Protein stability depends upon various factors like pH, temperature, composition of the environment, etc. Thus the change in any of these parameters leads to physical changes such as denaturation, resulting in loss of its characteristic biological activity. The determination of the factors governing the conformational stability of biopolymers is of fundamental importance for many biological phenomena. The study of the solute-solvent and solute-solute interactions is of primary importance in the maintenance of native conformation of proteins and nucleic acids. Various thermodynamic and transport properties like free energy, volume, compressibility, heat capacity, viscosity, etc. are very useful tools to study the solution behavior of solutes. Such data are quite helpful in understanding the water-protein interactions. In view of this, attempts are being made to study the various thermodynamic properties of amino acids, peptides and their derivatives in aqueous and mixed aqueous solutions. A brief review of representative physicochemical studies on protein model compounds i.e., amino acids, peptides etc. is being presented below.

Chalikian et al. have reported the partial molar volumes, expansibilities, and adiabatic compressibilities of glycine, diglycine, triglycine, tetruglycine, and pentaglycine in aqueous solutions at 18-55°C. These data were analyzed and interpreted in terms of the hydration of these short oligoglycines and their constituent groups. From the temperature dependence of the partial molar volume, they have reported that water that solvates the polar groups of a peptide linkage behaves more like a “normal” liquid than does bulk water, which exhibits its well known anomalous liquid properties.

Chalikian et al. observed that ionization of amino groups leads to a considerably larger volume contraction than ionization of the carboxylate groups of amino acids. Further, from the temperature and pressure dependence of the partial molar properties of glycine and α-alanine, Chalikian et al. have reported that the hydration of glycine is completely dominated by the electrostatic solute-solvent interactions and the hydration of the methyl group in α-alanine is influenced by the ionic hydration shell. Likhodi and Chalikian have reported the hydration properties of some amino acids and oligoglycines in D2O and specifically, the partial molar volumes, \( V^o_2 \) and partial molar adiabatic compressibilities, \( K^o_{s,2} \) at 25°C. The resulting data have been used to estimate the volume and compressibility contributions of the components: nonpolar (methylene group), polar (peptide group), and
charged ( oppositely charged amino and carboxyl terminal groups) chemical groups. It was found that the volume and compressibility contributions of these charged, polar, and nonpolar groups in D$_2$O are “measurably” distinct from those in H$_2$O.

Hedwig$^7$ has reported the partial molar isentropic compressibilities at infinite dilution, $K_{o,2}^e$ for the peptides: serylglycine, serylglycylglycine and serylglycylglycylglycine in aqueous solutions at 25°C. The partial molar volumes at infinite dilution, $V_{o,2}$, have also been determined for these peptides in aqueous solution at the temperatures 15, 30 and 40°C. The $K_{o,2}^e$ and partial molar isothermal compressibilities, $K_{o,T,2}^e$ results were used to obtain the partial molar compressibilities of the glycyl group CH$_2$CONH at 25°C. The results are compared with those obtained using data for other series of peptides of sequence ala(gly)$_n$, $n = 1-4$, and (gly)$_n$, $n = 2-5$.

Millero et al.$^8$ have reported the apparent molar volumes and adiabatic compressibilities of several amino acids in water. They calculated the number of hydrated water molecules, electrostriction partial molar volume and compressibility from partial molar volume and compressibility data. They have also estimated various group contributions for the partial molar volume and compressibility by different methods for the studied amino acids.

Parr et al.$^9$ have determined the solution densities for aqueous solutions of the tripeptides of sequence glycyl-x-glycine, where x is one of the amino acids serine, threonine, asparagine, glutamine, cysteine, histidine, and tyrosine, at $T = (288.15, 303.15, \text{ and } 313.15)$ K. These solution densities were used to calculate the partial molar volumes at infinite dilution, $V_{o,2}$, for the tripeptides. The $V_{o,2}$ results were combined with those determined in previous work for $T = 298.15$ K to obtain the partial molar isobaric expansions at infinite dilution, $E_{o,2}^e$ {\footnotesize $E_{o,2}^e = \left(\frac{\partial V_{o,2}^e}{\partial T}\right)_P$}, for the tripeptides at 298.15 K. The contribution of amino acid side-chain hydration to the $E_{o,2}^e$ results has been discussed.

Iqbal and Verrall$^{10}$ have studied the protein-solvent and protein-protein interactions from the partial specific volumes, adiabatic compressibilities and expansibilities of some proteins in water. The results provide some information about the structural and dynamic features of these proteins and show a greater dependence of volumetric data on the hydrophobicity than on any other protein characteristics.

Kikuchi et al.$^{11}$ reported the densities and sound velocities in dilute aqueous solutions of some amino acids at $T = (278.15, 288.15, 298.15, 303.15$ and $318.15)$ K. Partial molar
volumes and adiabatic compressibilities at infinite dilution were evaluated and their temperature and concentration dependences have been interpreted in terms of the solute-solute interactions.

Dhondge et al.\textsuperscript{11} have reported the apparent molar volume of solute ($\phi_v$), isentropic compressibility of solution ($\beta_s$) and apparent molar isentropic compressibilities of solute ($\phi_{ks}$) for aqueous solutions of glycine, L-alanine and $\beta$-alanine at lower temperatures i.e. $T = (275.15$, $279.15$, and $283.15)$ K. The limiting values of apparent molar volume of solute ($\phi_0 v$), apparent molar isentropic compressibility of solute ($\phi_0 ks$) and apparent molar expansivity ($\phi_0 e$) in the aqueous medium have also been obtained. The temperature coefficients of these limiting properties have also been computed. The results obtained were interpreted in terms of solute-solvent and solute-solute interactions, and structure making and breaking abilities of the solute in aqueous medium.

