ) 308.15 and (∇) 313.15K

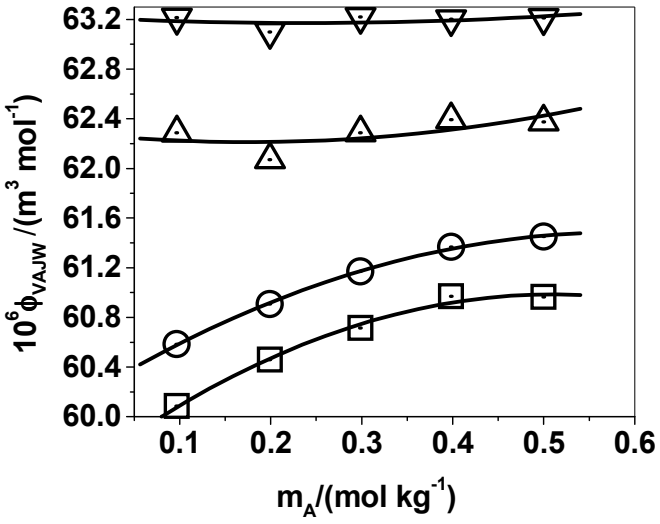


Fig. 32: Plots of ϕ_{VAJW} (L-seline) *versus* m_A at m_J= 0.2 mol kg^{-1} in glucose system and different temperatures (□) 298.15, (○) 303.15, (Δ) 308.15 and (∇) 313.15K

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Chapter 5

COMPRESSIBILITY

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

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

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 (Eq. 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 Eq. (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.

Apparent molar compressibilty of the aminoacid/peptide-Tetra-n-alkyl ammonium bromide systems

The measured speed of sound, u and κ_s values calculated therefrom at different concentrations of glycine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ are listed in **Table**

1. The ϕ_{KAJW} and ϕ_{KJAW} are calculated using Eq. (2b). The variation of ϕ_{KAJW} with m_A for glycine in $(CH_3)_4NBr$ is shown in **Fig. 1**. The ϕ_{KAJW} of glycine changes from -4.5 x 10^{-14} to -1 x 10^{-14} m^3 mol^{-1} Pa^{-1} in the presence of different concentrations of $(CH_3)_4NBr$. The ϕ_{KAJW} values of glycine increase with the increase in m_A as well as m_J. The plots given in Fig. 1 show that the glycine molecules are less compressed with the increase in the concentrations of $(CH_3)_4NBr$.

Table 1: Experimental speed of sound of aqueous glycine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ solutions 298.15 K.

m_J (mol kg^{-1})	u (m s^{-1})	m_J (mol kg^{-1})	u (m s^{-1})
Glycine+ $(CH_3)_4NBr$			
m_A= 0.5 mol kg^{-1}		**m_A= 0.75 mol kg^{-1}**	
0.2498	1536.2	0.2498	1550.2
0.4997	1550.4	0.4998	1558.6
0.7997	1560.7	0.7998	1572.4
0.9986	1576.4	1.0003	1588.8
1.4996	1592.0	1.4994	1600.1
m_A= 1.0 mol kg^{-1}		**m_A= 1.5 mol kg^{-1}**	
0.2499	1568.1	0.2499	1588.4

0.4998	1572.4	0.4997	1596.8
0.7997	1592.7	0.8002	1608.6
0.9995	1600.0	0.9994	1616.3
1.4991	1624.4	1.5000	1636.6

m_A= 2.00 mol kg^{-1}

0.2499	1604.5
0.4997	1614.0
0.7995	1622.2
0.9996	1632.5
1.4992	1648.3

Glycine+$(C_2H_5)_4NBr$

m_A= 0.5 mol kg^{-1}		m_A= 0.75 mol kg^{-1}	
0.2497	1548.5	0.2497	1554.5
0.3497	1560.0	0.3497	1570.3
0.5000	1584.2	0.5000	1592.8
0.7498	1604.8	0.7500	1612.1
1.0001	1624.5	0.9995	1632.2
m_A= 1.0 mol kg^{-1}		m_A= 1.5 mol kg^{-1}	
0.2498	1562.6	0.2498	1580.5
0.3497	1576.4	0.3497	1592.7
0.5000	1598.8	0.4996	1612.1
0.7499	1616.5	0.7499	1628.0
0.9999	1640.7	0.9995	1648.5

m_A= 2.00 mol kg^{-1}

0.2498	1598.2
0.3497	1616.7
0.4997	1626.5
0.7495	1636.8
0.9997	1658.5

Glycine+$(C_4H_9)_4NBr$

m_A= 0.5 mol kg^{-1}		m_A= 0.75 mol kg^{-1}	
0.0987	1547.3	0.0999	1558.3
0.2491	1576.1	0.2497	1584.5
0.3499	1602.7	0.3499	1612.1
0.4996	1616.0	0.4998	1624.6
0.6999	1648.4	0.6998	1656.0
m_A= 1.00 mol kg^{-1}		m_A= 1.5 mol kg^{-1}	
0.0999	1569.4	0.0999	1590.4
0.2497	1592.1	0.2497	1612.7
0.3499	1620.5	0.3498	1632.9
0.4997	1632.4	0.4997	1651.1
0.6998	1664.7	0.6998	1672.2

m_A= 2.00 mol kg^{-1}

0.0999	1612.6
0.2494	1632.4
0.3498	1648.0
0.4997	1664.5
0.6994	1688.6

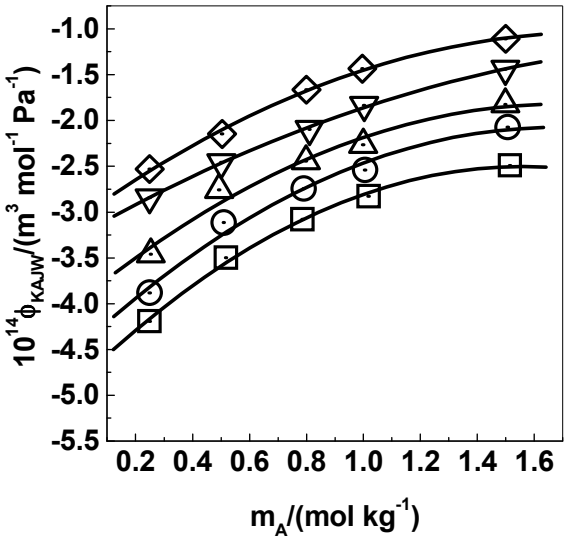

Fig. 1: The ϕ_{KAJW} vs. m_A plots for glycine in different concentrations, m_J of $(CH_3)_4NBr$; for m_J (□) 0.25, (○) 0.5 , (Δ) 0.8 , (▽) 1, (◇) 1.5 mol kg^{-1}

Further, the values of ϕ_{KJAW} of $(CH_3)_4NBr$ in glycine as a function of m_J at different concentrations of glycine are depicted in Fig. 2. There is a mild decrease in ϕ_{KJAW} of $(CH_3)_4NBr$ with m_J in the presence of glycine. This mild effect may be due to the large size of $(CH_3)_4NBr$, the compressibility of which in water is positive. The range of ϕ_{KJAW} of $(CH_3)_4NBr$ in glycine is from 1 to 1.8 x 10^{-14} m^3 mol^{-1} Pa^{-1}. The ϕ_{KJAW} values

of $(CH_3)_4NBr$, however, increase with an increase in the concentration of glycine at a constant concentration of $(CH_3)_4NBr$.

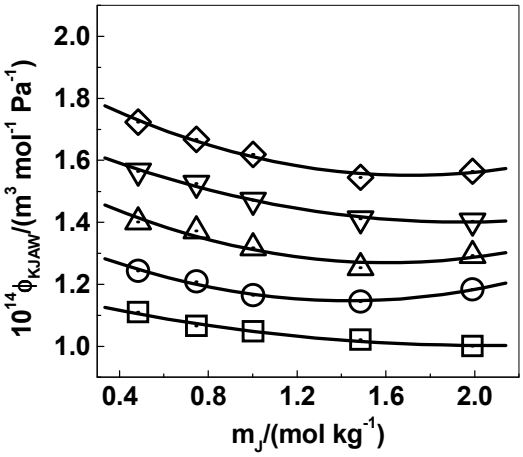

Fig. 2: The ϕ_{KJAW} vs. m_J plots for $(CH_3)_4NBr$ in glycine in different concentrations, m_A of glycine; for m_A (□) 0.5, (○) 0.75, (Δ) 1, (∇) 1.5, (◇) 2 mol kg^{-1}

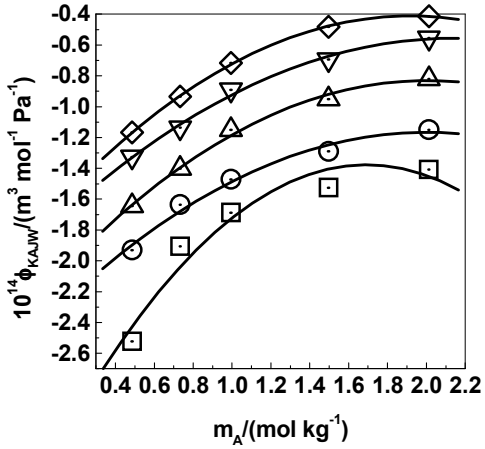

Fig. 3: The ϕ_{KAJW} vs. m_A plots for glycine in different concentrations, m_J of $(C_2H_5)_4NBr$; for m_J (□) 0.25, (○) 0.35, (Δ) 0.5, (∇)0.75, (◇) 1 mol kg^{-1}

The ϕ_{KAJW} values for glycine in $(C_2H_5)_4NBr$ solutions (Fig. 3) increase with an increase in m_A . This increase in quite significant at low concentrations of

$(C_2H_5)_4NBr$. Glycine solution becomes less compressed upon addition of $(C_2H_5)_4NBr$. The plots of ϕ_{KJAW} versus m_J at different concentrations of $(C_2H_5)_4NBr$ (Fig. 4) are quite similar to those observed in the case of $(CH_3)_4NBr$. Fig. 5 shows a monotonous variation in the ϕ_{KAJW} values for glycine in $(C_4H_9)_4NBr$ up to high concentrations. However, the ϕ_{KJAW} values for $(C_4H_9)_4NBr$ in glycine show interesting trend, .as the ϕ_{KJAW} values vary from negative to positive while going through from low to high concentrations of glycine. (Fig. 6). This effect is important at low concentrations of $(C_4H_9)_4NBr$, possibily due to hydrophobic hydration.

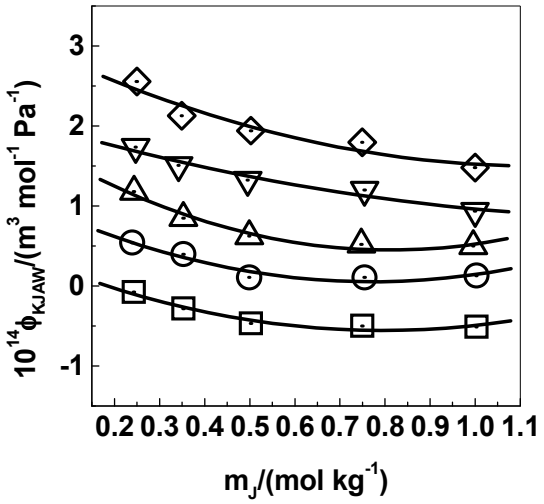

Fig. 4: The ϕ_{KJAW} vs. m_J plots for $(C_2H_5)_4NBr$ in glycine in different concentrations, m_A of glycine; for m_A (□) 0.5, (○) 0.75, (Δ) 1, (∇) 1.5, (◇) 2 mol kg^{-1}

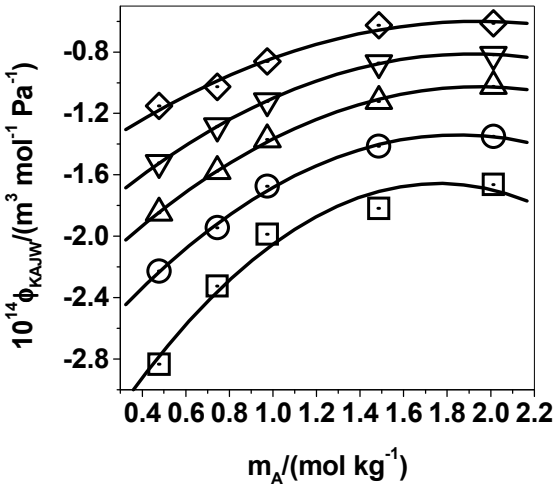

Fig. 5: The ϕ_{KAJW} vs. m_A plots for glycine in different concentrations, m_J of $(C_4H_9)_4NBr$; for m_J (□) 0.1 , (○) 0.25, (Δ) 0.35, (∇) 0.5, (◇) 0.7 mol kg^{-1}

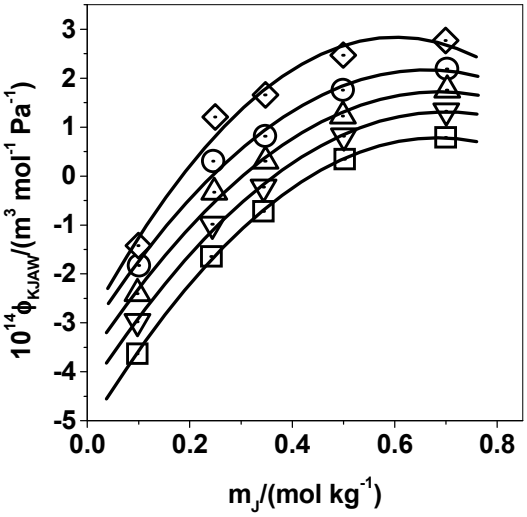

Fig. 6: The ϕ_{KJAW} vs. m_J plots for $(C_4H_9)_4NBr$ in glycine in different concentrations, m_A of glycine; for m_A (□) 0.5, (○) 0.75, (Δ) 1, (∇) 1.5, (◇) 2 mol kg^{-1}

In Table 2, the experimental sound speed, u for aqueous systems comprising of $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ in L-alanine are enumerated. In Fig. 7 are plotted the calculated ϕ_{KAJW} values as a function of m_A at constant m_J values for L-alanine in $(CH_3)_4NBr$. At low m_J values, the ϕ_{KAJW} values increase with m_A, but at high concentrations of the salt, these values show a sharp decrease with m_A. This suggests that L-alanine is more compressed at high concentrations of salt. This behaviour is different from the one observed in the case of glycine. A similar behaviour is seen in the ϕ_{KJAW} values plotted against m_J of$(CH_3)_4NBr$ (Fig. 8). The ϕ_{KAJW} of L-alanine in $(C_2H_5)_4NBr$ depicts (Fig. 9) almost similar behaviour as shown by $(CH_3)_4NBr$. In Fig. 10 are plotted the ϕ_{KJAW} values of $(C_2H_5)_4NBr$ in L-alanine .Except at low concentrations of L-alanine, the ϕ_{KJAW} values of $(C_2H_5)_4NBr$ in L-alanine are noted to be less sensitive . L-alanine in $(C_4H_9)_4NBr$ as seen from Fig. 11 behaves like it does in other two salts. This is also true for the ϕ_{KJAW} versus m_J in the case of $(C_4H_9)_4NBr$ in L-Alanine system at all the concentrations (Fig.12).

Table 2: **Experimental speed of sound, u at different molality of L-alanine m_A and electrolyte m_J at 298.15K**

m_J (mol kg^{-1})	u (m s^{-1})	m_J (mol kg^{-1})	u (m s^{-1})
L-alanine+$(CH_3)_4NBr$			
m_A=0.15 mol kg^{-1}		m_A=0.3 mol kg^{-1}	

0.2499	**1528.2**	**0.2505**	**1536.4**
0.4999	**1536.4**	**0.4991**	**1546.7**
0.7490	**1544.2**	**0.7497**	**1556.4**
0.9994	**1556.3**	**0.9995**	**1566.1**
1.4991	**1576.9**	**1.4987**	**1584.1**
	m_A= 0.50 mol kg^{-1}		**m_A= 0.75 mol kg^{-1}**
0.2499	**1544.2**	**0.2498**	**1554.6**
0.4998	**1554.4**	**0.4998**	**1564.1**
0.7496	**1566.8**	**0.7491**	**1576.8**
0.9996	**1578.0**	**1.0000**	**1588.3**
1.4994	**1596.3**	**1.5001**	**1608.9**

m_A= 1.0 mol kg^{-1}

0.2499	**1568.4**
0.4997	**1580.7**
0.7496	**1590.2**
0.9994	**1598.5**
1.4980	**1616.6**

L-alanine+$(C_2H_5)_4NBr$

	m_A=0.15 mol kg^{-1}		**m_A=0.3 mol kg^{-1}**
0.2498	**1536.3**	**0.2498**	**1544.3**
0.3502	**1544.0**	**0.3501**	**1552.6**
0.5001	**1558.5**	**0.4999**	**1564.9**
0.7499	**1578.4**	**0.7497**	**1586.0**
0.9999	**1600.9**	**0.9990**	**1608.1**

m_A= 0.50 mol kg^{-1}		m_A= 0.75 mol kg^{-1}	
0.2498	1552.2	0.2498	1568.0
0.3497	1560.2	0.3497	1576.2
0.4996	1576.4	0.4996	1588.4
0.7498	1598.7	0.7498	1608.5
0.9998	1616.3	0.9997	1624.8

m_A= 1.0 mol kg^{-1}

0.2498	1584.2
0.3498	1590.4
0.4999	1600.0
0.7498	1616.2
0.9997	1636.3

L-alanine+ $(C_4H_9)_4NBr$

m_A=0.15 mol kg^{-1}		m_A=0.3 mol kg^{-1}	
0.0999	1528.2	0.0999	1536.4
0.2497	1556.3	0.2500	1568.6
0.3496	1576.1	0.3498	1584.0
0.4999	1600.7	0.4996	1608.1
0.6998	1632.3	0.6998	1640.4

m_A= 0.50 mol kg^{-1}		m_A= 0.75 mol kg^{-1}	
0.0999	1548.6	0.0999	1564.0
0.2497	1580.2	0.2497	1596.1
0.3499	1600.6	0.3499	1608.1
0.4997	1620.2	0.4997	1632.2

0.6999	**1648.5**	**0.6886**	**1656.3**

m_A= 1.0 mol kg^{-1}

0.0999	**1576.6**
0.2497	**1604.0**
0.3468	**1624.1**
0.4994	**1648.8**
0.6980	**1672.3**

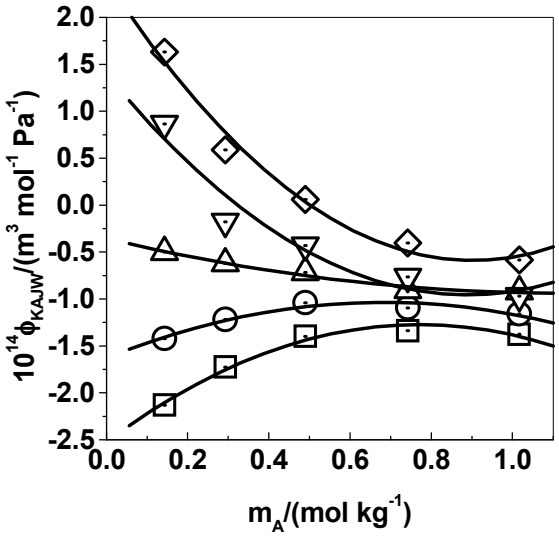

Fig. 7: The ϕ_{KAJW} vs. m_A plots for L-alanine in different concentrations, m_J of $(CH_3)_4NBr$; for m_J (□) 0.25, (○) 0.5, (Δ) 0.75, (∇) 1, (◇) 1.5 mol kg^{-1}

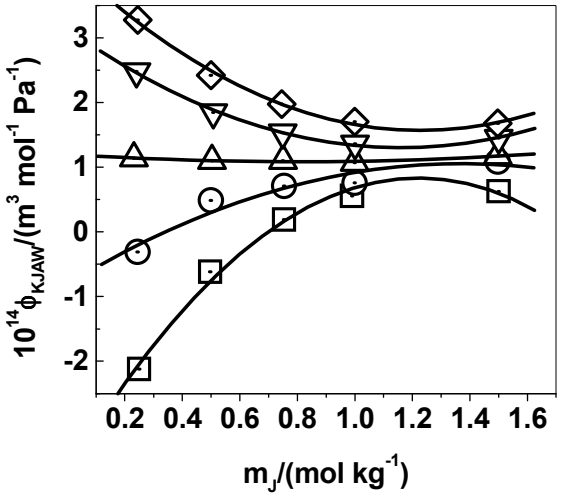

Fig. 8: The ϕ_{KJAW} vs. m_J plots for $(CH_3)_4NBr$ in L-alanine in different concentrations, m_A of glycine; for m_A (□) 0.15, (○) 0.3, (Δ) 0.5, (▽) 0.75, (◇) 1 mol kg^{-1}