Liu et al.\textsuperscript{12} have reported the partial molar volumes, $V_{o2}$ and heat capacities, $C_{o p2}$ at infinite dilution for some N-acetyl amino acid amides in aqueous solutions at $T = (288.15$, $298.15$, $313.15$, and $328.15)$ K. These results, along with the literature data for the compounds N-acetyl glycinamide, have been used to calculate the amino acid side-chain contributions to the thermodynamic properties. These side-chain contributions are compared with those obtained using small peptides as side-chains model compounds. Liu et al.\textsuperscript{13} have reported the densities of aqueous solutions of the tripeptides of sequence glycyl-x-glycine, where x is one of the amino acids alanine, valine, leucine, isoleucine, phenylalanine, methionine and proline at $T = (288.15$, $303.15$, and $313.15)$ K. The partial molar isobaric expansions at infinite dilution, ($\partial V_{o2} / \partial T$)$_p$ for the tripeptides were calculated at 298.15 K.

Liu et al.\textsuperscript{14} have reported the mixing and dilution enthalpies of ternary system i.e., $\alpha$-amino acids (L-valine and L-threonine) + monosaccharide (fructose and sorbose) + H$_2$O at 298.15 K. They have reported the enthalpic pairwise interaction coefficients, $h_{xy}$ of L-valine and L-threonine with saccharides using McMillan-Mayer theory. They have observed $h_{xy}$ values of L-valine with saccharides to be positive and those of L-threonine be negative. The variations of the enthalpic pairwise interaction coefficients are interpreted in terms of solute-solvent interactions.

Yan et al.\textsuperscript{15-17} have determined the densities and viscosities for solutions of some $\alpha$-amino acids in water, calcium chloride and in sodium acetate at $T = (278.15$, $288.15$, $298.15$, and $308.15)$ K. These data have been used to calculate the apparent molar volumes and viscosity $B$-coefficients of the amino acids. The volumetric data have been interpreted in terms of the hydration of the hydrophobic parts of the amino acids. From the viscosity data,
structural effects of the amino acids in the solutions have been discussed. The results have been interpreted in the light of the solute-solvent interactions in aqueous media.

Yan et al.\textsuperscript{2,18} have also reported the densities and conductivities for the sodium butyrate-glycyl dipeptides (glycyl-glycine, glycyl-L-valine, glycyl-L-leucine) water systems at 298.15 K. These data have been used to calculate apparent molar volumes of the dipeptides and limiting molar conductivity ($\Lambda_o$) of sodium butyrate using the $V^o_2$ values of the amino acids and an additivity relationship, the standard partial molar volumes of peptides were estimated. The decrease in ($\Lambda_o$) with an increase in dipeptide concentration is attributed to the interactions of sodium butyrate with the dipeptide and friction resistance of the solvent medium.

Yan et al.\textsuperscript{17-19} have reported the densities and viscosities of aqueous solutions of $\alpha$-amino acids having nonpolar side chains in aqueous solutions of sodium acetate, sodium butyrate as a function of concentrations of amino acid and electrolyte at 298.15 and 308.15 K. The $V^o_2$, $\Delta V^o_2$ and the $B$-coefficients vary linearly with increasing number of carbon atoms in the alkyl chain of the amino acids, and they were split into contributions from the charged end groups (NH$_3^+$, COO$^-$) and CH$_2$ groups of the amino acids. The results have been interpreted in the light of the solute-solvent interactions in aqueous media.

Yan et al.\textsuperscript{20} have reported the infinite dilution apparent molar volumes, $V^o_{2,\phi}$ for glycine, DL-alanine, DL-$\alpha$-amino-$n$-butyric acid, DL-valine, DL-leucine, and L-serine in 6 mol·kg$^{-1}$ aqueous guanidine hydrochloride at 5, 15, 25, 35$^\circ$C from precise measurements. The results show that the apparent molar volumes at infinite dilution for (NH$_3^+$, COO$^-$) groups increase with increasing temperature and those for CH$_2$ and the other alkyl chains are almost constant. These results also show that guanidine hydrochloride has stronger interactions with amino acids than urea.

Yan et al.\textsuperscript{21} have determined the densities and conductivity data for aqueous solutions of 2-[(2-aminoacetyl)amino]acetic acid (commonly known as glycylglycine), 2-[(2-aminoacetyl)amino]-3-methylbutanoic acid (common name glycyl-L-valine), and (2S)-2-[(2-aminoacetyl)amino]-4-methylpentanoic acid (commonly known as glycyl-L-leucine) with sodium hexanoate (commonly known as sodium caproate) at $T = 298.15$ K. The apparent molar volumes of the dipeptides ($V_{2,\phi}$) and limiting molar conductivity of sodium caproate ($\Lambda_o$) have also been derived. The standard partial molar volumes $V^o_{2,\phi}$ obtained from $V_{2,\phi}$ have been used to calculate the standard partial molar volumes of transfer, $\Delta V^o$, for glycyl dipeptides from water to aqueous sodium caproate solutions. The hydration numbers, $n_H$, and
volumetric interaction coefficients have also been calculated. The dependence of above thermodynamic functions on concentration and nature of solute has been discussed in terms of various interactions taking place between hydrophobic and hydrophilic parts of peptides and sodium caproate. The decrease in $\Lambda_o$ values of sodium caproate with an increase in dipeptide concentration is attributed to the interaction of sodium caproate with the dipeptides and increasing viscosity of solvent. The limiting ionic molar conductivities and the Stokes’ radii of $\text{Na}^+$ and the caproate anion have also been estimated and discussed.