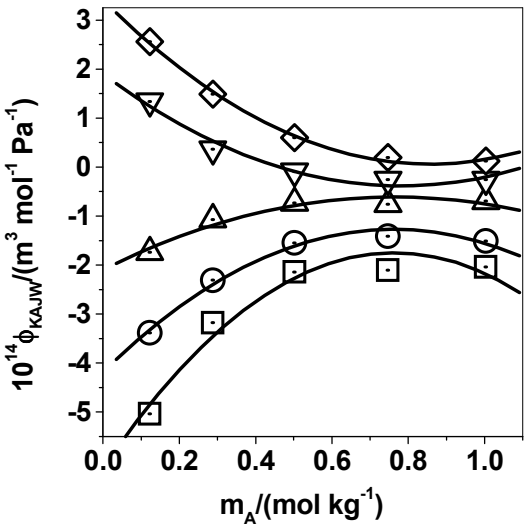

Fig. 9: The ϕ_{KAJW} vs. m_A plots for L-alanine in different concentrations, m_J of $(C_2H_5)_4NBr$; for m_J (□) 0.25, (○) 0.35, (Δ) 0.5, (∇) 0.75, (◇) 1 mol kg^{-1}

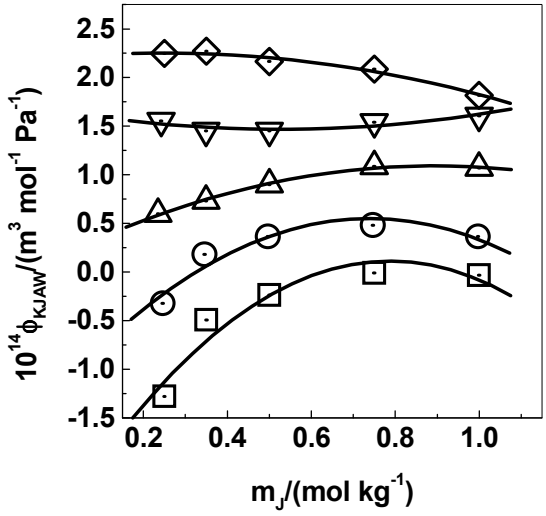

Fig. 10: The ϕ_{KJAW} vs m_J plots for $(C_2H_5)_4NBr$ in L-alanine in different concentrations, m_A of glycine; for m_A (□) 0.15, (○) 0.3, (Δ) 0.5, (∇) 0.75, (◇) 1 mol kg^{-1}

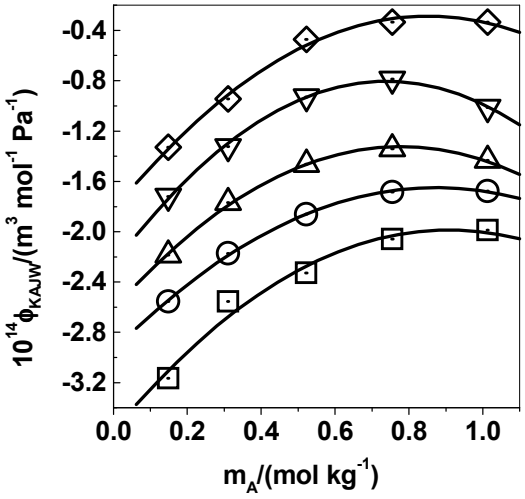

Fig. 11: The ϕ_{KAJW} vs. m_A plots for L-alanine in different concentrations, m_J of $(C_4H_9)_4NBr$; for m_J (□) 0.1, (○) 0.25, (Δ) 0.35, (∇) 0.5, (◇) 0.7 mol kg^{-1}

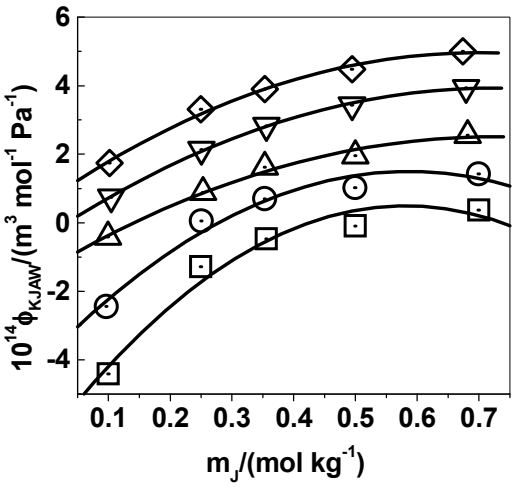

Fig. 12: The ϕ_{KJAW} vs m_J plots for $(C_4H_9)_4NBr$ in L-alanine in different concentrations, m_A of glycine; for m_A (□) 0.15, (○) 0.3, (Δ) 0.5, (∇) 0.75, (◇) 1 mol kg^{-1}

The speed of sound for glycylglycine in $(CH_3)_4NBr$, $(C_2H_5)_4NBr$ and $(C_4H_9)_4NBr$ solutions are listed in Table 3. The changes in the ϕ_{KAJW} values with respect to the concentrations of glycylglycine and salts are different from those noted in the cases of glycine and L-alanine. The ϕ_{KAJW} values for glycylglycine decrease with an increase in its concentration at a constant concentration of $(CH_3)_4NBr$ (Fig. 13), while ϕ_{KJAW} for $(CH_3)_4NBr$ increase with an increase in the concentrations of $(CH_3)_4NBr$ at a given m_A (Figs. 13 and 14). Figs. 15 and 16 also display similar behaviour with regard to the changes in the ϕ_{KAJW} and ϕ_{KJAW} values with respect to the concentrations of

glycylglycine and $(C_2H_5)_4NBr$ solutions. The pattern is also similar in the case of glycylglycine with $(C_4H_9)_4NBr$ (Figs. 17 and 18).

However an interesting aspect of the data collected is that since $(C_4H_9)_4NBr$ is a strong structure maker due to bulky butyl groups, the effect of this salt is more prominent in glycine, L-L-alanine and glycylglycine solutions This can also be explained in terms of the viscosity B-coefficients extracted from the viscosity data of these salts in water. Several reports are available in the literature..

Table 3: **Experimental speed of sound, u at different molality of glycyglylcine m_A and electrolyte m_J at 298.15K.**

m_J (mol kg^{-1})	u (m s^{-1})	m_J (mol kg^{-1})	u (m s^{-1})
Glycylglycine+$(CH_3)_4NBr$			
	m_A= 0.1 mol kg^{-1}		**m_A= 0.3 mol kg^{-1}**
0.2505	**1520.3**	**0.2505**	**1536.2**
0.4996	**1532.4**	**0.4999**	**1544.5**
0.7995	**1544.0**	**0.7997**	**1556.7**
1.0991	**1552.2**	**1.0999**	**1568.4**
1.4997	**1568.1**	**1.4997**	**1584.3**
	m_A= 0.5 mol kg^{-1}		**m_A= 0.6 mol kg^{-1}**
0.2505	**1552.2**	**0.2505**	**1562.1**
0.4996	**1560.0**	**0.4999**	**1570.3**

0.7998	**1572.3**	**0.7998**	**1582.0**
1.0094	**1584.5**	**1.0090**	**1594.3**
1.4997	**1600.0**	**1.5001**	**1608.5**

m_A= 0.75 mol kg^{-1}

0.2517	**1576.2**
0.4996	**1584.7**
0.7998	**1596.1**
1.0989	**1608.7**
1.4988	**1620.1**

Glycylglyine+$(C_2H_5)_4NBr$

m_A= 0.1 mol kg^{-1}		**m_A= 0.3 mol kg^{-1}**	
0.0994	**1520.2**	**0.0952**	**1536.3**
0.2497	**1528.3**	**0.2493**	**1548.5**
0.5495	**1552.1**	**0.5472**	**1568.7**
0.7497	**1568.0**	**0.7499**	**1584.4**
1.1986	**1608.5**	**1.1988**	**1624.2**

m_A= 0.5 mol kg^{-1}		**m_A= 0.6 mol kg^{-1}**	
0.0999	**1544.3**	**0.1004**	**1552.2**
0.2493	**1560.0**	**0.2498**	**1568.4**
0.5486	**1584.3**	**0.5500**	**1592.3**
0.7498	**1600.5**	**0.7499**	**1608.0**
1.1997	**1640.8**	**1.1996**	**1648.8**

m_A= 0.75 mol kg^{-1}

0.1008	**1560.7**

0.2502	**1576.5**
0.5433	**1600.2**
0.7429	**1616.2**
1.1995	**1656.2**

Glycylglycine+$(C_4H_9)_4NBr$

m_A= 0.1 mol kg^{-1}		**m_A= 0.3 mol kg^{-1}**	
0.0496	**1520.3**	**0.0497**	**1536.3**
0.2699	**1552.4**	**0.2700**	**1568.1**
0.3499	**1566.6**	**0.3500**	**1582.4**
0.5794	**1600.8**	**0.5797**	**1614.1**
0.6999	**1616.0**	**0.7004**	**1632.4**
	m_A= 0.5 mol kg^{-1}		**m_A= 0.6 mol kg^{-1}**
0.0496	**1552.2**	**0.0496**	**1560.3**
0.2699	**1584.4**	**0.2699**	**1592.3**
0.3500	**1598.3**	**0.3499**	**1606.1**
0.5800	**1626.1**	**0.5793**	**1636.6**
0.6999	**1648.2**	**0.7001**	**1656.4**

m_A= 0.75 mol kg^{-1}

0.0497	**1568.1**
0.2700	**1600.9**
0.3499	**1614.2**
0.5798	**1648.8**
0.7001	1664.5

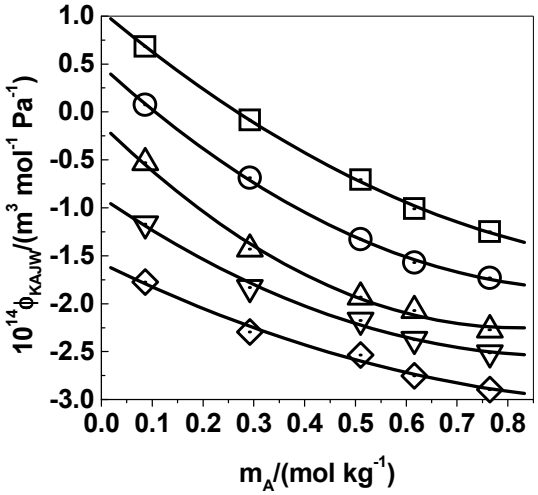

Fig. 13: The ϕ_{KAJW} vs. m_A plots for glycylglycine in different concentrations, m_J of $(CH_3)_4NBr$; for m_J (◇) 0.25, (▽) 0.5, (Δ) 0.8, (○) 1, (□) 1.5 mol kg^{-1}

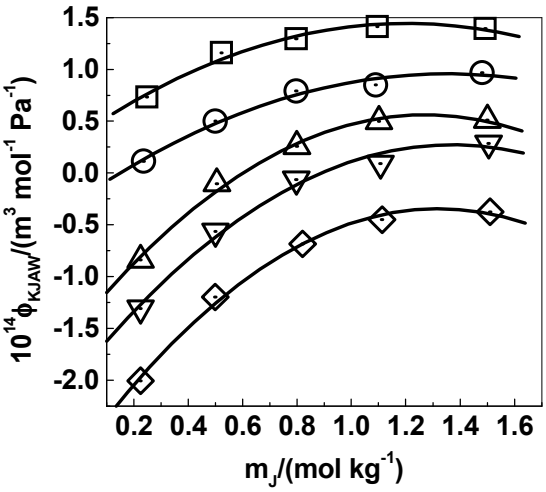

Fig. 14: The ϕ_{KJAW} vs. m_J plots for $(CH_3)_4NBr$ in glycylglycine in different concentrations, m_A of glycylglycine; for m_A

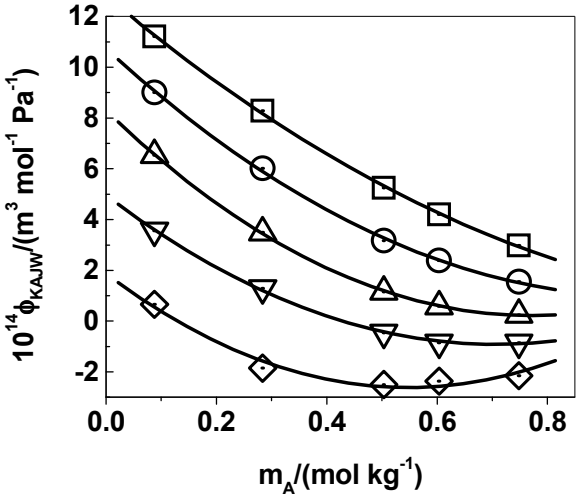

Fig. 15: The ϕ_{KAJW} vs. m_A plots for glycylglycine in different concentrations, m_J of $(C_2H_5)_4NBr$; for m_J (◇) 0.25, (▽) 0.5, (Δ) 0.8, (○) 1, (□) 1.5 mol kg^{-1}

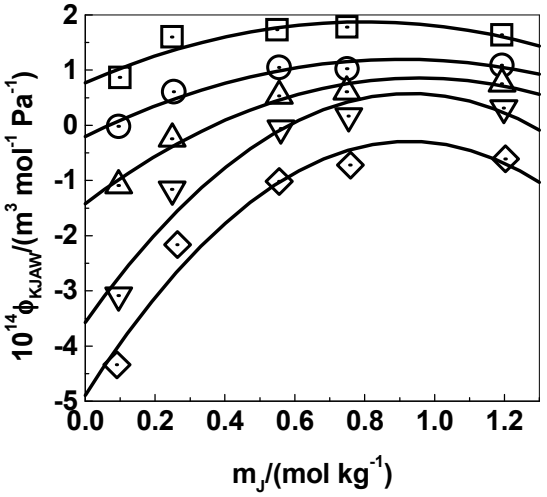

Fig. 16: The ϕ_{KJAW} vs. m_J plots for $(C_2H_5)_4NBr$ in glycylglycine in different concentrations, m_A of glycylglycine; for m_A (□) 0.1, (○) 0.3, (Δ) 0.5, (∇) 0.6, (◇) 0.75 mol kg^{-1}

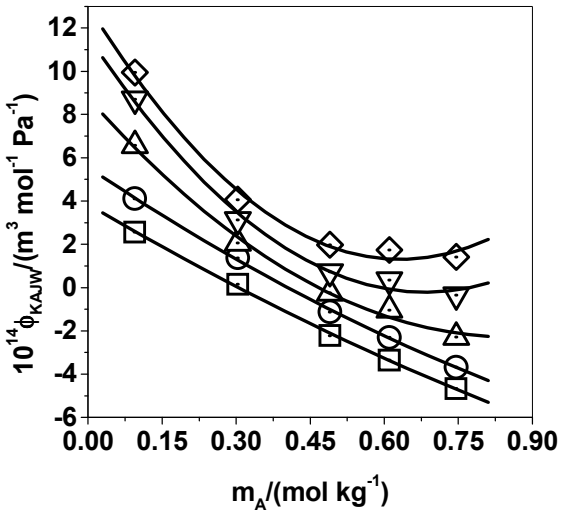

Fig. 17: The ϕ_{KAJW} vs. m_A plots for glycylglycine in different concentrations, m_J of $(C_4H_9)_4NBr$; for m_J (□) 0.05, (○) 0.27, (Δ) 0.35, (∇) 0.58, (◇) 0.7 mol kg^{-1}

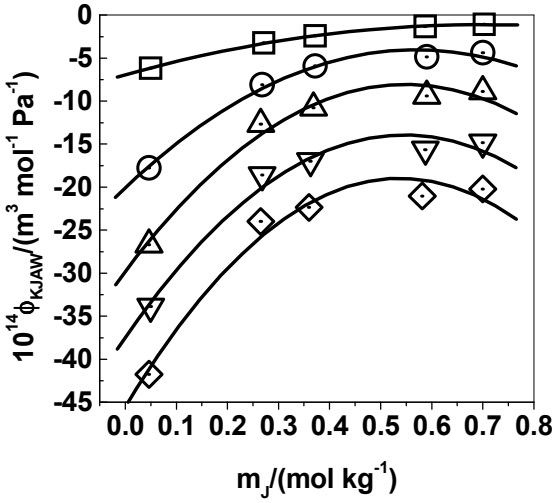

Fig. 18: The ϕ_{KJAW} vs. m_J plots for $(C_4H_9)_4NBr$ in glycylglycine in different concentrations, m_A of glycylglycine; for m_A (□) 0.1, (○) 0.3, (Δ) 0.5, (∇) 0.6, (◇) 0.75 mol kg^{-1}

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

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

The effect of different salts and their concentrations on $\phi_K{}^o{}_{tr.AJW}$ is shown in **Fig. 19**. 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.

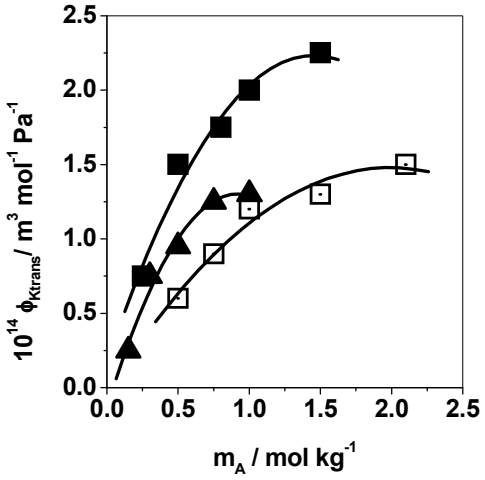

Fig. 19: Plots of $\phi_K{}^o{}_{tr.AJW}$ of glycine + in $(CH_3)_4NBr$ (■), L-L-alanine + $(C_2H_5)_4NBr$ (▲), glycylglycine + $(C_4H_9)_4NBr$ (□)

Thus, it can be concluded that the transfer compressibilities of glycine are dependent on the nature and size of the cations involved.

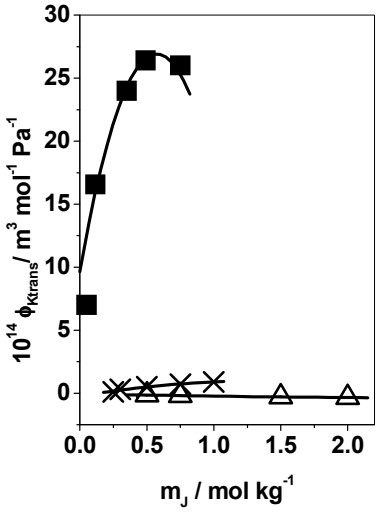

Fig. 20: Plots of $\phi_K{}^o{}_{tr.JAW}$ of glycine + $(C_2H_5)_4NBr$ (X), L-alanine + $(CH_3)_4NBr$ (Δ), glycine + $(C_4H_9)_4NBr$ (■)

Eqn (6) can also be used to compute $\phi_K{}^o{}_{tr.JAW}$ values for the salts in different amino acids and peptide (see Fig. 20).

Effect of NaBr, KCl, KBr and $MgCl_2$ on Viscosities of Aqueous Glycine and L-alanine Solutions at 298.15 K

Viscosity, η is another important property, which can yield information on solute–solute interactions. There are some reports on the viscosities of dilute aqueous solutions of amino acids and electrolytes.[1-10] However, no viscosity reports are available at high concentrations of amino acid and electrolyte. In this work the viscosities of

aqueous glycine and L-alanine in the solutions of NaBr, KCl, KBr and $MgCl_2$ up to high concentrations are presented. The mixture viscosities of these solutions are accurately fitted using a simple two-parameter equation. The viscosity data were required in order to test a model under developmental stage in this laboratory for calculating viscosities of concentrated mixtures of the simple amino acids in strong electrolytes.

The viscosities of aqueous glycine and L-alanine in NaBr, KCl, KBr and $MgCl_2$ solutions are listed in Table 4. Ogawa et al. measured viscosities of several amino acids in aqueous LiCl, NaCl and KCl solutions with their concentrations

Table 4: Experimental viscosity, η of aqueous glycine and L-alanine in NaBr, KBr, KCl and $MgCl_2$ solutions at 298.15 K

m_J / (mol· kg^{-1})	η/ (mPa· s)	m_J /(mol· kg^{-1})	η / (mPa· s)	m_J / (mol· kg^{-1})	η/ (mPa· s)	m_J / (mol· kg^{-1})	η / (mPa· s)
(Glycine + NaBr)							
m_A = 0.4994 mol· kg^{-1}		m_A = 0.9999 mol· kg^{-1}		m_A = 1.9989 mol· kg^{-1}		m_A = 2.9998 mol· kg^{-1}	
0.4994	0.999	0.4974	1.074	0.4994	1.232	0.5003	1.445
0.9988	1.032	0.9999	1.115	0.9999	1.285	0.9979	1.503
2.0007	1.114	2.0009	1.222	1.9998	1.427	2.0001	1.670
2.9997	1.238	2.9987	1.328	3.0001	1.565	3.0016	1.847
3.9972	1.365	3.9984	1.481	4.0001	1.743	3.9992	2.038
(Glycine + KCl)							
m_A=0.4991 mol· kg^{-1}		m_A = 1.0004 mol· kg^{-1}		m_A = 1.9993 mol· kg^{-1}		m_A = 2.9999 mol· kg^{-1}	

0	0.956	0	1.189	0	1.189	0	1.374
0.5003	0.967	0.5002	1.040	0.5002	1.201	0.1001	1.375
1.0006	0.972	0.9994	1.041	0.9979	1.211	0.4999	1.396
1.9999	0.979	1.9999	1.055	1.9993	1.220	1.0002	1.390
3.0006	0.997	3.0006	1.083	3.0009	1.252	2.0004	1.415
3.9981	1.023	3.9985	1.099	3.9995	1.290	3.0001	1.467

(Glycine + KBr)

m_A = 0.4995 mol· kg^{-1}		m_A = 0.9990 mol· kg^{-1}		m_A = 1.9996 mol· kg^{-1}		m_A = 2.9998 mol· kg^{-1}	
0.4999	0.952	0.4999	1.017	0.5001	1.190	0.4995	1.372
1.0001	0.962	0.9998	1.013	0.9996	1.203	1.0001	1.365
1.9992	0.947	2.0001	1.012	1.9998	1.178	2.0001	1.386
2.9988	0.970	2.9992	1.023	2.9997	1.189	3.0002	1.391
4.0005	0.976	3.9993	1.044	4.0001	1.225	3.9997	1.422

(Glycine + $MgCl_2$)

m_A = 0.4999 mol· kg^{-1}		m_A = 0.9998 mol· kg^{-1}		m_A = 1.9990 mol· kg^{-1}		m_A = 3.0002 mol· kg^{-1}	
0.0987	0.991	0.0998	1.060	0.0998	1.230	0.0998	1.424
0.5010	1.086	0.5001	1.180	0.4999	1.334	0.4989	1.539
1.0001	1.196	0.9988	1.292	0.9987	1.466	0.9999	1.696
1.5001	1.333	1.5007	1.418	1.4976	1.621	1.4989	1.881

(L-alanine + KCl)

m_A =0.1003 mol· kg^{-1}		m_A = 0.4995 mol· kg^{-1}		m_A = 0.7497 mol· kg^{-1}		m_A = 1.0002 mol· kg^{-1}	
0	0.918	0	1.017	0	1.079	0	1.152

0.5003	0.924	0.5003	1.016	0.5002	1.091	0.5003	1.154
0.9992	0.916	0.9992	1.012	1.0005	1.082	1.0006	1.155
1.9984	0.933	1.9995	1.025	1.9995	1.108	2.0001	1.164
2.9999	0.947	2.9989	1.044	2.9995	1.118	3.0002	1.188
3.9999	0.943	4.0016	1.077	3.9999	1.149	3.9999	1.217

(L-alanine + $MgCl_2$)

m_A = 0.1003 mol·kg^{-1}		m_A = 0.4995 mol·kg^{-1}		m_A = 0.7498 mol·kg^{-1}		m_A = 1.0002 mol·kg^{-1}	
0.0494	0.942	0.0504	1.035	0.0515	1.104	0.0504	1.171
0.5010	1.043	0.4999	1.154	0.4999	1.224	0.5001	1.300
0.9999	1.161	1.0009	1.287	0.9999	1.361	0.9989	1.453
1.4990	1.290	1.4999	1.419	1.5001	1.512	1.4998	1.626

ranging up to 2 mol·kg^{-1} of water.[1] These authors have not reported any direct viscosity data, but have listed the viscosity B- and D-coefficients. If the viscosities of glycine and L-alanine in aqueous KCl are calculated using these coefficients and their equation, the resultant viscosities agree to within 0.009 mPa·s. It may be noted that the agreement between our viscosity data and the calculated ones from the work of Ogawa et al.[1] was obtained up to 2 mol·kg^{-1} of aqueous KCl, using our molalities. Again, the number of data points has not been mentioned in their report. A direct comparison of our viscosity data of glycine and L-alanine in aqueous KCl solution is however, possible with the recent data of Banipal et al.[10] An average agreement of 0.007 mPa·s was obtained for both the amino acids in aqueous KCl solutions. Such a comparison however could not be

possible with the data of Rodriguez et al., who measured the viscosity data of DL-alanine in NaCl solutions and not in other electrolytes of our interest.[11] The effect of electrolytes on the viscosities of amino acid + electrolyte mixtures are shown in Fig. 21 (a and b). The viscosities of glycine and L-alanine in the electrolyte solutions increase with increase in concentration of amino acid as well as electrolyte. An examination of Fig. 21 (a and b) signifies

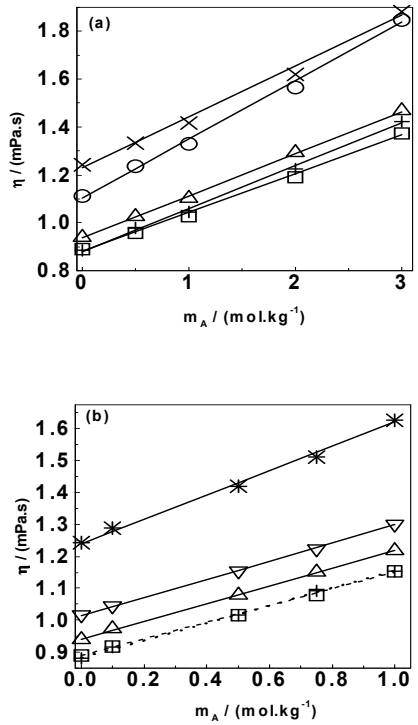

Fig. 21: Effect of electrolytes on η of the mixture of aqueous amino acids + electrolytes (a) aqueous glycine (o), glycine + 4 mol·kg^{-1} KCl (Δ), + 3 mol·kg^{-1} NaBr (O), 4 mol·kg^{-1} KBr (+), + 1.5 mol·kg^{-1} $MgCl_2$ (X) (b) aqueous L-alanine (o), L-alanine + 0.5 mol·kg^{-1} KCl (+), + 4 mol·kg^{-1} KCl (Δ), + 0.5 mol·kg^{-1} $MgCl_2$ (∇), 1.5 mol·kg^{-1} $MgCl_2$ (◇)

higher effect of $MgCl_2$ on the viscosity of the amino acid-electrolyte mixture as compared to 1:1 electrolytes. For example, the $\partial\eta/\partial m_A$ value at 1 mol·kg^{-1} of glycine in water is 0.156 mPa·s· kg· mol^{-1}, which increases to 0.181, 0.168 and 0.172 mPa·s· kg· mol^{-1} on addition of 1:1 electrolytes NaBr, KCl and KBr, respectively. The maximum value of $\partial\eta/\partial m_A$ of 0.198 mPa·s·kg·mol^{-1} for glycine solutions is observed due to the addition of $MgCl_2$. In the case of 1 mol·kg^{-1} of L-alanine, the $\partial\eta/\partial m_A$ value changes from 0.258 mPa· s· kg· mol^{-1} in water to 0.272 mPa· s· kg· mol^{-1} in 1 mol·kg^{-1} of KCl and 0.310 mPa· s· kg· mol^{-1} in 1 mol·kg^{-1} of $MgCl_2$. The $\partial\eta/\partial m_A$ values of aqueous amino acid + electrolyte mixtures do not show very large increase with these added electrolytes in contrast to those seen on addition of tetra-n-alkylammonium bromide.[11]

The structure-making or -breaking ability of solutes can be rationalized in terms of the Jones-Dole viscosity B-coefficient. The B-coefficient of amino acids in 1 mol·kg^{-1} of electrolyte is obtained using the following equation:

$$\eta / \eta^0 = 1 + B\,c + D\,c^2 \qquad (7)$$

where η^0 is the viscosity of solvent (electrolyte + water). The molar concentration, c is calculated from molality using the density of solution published in our recent reports.[12-14] The B-coefficients of aqueous glycine and L-alanine observed in this work are 0.136 dm^3·mol^{-1} and 0.271 dm^3·mol^{-1}, respectively. The B-coefficient values are in close agreement with the literature values (0.135 dm^3·mol^{-1} and 0.247 dm^3·mol^{-1} for aqueous glycine and L-alanine, respectively).[12-14] The viscosity B-coefficients for glycine and L-

alanine on addition of 1 mol· kg^{-1} of electrolytes are listed in Table 5. The B-coefficients of glycine and L-alanine also increase on addition of NaBr, KCl and KBr, while it does not change on addition of $MgCl_2$. This again confirms that the 1:1 electrolytes promote structure-making ability of the amino acid solution, while $MgCl_2$ has no influence.

The viscosity of these mixtures can be analysed by a simple equation. If an amino acid is added to water making a concentrated aqueous amino acid solution having molality m_A then the viscosity of aqueous amino acid solutions, η_{AW} can be given by:

$$\eta_{AW} = \eta^0_W + q_{A1}\, m_A + q_{A2}\, m_A^2 \qquad (8)$$

where η^0_W is the viscosity of water (0.8903 mPa·s at 298.15 K) and q_{A1} and q_{A2} are the empirical parameters required to account for the concentration dependence of viscosity of aqueous amino acid. Similarly the viscosity of concentrated aqueous electrolyte solution can be correlated by eq 8:

$$\eta_{JW} = \eta^0_W + q_{J1}\, m_J + q_{J2}\, m_J^2 \qquad (9)$$

One can write the modified viscosity of aqueous amino acid, η'_{AJW}. Let the viscosity of amino acid in the mixture be given as:

$$\eta'_{AJW} = \eta_{AW} + \delta^0_{AJW}\, m_A\, m_J + \delta^1_{AJW}\, m_A^2\, m_J^2 \qquad (10a)$$

and of electrolyte as

$$\eta'_{JAW} = \eta_{JW} + \delta^0_{JAW}\, m_A\, m_J + \delta^1_{JAW}\, m_A^2\, m_J^2 \qquad (10b)$$

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

The bulk viscosity, η of such a mixture is given by

$$\eta = (m_A \eta'_{AJW} + m_J \eta'_{JAW}) / (m_A + m_J) \quad (11)$$

Substitution of eqs 10a and b into eq 11 and simplifying gives

$$\eta = \eta_{ideal} + m_A m_J [\delta^0_{JAW} + \delta^1_{JAW} m_A m_J] \quad (12)$$

where η_{ideal} is given by

$$\eta_{ideal} = (m_A \eta_{AW} + m_J \eta_{JW}) / (m_A + m_J) \quad (13)$$

Table 5: Viscosity B-coefficients for aqueous glycine and L-alanine on addition of 1 $mol \cdot kg^{-1}$ of electrolytes at 298.15 K

Electrolyte	B / ($dm^3 \cdot mol^{-1}$)	Electrolyte	B / ($dm^3 \cdot mol^{-1}$)
Glycine		L-alanine	
NaBr	0.161	KCl	0.325
KCl	0.177	$MgCl_2$	0.279
KBr	0.210		
$MgCl_2$	0.121		

Table 6: The amino acid + electrolyte interaction parameters, δ^0_{AJW} and δ^1_{AJW} for aqueous glycine and L-alanine in the presence of different electrolytes at 298.15 K. (values given in parentheses are the standard errors in the parameters)

System	δ^0_{AJW} / (mPa s kg^2 mol^{-2})	δ^1_{AJW} / (mPa s kg^4 mol^{-4})	rmsd / (mPa· s)
Glycine + NaBr	0.0881 (0.0034)	-0.0023 (0.0004)	0.02
Glycine + KCl	0.0554 (0.0041)	-0.0025 (0.0006)	0.02
Glycine + KBr	0.0498 (0.0035)	-0.0020 (0.0004)	0.02
Glycine + $MgCl_2$	0.1956 (0.0137)	-0.0177 (0.0040)	0.03
L-alanine + KCl	0.1266 (0.0113)	-0.0186 (0.0038)	0.03
L-alanine + $MgCl_2$	0.4352 (0.0244)	-0.1128 (0.0212)	0.02

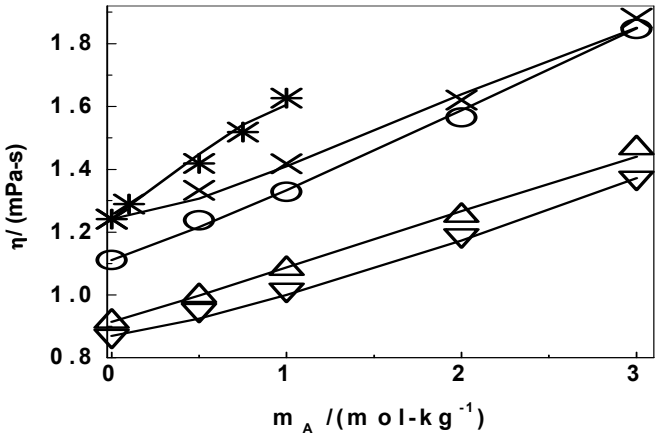

Fig. 22: Experimental and fitted viscosities (points experimental and lines fitted viscosities by eq 6 glycine + 3 mol·kg^{-1} KCl (Δ), glycine + 0.5 mol·kg^{-1} KBr (∇), glycine + 3 mol·kg^{-1} NaBr (O), glycine + 1.5 mol·kg^{-1} $MgCl_2$ (X), L-alanine + 1.5 mol·kg^{-1} $MgCl_2$ (◇)

The parameters δ^0_{AJW} and δ^1_{AJW} are obtained by the regression of the viscosity data listed in Table 4. The δ^0_{AJW} and δ^1_{AJW} parameters obtained for glycine and L-alanine in different electrolytes are listed in Table 6. These parameters depend on the nature of amino acid and electrolyte. These parameters are independent of the concentration of electrolytes. The correlation power of eq 6 is shown in Fig. 22, where the points show the experimental data and lines are the fitted values. The figure depicts the close agreement between the experimental and fitted viscosities of glycine and L-alanine in different electrolytes. The viscosities of aqueous glycine in the solutions of 1:1 electrolytes studied here can be estimated using parameters listed in Table 6 with an average rmsd (rmsd = $[(\sum(\eta_{exp.} - \eta_{fitted})^2)/N)]^{0.5}$, where N = number of data points) of (0.020 mPa· s), whereas in solution of $MgCl_2$ of (0.04 mPa·s). In the case of L-alanine in the above electrolytes, an average rmsd of (0.03 mPa·s) is obtained.

The δ^0_{AJW} and δ^1_{AJW} parameters signify the interactions between the amino acid and electrolyte in their solutions. The δ^0_{AJW} parameter decreases with an increase in the ionic size for a given amino acid. This observation is supported by volumetric study, where $MgCl_2$ shows maximum interactions with the charged centers of amino acids giving higher transfer volumes as compared to larger cations like K^+ or Na^+.

At last, the speeds of sound for aqueous glycine (0.10 mol kg-1) were also measured in aqueous methanol. Other amino acids and organic solvents were not taken for a detailed study due to some solubility restrictions. Fig. 23 shows a variation in ϕ_{KAJW} with composition of aqueous methanol. A linear variation is seen between the two.

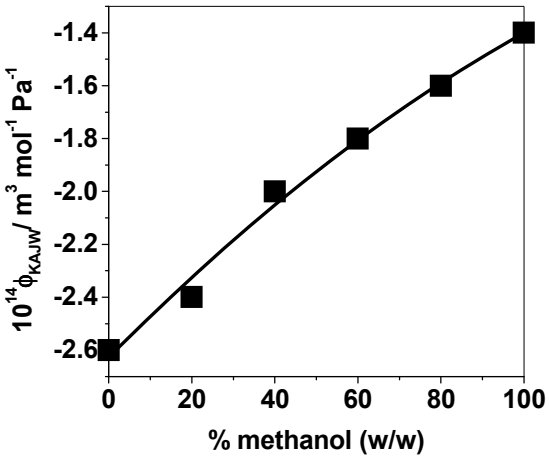

Fig. 23: Variation in ϕ_{KAJW} with composition of aqueous methanol for glycine (0.10 mol kg^{-1})

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Chapter 6

MODEL

This chapter deals with the development of a framework of suitable equations that are required to correlate equilibrium thermodynamic properties of mixtures of amino acid with electrolyte solutions. The developed equations are simple in nature and easy to apply to a variety of thermodynamic properties of many amino acid + electrolyte systems.

The solution properties of amino acids are greatly influenced by ionic solutions. As amino acids are the building blocks of proteins, the mutual interactions among amino acid, ions and water bear significant impact on the native properties of proteins. As discussed in Chapter I, several models are available in the literature to predict the thermodynamic activities of aqueous solutions of either amino acids or of electrolytes with good accuracy. These models are based on the local composition concept and have considered the chemical equilibria in these solutions at pH other than ~ 7. The amino acids in water are considered as non-electrolytes while treating their thermodynamic properties. Thermodynamic of ions in water in concentrated solutions has received adequate treatment more notably within the context of the Pitzer formalism. (Please see Chapter I)

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.[1] Talukdar et. al.[2] used The Scaled Particle Theory has been used for correlating excess free energy and entropy of mixing of amino acids from water to aqueous salt solutions. The UNIFAC model for correlation of activity coefficients of amino acids has also been

used[3]. 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[4-11]. 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.

A careful search of the published literature, however has revealed the following facts: i) several thermodynamic properties of amino acids in ionic solutions have been measured in dilute concentrations, ii) simple equations have been used to fit the properties of amino acids in electrolyte solutions of the dilute solution data, iii) these thermodynamic data have not been studied and correlated in high concentrations of both amino acids and electrolytes, and iv) No model or equations are available that can correlate these properties with the concentrations of electrolyte solutions or amino acids. These above observations led us recently to examine the volumetric properties of amino acids in electrolyte solutions in high concentrations. In this paper, we undertake the following issues: i) to develop suitable equations to account the concentration dependence of a given thermodynamic property of amino acid in electrolyte solution applicable up to high concentrations, or how thermodynamic properties of an amino acid are altered on addition of an electrolyte up to high concentrations and ii) to develop suitable equations

to account the concentration dependence of a given thermodynamic property of electrolyte in amino acid applicable up to high concentrations; this issue has never been addressed before in the literature to the best of our knowledge.

Model and Equations:

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. 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. In case of aqueous amino acids solutions it is important to consider the speciation (different species available in aqueous medium) in the calculation procedure. Amino acid in water can loose a proton there by forming a negatively charged molecule or 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 (acid), proton acceptor (base), or functional groups more than 99% of amino acid molecules stay in zwitterionic form in the pH range of 6.8-7.2.

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[12], 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 the case of mixed electrolyte solutions, binary interactions between like charged ions and ternary interactions among three ions are considered.

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 is 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.

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:

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

where m_A is the molality of amino acid and q_n are the adjustable parameters. Similarly, the excess 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:

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

i j i j k

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 $I = 0.5 \sum m_i z_i^2$ 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

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

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 expression 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. α = 2.0 $(kg\ mol^{-1})^{0.5}$. $\beta^{(1)}_{MX}$ is necessary in dilute solutions, while C^{φ}_{MX} is required at high concentrations. 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 :

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

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

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

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 $\lambda_{AJW} = \lambda_{JAW}$.