Yan et al.\textsuperscript{22} have also investigated the interactions of above glycyl dipeptides with sodium dodecyl sulfate (SDS) as a function of temperature in aqueous solution by a combination of density, conductivity, and fluorescence methods. The standard partial molar volume ($V_{2,\phi}^o$), standard partial molar volumes of transfer for dipeptide from water to aqueous SDS solutions ($\Delta_t V^o$), partial molar expansibility ($E_{\phi}^o$), and Hepler’s constant have been calculated from density data. Electrical conductivity was used to estimate the critical micellar concentration (cmc) and the thermodynamic parameters of micellization of SDS in aqueous peptide solutions. The change of micropolarity produced by the interaction was monitored by the measurement of emission intensity ratio between the first and the third bands ($I_1/I_3$) of pyrene fluorescence. The volumetric studies conclude that the dipeptides act as structure makers in SDS solutions and, ion-ion and ion-peptide group interactions predominate in these systems. The standard enthalpy of micellization is found to be positive at lower temperatures, and it becomes negative at higher temperatures. A positive entropy of micellization was observed. The marked reduction in cmc as well as the $I_1/I_3$ ratio with the increase in size of the alkyl chain length of the dipeptides is probably due to the hydrophobic bonding of these dipeptides with the exposed hydrocarbon on the micelle surface. A longer alkyl chain of peptides is markedly effective in promoting the micellar formation.

Wang et al.\textsuperscript{23} have reported the positive $\Delta_t V_{2,\phi}^o$ values for some amino acids having nonpolar side chains in aqueous solutions of sodium caproate. They observed that volumetric properties increase with increasing side chain length of the carboxylate anion. The results have been discussed in terms of the destructive effect exerted by the hydrocarbon chain of carboxylate ion on the hydration sphere of amino acids.

Qiu et al.\textsuperscript{24} have reported enthalpies of solution of glycine, L-alanine, L-serine, L-threonine, diglycine and triglycine in aqueous solutions of D-sorbitol, D-mannitol, and xylitol by calorimetry at 298.15 K. It has been observed that the derived transfer enthalpies have negative values and decrease with increase of the concentration of sugar alcohol solutions,
which indicate that the primary interactions are those between the zwitterionic group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule. The hydrophilic side chains also make negative contributions to the transfer enthalpies.

Qiu et al.\textsuperscript{25} have also observed the endothermic solution process of five amino acids, glycine, L-alanine, L-valine, L-serine and L-threonine in aqueous solutions of three quaternary ammonium surfactants \([\text{C}_n\text{H}_{2n+1}(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{Br}\) \((n = 12, 14, 16)\) at 298.15 K with a microcalorimeter. The values of the enthalpy of transfer from water to the aqueous surfactant solutions reflect the change of microenvironment of the amino acid molecule. These results are discussed in terms of a delicate balance of hydrophobic and hydrophilic interactions and differences in the molecular structure of amino acids.

Ramasami and Kakkar\textsuperscript{26} have studied the partial molar volumes and adiabatic compressibilities at infinite dilutions of some \(\alpha\)-aminocarboxylic acids with non-branched aliphatic chains, \(\alpha,\omega\)-aminocarboxylic acids and a dipeptide namely glycylglycine in water and aqueous solutions of sodium sulphate at \(T = (288.15, 298.15, \text{and} \ 308.15)\) K. This work distinguishes the behaviour of \(\alpha\)-amino acids and of the “less polar” 5-amino pentanoic acid from that of the analogues, but “more polar” glycylglycine in solution. The data obtained support the water structure making ability of sodium sulphate. Wadi and Ramasami\textsuperscript{27} have reported the partial molal volumes, \(\phi^\circ\) and adiabatic compressibilities, \(\phi^\circ_{k,s}\) of glycine and DL-alanine in water and aqueous solutions of 0.5, 1.0 and 1.5 mol·kg\(^{-1}\) sodium sulfate at 288.15, 298.15 and 308.15 K. The results have been interpreted in terms of the hydration of the hydrophobic and hydrophilic parts of the amino acids.

Singh et al.\textsuperscript{28} have reported the densities of glycine, alanine, and leucine in aqueous solutions of potassium chloride (KCl) (0.01 to 0.10 mol·kg\(^{-1}\)) at 310.15 K. Apparent molar volumes, limiting partial molar volumes and group contributions to partial molar volumes have been determined for the amino acids. Pair and triplet interaction coefficients have also been calculated from transfer parameters.

Lee et al.\textsuperscript{29} have determined the volumetric properties and adiabatic compressibilities of N-acetyl amino acid amides, N-acetyl amino acid methyl amides, and N-acetyl amino acids with neutralized carboxyl termini between 18-55°C . The individual compounds in the three classes were selected so as to collectively cover the 20 naturally occurring amino acid side chains. They have also determined changes in volume and compressibility accompanying the protonation/deprotonation reactions of amino acids with ionizable side chains. They used their data to develop an additive scheme i.e. further used to calculate the
partial specific volumes, \( v^o \) and adiabatic compressibilities, \( K^o_s \), for the fully extended conformation of apomyoglobin and apocytochrome c as a function of pH at 25°C. From the comparison between the calculated and experimental volumetric characteristics, it has been suggested that neither apocytochrome c nor apomyoglobin are fully unfolded and retain a sizeable core of solvent–inaccessible groups.

Riyazudddeen and Altamash\(^3^0\) have reported the ultrasonic velocity and density of L-histidine or L-glutamic acid or L-tryptophan or glycynglycine + 2 mol·L\(^{-1}\) aqueous KCl or 2 mol·L\(^{-1}\) aqueous KNO\(_3\) solutions as functions of amino acid or dipeptide concentration and temperature from \( T = (298.15 \text{ to } 323.15) \) K. The isentropic compressibility (\( K_s \)) values have been computed. The decrease in \( K_s \) values with an increase in concentration of amino acid/dipeptide in aqueous solutions of KCl and KNO\(_3\) has been ascribed to an increase in the number of incompressible zwitterions in the solutions. Riyazudddeen and Khan\(^3^1\) have also reported the ultrasonic velocity and density values of amino acids: L-alanine/L-proline/L-valine/L-leucine in 2.0 M aqueous KCl and 2.0 M aqueous KNO\(_3\) solutions for several concentrations of amino acids at different temperatures: 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15 K. Using ultrasonic velocity and density data, the thermodynamic parameters such as isentropic compressibility (\( K_s \)), change in isentropic compressibility (\( \Delta K_s / K^o_s \)) have been computed and the trends in their behavior with changes in the concentration of amino acids/zwitterions as well as in temperature have been discussed in terms of zwitterions-ions, zwitterions-water dipoles, ions-ions, ions-water dipoles intermolecular/interionic interactions. Riyazudddeen and Usmani\(^3^2\) have also reported partial molar volumes and partial molar isentropic compressibilities for L-alanine and L-threonine in aqueous glucose and sucrose solutions at different temperatures from 298.15 to 323.15 K. They have evaluated the corresponding transfer functions and related parameters. These parameters have been discussed in terms of ionic-hydrophilic, hydrophilic-hydrophilic, and hydrophobic-hydrophilic interactions.

Hakin and Liu\(^3^3\) have reported the relative densities and relative massic heat capacities for the amino acids; \( \beta \)-alanine, 4-aminobutanoic acid, dl-norvaline and dl-norleucine in dilute aqueous solutions at \( P = 0.1 \) MPa and \( T = (288.15, 298.15, 313.15, \text{ and } 328.15) \) K. Apparent molar volumes and heat capacities have been calculated and the isothermal concentration dependences of these properties have been modeled to yield apparent molar properties at infinite dilution. Trends in the temperature dependences of the
infinite dilution properties are discussed in terms of methylene group contributions and the variations in these contributions caused by the presence of ionic end groups.

Hakin et al.\textsuperscript{34} have reported the apparent molar volumes, $V_{2,\phi}$, and apparent molar heat capacities, $C_{p,2,\phi}$ of L-asparagine, L-glutamine, glycylglycine, glycyl-L-valine, glycyl-L-asparagine, and glycyl-DL-leucine at 288.15, 298.15, 313.15, and 328.15 K. The semi-empirical modelling procedures of Helgeson, Kirkham, and Flowers have been used to subdivide the calculated standard state volume and heat capacity data into solvation and nonsolvation contributions. These analyses yield structural contributions to standard state volumes and heat capacities for the CH(NH$_2$)CO$_2$H, CH$_2$, OH, COOH, CH, CONH$_2$, and CONH groups. Some comments are reported concerning the practicality of using the thermodynamic properties of aqueous amino acid and peptide systems as the basis for modelling standard state thermodynamic properties of aqueous protein systems.

Badarayani and Kumar\textsuperscript{35-36} have reported densities and sound velocities of glycine and L-alanine in aqueous concentrated solutions of NaBr, KCl, KBr and MgCl$_2$ at 298.15 K. They observed that MgCl$_2$ influence the apparent molar and transfer properties of the volumes and compressibilities more strongly than 1:1 electrolytes. Kumar\textsuperscript{37} and coworkers from the volumetric studies of o-amino acids in aqueous electrolyte systems, has shown that guanidine hydrochloride is structure-breaker and interact with charged end groups of zwitterionic amino acids, causing a net decrease in electrostriction of solvent, while sodium sulphate is a water structure-maker.

Jiang et al.\textsuperscript{38} have reported the transfer enthalpies of cesium chloride (CsCl) and rubidium chloride (RbCl) from pure water to aqueous L-alanine solutions from (298.15 to 313.15) K and the thermodynamic parameters (including enthalpy ($h_{EA}$) and heat capacity ($C_{p,EA}$) interaction parameters for (electrolyte + L-alanine + water) in terms of the McMillan-Mayer theory. The results show that the interaction between RbCl or CsCl and L-alanine is exothermic, and the enthalpic interaction parameter decreases with increasing temperature from 298.15 K to 308.15 K. The values of $h_{EA}$ and $C_{p,EA}$ become more negative as the size of the electrolyte ions increases from Rb$^+$ to Cs$^+$.

Sadeghi and Goodarzi\textsuperscript{39} have reported the positive transfer volumes at infinite dilution of electrolytes (potassium dihydrogen citrate (KH$_2$Cit), tripotassium citrate (K$_3$Cit) in aqueous solutions of (0.0, 0.23, 0.47 and 0.72 mol·kg$^{-1}$) Alanine, and these values increase with the concentration of alanine. They have also reported a negative value for the apparent molar isentropic compressibility which implies that the water molecules around the ions are
less compressible than the water molecules in the bulk solutions. They concluded that the
effect of alanine concentration on the volume and isentropic compressibility of K$_3$Cit is more
than those of KH$_2$Cit.