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, $\gamma_{\pm J}$ in mixture as:

$$\ln \gamma_{AJW} = \ln \gamma^{0}_{AJW} + 2\, s_{\phi}\, m_A + 3\, s_{\phi}^{'}\, m_A^{2} + 2\, \lambda_{AJW}\, m_J \qquad (7)$$

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

$$\begin{aligned} \ln\gamma_{\pm JAW} = \ln\gamma_{\pm}{}^{0}{}_{JAW} \; - \; & \left| Z_M\, Z_X \right| \; A_{\phi} \left(I^{0.5} / (1 + b\, I^{0.5}) + (2 / b) \ln (1 + b\, I^{0.5}) \right) + \\ & 4\, \nu_M\, \nu_X\, m_J \left[\beta^{(0)}_{MXA} - (2\, \beta^{(1)}_{MXA} / \alpha^2\, I) \left[1 - (1 + \alpha\, I^{0.5}) \exp (-\alpha\, I^{0.5}) \right] \right] + \\ & 3\, m_J^{2}\, (\nu_M\, \nu_X)^{1.5}\, C^{\varphi}_{MXA} \Big] + 2\, \lambda_{AJW}\, m_A \end{aligned} \qquad (8)$$

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 $kg^{0.5}$ $mol^{-0.5}$ [13] at 298.15 K. The expression for correlating ϕ_{VAJW} with m_A and m_J can be obtained from the above equations. These expressions are:

$$\phi_{VAJW} = \phi_V{}^{0}{}_{AJW} + 2\, s_V\, m_A + 3\, s_V{}'\, m_A{}^2 + 2\, R\, T\, \lambda^V{}_{AJW}\, m_J \qquad (9)$$

In equation (9) $\lambda^V{}_{AJW}$, s_V and $s_V{}'$ are defined as: $\lambda^V{}_{AJW} = (\partial\lambda_{AJW} / \partial P)$, $s_V = (\partial s_{\varphi} / \partial P)$ 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:

$$\begin{aligned}\phi_{VJAW} = \phi_V{}^{0}{}_{JAW} + \nu\, |Z_M\, Z_X|\, (A_V / 2\, b) \ln (1 + b\, I^{0.5}) + 4\nu_M\, \nu_X\, R\, T\, m_J \\ [\beta^{(0)V}{}_{MXA} + 2\, \beta^{(1)V}{}_{MXA} [\, [1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] / (\alpha^2\, I)\,] \\ + 3 m_J{}^2\, [(\nu_M\, Z_M) / 2\, |Z_M\, Z_X|^{0.5}\, C^{\varphi V}{}_{MXA}] + 2\, R\, T\, \lambda^V{}_{AJW}\, m_A\end{aligned} \qquad (10)$$

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 $kg^{0.5}$ $mol^{-1.5}$ [13] at 298.15 K.

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:

$$\phi_{KAJW} = \phi_K{}^0{}_{AJW} + 2\, s_K\, m_A + 3\, s_K{}'\, m_A{}^2 + 2\, R\, T\, \lambda^K{}_{AJW}\, m_J \qquad (11)$$

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

$$\phi_{KJAW} = \phi_K{}^0{}_{JAW} + \nu\, |Z_M\, Z_X|\, (A_K / 2\, b) \ln (1 + b\, I^{0.5}) + 4\, \nu_M\, \nu_X\, R\, T\, m_J$$
$$[\beta^{(0)K}{}_{MXA} + 2\, \beta^{(1)K}{}_{MXA} [\, [1 - (1 + \alpha\, I^{0.5}) \exp(-\alpha\, I^{0.5})] / (\alpha^2\, I)]$$
$$+ 3\, m_J{}^2\, [(\nu_M\, Z_M) / 2\, |Z_M\, Z_X|^{0.5}\, C^{\varphi K}{}_{MXA}] + 2\, R\, T\, \lambda^K{}_{AJW}\, m_A \qquad (12)$$

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} $m^3\, kg^{0.5}\, mol^{-1.5}\, Pa^{-1}$ [13] at 298.15 K. 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:

$$\text{Objective function} = (\sum (y_{exp.} - y_{cal.})^2 / N)^{0.5} \quad (13)$$

With N being number of experimental data points.

Results and Discussion:

In this work equations (7-12) 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. Though a large number of experimental data on activity coefficient, volume and compressibility of the amino acid – electrolyte – water solutions are reported in the literature, some representative systems have been analysed in this work. were subjected to these equations. A summary of the experimental data and literature data together with their sources and the accuracy of measurements are described in Table 1.

Table 1: List of systems analyzed for testing equations (7-12) for different properties

No.	System	m_A	m_J	Property	Reported accuracy of the basic property[a]
1.	Glycine – NaCl - H_2O[14,15]	0.5 – 3	0.2 – 1	γ, ϕ_V , ϕ_K	0.0008, 0.100, 1.0

2.	Glycine – $NaNO_3$ – H_2O[15]	0.5 – 3	0.2 – 1	ϕ_V , ϕ_K	0.100, 1.0
3.	Glycine – NaBr – H_2O	0.5 – 3	0.5 – 4	ϕ_V , ϕ_K	0.010, 0.5
4.	Glycine – KCl – H_2O[15]	0.5 – 3	0.2-1	ϕ_V , ϕ_K	0.100, 1.0
5.	Glycine – KCl – H_2O[16]	0.5 – 3	0.5 – 4	ϕ_V , ϕ_K	0.010, 0.5
6.	Glycine – KNO_3 – H_2O[15]	0.5 – 3	0.2 – 1	ϕ_V , ϕ_K	0.100, 1.0
7.	Glycine – KBr – H_2O	0.5 – 3	0.5 – 4	ϕ_V , ϕ_K	0.010, 0.5
8.	Glycine – $MgCl_2$ – H_2O	0.5 – 3	0.1 – 1.5	ϕ_V , ϕ_K	0.010, 0.5
9.	Alanine – KCl – H_2O	0.1 – 1	1 – 4	ϕ_V , ϕ_K	0.010, 0.5
10.	Alanine – $MgCl_2$ – H_2O	0.1 – 1	0.05–1.5	ϕ_V , ϕ_K	0.010, 0.5
11.	Glycylglycine–KCl– H_2O	0.5 –1.2	0.5 – 2	ϕ_V , ϕ_K	0.010, 0.5
12.	Glycylglycine–KBr- H_2O	0.5 – 1.2	0.5 – 2	ϕ_V , ϕ_K	0.010, 0.5
13.	Glycylglycine–$MgCl_2$– H_2O	0.5 – 1	0.5 - 1.5	ϕ_V , ϕ_K	0.010, 0.5
14.	Glycylglycine – Na_2SO_4 – H_2O	0.5 – 1	0.5 – 2	ϕ_V , ϕ_K	0.010, 0.5
15.	Glycine–$(CH_3)_4NBr$- H_2O	0.5 – 2	0.25 –1.8	ϕ_V	0.010

16.	Glycine – $(C_2H_5)_4NBr$ - H_2O	0.5 – 1.5	0.5 – 1.5	ϕ_V	0.010
17.	Glycine – $(C_4H_9)_4NBr$ – H_2O	0.5 –1.5	0.05 – 0.73	ϕ_V	0.010
18.	Alanine – $(CH_3)_4NBr$ – H_2O	0.5 –1	0.25 – 1.8	ϕ_V	0.010
19.	Alanine – $(C_2H_5)_4NBr$ - H_2O	0.1 – 1	0.1 –1.2	ϕ_V	0.010
20.	Alanine – $(C_4H_9)_4NBr$ – H_2O	0.1 – 1	0.05 – 0.73	ϕ_V	0.010
21.	Glycylglycine – $(CH_3)_4NBr$ - H_2O	0.1 – 0.75	0.25 – 0.8	ϕ_V	0.010
22.	Glycylglycine – $(C_2H_5)_4NBr$ - H_2O	0.1 – 0.75	0.1 – 1.2	ϕ_V	0.010
23.	Glycylglycine – $(C_4H_9)_4NBr$ – H_2O	0.1 – 0.75	0.05 - 0.5	ϕ_V	0.010
24.	Glycine – KSCN – H_2O	0.1 – 0.3	1 – 5	ϕ_V	0.007
25.	Alanine – KSCN – H_2O[17]	0.075 –	1 – 5	ϕ_V	0.007

		0.25			
26.	Proline – KSCN – H_2O[17]	0.05 – 0.3	1 – 5	ϕ_V	0.007
27	Threonine – KSCN – H_2O[17]	0.05 – 0.25	1 – 5	ϕ_V	0.007
28.	β-Alanine – KSCN – H_2O[17]	0.1 – 0.35	1 – 5	ϕ_V	0.007
29.	γ-amino-n-butyric acid – KSCN – H_2O[17]	0.1 – 0.3	1 – 5	ϕ_V	0.007
30.	ε-aminocaproic acid – KSCN – H_2O[17]	0.05 – 0.25	1 – 5	ϕ_V	0.007
31.	Glycine – sodium butyrate – H_2O[18]	0.1 – 0.35	0.5 – 2	ϕ_V	0.003
32.	DL α-Alanine– sodium butyrate – H_2O[18]	0.1- 0.35	0.5 – 2	ϕ_V	0.003
33.	DL α-amino-n-butyric acid–sodium butyrate – H_2O[18]	0.1- 0.35	0.5 – 2	ϕ_V	0.003
34.	Leucine – sodium butyrate – H_2O[18]	0.02 - 0.05	0.5 - 2	ϕ_V	0.003
35.	Valine – sodium butyrate – H_2O[18]	0.1 – 0.35	0.5 - 2	ϕ_V	0.003
36.	β-Alanine – NaCl – H_2O[19]	0 –4	0 – 4	γ	0.003

37.	2-amino-n-butyric acid – NaCl – H_2O[20]	0 –1.5	0 – 4	γ	0.0008

[a]For ϕ_V and ϕ_K the accuracies of measurements of density given in kg m^{-3} and speed of sound in m s^{-1}, respectively.)

A stringent test was first performed on the ln γ_{AJW} in electrolyte solutions. The amino acids investigated were glycine, β-alanine and DL-α-amino butyric acid in aqueous NaCl. The ln γ_{AJW} data of amino acids in NaCl were first analysed using equation (7). In Annexure I (given at the end of this Chapter) are given the values of the s_ϕ, s_ϕ' and λ_{AJW} parameters for some amino acids in aqueous NaCl solutions together with root mean squares deviation, σ of the fit. The maximum concentrations of amino acids and electrolytes were 2 mol kg^{-1} and 4 mol kg^{-1}, respectively. Fig. 1 shows the applicability of equation (7) in duplicating the experimental ln γ_{AJW} data for glycine in NaCl solutions of different concentrations. 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 σ of 0.001, which is an excellent agreement with the experimental data. An addition of glycine at any constant NaCl concentration decreases the activity of glycine in NaCl showing the association of amino acid. In aqueous β-alanine – NaCl system, an increase in the ln γ_{AJW} values with the enhanced concentration of amino acid indicates anti-association effect. The use of equation (7) to these data shows good fits (Fig. 2) average σ = 0.014) . In the case of DL-α-amino butyric acid (Fig. 3), the changes in its ln γ_{AJW} with increasing

concentration of the amino acid can be correlated with average σ value of 0.001 in ln

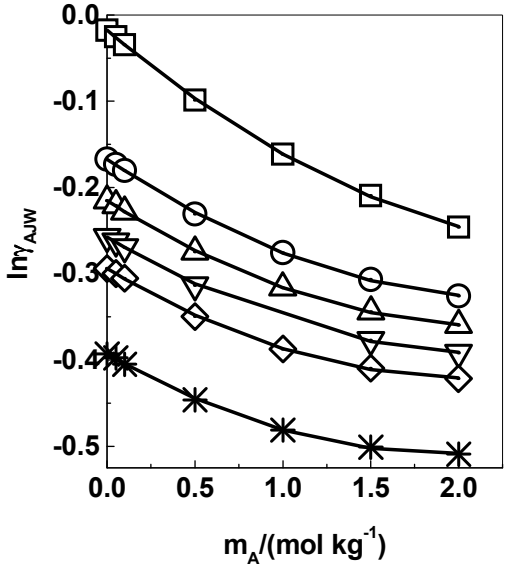


Fig 1: The plot of $\ln\gamma_{AJW}$ *vs*. m_A of glycine in aqueous NaCl system at constant m_J: 0.05 (□), 1.0 (○), 1.5 (△), 2.0 (▽), 2.5 (◇), 4.0 mol kg^{-1}(✳)

γ_{AJW}. As seen from the above three examples, equation (7) can correlate the activity coefficients of different types of amino acids in NaCl with excellent accuracy. Equation (7) is capable to analyze both the increase and decrease in activity coefficient values of amino acids with increase in their concentration in aqueous salt solutions.

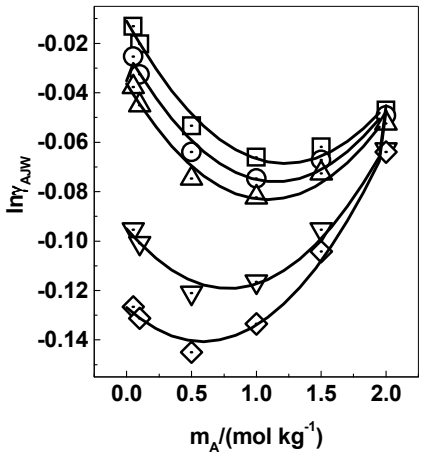


Fig 2: The variation of $\ln\gamma_{AJW}$ with m_A of alanine in NaCl at constant m_J: 0.01(□), 0.05 (○), 0.1 (△), 0.5 (▽), 1.0 mol kg^{-1} (◇)

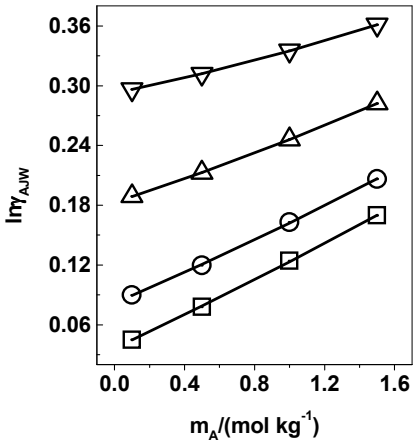


Fig 3: The plots of $\ln\gamma_{AJW}$ *vs*. m_A of DL-α-amino-n-butyric acid in aqueous NaCl solutions at constant m_J: 1.5 (□), 2.0 (○), 3.0 (△), 4.0 mol kg^{-1} (▽)

Variation of λ_{AJW} of three amino acids as a function of NaCl concentration is shown in Fig. 4 The λ_{AJW} parameter for glycine decreases with m_J in dilute solutions, while in concentrated solution (m_J >2 mol kg^{-1}) 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. Alanine and DL-α-amino butyric acid being bulkier do 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.

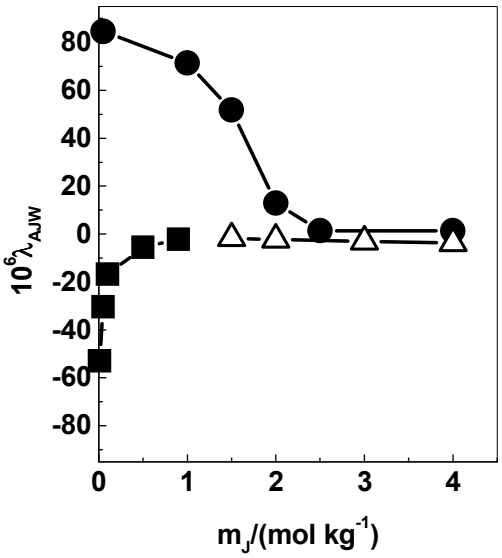


Fig 4: The dependence of λ_{AJW} on m_J for alanine (■), glycine (●) and DL-α-amino-n-butyric acid (△) in aqueous NaCl systems

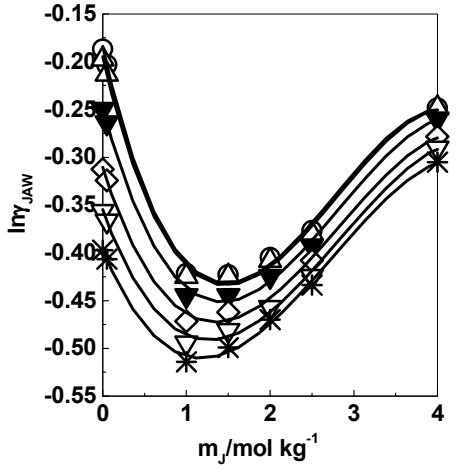


Fig 5: The plots of $\ln\gamma_{JAW}$ *vs.* m_J of glycine in aqueous NaCl solutions at constant m_A: 0.05 (○), 0.1 (△), 0.5 (▼), 1.0 (◇), 1.5 (▽), 2.0 mol kg^{-1}(✳)

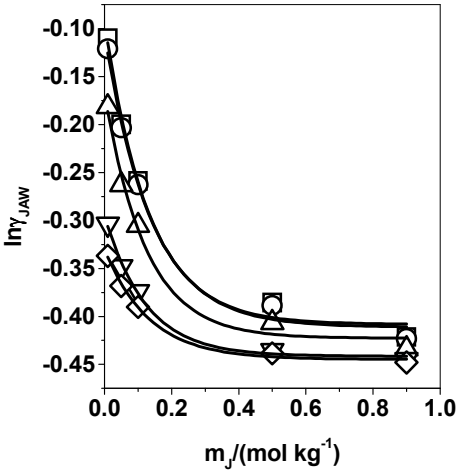


Fig 6: The plots of $\ln\gamma_{JAW}$ *vs*. m_J of alanine in aqueous NaCl solutions at constant m_A: 0.05 (□), 0.1 (○), 0.5 (△), 1.0 (▽), 1.5 mol kg^{-1}(◇)

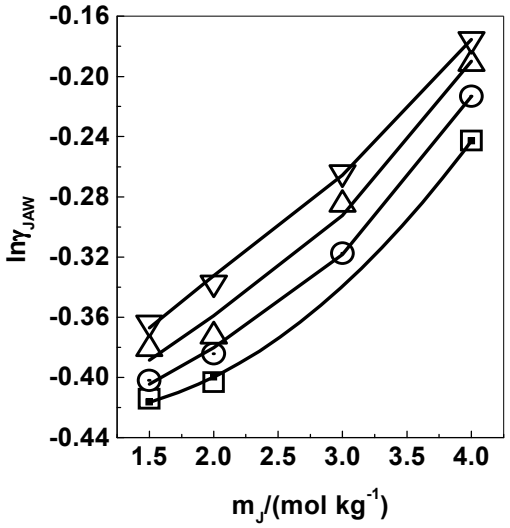


Fig 7: The estimated $\ln\gamma_{\pm JAW}$ of NaCl as a function of m_J in DL-α-amino-n- butyric acid at m_A: 0.1 (□), 0.5 (○), 1.0 ((△), 1.5 mol kg^{-1} (▽)

The values of λ_{AJW} obtained from equation (7) were treated as input data in equation (8) for the fitting of activity coefficients of electrolyte, J in amino acid solutions by evaluating the Pitzer coefficients. The resulting Pitzer coefficients are listed in Annexure II. The experimental ln γ_{JAW} values of NaCl in aqueous glycine at constant m_A concentrations are depicted in Fig 5. The close agreement between experimental data shown by symbols and the estimated ones shown by lines indicate the successful application of our approach. A clear agreement between the two is witnessed. In Fig 6, we show the estimated ln γ_{JAW} values of NaCl against those of experimental in alanine at its constant concentrations. A linear relationship with ± 2% indicates the successful

application of the proposed equation in dilute NaCl solutions, where long-range interactions are predominant over short-range interactions. The estimated ln γ_{JAW} values of NaCl in DL-α-amino butyric acid at several m_A are depicted in Fig 7, in which the estimated values are shown in contrast with solid experimental points. Equation (8) reproduces the activity coefficients of NaCl in all the amino acids. This is due to the fact that equation (8) contains a Debye - Hückel term sufficing the duplication of long-range interactions in dilute NaCl solutions. In the concentrated NaCl solutions, the role of the Pitzer coefficients becomes dominant. In short the activity coefficients of both amino acid electrolyte in their aqueous mixtures can be fitted with an average σ value of 0.005.

To make a clear depiction of the capability of our equations, the ln $\gamma_{JAW,exp}$ values of NaCl in different amino acids have been plotted against their estimated values. The graph shows over all a good agreement (Fig. 8).