Kumar et al.\textsuperscript{40} have measured the densities and viscosities of glycine and L-valine at
308.15 and 318.15 K in aqueous tripotassium citrate solutions ranging from 0.2 to 0.8 mol
kg$^{-1}$ of tripotassium citrate. The values of apparent molar volume, partial molar volume at
infinite dilution, transfer volumes and relative viscosities of each amino acid in various
aqueous tripotassium citrate solutions have been evaluated. Transfer volume data have been
used to calculate the pair and triplet interactions. The viscosity data have been analyzed by
Jones-Dole equation. The activation parameters of viscous flow have been obtained to throw
light on the mechanism of viscous flow. The results have been discussed in terms of solute-
solute and solute-solvent interactions and the structural changes of the solutes in solutions.

Zhuo et al.\textsuperscript{41} have reported the positive transfer volumes and viscosity $B$-coefficients
of saccharides (D-(+)-glucose, D-(+)-galactose, D-(+)-xylose, and D-(−)-ribose in aqueous
amino acids (glycine and L-alanine) solutions. They observed that values of transfer
parameters increase with increasing amino acids contents. The results have been discussed in
terms of structural interaction model and the stereostructure of monosaccharide molecules.

Yu et al.\textsuperscript{42} have reported the enthalpies of dilution of aqueous solutions of amino
acids with 2-butanone and enthalpies of mixing at 298.15 K, using a mixing flow
microcalorimeter. The experimental data were treated according to the McMillan-Mayer
theory, to obtain the enthalpic interaction coefficients. Combining the enthalpic pairwise
interactions coefficients, $h_{XY}$ of amino acids with cyclohexanone from the literature, the
following sequence has been observed: $h_{XY}$ (cyclohexanone) < $h_{XY}$ (2-butanone). These
results have been attributed to the difference in molecular structure and conformation of
cyclohexanone and 2-butanone.

Sastry et al.\textsuperscript{43} have determined the apparent molar volumes and partial molar volumes
at infinite dilution, for amino acids (glycine, l-valine, l-leucine, l-phenylalanine and l-
asparagine) in aqueous solutions of sucrose (5-20 % (w/w)), urea (5 %), 2,3-butanediol (5 %)
and 2-butoxyethanol (5%) from the experimental densities at $T = (283.15-233.15)$ K. Limiting
partial molar expansibilities, $E_{2}^{o}$, and transfer volumes (from water to aqueous
additive environment), $\Delta V^o$ for the amino acids and their side chains have also been
calculated. Relative viscosities for same systems were also calculated over the same
temperature range and were analyzed in terms of Jones-Dole equation to calculate $B$-
coefficients. The analysis of volumetric functions and $B$-coefficients suggests that the solute-cosolute interactions are more favoured at elevated temperatures and in presence of high concentration of sucrose. Otherwise the hydrophobic side chains facilitate the solute-solute interactions and also time induced hydrophobic hydration in the bulk water.

Huang et al.\textsuperscript{44} have reported the apparent molar volumes of glycine, L-alanine and L-serine in DMSO-water mixtures. The transfer volumes from water to the mixtures were also evaluated. Together with static light scattering measurement, the results were utilized to reveal the microscopic solvent structure of DMSO-water mixtures and its influence on the interaction between DMSO and amino acids from a clustering point of view. The results demonstrate that the interaction between amino acids and DMSO is greatly related to the clustering structure of the mixed solvent and that amino acids interacted with already established solvent clusters. The linear dependence of transfer volume of amino acids on DMSO concentration up to 2.0 mol dm\textsuperscript{-3} could be attributed to the increasing interaction with (DMSO)$_m$(H$_2$O)$_n$ clusters. The formation of (DMSO)$_m$(H$_2$O)$_n$ cluster via hydrophobic aggregating at higher DMSO concentration led to a decrease in hydrophobic effect of DMSO and its hydrophobic-hydrophilic and hydrophobic-hydrophobic interaction with amino acids. The structure change of solvent and the interaction between amino acid residues and DMSO was reflected by the solvation of proteins. It was found that dependence of hydrodynamic radius of bovine serum albumin and lysozyme on DMSO concentration was the same and similar to that of static light scattered by the mixed solvent, regardless of the difference in conformational change between the two proteins.

Venkatesu et al.\textsuperscript{45} have determined the densities of amino acids in aqueous electrolyte solutions, by using a high precision vibrating tube digital densimeter at $T = 298.15$ K under atmospheric pressure. The investigated systems contained amino acids of zwitterionic glycine peptides: glycine (Gly), diglycine (Gly$_2$), triglycine (Gly$_3$), and tetraglycine (Gly$_4$) and cyclic glycylglycine (c(GG)) with potassium chloride (KCl), potassium bromide (KBr) and potassium acetate (KAc). The density increments resulting from the addition of the different model compounds of amino acids and the ionic salts were investigated, respectively.

Valdez et al.\textsuperscript{46} have reported the partial specific volumes and adiabatic compressibilities of three basic proteins: cytochrome c, lysozyme, and myelin in reverse micelles made of sodium bis (2-ethylhexyl) sulfosuccinate, water, and isoctane and in aqueous solvents. They reported the volumetric data for the transition of myelin basic protein from its initially unfolded state in water free of denaturants, to a folded, compact
conformation within the water-controlled microenvironment of reverse micelles. These results disclose yet another aspect of the protein structural properties observed in membrane-mimetic molecular assemblies.