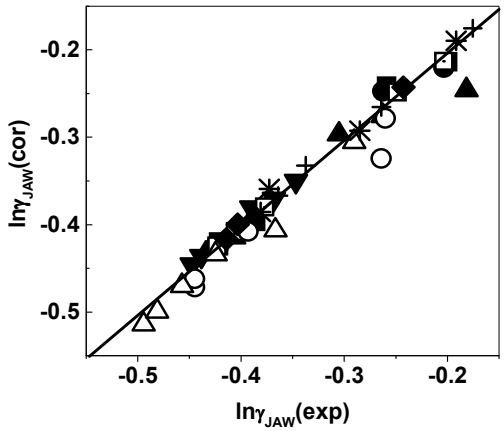


Fig 8: The plot of $\ln\gamma_{\pm JAW}$ (exp) *vs.* $\ln\gamma_{\pm JAW}$(cor) of NaCl in alanine at m_A: 0.05 (■), 0.1 (●), 0.5 (▲), 1.5 mol kg^{-1} (▼) NaCl in glycine at m_A: 0.05 (□),1.5 (○), 2.0 mol kg^{-1} (△); NaCl in DL-α-amino-n-butyric acid at m_A:1.5 (◆), 3.0 (✳), 4.0 mol kg^{-1}(+)

After a successful demonstration of equations (7) and (8) 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 (9). The term s_V in Masson's equation[21] ($\phi_{VAW} = \phi_V{}^0{}_{AW} + s_V\, m_A$) signifies the amino acid – amino acid (solute – solute) interactions in very dilute aqueous amino acid solutions. The fitting of the concentrated amino acid solutions requires an additional s_V' and $m^2{}_A$ terms. Both these coefficients are adjustable parameters. The coefficients of equation (10) obtained for the experimental data are listed in Annexure III. 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 for glycine (43.19 x 10^{-6} m^3 mol^{-1} [21], 43.23 x 10^{-6} m^3 mol^{-1} [15], 43.14 x 10^{-6} m^3 mol^{-1} [22] and 43.23 x 10^{-6} m^3 mol^{-1} [23]). For L-alanine, the $\phi_V{}^0{}_{AW}$ values from the literature are 60.47 x 10^{-6} m^3 mol^{-1} [21] and 60.50 x 10^{-6} m^3 mol^{-1} [23], while for glycylglycine the $\phi_V{}^0{}_{AW}$ values as 76.63 x 10^{-6} m^3 mol^{-1} [22], 76.34 x 10^{-6} m^3 mol^{-1} [24], 76.76 x 10^{-6} m^3 mol^{-1} [25] 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 which agreed well with that of Soto et al. is 46.78 x 10^{-6} m^3 mol^{-1} in 1 mol kg^{-1} KCl[16]. Ogawa et. al. have published slightly different $\phi_V{}^0{}_{AJW}$ value of glycine (44.89 x 10^{-6} m^3 mol^{-1}) in 1 mol kg^{-1} of KCl[23]. Several electrolytes

dissolved in amino acids and peptide, mentioned in Table 1 were regressed for their ϕ_V values.

Fig 9 displays a contrast between the ϕ_{VAJW}(exp) (shown by symbols) and ϕ_{VAJW}(est) (shown by lines) for aqueous glycine as a function of m_A in KBr at different salt concentrations. Fig. 10 shows the values of ϕ_{VAJW}(exp) (symbols) in contrast to the correlated ones (lines) as a function of m_A for glycine in NaCl solutions. A close examination of Figs 9 and 10 shows that ϕ_{VAJW} of glycine in aqueous KBr solutions can be accurately represented by equation (9).

Further, application of equation 10 is further confirmed by analyzing the ϕ_{VAJW} of alanine as a function of m_A in NaCl at different salt concentrations of NaCl. A good agreement is seen between the two quantitites.

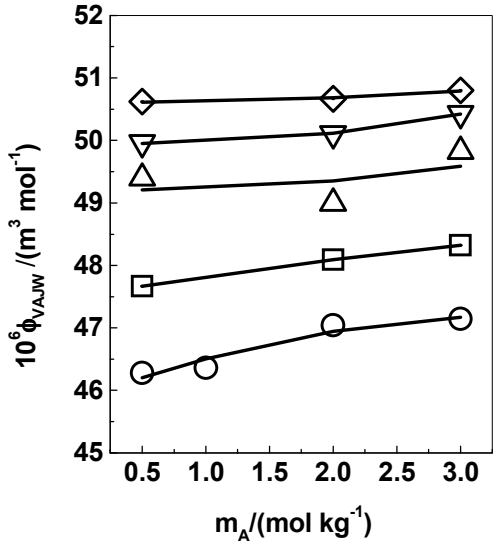


Fig 9: The plots of ϕ_{VAJW} *vs*. m_A of

glycine in aqueous KBr at constant m_J: 0.5 (○), 1.0 (□), 2.0 (△), 3.0 (▽), 4.0 mol kg^{-1} (◇); symbols expt., lines est.

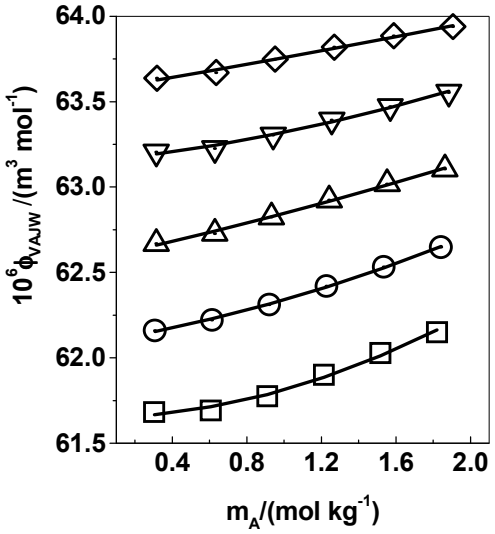


Fig 10 : The plots of ϕ_{VAJW} vs. m_A of alanine in NaCl at m_J: 0.2 (□), 0.4 (○), 0.6 (△), 0.8 (▽), 1.0 mol kg^{-1} (◇)

Besides these two amino acids studied in NaCl solutions, the effect of $MgCl_2$ on ϕ_{VAJW} of glycine and of Na_2SO_4 on glycylglycine was investigated using the developed equations. The success of our equations is demonstrated in Fig. 11, in which one can witness excellent agreement between the experimental and estimated quantities as shown by the symbols and lines.

Similarly, the ϕ_{VAJW} data of glycylglycine in KCl were also subjected to the equations developed above. The purpose of using KCl data was to see whether these

equations can describe the volumetric properties of glycylglycine in a structure-breaking electrolyte, like KCl. Earlier electrolytes used in the investigations were structure makers. It is interesting to find that the equations can successfully analyse the ϕ_{VAJW} data of glycylglycine in KCl (See Fig. 12).

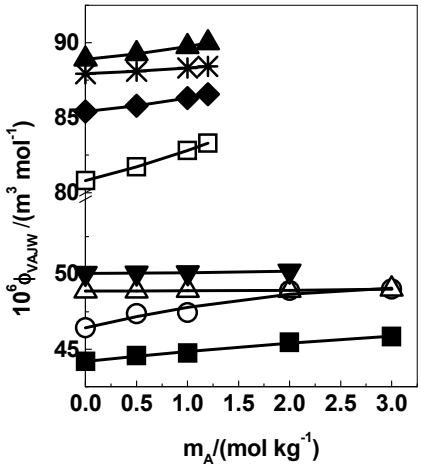


Fig 11: The plot of ϕ_{VAJW} *vs.* m_A of: glycine in $MgCl_2$ at m_J: 0.1(■), 0.5 (○), 1.0 (△), 1.5 mol kg^{-1} (▼), glycylglycine in Na_2SO_4 at m_J: 0.5 (□), 1.0 (◆), 1.5 (✳), 2.0 (▲)

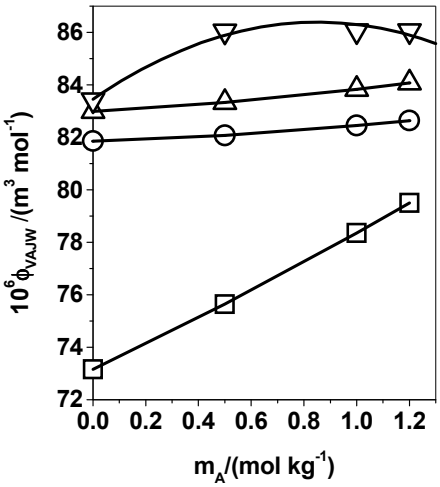


Fig 12: The plot of ϕ_{VAJW} *vs*. m_A of glycylglycine in KCl at m_J: 0.5 (□), 1.0 (○), 1.5 (△), 2.0 mol kg^{-1} (▽)

Besides checking the validity of these equations to estimate volumes of amino acids and peptides in simple electrolyte solutions, complex electrolytes like tetra-n-alkylammonium salts were also investigated. 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. Fig. 13 demonstrates the effect of ϕ_{VAJW} for glycine and alanine in $(C_2H_5)_4NBr$ solutions of varying concentrations. A cursory look on the plots drawn in Fig. 13 confirms the applications of these equations to such electrolytes.

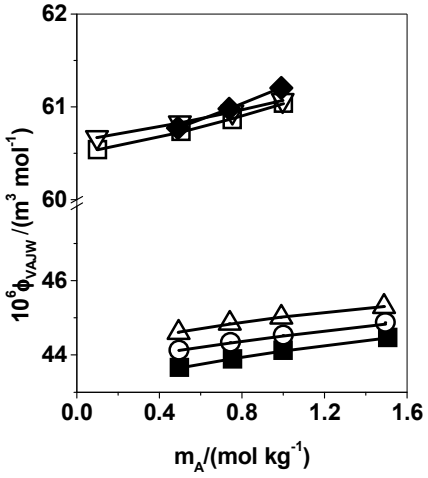


Fig 13: The plots of ϕ_{VAJW} *vs*. m_A of glycine in $(C_2H_5)_4NBr$ at m_J: 0.1 (■), 0.5 (○), 1.2 mol kg^{-1} (△), alanine in $(C_2H_5)_4NBr$ at m_J: 0.1 (□), 0.3 (▽), 1.2 mol kg^{-1} (◆)

Further, the equations were also applied to the ϕ_{VAJW} data of glycine and glycylglycine in $(C_4H_9)_4NBr$ at various ionic concentrations (Fig. 14). Again, excellent agreement was

noted between experimental and estimated ϕ_{VAJW} data of these systems. It should be noted that both these electrolytes act as strong structure makers. This establishes the goodness of the developed equations for a range of electrolytes.

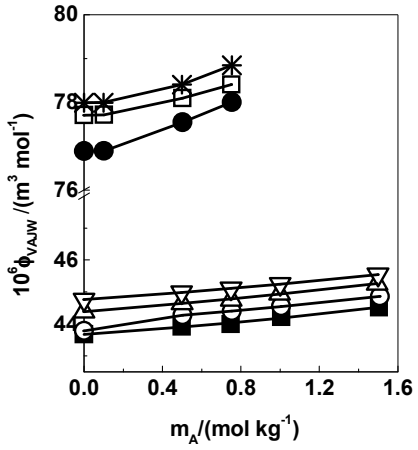


Fig 14: The plots of ϕ_{VAJW} *vs*. m_A of glycine in $(C_4H_9)_4NBr$ at m_J : 0.05 (■), 0.3 (○), 0.6 (△), 0.7 mol kg^{-1} (▽), glycylglycine in $(C_4H_9)_4NBr$ at m_J: 0.05 (●), 0.3 (□), 0.6 mol kg^{-1} (✳)

It would be of interest to examine the dependence of λ_{AJW} (the amino acid – electrolyte interaction parameter) on the concentration of electrolytes. Fig. 15 shows exponential dependence of λ_{AJW} on m_J for glycine in aqueous KBr. It seems that the interaction of amino acid dramatically changes in dilute electrolyte solutions. Later, no appreciable change in λ_{AJW} with respect to the electrolyte molality is noted. Figs. 15 to 18 also display the dependence of the λ_{AJW} parameters on molalities for amino acids in different types of electrolytes. The average σ in ϕ_{VAJW} correlating for several amino acids in electrolyte solutions listed in Table 1 is 0.02 x 10^{-6} m^3 mol^{-1}. 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 2 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}. The densities can be calculated with an accuracy of 75 x 10^{-3} kg m^{-3} in general.

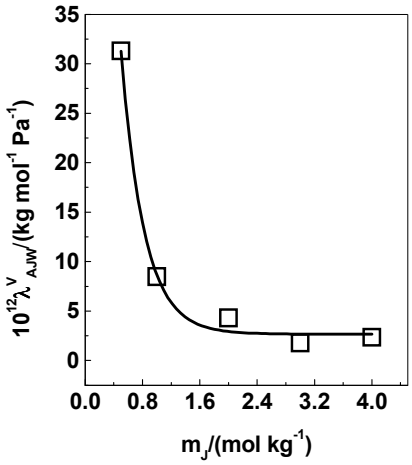


Fig 15: Variation of λ^{V}_{AJW} as a function of m_J for glycine in aqueous KBr solutions

The λ^{V}_{AJW} obtained using equation (9) are transferred to equation (10) in order to fit the ϕ_{VJAW} - m_J data. The Pitzer coefficients i.e. $\beta^{(0)V}_{MXA}$, $\beta^{(1)V}_{MXA}$ 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 Annexure IV.

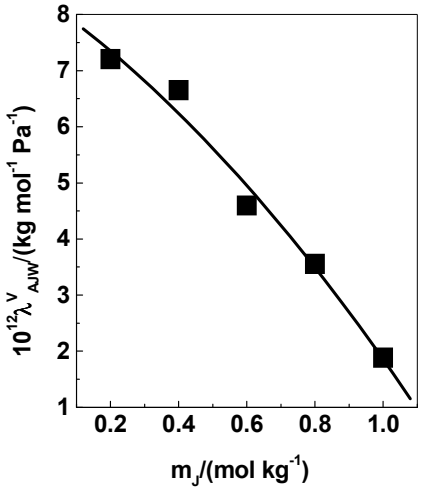


Fig 16: Variation of λ^{V}_{AJW} as a function of m_J for alanine in aqueous NaCl solutions

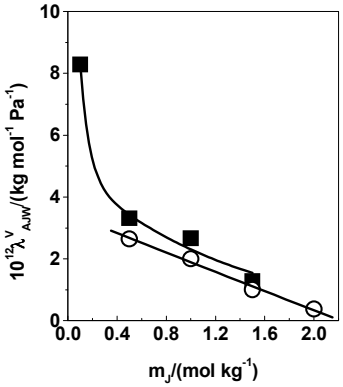


Fig 17: Variation of λ^{V}_{AJW} as a function of m_J for glycine in aqueous $MgCl_2$: (■), glycylglycine in aqueous Na_2SO_4 (○) solutions

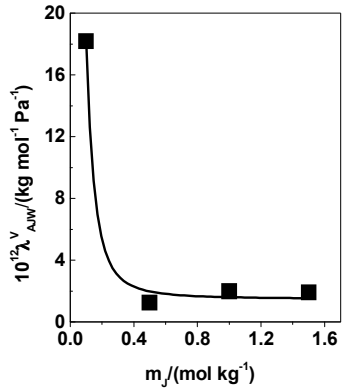


Fig 18: Variation of λ^{V}_{AJW} as a function of m_J for aqueous glycylglycine in KCl solutions (■)

.

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} [26], 23.45 x 10^{-6} m^3 mol^{-1} [27]), KCl = 26.85 x 10^{-6} m^3 mol^{-1}(26.90 x 10^{-6} m^3 mol^{-1} [28], 26.89 x 10^{-6} m^3 mol^{-1} [29]), KBr = 33.73 x 10^{-6} m^3 mol^{-1}(33.73 x 10^{-6} m^3 mol^{-1} [26] 33.75 x 10^{-6} m^3 mol^{-1} [30]), $MgCl_2$ = 14.52 x 10^{-6} m^3 mol^{-1} (14.49 x 10^{-6} m^3 mol^{-1} [31], 14.6 x 10^{-6} m^3 mol^{-1} [32],) and that for Na_2SO_4 = 11.56 x 10^{-6} m^3 mol^{-1} (11.62 x 10^{-6} m^3 mol^{-1} [31], 11.64 x 10^{-6} m^3 mol^{-1} [26], are in close agreement with the literature values. 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} [29], 114.8 x 10^{-6} m^3 mol^{-1} [33] and 114.25 x 10^{-6} m^3 mol^{-1} [34]. 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 [35-37]. An excellent agreement is noticed between the $\phi_V^0{}_{JW}$ value of $(C_4H_9)_4NBr$ obtained in the current work 300 x 10^{-6} m^3 mol^{-1} and that 300 x 10^{-6} m^3 mol^{-1} reported earlier [31].

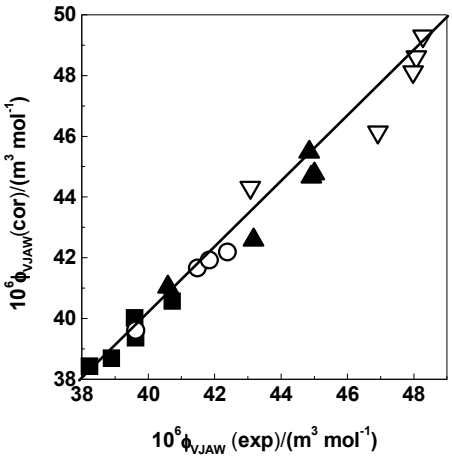


Fig 19: The plot of ϕ_{VJAW} (exp) *vs*. ϕ_{VJAW} (cor) of KBr in aqueous glycine at m_A: 0.5 (■), 1.0 (○), 2.0 (▲), 3.0 mol kg^{-1} (▽)

Fig. 19 shows a contrasting plot between the experimental ϕ_{VJAW} and estimated ϕ_{VJAW} for KBr in aqueous glycine in different amino acid concentrations. Fig. 20 depicts the variations in ϕ_{VJAW} with m_J of NaCl in alanine at different concentrations of alanine. An examination of both the figures demonstrates that the proposed equations can act as successful correlating expressions for the ϕ_{VJAW} and m_J data. The ϕ_{VJAW} values for these two amino acids vary from 18 to 50 x 10^{-6} m^3 mol^{-1}. An application of these equations

suggests that the framework is applicable to a wide range of ϕ_{VJAW} values and at varying concentrations of amino acids.

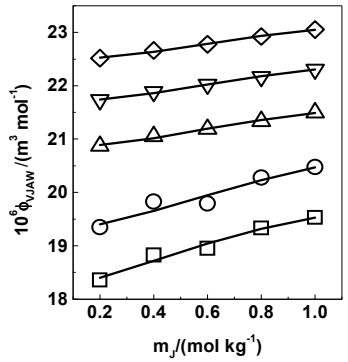


Fig 20: The plots of ϕ_{VJAW} *vs*. m_J of NaCl in alanine at m_A: 0.3 (□), 0.5 (○), 0.9 (△), 1.6 (▽), 1.9 mol kg^{-1} (◇)

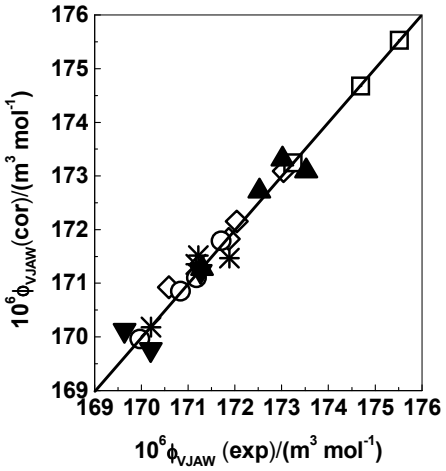


Fig 21: The plots of $\phi_{VJAW}(exp)$ *vs*. $\phi_{VJAW}(cor)$ of: $(C_2H_5)_4NBr$ in glycine at m_A: 0.7 (◇), 1.0 (○), 1.5 mol kg^{-1} (▼), $(C_2H_5)_4NBr$ in alanine at m_A: 0.1 (□), 0.5 (▲), 1.0 mol kg^{-1} (✳)

The correlated values of ϕ_{VJAW} as calculated from λ^{V}_{AJW} and the Pitzer coefficients agree very well with the experimental ϕ_{VJAW} values for$(C_2H_5)_4NBr$ in glycine solutions (Fig. 21) The similar results are obtained for the systems comprising $(C_4H_9)_4NBr$ in glycine and glycylglycine throughout the concentration range (Fig. 22). These R_4NX, though show hydrophobic hydarion characteristics in water, their equilibrium properties can be easily estimated by the equations proposed by us. As well established over the years, these electrolytes are strong structure makers as evidenced by their B-coefficients. This means that the cations can arrange the water molecules around themselves quite strongly. It is satisfactory to note that the proposed equations are applicable to such solutions as well.

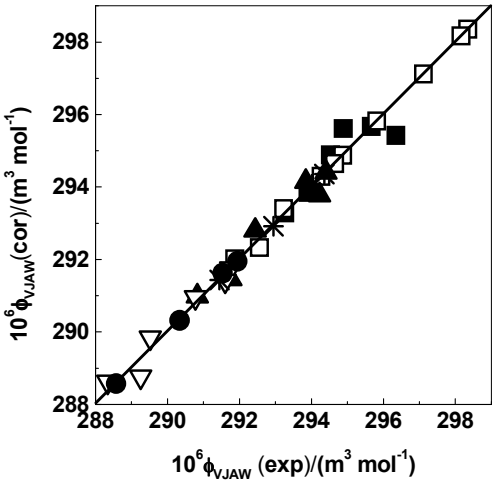


Fig 22: The plot of ϕ_{VJA} n_A : 0.7 (■), 1.0 (●), 1.5 mol kg^{-1} (△), $(C_4H_9)_4$ mol kg^{-1} (+)

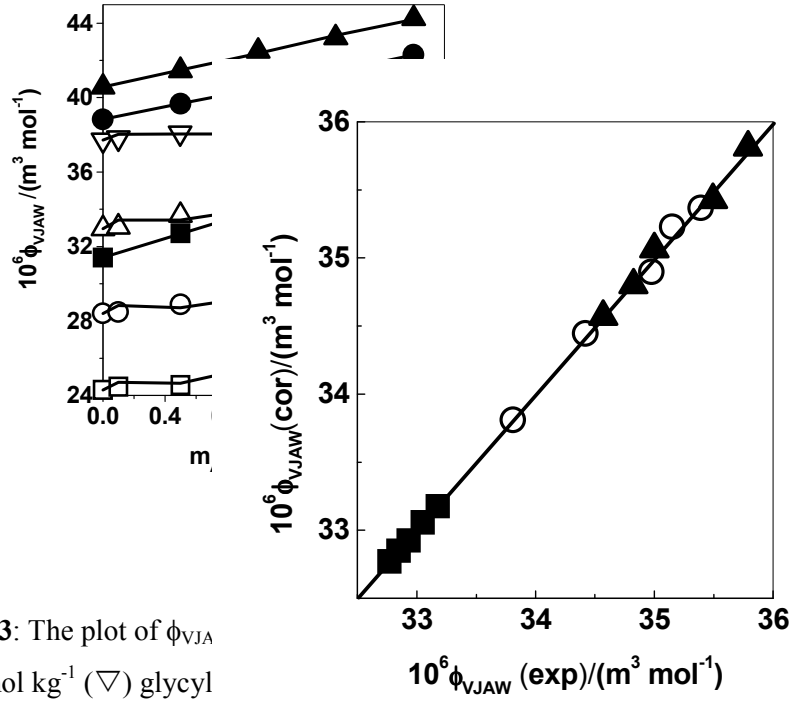


Fig 23: The plot of ϕ_{VJA} 1.0 (○), 2.0 (△), 3.0 mol kg^{-1} (▽) glycyl .2 mol kg^{-1} (▲)

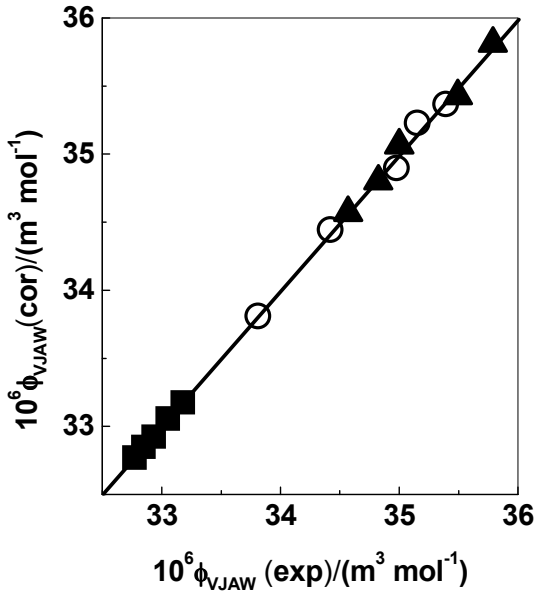


Fig 24: The plot of ϕ_{VJAW} (exp) *vs*. ϕ_{VJAW} (cor) of KCl in aqueous glycylglycine at m_A: 0.5 (■), 1.0 (○), 1.5 mol kg^{-1} (▲)

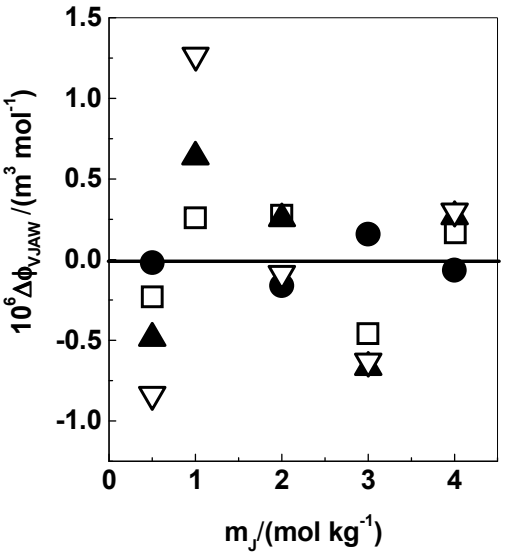


Fig 25: The plot of $\triangle\phi_{VJAW}$ *vs*. m_J of KBr in aqueous glycine solutions at m_A: 0.5 (□), 1.0 (●), 2.0 (▲), 3.0 mol kg^{-1} (▽)

The effect of different concentrations of glycine on ϕ_{VJAW} of $MgCl_2$ is demonstrated in Fig. 23. The proposed equations can correlate ϕ_{VJAW} within a range of 24 to 44 $x10^{-6}$ m^3 mol^{-1} with good accuracy. It is also possible to correlate the ϕ_{VJAW} of KCl in aqueous glycylglycine at different concentrations (Fig. 24). Similar results are obtained in the case of KBr in aqueous glycine solutions (Fig. 25).

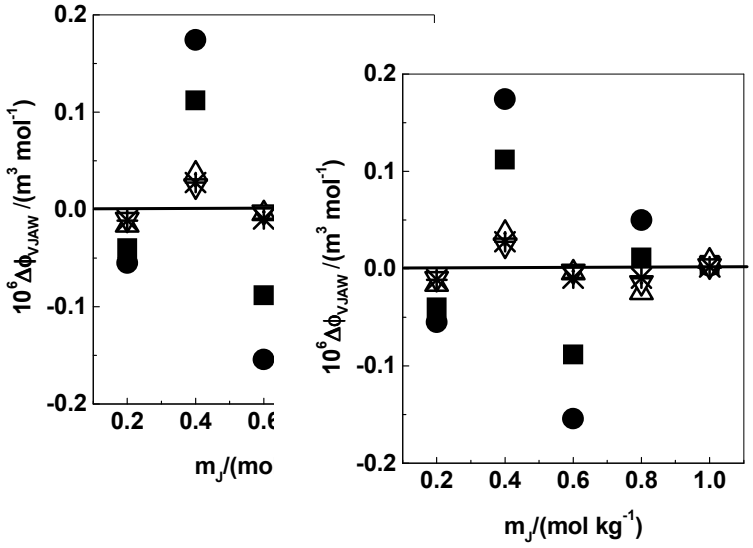


Fig 26: The plot of $\Delta\phi_{VJAW}$ *vs*. m_J of NaCl in alanine at m_A: 0.3 (■), 0.5 (●), 0.9 (△), 1.6 (▽), 1.9 mol kg^{-1} (✳)

An important stringent test of the proposed equations can be seen by the plots drawn in Fig. 26, in which the $\Delta\phi_{VJAW}$ values of NaCl in alanine are shown with respect to m_J. The $\Delta\phi_{VJAW}$ values are random in their distribution showing successful application of the proposed equations. One obtains –0.2 to +0.2 $x10^{-6}$ m^3 mol^{-1} as a range of distribution. The $\Delta\phi_{VJAW}$ values in the cases of $(C_2H_5)_4NBr$ in glycine and in alanine are noted to be random, as seen in Fig. 27. The similar situation can be witnessed in Fig. 28 for $(C_4H_9)_4NBr$ in aqueous glycine and glycylglycine.

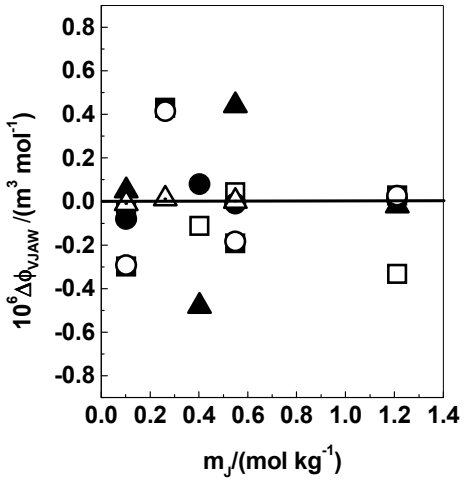


Fig 27: The plot of $\triangle\phi_{VJAW}$ *vs*. m_J of $(C_2H_5)_4NBr$ in glycine at m_A: 0.7 (□), 1.0 (●), 1.5 mol kg^{-1} (△) $(C_2H_5)_4NBr$ in alanine at m_A: 0.1 (△), 0.3 (■), 1.2 mol kg^{-1} (○)

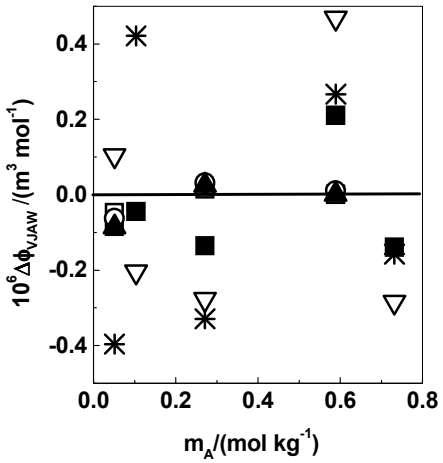
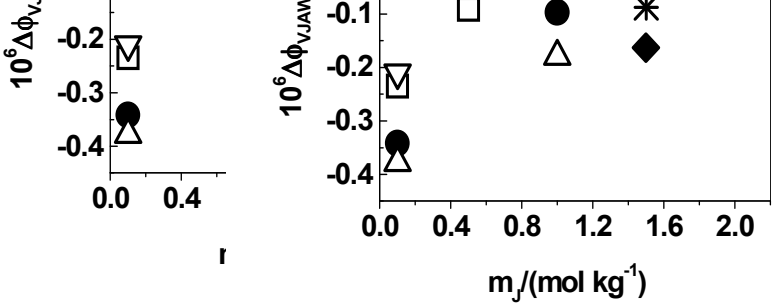


Fig 28 The plot of $\triangle\phi_{VJAW}$ *vs*. m_J of $(C_4H_9)_4NBr$ in glycine m_A: 0.7 (■), 1.0 (✳), 1.5 mol kg^{-1} (▽); $(C_4H_9)_4NBr$ in glycylglycine at m_A: 0.1 (□), 0.5 (○), 0.8 mol kg^{-1} (▲)



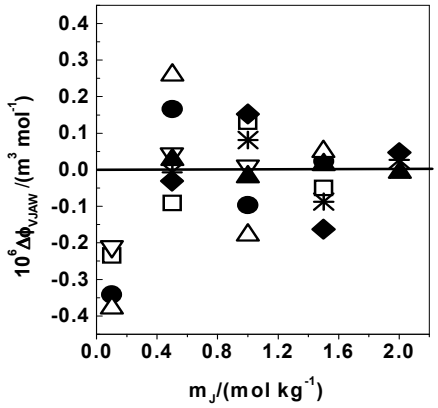


Fig 29: The plots of $\triangle\phi_{VJAW}$ *vs.* m_J of $MgCl_2$ in glycine at m_A: 0.5 (□), 1.0 (●), 2.0 (△), 3.0 mol kg^{-1} (▽); Na_2SO_4 in glycylglycine at m_J: 0.5 (▲), 1.0 (✳), 1.2 mol kg^{-1} (♦)

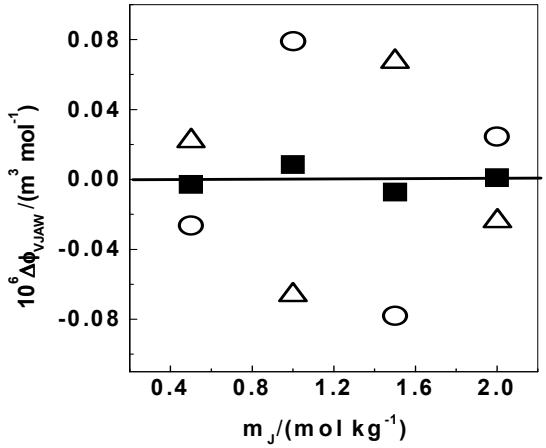


Fig 30: The plot of $\Delta\phi_{VJAW}$ *vs.* m_J of KCl in glycylglycine at m_A: 0.5 (■), 1.0 (○), 1.5 mol kg^{-1} (△).

Random distributions of the difference parameter, $\triangle\phi_{VJAW}$ can also be seen in the cases of $MgCl_2$ in aqueous glycine and of Na_2SO_4 in glycylglycine (Fig. 29). Similar distributions are plotted for KCl in glycylglycine, where again a random distribution is seen (Fig. 30).

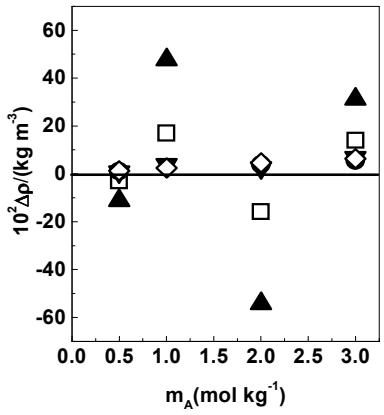


Fig 31: The plot of $\Delta\rho$ *vs*. m_A of glycine in aqueous KBr at m_J: 0.5 (□), 1.0 (●), 2.0 (▲), 3.0 (◇), 4.0 (▽) mol kg^{-1}

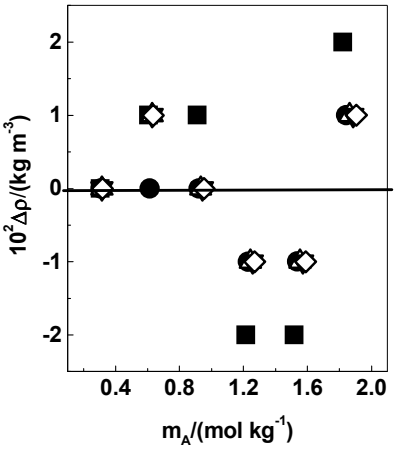


Fig 32: The plot of $\Delta\rho$ *vs*. m_A of alanine in aqueous NaCl at m_J:0.2 (■), 0.4 (●), 0.6 (△), 0.8 (▼), 1.0 mol kg^{-1} (◇)

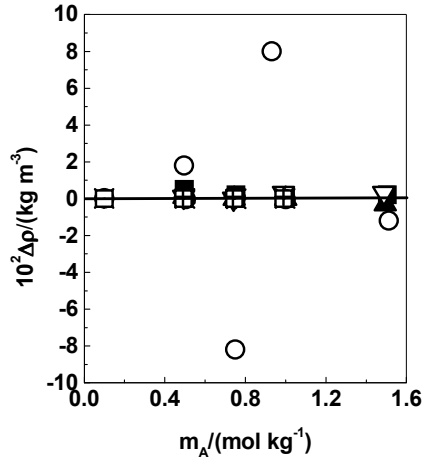


Fig 33: The plot of $\triangle\rho$ *vs*. m_A of: glycine in $(C_2H_5)_4NBr$ at m_J: 0.1 (■), 0.4 (○), 0.5 (▲), 1.2 mol kg^{-1}(▽), alanine in $(C_2H_5)_4NBr$ at m_J: 0.1 (●), 0.3 (✳), 0.5 (□), 1.2 mol kg^{-1}(+)

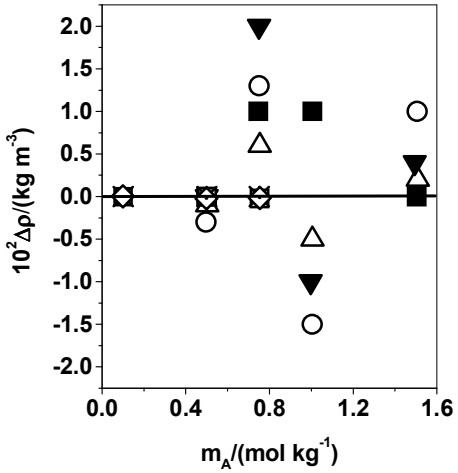


Fig 34: The plot of $\triangle\rho$ *vs*. m_A of: glycine in

$(C_4H_9)_4NBr$ at m_J: 0.05 (■), 0.1 (○), 0.3 (△), 0.6 mol kg^{-1} (▼), glycylglycine in $(C_4H_9)_4NBr$ at m_J: 0.05 (□), 0.3 (✳), 0.6 mol kg^{-1} (◇)

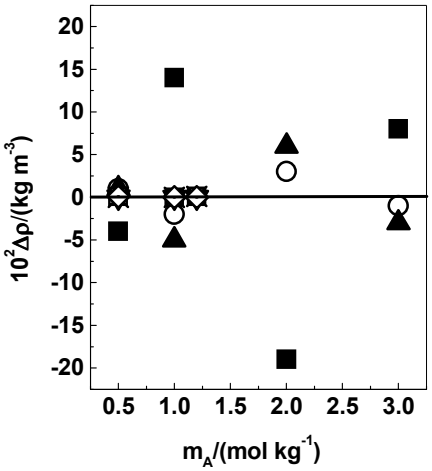


Fig 35: The plot of Δρ *vs*. m_A of: glycine in $MgCl_2$ at m_J: 0.1 (■), 0.5 (○), 1.0 mol kg^{-1} (▲), glycylglycine in Na_2SO_4 at m_J: 0.5 (□), 1.0 (▼), 1.5 (✳), 2.0 mol kg^{-1} (◇)

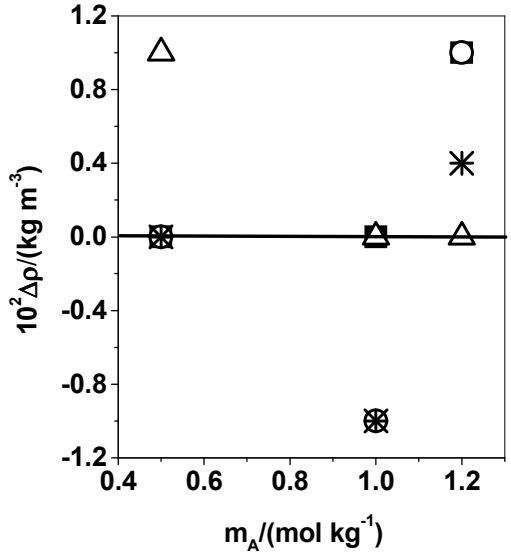


Fig 36: The plot of $\triangle\rho$ *vs*. m_A of glycylglycine in KCl at m_J: 0.5 (■), 1.0 (○), 1.5 (△), 2.0 mol kg^{-1} (✳)

The degree of fits of the proposed equations is also demonstrated in Figs. 31 to 36, in which the values of $\triangle\rho$ ($=\rho_{expt}-\rho_{cor}$) plotted as a function of m_J. A closer examination of these drawings demonstrate that all the deviations are random in nature, and hence one can have confidence in the proposed equations.

In the above illustration pressure derivative of equations (7) and (8) (i.e. volume) were elaborated. It is also important to study the second pressure derivatives of equations (7) and (8) 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 (11) and (12), respectively. The coefficients obtained from equation (11) ${\phi_K}^0_{AJW}$, S_K, S_K' and ${\lambda^K}_{AJW}$ for different experimental systems are listed in Annexure V. 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 -15.29×10^{-15} m^3 mol^{-1} Pa^{-1} while the value in literature is -11.03×10^{-15} m^3 mol^{-1} Pa^{-1} [186]. The ${\phi_K}^0_{AW}$ of amino acids (glycine = -27.00×10^{-15} m^3 mol^{-1} Pa^{-1}, L-alanine = -25.16×10^{-15} m^3 mol^{-1} Pa^{-1} and glycylglycine = -33.5×10^{-15} m^3 mol^{-1} Pa^{-1}) are in good agreement with those reported earlier [48,70].

The ${\phi_K}^0_{AJW}$, ${\beta^{(0)K}}_{MXA}$, ${\beta^{(1)K}}_{MXA}$ and ${C^{\varphi K}}_{MXA}$ for NaCl in aqueous alanine are listed in Annexure VI.

The accuracy of estimation of ϕ_{KAJW} can be seen from Fig. 37, in which the ϕ_{KAJW} values for alanine in aqueous NaCl are plotted against m_A. In order to appreciate the accuracy of the proposed equations, a plot of $\Delta\phi_{KAJW}$ ($\phi_{KAJW,exp} - \phi_{KAJWcor}$) *vs.* m_A of alanine in NaCl is shown in Fig. 38 for the same system. It is interesting to note that the difference function is random in nature confirming the success of the equation meant to calculate the second pressure dependence of equations (7) and (8) .