Recently, Zhao\textsuperscript{47} in his review systematically reported the viscosity $B$-coefficients and standard partial molar volumes of amino acids at various temperatures. He also discussed the effect of organic solutes and various ions on the viscometric and volumetric properties of the amino acids in terms of their kosmotropic effects on the hydration of amino acids. The studies provide better understanding of why some amino acids are protein/enzyme’s stabilizers, although not all amino acids and short peptides stabilize globular proteins.

Soto\textit{et al.}\textsuperscript{48} reported the experimental data for the density, speed of sound and refractive index of aqueous diglycine $+$ NaCl and triglycine $+$ NaCl solutions. The results indicated that interactions between the peptides and NaCl strongly affect their behavior in aqueous solutions. The analysis of the results proved that the electrostatic forces between the charged groups of both peptides and the counterions are the dominant interactions in solution. The linear dependence of the apparent molar volume of peptides on the number of gly units in their structure suggests that the gly groups are hydrated independently.

Soto\textit{et al.}\textsuperscript{49} have reported the experimental data of density, velocity of sound and refractive index of glycine in aqueous solutions KCl, KNO$_3$ and NaNO$_3$ at 298.15 K. The results also showed that the nature of both the cation and anion of the electrolyte play an important role in the interactions between an electrolyte and glycine. For all the electrolytes studied, it was found that these interactions result in a positive transfer volume of glycine from one electrolyte solution to another with higher electrolyte concentration.

Talukdar\textit{et al.}\textsuperscript{50} have reported the standard free energies ($\Delta G^{\circ}_1$) and entropies ($\Delta S^{\circ}_1$) of transfer of glycine (G), diglycine (DG), and triglycine (TG), from water to aqueous mixture of glycerol (GL) and urea (UH) from solubility measurements at different temperatures. This was also extended to ionic cosolvent systems like aqueous sodium nitrate solutions for G and DG. The observed $\Delta G^{\circ}_1$ and $T\Delta S^{\circ}_1$ composition profiles, as well as those obtained after correcting for the “cavity effect” as estimated by scaled particle theory (SPT), were examined in the light of various interactions. The corrected $\Delta G^{\circ}_1$ and $T\Delta S^{\circ}_1$ values show a regular function of the peptide chain length of the amino acids and impart useful information regarding the involved relative structural effects of these ionic and nonionic cosolvents.

Natarajan\textit{et al.}\textsuperscript{51} have determined the apparent molar volumes and viscosity $B$-coefficients of some $\alpha$-, substituted $\alpha$-, and $\alpha,\omega$-amino acids in water and aqueous ammonium
chloride solutions at 298.15 K. An increase in the volume of transfer of amino acids from water to aqueous ammonium chloride solutions and of viscosity $B$-coefficients with increasing electrolyte concentration has been explained due to strong interactions of $\text{NH}_4^+$ and $\text{Cl}^-$ ions with the charged centers of the zwitterions compared to ion-nonpolar group interactions. The interactions have been rationalized in terms of the cosphere overlap model.

Bhat and Ahluwalia$^{52-53}$ have also studied partial molar volumes and heat capacities for several amino acids and peptides in the presence of aqueous NaCl and CaCl$_2$ solutions. The results have been explained on the basis of ability of CaCl$_2$ to act as a strong destabilizer of protein as compared to NaCl.

Palecz et al.$^{54}$ have determined the enthalpies of solution of L-$\alpha$-isoleucine, L-$\alpha$-cysteine, L-$\alpha$-aspartic acid, and L-$\alpha$-glutamic acid in aqueous sodium chloride solutions at 298.15 K. From the obtained experimental results the standard dissolution enthalpies of amino acids in aqueous NaCl solutions have been determined. These data were used to calculate the heterogeneous enthalpic pair interaction coefficients based on McMillan-Mayer’s theory. These values were interpreted in the terms of the hydrophobic or hydrophilic effects of the side chains of amino acids on their interactions with dissociated sodium chloride in water.

Liu et al.$^{55}$ have determined the densities of glycine, L-alanine, and L-serine in aqueous solutions of N-methylformamide (NMF) at 298.15 K. The standard partial molar volumes ($V_\phi^o$), standard partial molar volumes of transfer ($\Delta_n V_\phi^o$) and hydration numbers for the amino acids have also been determined. The positive $\Delta_n V_\phi^o$ of glycine and L-serine suggests that hydrophilic-hydrophilic interactions are predominant and that NMF has a dehydration effect on the two amino acids. The negative $\Delta_n V_\phi^o$ of L-alanine in NMF solutions with $m < 1.5 \text{ mol} \cdot \text{kg}^{-1}$ shows that the $-\text{CH}_3$ group of L-alanine weakens the interaction between its charged group and the hydrophilic group of NMF, thereby enhancing the hydrophobic-hydrophobic and hydrophobic- hydrophilic interactions; this was confirmed by the changes in hydration number. In NMF solutions with $m > 1.5 \text{ mol} \cdot \text{kg}^{-1}$, the $\Delta_n V_\phi^o$ value for L-alanine is positive, and the dehydration effect of NMF increases as a result of association between NMF molecules. The results are interpreted in terms of a cosphere overlap model.

Santosh et al.$^{56-58}$ have determined the densities, refractive indices, ultrasonic velocity and viscosity for glycylglycine in aqueous FeCl$_2$, FeCl$_3$ solutions and CoCl$_2$ aqueous ethanol solution as a function of concentration at $T = (288.15$ to $318.15)$ K. The apparent molar
volumes and partial molar volumes were obtained from these density data. The limited partial molar expansivities have been calculated from the temperature dependence of the partial molar volume. The molar refractions were calculated from the experimental refractive index values for the studied mixture. The excess volumes and molar refractions were also calculated. The behavior of the excess parameters suggests strong solute-solvent interactions. The negative $V_E$ values suggest that glycylglycine acts as a structure maker in water through hydrogen bonding and large dispersive forces.