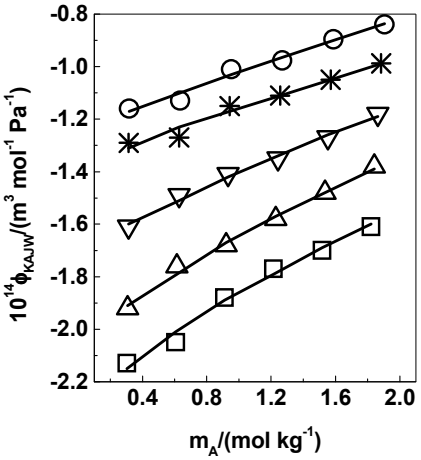


Fig 37: The plot of ϕ_{KAJW} *vs.* m_A of alanine in aqueous NaCl at m_J: 0.2 (□), 0.4 (△), 0.6 (▽), 0.8 (✳), 1.0 mol kg^{-1} (○)

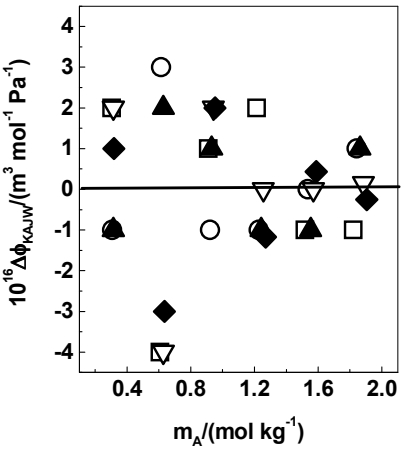


Fig 38: The plot of $\Delta\phi_{KAJW}$ *vs*. m_A of alanine in NaCl at m_J: 0.2 (□), 0.4 (○), 0.6 (▲), 0.8 (▽), 1.0 mol kg^{-1} (◆)

Since the measured quantity of the experiment is the speed of sound, u, it is better to demonstrate the utility of our equations in the form of a plot with Δu as a function of m_A. Fig. 39 shows such a plot for aqueous alanine in NaCl solutions. There is a complete absence of any systematic deviation in the plot, thus confirming the application of the equation.

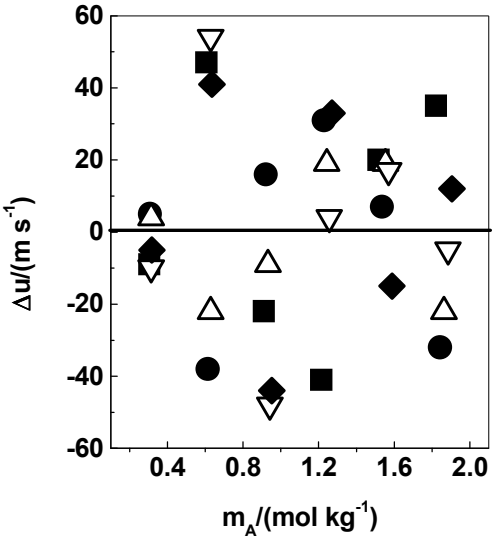


Fig 39: The plot of Δu *vs*. m_A of alanine in aqueous NaCl at m_J: 0.2 mol (■), 0.4 mol (●), 0.6 mol (△), 0.8 (▽), 1.0 mol kg^{-1} (◆)

The semiempirical parameters thus obtained from the analysis of the equations were then fed together with interaction parameters to calculate ϕ_{KJAW} values. An example of this exercise is shown in Fig. 40, where the ϕ_{KJAW} values for NaCl in aqueous alanine at different concentrations of amino acids are shown. Ones sees a good agreement between

the experimental points (symbols) and the lines (estimated values). This is also confirmed by a plot shown in Fig. 41, in which the $\Delta\phi_{KJAW}$ values of NaCl in alanine are plotted

demonstrating an absence of a systematic deviation. The Δu ($u_{exp} - u_{cor}$) values for the system regressed are listed in Table 2.

Table 2: Average differences in the experimental and correlated densities and sound speeds for the data from literature at 298.15 K.

Systems	10^{-3} $\Delta\rho$ / kg m^{-3}	$10^{-3}\Delta u$ / m s^{-1}	10^{-3} $\Delta\rho$ / kg m^{-3}	10^{-3} Δu m s^{-1}
	Back calculated from ϕ_{AJW}		Back calculated from ϕ_{JAW}	
Glycine – NaCl – H_2O	35	0.8	42	0.2
Glycine – $NaNO_3$ – H_2O	27	0.3	34	1.0
Glycine – KCl – H_2O	35	0.3	46	1.0
Glycine – KNO_3 – H_2O	26	0.4	57	1.2
Alanine – KSCN – H_2O	12		61	
Proline – KSCN – H_2O	8		34	
Glycine – KSCN – H_2O	6		33	
Threonine – KSCN – H_2O	9		44	
6-aminocaproic acid – KSCN – H_2O	8		76	
γ-amino butyric acid – KSCN – H_2O	33		11	
β - alanine	12		31	
Glycine – sodium butyrate – H_2O	6		45	
DL-alanine – sodium butyrate – H_2O	10		27	
Leucine – sodium butyrate – H_2O	9		49	
Valine – sodium butyrate – H_2O	8		53	
α-amino butyric acid – sodium butyrate – H_2O	6		57	

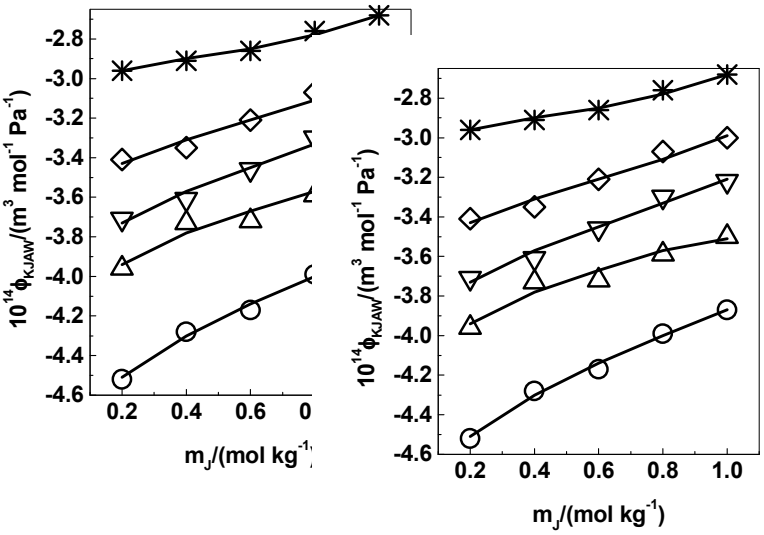


Fig 40: The plot of ϕ_{KJAW} *vs*. m_J of NaCl in aqueous alanine at m_A: 0.3 (○), 0.6 (△), 0.9 (▽), 1.2 (◇), 1.6 mol kg^{-1} (✳)

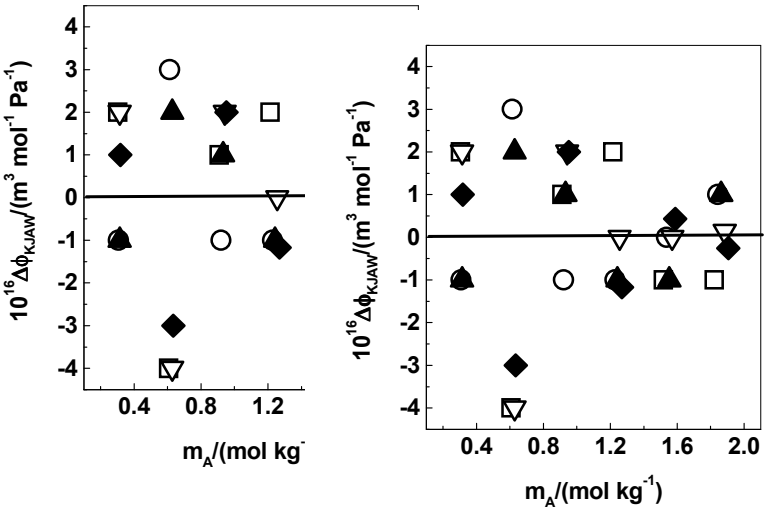


Fig 41: The plot of $\Delta\phi_{KJAW}$ *vs*. m_J of NaCl in alanine at m_A: 0.3 (■), 0.6 (●), 0.9 (△), 1.2 (○), 1.6 mol kg^{-1}(▲)

The average σ 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.

For some other literature data, the average σ 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.

Variation of λ^K_{AJW} as a function of m_J is shown in Fig. 42. The aqueous NaCl-alanine systems show an increase in the λ^K_{AJW} values with increasing m_J values. The behaviour is consistent with the one noted in the case of λ^V_{AJW}.

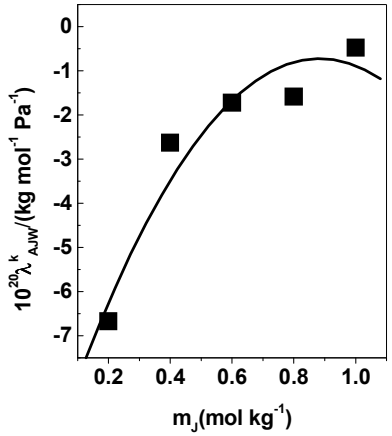


Fig 42: Variation of λ^k_{AJW} as a function of m_J for aqueous alanine in NaCl solutions

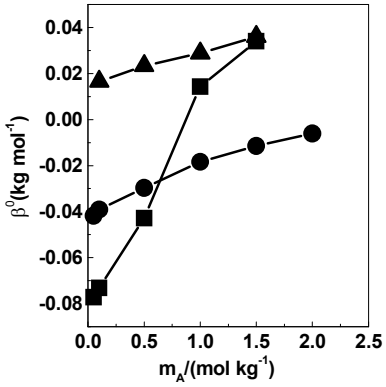


Fig 43: The Pitzer β^o coefficients of aqueous NaCl

as a function of m_A for alanine (■), glycine (●) and DL-α-amino-n-butyric acid (▲)

The Pitzer coefficients for any single electrolyte solution indicate short range interactions. It is expected that their values should change with a change in solvent. In this case, their values in water should differ from those calculated in amino acid alone. For example, the interactions shown by the β^0 of NaCl are weaken on addition of alanine, glycine and D-L- -α-amino-n-butyric acid (Fig. 43). Fig. 44 displays variation in the β^1 parameter with the amino acid concentration. This parameter is significant in very dilute solutions only. Though the β^1 vs. m_A patterns for both glycine and D-L- -α-amino-n-butyric acid are similar, one notes a sharp decrease in the β^1parameter becomes significant in high concentrations used in the collection of data. This behaviour is also witnessed in the plots of C^{φ} vs. m_A for these three amino acids as depicted in Fig. 45.

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 Figs. 47-56. The changes in the ${\phi_V}^0_{JAW}$ values of KBr (Fig. 46) and $MgCl_2$ (Fig. 50) in glycine show similar trend while that of $(C_4H_9)_4NBr$ in glycylglycine (Fig. 54) is a linear function of m_A. In the current situation, $\beta^{(1)V}$ has less importance, as the objective of the work was centered around concentrated solutions. However, its variation with m_A is shown in Figs. 48, 52 and 56 for KBr (in glycine), $MgCl_2$ in (glycine) and $(C_4H_9)_4NBr$ in glycylglycine. With respect to the volume $C^{\varphi V}$ parameter, the ternary interactions in are enhanced with an increase in the concentrations of amino acids (Figs. 49, 53 and 57).

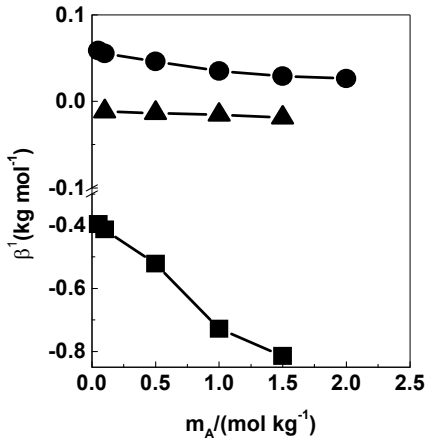


Fig 44: The Pitzer β^1 coefficients of aqueous NaCl as a function of m_A for alanine (■), glycine (●) and DL-α-amino-n-butyric acid (▲)

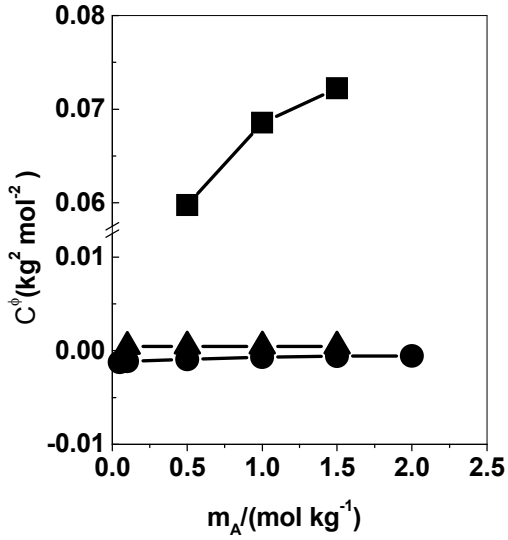


Fig 45: The Pitzer C^{ϕ} coefficients of aqueous NaCl as a function of m_A for alanine (■), glycine (●) and DL-(-amino-n-butyric acid (▲)

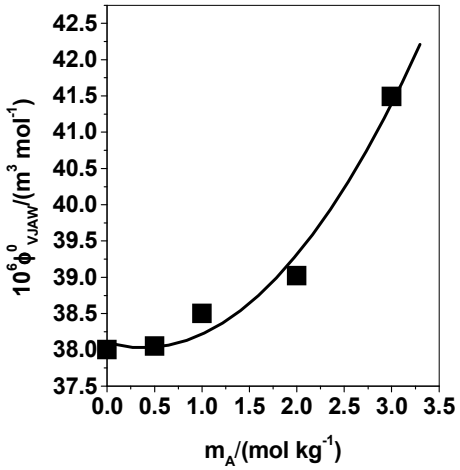


Fig 46: The $_{\lambda W}$ values of aqueous KBr as a function $_{lA}$ for glycine

$m_A/(mol\ kg^{-1})$

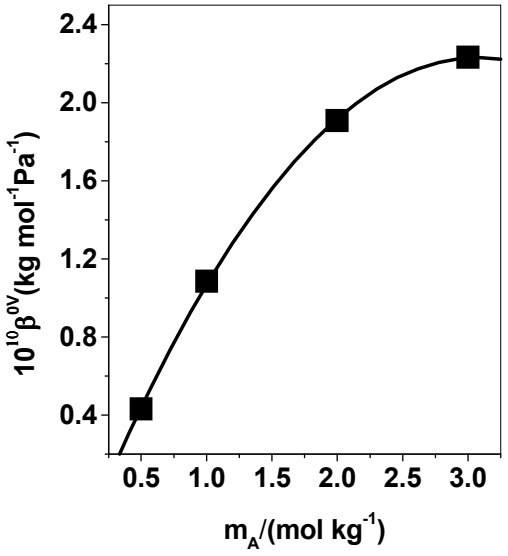


Fig 47: The Pitzer β^{oV} coefficients of aqueous KBr as a function of m_A for glycine (■)

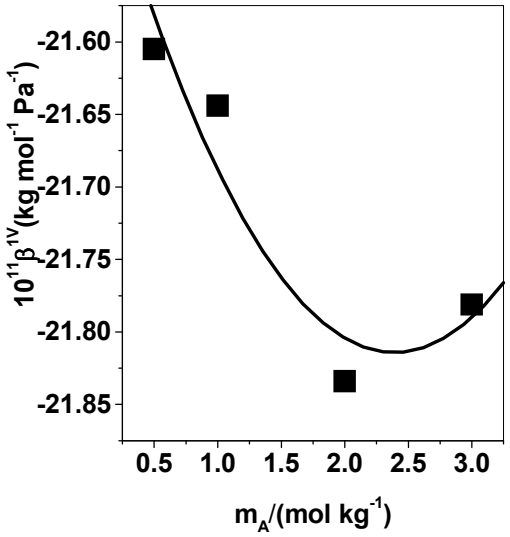


Fig 48: The Pitzer β^{1V} coefficients of aqueous KBr as a function of m_A for glycine (■)

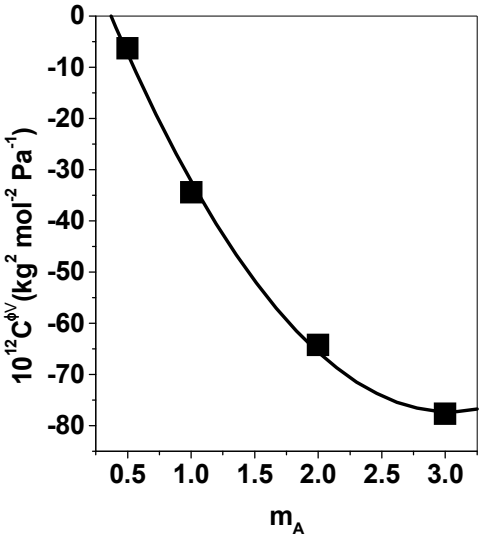


Fig 49: The Pitzer $C^{\phi V}$ coefficients of aqueous KBr as a function of m_A for glycine (■)

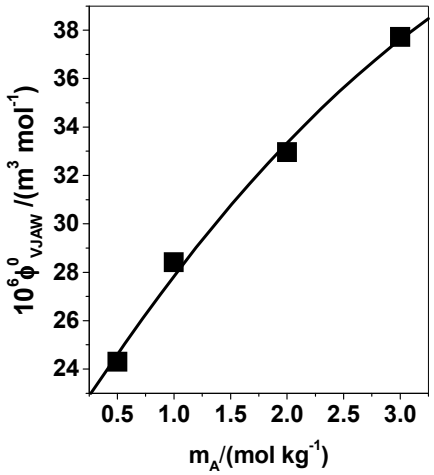


Fig 50: The ϕ^0_{VJAW} values of aqueous $MgCl_2$ as a function of m_A for glycine (■)

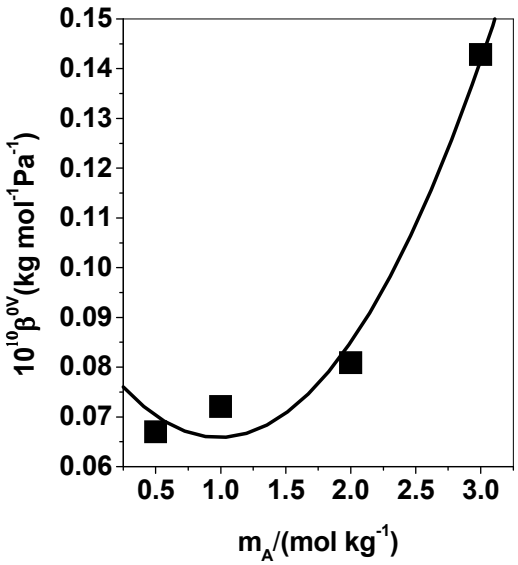


Fig 51: The Pitzer β^{0V} coefficients of $MgCl_2$ as a function of m_A for glycine (■)

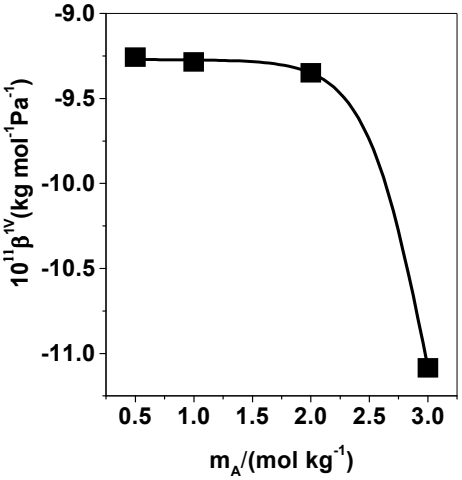


Fig 52: The Pitzer β^{1V} coefficients of aqueous $MgCl_2$ as a function of m_A for glycine (■)

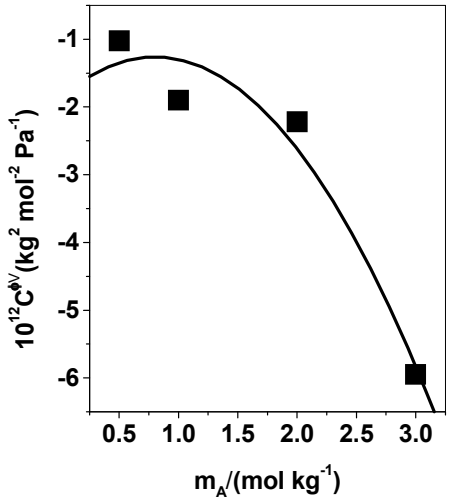


Fig 53: The Pitzer $C^{\phi V}$ coefficients of aqueous $MgCl_2$ as a function of m_A for glycine (■)

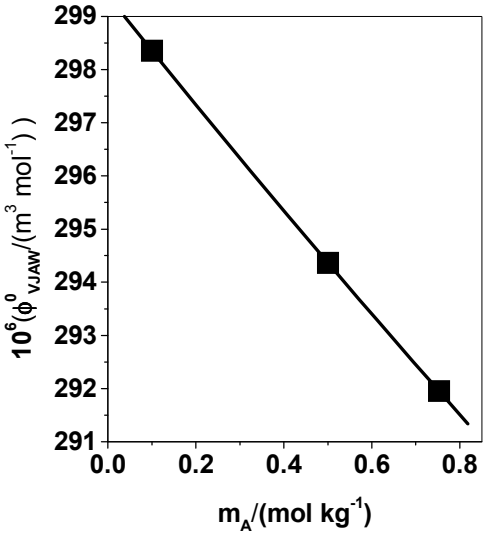


Fig 54: The ϕ^0_{VJAW} values of $(C_4H_9)_4NBr$ as a function of m_A for glycylglycine (■)

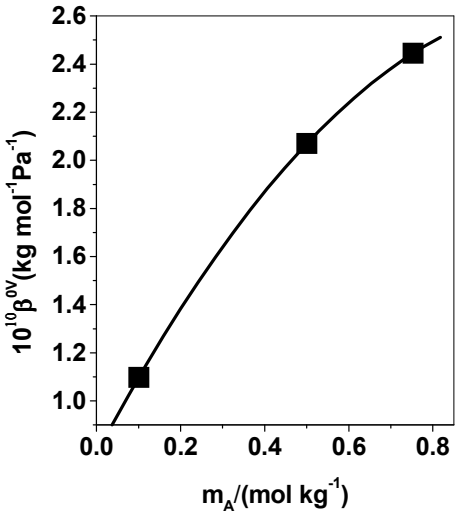


Fig 55: The Pitzer β^{0V} coefficients of aqueous $(C_4H_9)_4NBr$ as a function of m_A for glycylglycine (■)

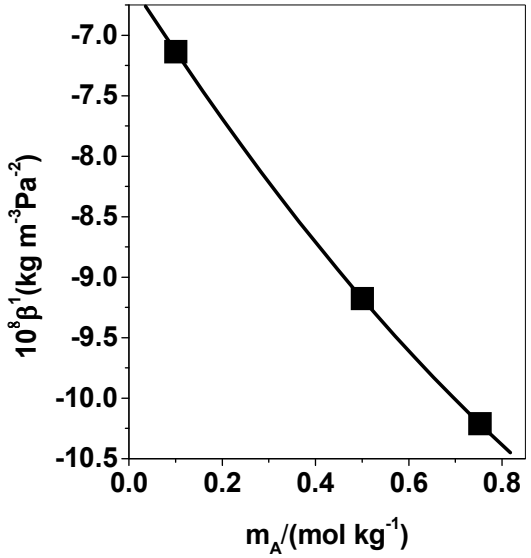


Fig 56: The Pitzer β^{1V} coefficients of aqueous $(C_4H_9)_4NBr$ as a function of m_A for glycylglycine (■)

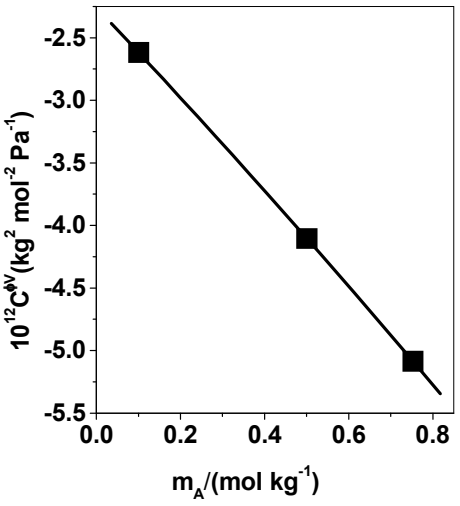


Fig 57: The Pitzer $C^{\phi V}$ coefficients of aqueous $(C_4H_9)_4NBr$ as a function of m_A for glycylglycine (■)

The ϕ^0_{KJAW} values of NaCl decrease with an increase in the concentration of amino acid. Aqueous NaCl is less compressed in amino acid solutions. A linear increase

in ϕ^0_{KJAW} with m_A can be witnessed in Fig. 58. It is interesting to note that the β^{0V} parameter is further reduced in the environment of amino acid. This parameter assumes more significance in aqueous amino acids (Fig. 59). The variation in the β^{1K} parameter with m_A is not very smooth as seen in Fig. 60. The Pitzer $C^{\phi K}$ coefficient of NaCl in aqueous alanine becomes important with increasing concentration of amino acid (Fig. 61).

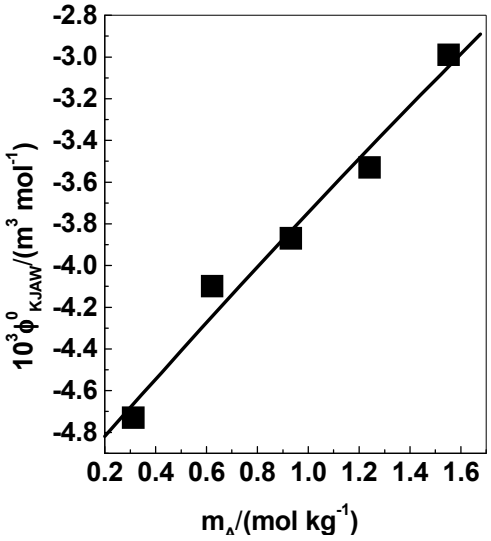


Fig 58: The ϕ^0_{KJAW} values of NaCl as a function of m_A of alanine (■)

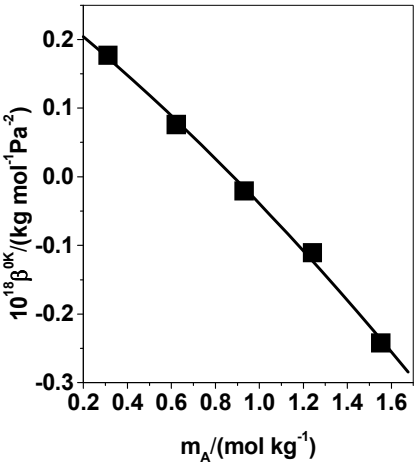


Fig 59: The Pitzer $\beta^{K(0)}$ coefficients of NaCl as a function of m_A for alanine (■)

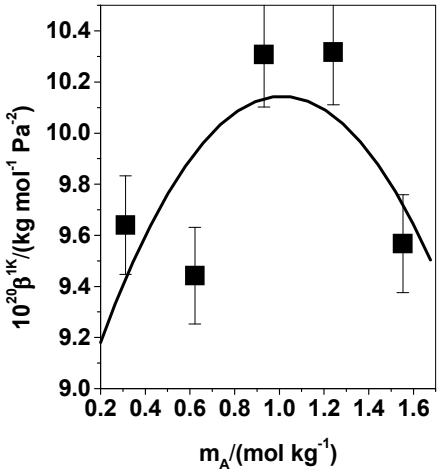


Fig 60: The Pitzer β^{1K}coefficients of NaCl as a function of m_A for alanine (■)

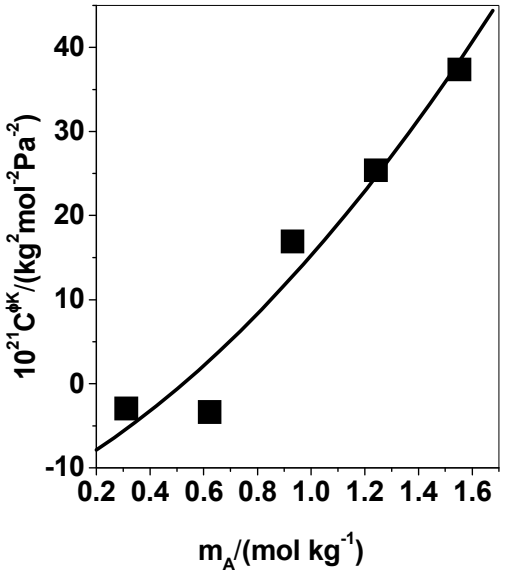


Fig 61: The Pitzer $C^{\phi K}$coefficients of NaCl as a function of m_A for alanine (■)

In nutshell, thermodynamic properties of the amino acid/peptide in aqueous electrolyte solutions and of electrolyte in aqueous amino acid/peptide solutions up to high concentrations can be correlated 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.

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ANNEXURE I

Activity coefficient (lnγ):

(1) Alanine-NaCl-H_2O

m_J	$-10^2 \ln\gamma^o$	$-10^3 S_\phi$	$10^4 S'_\phi$	$-10^5 \lambda^\phi_{AJW}$
0.01	1.104	47.19	128.9	5.3000
0.05	2.352	45.69	132.6	3.0408
0.10	3.642	43.10	132.2	1.6819
0.50	9.504	30.81	131.1	0.5568
0.90	1.2691	23.33	131.8	0.2125

(2) Glycine-NaCl-H_20

m_J	$-10^2 \ln\gamma^o$	$-10^3 S_\phi$	$10^4 S'_\phi$	$10^5 \lambda^\phi_{AJW}$
0.05	1.752	87.04	100.41	8.452
1.0	16.701	69.40	99.66	7.134
1.5	21.515	65.22	97.55	5.174
2.0	25.735	61.32	93.186	1.289
2.5	29.395	61.27	98.591	0.137
3.999	39.291	59.45	101.94	0.132

(3) DL-α-amino-n-butyric acid-NaCl-H_2O

m_J	$10^2 \ln\gamma^o$	$10^3 S_\phi$	$10^4 S'_\phi$	$-10^5 \lambda^\phi_{AJW}$
1.5	3.635	41.271	14.538	0.17621
2.0	8.196	37.166	19.311	0.23139
3.0	18.32	28.007	22.201	0.30642
4.0	29.27	17.568	23.359	0.37969

Annexure II

(1) Alanine-NaCl-H_2O

m_A	$-\ln\gamma^o$	$10^2\beta^O$	$-10^3\beta^1$	10^4C^ϕ
0.05	14.571	-7.7215	396.07	543.93
0.10	15.316	-7.3153	412.71	551.00
0.50	21.433	-4.2821	521.86	597.48
1.00	32.077	1.4316	728.53	685.62
1.50	34.87	3.3972	814.53	722.31

(2) Glycine-NaCl-H_20

m_A	$-\ln\gamma^o$	$-10^2\beta^O$	$10^3\beta^1$	-10^4C^ϕ
0.05	0.1868	4.1810	58.827	12.527
0.10	0.1973	3.9150	55.295	11.609
0.50	0.2498	2.9760	46.014	9.5204
1.000	0.3125	1.8395	35.095	7.1774
1.500	0.3567	1.1543	29.142	5.9353
2.000	0.3973	0.6127	26.353	5.6717

(3) DL-α-amino-n-butyric acid-NaCl-H_2O

m_A	$-\ln\gamma^o$	$10^2\beta^O$	$-10^3\beta^1$	10^4C^ϕ
0.1	0.3771	1.653	11.541	4.543
0.5	0.3996	2.333	13.608	4.587
1.0	0.4108	2.885	15.563	4.628
1.5	0.4224	3.608	18.834	4.700

Annexure III

Apparent molal volume:

(1) Alanine-$(C_2H_5)_4NBr$-H_2O

m_J	$10^6\phi^o_{VAJW}$ $m^3\ mol^{-1}$	$10^6\ S_V^o$	$10^6 S'^o_V$	$10^{12}\ \lambda^V_{AJW}$
0.1020	60.49	0.7477	2.1765	17.3933
0.2622	60.63	0.6681	1.3714	
0.5490	60.66	0.1090	4.2132	4.68892
1.2115	60.40	1.3823	1.6246	3.56602
				1.28487

(2) Alanine-NaCl- H_2O

0.2	61.64	0.0456	1.9261	7.2032
0.4	62.08	0.3627	0.9025	6.6515
0.6	62.57	0.4776	0.3361	4.5953
0.8	63.14	0.2195	0.7641	3.5540
1.0	63.56	0.3607	0.1302	1.8842

(3) Glycine-$(C_4H_9)_4NBr$- H_2O

0.0509	43.67	0.7765	1.5589	27.251
0.1034	43.78	0.8382	1.0973	8.5443
0.2709	44.02	0.9021	0.9599	3.0586
0.5890	44.38	0.9362	1.0941	1.9360
0.7318	44.76	0.8275	0.9878	0.1408

(4) Glycine-$(C_2H_5)_4NBr$-H_2O

0.1020	43.10	2.4625	2.8131	4.5977
0.4023	30.56	18.900	1.8793	1.5663
0.5490	43.66	1.9913	1.6337	2.0218
1.2115	44.05	2.5531	3.8917	0.7694

(5) Glycine-$MgCl_2$-H_2O

0.1002	44.19	1.3823	-0.5775	8.2865
0.4996	46.43	3.2230	-3.2258	3.3100
0.9999	48.87	-0.0248	0.2261	2.6646
1.5004	50.06	-0.0637	0.6703	1.2827

(6) Glycine-KBr-H_2O

0.5016	45.84	1.5399	1.4447	3.1293
1.0009	47.50	0.6770	0.28401	0.8481
2.0006	49.04	0.6933	0.4833	0.4299
3.0004	49.78	0.6968	0.1731	0.1777
4.0004	50.53	0.3330	0.2546	0.2350

(7) Glycylglycine-$(C_4H_9)_4NBr$-H_2O

0.0509	76.89	2.9792	3.6429	602.77
0.2710	77.71	1.3707	5.9637	491.10
0.5889	77.99	7.6435	14.6135	15.4032

(8) Glycylglycine-KCl-H_2O

0.5003	73.16	9.5353	6.1699	1.9920
1.0003	81.86	5.6049	4.1568	0.1062
1.5003	82.99	1.0669	4.1991	0.1401
2.0003	83.42	6.69865	-17.921	0.5717

(9) Glycylglycine-Na_2SO_4-H_2O

0.4998	80.8	3.2880	4.9560	2.6416
1.0000	85.41	1.1793	4.1797	2.0016
1.5006	87.93	0.4853	1.7488	1.0004
2.0016	88.9	1.3631	3.7406	0.3735

Annexure IV

(1) Alanine-$(C_2H_5)_4NBr$-H_2O

m_A	$10^6\phi^o_{VJAW}$ $m^3\ mol^{-1}$	$10^{10}4\beta^O$	$-10^{11}2\beta^1$	$-10^{12}3C^\phi$
0.0997	176.0	1.1169	75.96	325.27
0.4973	173.3	1.0060	43.63	157.95
0.7479	173.2	1.4183	43.97	542.25
0.9948	171.3	1.5662	44.41	201.24

(2) Alanine-NaCl- H_2O

0.3122	18.00	4.0050	107.6	276.70
0.62246	19.10	3.8303	107.8	244.01
0.93158	20.71	3.5936	108.3	242.17
1.55258	21.56	3.4332	105.2	230.86
1.86298	22.34	3.3981	104.9	229.13

(3) Glycine-$(C_4H_9)_4NBr$- H_2O

0.4990	295.6	1.434	64.550	303.37
0.7502	294.8	-0.0840	64.104	35.54
1.0024	294.4	-0.1514	64.687	23.49
1.5020	291.7	-0.9371	65.643	243.06

(4) Glycine-$(C_2H_5)_4NBr$-H_2O

0.1020	173.2	0.2215	43.23	47.089
0.4023	173.3	-0.1355	43.61	9.0111
0.5490	171.9	0.3164	43.43	41.705
1.2115	171.5	-0.4644	43.97	57.833

(5) Glycine-$MgCl_2$-H_2O

0.5004	24.31	0.6695	92.58	10.258
1.0005	28.41	0.7207	92.87	19.008

2.0006	32.96	0.8088	93.49	22.188
3.0002	37.72	1.4283	110.85	59.496

(6) Glycine-KBr-H_2O

0.4998	38.05	0.4316	21.605	6.3001
1.0010	38.51	1.0853	21.644	34.45
2.0001	39.02	1.9077	21.834	64.252
3.0004	41.92	2.2329	21.781	77.683

(7) Glycylglycine-$(C_4H_9)_4NBr$-H_2O

0.1008	298.3	5.3230	171.36	708.177
0.5007	294.3	6.3258	191.77	856.800
0.753	291.9	6.7002	202.13	954.870

(8) Glycylglycine-KCl-H_2O

0.5	32.77	0.4424	27.030	15.101
1.0	33.81	0.9658	27.080	44.081
1.2	34.57	0.5504	27.039	89.915

(9) Glycylglycine-Na_2SO_4-H_2O

0.5	31.41	0.5376	73.255	2.643
1.0	38.84	0.3615	73.491	2.725
1.2	40.57	0.4045	73.601	3.530

Annexure V

Apparent Molal Compressibility:

Alanine-NaCl- H_2O

m_J	$-10^{15}\phi^{o}_{KAJW}$ $m^3\ mol^{-1}\ Pa^{-1}$	$10^{15}S_k$	$-10^{15}\ S'_k$	$-10^{20}\lambda^{k}_{AJW}$
0.2	2.285	1.0072	0.9129	6.676
0.4	2.03	0.8727	0.5934	2.627
0.6	1.70	0.6844	0.4579	1.728
0.8	1.37	0.4654	0.1801	1.591
1.0	1.24	0.4583	0.1022	0.482

Annexure VI

Alanine-NaCl- H_2O

m_A	$-10^{15}\phi^{o}_{kJAW}$ $m^3\ mol^{-1}\ Pa^{-1}$	$10^{18}\beta^{O}$	$10^{20}\ \beta^{1}$	$10^{21}C^{\phi}$
0.3133	4.73	0.1767	9.6401	-2.960
0.6224	4.10	0.0761	9.4420	-3.392
0.9315	3.87	-0.0208	10.308	16.88
1.2420	3.53	-0.1107	10.317	25.37
1.5525	2.99	-0.2422	9.5676	37.35

Chapter 7

CONCLUSIONS

In this thesis, investigations on the interactions between amino acid/peptide and electrolyte solutions have been made. The purpose to investigate the above systems is based upon the pivotal role that ionic species play in controlling chemical, physical and biological behavior of proteins, nucleic acid etc. For instance certain ions are known to stabilize protein structure and DNA duplex, while proteins are denatured and DNA duplex is destabilized in the presence of certain other ionic species. Protein molecules are complex in nature and therefore it is cumbersome role to investigate protein ion interactions. In order to better understand these interactions it is preferred to undertake detailed study of amino acid-ion-water system. It is known that small assemblies of amino acids are building blocks of proteins. These amino acids are joined together by peptide linkage. It is therefore expected that ions by way of their structure making and breaking abilities will influence the physical, chemical and biological behavior of amino acids and hence of proteins.

In view of scarcity 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. Also, the measurements have been made in quaternary ammonium electrolytes due to their hydrophobic hydration nature.

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.

List of Publications

1. Rohini Badarayani, Dilip Satpute, and Anil Kumar, Effect of NaBr, KCl, KBr, and $MgCl_2$ on viscosities of aqueous Glycine and L-Alanine solutions at 298.15 K,J.Chem.Eng.Data,2005,50, 1083-1086.

Manuscripts to be Communicated:

1. Dilip Satpute, Anil Kumar, Effect of tetra-n-alkylammonium bromides on the volumetric property and compressibility of glycine in aqueous solution.
2. Dilip Satpute, Anil Kumar, Effect of tetra-n-alkylammonium bromides on the volumetric property and compressibility of alanine in aqueous solution
3. Dilip Satpute, Anil Kumar, Effect of tetra-n-alkylammonium bromides on the volumetric property and compressibility of glycylglycine in aqueous solution
4. Dilip Satpute, Anil Kumar, Effect of Temperature on the volumetric property and compressibility of glycine, DL-alanine, L-Serine and DL-Valine in aqueous glucose solution
5. Dilip Satpute, Anil Kumar, Thermodynamics of amino acids in concentrated ionic solution; correlations