Rajagopal and Gladson have determined the density and ultrasonic speed of four amino acids (glycine, L-alanine, L-valine, and L-leucine) in aqueous sodium fluoride solutions \{0.1 to 0.5\} M at $T = (308.15, 313.15, and 318.15)$ K. Apparent molar volumes ($V_\phi$), partial molar volumes ($V_\phi^o$), transfer volumes ($\Delta_t V_\phi^o$) and hydration number ($n_H$) are evaluated using density data. The reported values of partial molar volumes and partial molar compressibilities indicate the presence of strong solute-cosolute interactions in the solution. The compressibility parameters complement the results obtained from volumetric studies. The hydration number variations prove that sodium fluoride has dehydration effect on amino acids. Further, the zwitterionic end group contributions from partial molar volume and partial molar compressibility are greater than the methylene group contributions, which indicate that the interactions of the ions of aqueous sodium fluoride with the zwitterionic end groups of the amino acids are much stronger than with the hydrophobic groups.

Cibulka et al. have determined the density data for dilute aqueous solutions of two amino acids (glycine, L-alanine) using a flow vibrating-tube densimeter and obtained the partial molar volumes at infinite dilution (standard molar volumes, $V_{m,2}^o$). The experiments were performed at temperatures from (298 up to 443) K at pressures close to the saturation line of water, at pressures in the range from (15 to 17) MPa, and at 30 MPa. Values of isothermal compressibility, $K_{T,2}^o = -(1/V_{m,2}^o) (\partial V_{m,2}^o/\partial P)_T$, are also evaluated. Maxima on the curves $V_{m,2}^o(T)$ and $K_{T,2}^o$ are observed and discussed. The new data along with literature values of standard molar volumes and heat capacities are used for generating the recommended parameterization of an equation of state for standard molar thermodynamic properties of the aqueous amino acids.

Nain et al. have determined the densities, $\rho$, ultrasonic speeds, $u$, and viscosities, $\eta$, of aqueous-glucose (2.5, 5, 10, 15 and 20% of glucose, w/w in water) and of solutions of L-methionine in four aqueous-glucose solvents at 293.15, 298.15 303.15, 308.15, 313.15, and 318.15 K. From these experimental data, apparent molar volume, $V_A$ limiting apparent molar
volume, $V^\circ_\phi$, apparent molar compressibility, $K^\circ_\text{s,ph}$, limiting apparent molar compressibility, $K^\circ_\text{s,ph, tr}$, transfer volume, $V^\circ_\text{s,ph, tr}$, transfer compressibility, $K^\circ_\text{s,ph, tr}$, Falkenhagen coefficient, $A$, Jones-Dole coefficient, $B$, free energy of activation of viscous flow per mole of solvent, $\Delta\mu^{\text{vis}}_1$ and per mole of solute, $\Delta\mu^{\text{vis}}_2$ were calculated. The results are interpreted in terms of solute-solvent and solute-solute interactions in these systems. It is observed that there exist strong solute-solvent interactions in these systems, which increase with increase in glucose concentration. It is observed that L-methionine act as structure-breaker in aqueous-glucose solvents.

In another paper, Nain et al.\textsuperscript{62} have reported similar studies on L-histidine in aqueous sucrose solutions at different temperatures (293.15 to 318.15) K. Results have shown strong solute-solvent interactions which increase with the concentration of sucrose. It has been found that L-histidine acts structure-maker in these aqueous sucrose solutions.

Harutunyan et al.\textsuperscript{63} have studied the volumetric properties of amino acids (dl-glycine, dl-alanine, dl-serine, l-aspartic acid, l-lysine, and l-leucine) in aqueous solution of nonionic surfactant hexadecyl poly[oxyethylene(25)] alcohol (C\textsubscript{16A25}). The values of apparent molar volumes $V_\phi$, partial molar volumes $V^\circ_\text{o,2,m}$ and volumes of transfer $\Delta_t V^\circ_\text{o,2,m}$ are calculated. The changes of volumes of transfer are discussed in terms of hydrophilic-hydrophobic interactions. The linear correlation of $V^\circ_\text{o,2,m}$ for amino acids is utilized to calculate the contribution of the charged groups ($\text{NH}_3^+$, COO$^-$), CH\textsubscript{2} group and other alkyl chains of amino acids to $V^\circ_\text{o,2,m}$.

Smirnov and Badelin\textsuperscript{64} have carried out the calorimetric measurements at 298.15 K in aqueous solutions of glycylglycglycine containing formamide, N-methylformamide, N,N-dimethylformamide and N,N-diethylformamide at concentrations of amides as co-solvents up to 0.4 mole fractions. The results obtained have been used to calculate the standard enthalpies of solution ($\Delta_\text{sol}H^\circ$) and transfer ($\Delta_t H^\circ$) of the glycylglycglycine from water into the mixtures as well as enthalpy coefficients of pair-wise interaction ($h_{xy}$) of the solute with amide in aqueous media. The $h_{xy}$ values were correlated with the properties of organic solvents using Kamlet-Taft equation. The results of the calorimetric measurements have been discussed with regard to the intermolecular interactions occurring in these systems.

Romero and Cadena\textsuperscript{65} determined the partial molar volumes at infinite dilution of aqueous solutions of 3-aminopropanoic acid, 4-aminobutanoic acid, 5-aminopentanoic acid and 6-aminohexanoic acid at $T = (293.15, 298.15, 303.15$ and $308.15)$ K from density measurements. The thermodynamic behavior of the aqueous $\alpha,\omega$-amino acid solutions is
compared with that reported for \( \alpha \)-amino acids in water. The interaction volume is calculated and the influence of charged and uncharged groups of the amino acids is discussed in terms of solute-solvent interactions.

Various substances when added to aqueous protein solutions are known to stabilize or destabilize the protein and the effects of additives on proteins have been explained in terms of either direct binding or indirectly through solvent mediated effects by different workers, Lee and Lee\textsuperscript{66} and Gekko and Timasheff.\textsuperscript{67} Kishore and Sabulal\textsuperscript{68-69} have reported that chlorosubstituted alcohols are strong denaturants of proteins as compared to normal alcohols. Comparison of the results for interactions of lysozyme and \( \alpha \)-lactalbumin with n-propanol and chlorosubstituted alcohols indicate that the denaturating effect of these two proteins involve very different mechanism. Banipal and Singh\textsuperscript{70} have studied the thermal denaturation of lysozyme in the presence of n-propanol, 1, 2-propanediol and glycerol. They concluded that polyhydric alcohol-water interactions are stronger than monohydric alcohol-water interactions, so glycerol remains excluded from the surface of the protein, whereas n-propanol gets accumulated and interacts favorably with hydrophobic side chains exposed on denaturation.

Banipal \textit{et al.}\textsuperscript{70-73} have reported the partial molar volumes, \( V^o_2 \), partial molar adiabatic compressibilities, \( K^o_{S,2} \) and viscosity \( B \)-coefficients of nonpolar side chain, polar side chain amino acids, and peptides in water and in aqueous sodium acetate, magnesium acetate solutions and solvents like n-propanol, 1,2-propanediol and glycerol at 298.15 K. Further these data were used to calculate the corresponding transfer parameters (\( \Delta_t V^o_2 \), \( \Delta_t K^o_{S,2} \) and \( \Delta_t B \)), hydration numbers, \( n_{Ht} \), interaction coefficients, side chain group contributions, and other related activation parameters. The dependence of above properties on concentration and nature of cosolute has been discussed in terms of various interactions taking place between hydrophobic and hydrophilic parts of amino acids and ions of cosolutes. It has been observed that with an increase in the ionic potential of metal ion, the \( \Delta_t V^o_2 \) values increase in the order: SA < MA. It has been observed that \( \Delta_t V^o_2 \) values decrease with increase in the hydrophobic part of amino acids at all cosolute concentrations. Large transfer values of the amino acids studied in the case of MA suggest strong interactions between charged side chains and cosolute as compared to in case of SA. Hydration numbers, \( n_{Ht} \), of amino acids were found to decrease with concentration of cosolutes. Banipal and Kapoor\textsuperscript{74} reported the partial molal volume, \( V^o_2 \) and expansibilities of some amino acids in aqueous solutions at different temperatures. From these data, they have calculated the precise partial molar expansibilities
\( (\partial V^o/\partial T)_p \) at infinite dilution. The \( (\partial^2 V^o/\partial T^2)_p \) values have been used to predict the structural hydration effects. The \( (\partial V^o/\partial T)_p \) values have also been used to convert the partial molar adiabatic compressibilities, \( K^o_{s,2} \) of the studied solutes (amino acids) to partial molar isothermal compressibilities, \( K^o_{T,2} \) at infinite dilution, which is an ideal parameter for interpreting the solute-solvent interactions.

Though in literature, various thermodynamic and transport properties such as volumetric, viscometric and adiabatic compressibility of amino acids and peptides in aqueous solutions of alkali and alkaline earth metals\(^{17,19,21,36-38,50,52-55}\) as well as in different organic solvents\(^{39,42,48,56}\) have been extensively studied by many research groups, however, most of them are limited to 298.15 K. Similarly, most of the earlier studies on amino acids and peptides in aqueous solutions of transition metal halides are also confined to 298.15 K\(^{75,76}\). There are only few reports available on the amino acids and peptides in aqueous electrolyte solutions of transition metal halides at varied temperature range\(^{77}\).

Akhtar\(^{75}\) have reported the densities and viscosities of L-proline and L-glutamine in aqueous metal electrolyte 0.06 and 0.10 M (Cu (II) nitrate and Ni (II) chloride) solutions at 308.15 K. The results were discussed in terms of the dehydration effect of the electrolyte upon the amino acids. The properties of these amino acids in water and (water + electrolytes) solution systems were discussed in terms of the charge, size and hydrogen bonding effect.

Miecznik et al.\(^{77}\) have reported the ultrasonic speeds and densities of amides in aqueous ZnCl\(_2\) and ZnBr\(_2\) solutions. The various thermodynamic parameters such as adiabatic compressibility, molar volume and their excess functions have been calculated. All these parameters have been discussed to explain solute-solvent interactions, especially the effect of the presence of the Cl atom in the acetamide molecules and the replacement of Zn by Br atom in the process of complexation.

Olmo et al.\(^{78}\) in 1992 studied the influence of both zinc and mercury ions on the lysozyme structure for possible conformation transitions as well as variations of activity. From the results of intrinsic viscosity variations, partial specific volume and preferential adsorption coefficients, they showed that lysozyme can undergo a conformational transition at 10 mM concentration of Zn\(^{2+}\) and Hg\(^{2+}\).
References:


