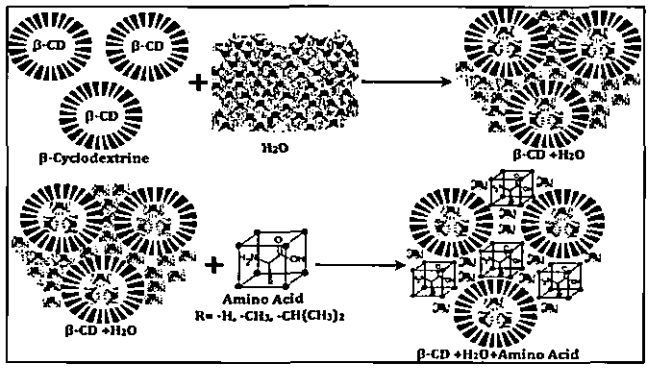
CHAPTER-IX

Molecular Interactions of α-Amino Acids Insight into Aqueous β-Cyclodextrin Systems



Qualitative and quantitative analysis of molecular interaction prevailing in glycine, L-alanine, L-valine and aqueous solution of β-cyclodextrin (β-CD), have been probed by thermophysical properties. Density (ρ), viscosity (η), ultrasonic speed (u) measurements have been reported at different temperatures. The extent of interaction (solute-solvent interaction) is expressed in terms of the limiting apparent molar volume (ϕ_V°), viscosity B-coefficient and limiting apparent molar adiabatic compressibility (ϕ_K°). The changes on the enthalpy (ΔH^*) and entropy (ΔS^*), of the encapsulation analysis give information about the driving forces governing the inclusion. The temperature dependence behaviour of partial molar quantities and group contributions to partial molar volumes have been determined for the amino acids. The trends in transfer volumes, $\Delta\phi_V^\circ$, have been interpreted in terms of solute-cosolute interactions on the basis of a cosphere overlap model. The role of the solvent (aqueous solution of β-CD), and the contribution of solute-solute and solute-solvent interactions to the solution complexes, have also been analyzed through the derived properties.

Ch-IX | Published in Amino Acids 2013, 45, 755-777.

IX.1 INTRODUCTION

Cyclodextrin molecules (CD) are cyclic oligosaccharides consist of six, seven, and eight glucopyranose units linked by α-1,4 linkages, which were called α, β and γ-cyclodextrin respectively. Due to a lack of free rotation about the glycosidic bonds, they have a toroidal, truncated, and cone shape,[IX.1]with an apolar, hydrophobic interior and two hydrophilic rims, formed by the primary -OH groups (narrow rim) and with all secondary -OH groups (wider rim)[IX.2] located at one end of the torus like molecule. Cyclodextrin molecules have a hydrophilic external surface but due to the presence of H atoms and -O- bonds, is slightly polar having a clear affinity to encapsulate hydrophobic moiety in a largely hydrophobic internal cavity, which makes the hydrophobic interaction between apolar moieties of host and guest molecules, that play an important role in the formation of inclusion complexes[IX.3, IX.4] with a wide variety of molecular species[IX.5] in different aqueous and non-aqueous solvent media.[IX.6] Among the three most important cyclodextrins, β-cyclodextrin (β-CD) (with a cavity diameter of 6.4-7.5 Å), is the most interest because its cavity size allows for the best special fit for many common guest moieties.[IX.7] For this reason, β-cyclodextrin is most commonly used as a complexing agent in hormones, vitamins, and many compounds frequently used in tissue and cell culture applications. This capability has also been of assistance for different applications in medicines, cosmetics, food technology, pharmaceutical, and chemical industries as well as in agriculture and environmental engineering as an encapsulating agent to protect sensitive molecules in hostile environment.[IX.8-IX.10] The molecular structure of β-CD is shown in **Scheme IX.1.**

The stabilization of native conformations of biological macromolecules is commonly related to several non-covalent interactions including hydrogen bonding, electrostatic and hydrophobic interactions.[IX.11]These interactions are affected by the surrounding solutes and solvent molecules; for this reason, the physico-chemical behaviors of proteins are strongly influenced by the presence of solutes. Because of direct solute–solvent interactions and/or alteration of the water structure, these solutes can change many properties of globular proteins such as their hydration, solubility, stability and the activity of enzymes.[IX.12, IX.13] However, due to the complex conformational and configurational three-dimensional structures of proteins, direct

investigations of the solute-solvent effect on these biological macromolecules are very challenging. Amino acids are basic component of proteins and are considered to be one of the important model compounds of protein molecules, which participate in all the physiological processes of living cells are quite helpful in understanding the water–protein-β-CD interactions in solutions. Especially viscometric and volumetric properties (such as viscosity *B*-coefficients and standard partial molar volumes) as well as changes in enthalpy and free energy in water and salts solutions can provide valuable clues for comprehending the protein unfolding[IX.14]and the hydrophobic interactions of non-polar side chains.[IX.15]

In the present study, we have attempted to ascertain the nature of solute–solvent/cosolute interactions of amino acids (glycine, L-alanine, and L-valine) in w_1= 0.005, 0.0075, 0.01 mass fraction of aqueous β-cyclodexrtin (β-CD) binary mixtures at 293.15, 298.15, 303.15, and 308.15K, as literature survey reveals that very scarce work has been carried out in the present ternary systems.

IX.2 EXPERIMENTAL SECTION

IX.2.1 Source and purity of samples

The studied salts (glycine, L-alanine, L-valine) and cosolute β-cyclodexrtin (β-CD), puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of salts were ≥ 0.99. The salts were dried from moisture at 373K for 48 h, and then they were cooled and store in a desiccator prior to use.

IX.2.2 Apparatus and Procedure

Aqueous binary solution of β-cyclodexrtin (β-CD) was prepared by mass (Mettler Toledo AG-285 with uncertainty ±0.0003g), which are used as solvent. Stock solutions of the salts (amino acids) were also prepared by mass and the working solutions were obtained by mass dilution. The conversion of molarity into molality was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molality of the solutions is evaluated to ±0.0001 mol·kg^{-3}.

The densities of the solutions (ρ) were measured by means of vibrating-u-tube Anton Paar digital density meter (DMA 4500M) with a precision of ±0.00005g cm^{-3} maintained at ±0.01K of the desired temperature. It was calibrated by triply-distilled water and passing dry air.

Solution viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated with triply distilled water, purified methanol and dry air with dryer. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to ±0.01K of the desired temperature. After attaining thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to ±0.1s. At least three repetitions of each data reproducible to ± 0.1s were taken to average the flow times. Adequate precautions were taken to minimize evaporation loses during the actual measurements. Viscosity of the solution is evaluated using the following appropriate equation as described earlier.[IX.16]

The ultrasonic speed (u) was measured by multi frequency ultrasonic interferometer (Model M-81) from Mittal Enterprises, India. The interferometer working at 5 MHz is based on the same principle as was used by Freyer et al.[IX.17] and Kiyoharo et al.[IX.18] The obtained speeds were corrected for diffraction errors as given by Subrahmayan et al.[IX.19] The uncertainty in the speed is ±0.2 $m \cdot s^{-1}$. The temperature was controlled within ±0.01 K using a Lauda thermostat during the measurement.

IX.3 RESULTS AND DISCUSSION

IX.3.1 Apparent molar volume

The salts are freely soluble in all proportions of the solvent mixtures. The physical properties of binary mixtures in different mass fractions (w_1=0.005, 0.0075, 0.01) of aqueous β-CD solutions at 293.15, 298.15, 303.15, 308.15 K are reported in Table IX.1. The measured experimental values of densities, viscosities, ultrasonic speeds of simple three amino acids in different mass fractions (w_1=0.005, 0.0075, 0.01) of aqueous β-CD mixture at 293.15 to 308.15 K as a function of concentration (molality) are listed in Table IX.2. Volumetric properties, such as, ϕ_V, ϕ_V^0, are regarded

as sensitive tools for the understanding of interactions in solutions. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecule and changes in the solvent volume due to its interaction with the solute. For this purpose, apparent molar volumes ϕ_V were determined from the solutions densities using the following equation and the values are given in Table IX.3.

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_o)}{m\rho\rho_o} \qquad \text{(IX.1)}$$

where M is the molar mass of the salt, m is the molality of the solution, ρ and ρ_0 are the density of the solution and aq. β-CD mixture respectively.

Table IX.3 shows that the values of ϕ_V are large and positive for all the systems, suggesting strong solute-solvent interactions. The apparent molar volumes ϕ_V were found to decrease with increasing molality (m) of amino acid in aqueous β-CD and increase with increasing temperature for all the amino acids under study. It is also found that the value increases linearly with increase in size of the alkyl chain of the amino acid and with increase in the mass fraction (w_1) of β-CD in solution. It indicates that the solute–solvent interactions increase with increasing concentration (w_1) of β-CD, size of the alkyl side chain of amino acids and temperature. The limiting apparent molar volumes ϕ_V^0 were obtained by a least-square treatment to the plots of ϕ_V versus $\sqrt{m}$ using the Masson equation;[IX.20]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{m} \qquad \text{(IX.2)}$$

where ϕ_V^0 ($= \bar{V}_2^0$) is the apparent molar volume at infinite dilution and S_V^* is the experimental slope. The ϕ_V^0 values have been determined by fitting the dilute data (m < 0.1 mol·kg^{-1}) to eq. IX.3. The standard deviations (σ) were determined using the following equation:

$$\sigma = \sqrt{\frac{\sum(Y_{exp} - Y_{obs})^2}{N-1}} \qquad \text{(IX.3)}$$

where N is the number of data points. The values of ϕ_V^0 and S_V^* are reported in Table IX.4. The plots of ϕ_V against $\sqrt{m}$ were found to be linear with negative slopes. At infinite dilution, each monomer of solute is surrounded only by the solvent

molecules, and being infinite distant with other ones. It follows, therefore, that ϕ_V^0 is unaffected by solute-solute interaction and it is a measure only of the solute-solvent interaction.[IX.21; IX.22] The ϕ_V^0 data are often embedded with important information of solute hydrophobicity, hydration properties and solute–solvent interactions[IX.23; IX.24] occurred in aqueous β-CD.

A perusal of Table IX.4 and Figure IX.1, IX.2, and IX.3, shows that the values of ϕ_V^0 are large and positive for all the amino acids at all the investigated temperatures, suggesting the presence of strong solute–solvent interaction.[IX.25] Furthermore, at each temperature, the values of ϕ_V^0 increase with increasing number of carbon atoms (or size of alkyl group) from Gly to Val. A similar increase in ϕ_V^0 with increasing number of carbon atoms for amino acids in aqueous glycerol, at 298.15 K, was also reported by Banipal et al.[IX.26] The behavior of ϕ_V^0 for the present systems can be explained employing the co-sphere model, proposed by Friedman and Krishnan[IX.26] according to which the effect of overlap of hydration cospheres is destructive. Mishra et al.[IX.27] using this model observed that an overlap of cospheres of two ionic species causes an increase in volume, whereas an overlap of hydrophobic–hydrophobic groups and ion–hydrophobic groups results in a net decrease in volume. Thus, the observed positive ϕ_V^0 values, (Table IX.4), is due to the effect of ion–hydrophilic interactions (between zwitterionic centres of the amino acids and the –OH groups of β-CD) which predominate over ion–hydrophobic interactions (between zwitterionic centres and non-polar parts of β-CD) and hydrophobic–hydrophobic interactions (between non-polar parts of the amino acids and β-CD) and increase in the order

glycine < L-alanine < L-valine

at each investigated temperature. The increase ϕ_V^0 with increasing temperature may be attributed to the release of some solvation molecules from the loose solvation layers of the solutes in solution. A plausible mechanism of interaction between β-CD and different amino acids as evident from the experimental observation is given in **Scheme IX.2.**

The values of ϕ_V^0 and S_V^* for the amino acids in pure water are adopted from the literature.[IX.28, IX.29] The parameter S_V^* is the volumetric virial coefficient, and it characterizes the pair wise interaction of solute species in solution.[IX.30, IX.31] S_V^* is found to be negative under investigations, which suggest that the pair wise interaction is restricted by the interaction of the charged functional group one molecule to side chain of the other amino acid molecules. From Table IX.4, a quantitative comparison between ϕ_V^0 and S_V^* values show that, the magnitude of ϕ_V^0 values is higher than S_V^*, suggesting that the solute-solvent interactions dominate over the solute-solute interactions in all solutions at the investigated temperatures. Furthermore, S_V^* values are negative at all temperatures, and the values slight increase with the increase of experimental temperatures which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of solute-solute interactions.

IX.3.1.1 Contributions of the zwitterionic end group, CH_2 groups and other alkyl chains of the amino acids to ϕ_V^0

The ϕ_V^0 value for the homologous series varies linearly with the number of carbon atoms in the alkyl chain (R) of the amino acids. Similar correlations have been reported earlier by a number of Workers,[IX.28, IX.29] and this linear variation can be represented as follows:

$$\phi_V^0 = \phi_V^0(NH_3^+, COO^-) + n_c\phi_V^0(CH_2) \qquad \text{(IX.4)}$$

where n_c is the number of carbon atoms in the alkyl chain of the amino acid, $\phi_V^0(NH_3^+, COO^-)$ and $\phi_V^0(CH_2)$ are the zwitterionic end group and methylene group contribution to ϕ_V^0, respectively. The values of $\phi_V^0(NH_3^+, COO^-)$ and $\phi_V^0(CH_2)$, calculated by a least-square regression analysis, are listed in Table IX.5, where those values in pure water are also provided from the literature[IX.32] It is well described in the literature[IX.32] that $\phi_V^0(CH_2)$ obtained by this scheme characterizes the mean contribution of the ϕ_V^0 (CH) and ϕ_V^0 (CH_3) values of the amino acids.

$$\phi_V^0(\mathrm{CH}) = 0.5\phi_V^0(\mathrm{CH_2}) \quad \text{(IX.5)}$$

$$\phi_V^0(\mathrm{CH_3}) = 1.5\phi_V^0(\mathrm{CH_2}) \quad \text{(IX.6)}$$

and are listed in Table IX.5. The table shows that the contribution of (NH_3^+, COO^-) to ϕ_V^0 is larger than that of the CH_2- group and increases with the increase in the mass fraction (w_1) of the cosolute β-CD, and investigated temperatures, which indicates that the interactions between the cosolute and charged end groups (NH_3^+, COO^-) of amino acids are much stronger than those between the cosolute and CH_2- group. Similar results were also reported [IX.33] for some α-amino acids in aqueous sodium caprylate solutions.

IX.3.1.2 Standard Transfer Volume

The standard transfer volume for the homologous series of amino acid, $\Delta\phi_V^0$, from pure water to aqueous β-CD solutions is defined by

$$\Delta\phi_V^0(\text{amino acid}) = \phi_V^0(\text{amino acis} + \text{aqueous } \beta\text{-CD}) - \phi_V^0(\text{water}) \quad \text{(IX.7)}$$

The results are illustrated in Table IX.6 and Figure as a function of molarity of aqueous β-CD solutions. The value of $\Delta\phi_V^0$ is, by definition, free from solute-solute interactions and therefore provides information regarding solute-solvent interactions.[IX.25] This agreement among the amino acids can be explained by the co-sphere model, as developed by Friedman and Krishnan[IX.26] according to which the effect of overlap of the hydration co-spheres is constructive. The overlap of hydration co-spheres of two ionic species results in an increase in volume, but that of hydration co-spheres of hydrophobic-hydrophobic groups and ion-hydrophobic groups results in a net volume decrease. Since amino acids exist predominantly as zwitterions in pure water and there is an overall decrease in volume of water due to electrostriction, the observed increasing positive volumes of transfer, indicate that in the ternary solutions (amino acid +aq. β-CD), indicates that the salts have, the ion-hydrophilic and hydrophilic-hydrophilic group interactions predominate over the ion-hydrophobic and hydrophobic-hydrophobic groups interactions, and the contribution increases with the molarity of β-CD in solutions. However, the negative $\Delta\phi_V^0$ values for L-valine indicate that ion-hydrophobic and hydrophobic-

hydrophobic interactions predominate over the ion-hydrophilic and hydrophilic-hydrophilic interactions. The observed trend can also be explained on the basis of the following equation;[IX.34, IX.35]

$$\phi_V^0 = \phi_{VW} + \phi_V - \phi_S \qquad \text{(IX.8)}$$

where ϕ_{VW} is the van der Waals volume; ϕ_V is the volume associated with voids or empty space; and ϕ_S is the shrinkage volume due to electrostriction. Assuming the ϕ_{VW} and ϕ_V have the same magnitudes in water and in aqueous β-CD solutions for the same class of solutes[IX.36] the observed positive $\Delta\phi_V^0$ values ascribed to the decrease in the volume of shrinkage, whereas negative $\Delta\phi_V^0$ values for L-valine may be attributed to shrinkage in volume. Banipal and co-workers[IX.37] also reported a decrease in the $\Delta\phi_V^0$ value with increasing size of the non-polar side chain of amino acids in aqueous glycerol. The introduction of a CH_3- group in L-alanine provides an additional tendency for hydrophobic-hydrophilic and hydrophobic-hydrophobic group interactions, and as a result, greater electrostriction of water is produced leading to smaller changes of $\Delta\phi_V^0$. Similarly, when the H-atom of glycine is replaced by the (CH_3CH_2CH-) group in L-valine, the additional propensity for hydrophobic-hydrophilic group interactions increases further and thus leads to change in $\Delta\phi_V^0$ values. This is in good agreement with the conclusion drawn by Li et. al. [IX.38] in a study of Glycine, L-Alanine and L-Serine in glycerol-water mixture at 298.15 K.

The standard partial molar volumes of transfer of the zwitterionic end group, $\Delta\phi_V^0(NH_3^+, COO^-)$, and other alkyl chain groups, $\Delta\phi_V^0(R)$, of amino acids from water to cosolute solutions have been calculated as follows

$$\Delta\phi_V^0(NH_3^+, COO^-) = \phi_V^0(NH_3^+, COO^-)[\text{in aqueous cosolute}] - \phi_V^0(NH_3^+, COO^-)[\text{in water}] \qquad \text{(IX.9)}$$

and are included in Table IX.7 and illustrated in Figure IX.4. The contribution of (NH_3^+, COO^-) to $\Delta\phi_V^0$, is positive throughout the studied concentration range of the aq. cosolute and increases with the increase in experimental temperature. The contribution of the alkyl chain groups to $\Delta\phi_V^0$ is negative for all the amino acids, and

shows the contribution of CH-, CH_2-, CH_3-, is negligible compare to the water.

The contribution of the other alkyl chain groups of the amino acids have been calculated from the difference between the limiting apparent molar volumes (ϕ_V^0) values of each amino acid and that of glycine using the following scheme

$$\Delta\phi_V^0(\mathrm{R}) = \phi_V^0(\text{amino acid}) - \phi_V^0(\text{glycine}) \qquad \text{(IX.10)}$$

where $\Delta\phi_V^0(\mathrm{R})$ defines the side chain transfer contribution to ϕ_V^0 of the respective amino acid relative to the H-atom of glycine. In this scheme, it is assumed that the volume contribution of the H-atom in glycine is negligible. The results are listed in Table IX.7. The table shows that the $\Delta\phi_V^0(\mathrm{R})$ values for L-alanine (CH_3CH-) and L-valine (CH_3CH_2CH-) is positive, which suggests the contribution of alkyl chain is greater than relative to the H-atom of glycine in solute-solvent interaction in solution.

IX.3.1.3 Hydration Number estimated from apparent molar volume

The number of water molecules (n_H) hydrated to the amino acids can be estimated from the value of measured standard partial molar volume. The values of ϕ_V^0 of the studied amino acids can be expressed as[IX.28]

$$\phi_V^0(\text{amino acid}) = \phi_V^0(\text{int}) + \phi_V^0(\text{elect}) \qquad \text{(IX.11)}$$

where $\phi_V^0(\text{int})$ is the intrinsic partial molar volumes of the amino acids and $\phi_V^0(\text{elect})$ is the electrostriction partial molar volume as a result of hydration of the amino acids. The $\phi_V^0(\text{int})$ consists of two terms: the van der Waals volume and the volume due to packing effects. The values of $\phi_V^0(\text{int})$ for the amino acids were calculated from their crystal molar volume by[IX.28] using the following relationship,

$$\phi_V^0(\text{int}) = \left(\frac{0.7}{0.634}\right)\phi_V^0(\text{cryst}) \qquad \text{(IX.12)}$$

where, 0.7 is the packing density in an organic crystal and 0.634 is the packing density of randomly packed spheres. The molar volume of crystals $\phi_V^0(\text{cryst})$ was calculated using the crystal densities of the amino acids represented by Berlin and Pallansch,[IX.39] Gucker et. al.[IX.40] at 298.15K. The $\phi_V^0(\text{elect})$ values can be

calculated[IX.41] from the intrinsic partial molar volumes of the amino acids $\phi_V^0(\text{int})$, and experimentally determined ϕ_V^0 values. Thus number of water molecules hydrated to the amino acids due to electrostriction causes decrease in volume can be related to the hydration numbers[IX.28] is estimated using the following relation

$$n_H = \frac{\phi_V^0(\text{elect})}{(V_e^0 - V_b^0)} \qquad \text{(IX.13)}$$

where V_e^0 is the molar volume of the electrostricted water and V_b^0 is the molar volume of bulk water. This model implies that for every water molecules taken from the bulk phase to the surroundings of amino acid, the volume is decreased by $(V_e^0 - V_b^0)$. The value of $(V_e^0 - V_b^0)$ is calculated[IX.28] to be -2.9, -3.0 or -3.3, and -4.0 $cm^3\ mol^{-1}$ at 293.15, 298.15, and 308.15 K respectively. We are assuming that this value is average -3.5 $cm^3\ mol^{-1}$ at 303.15K. The obtained n_H values are listed in Table IX.6, where n_H varies with the solvent composition, showing a tendency to decrease with an increase in the mass fraction (w_1) of β-CD, as well as temperature for all the amino acids under investigation. The observed decreasing tendency of n_H supports the view[IX.41] that the β-CD has a dehydration effect on these amino acids in aqueous β-CD solutions. Thus calculated values of n_H for the amino acids in aqueous β-CD are observed to vary in the following order:

n_H (glycine) > n_H (L-alanine) > n_H (L-valine)

The positive sign of the transfer volumes can be ascribed mainly to the fact that the hydration number n_H of the amino acids is reduced by the addition of β-CD; i.e., the electrostriction effect which brings about the shrinking in the volume of the solvent caused by the electric field of the dipolar solutes is reduced in the mixture as compared with that in pure water.

The schematic representation of solute-solvent interaction, for the studied amino acids in aqueous β-cyclodextrine binary mixtures, in view of various derived parameters is depicted in **Scheme IX.3**, where w_1 is the mass fraction of β-CD in aqueous solution.

IX.3.1.4 Temperature dependent limiting apparent molar volume

The variation of ϕ_V^0 with the temperature of the amino acids in aqueous β-CD mixture can be expressed by the general polynomial equation as follows,

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \qquad \text{(IX.14)}$$

where a_0, a_1, a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the cosolute β-CD, and T is the temperature range under study in Kelvin. The values of these coefficients of the above equation for the amino acids in aqueous β-CD mixtures are reported in Table IX.8.

The limiting apparent molar expansibilities, ϕ_E^0, can be obtained by the following equation,

$$\phi_E^0 = \left(\frac{\delta \phi_V^0}{\delta T}\right)_P = a_1 + 2a_2 T \qquad \text{(IX.15)}$$

The limiting apparent molar expansibilities, ϕ_E^0, change in magnitude with the change of temperature. The values of ϕ_E^0 for different solutions of the studied amino acids at (293.15, 298.15, 303.15, and 308.15) K are reported in Table IX.9. The table reveals that ϕ_E^0 is positive for all the amino acids in aqueous β-CD and studied temperature. This fact can ascribed to the absence of caging or packing effect[IX.24] for the amino acids in solutions.

During the past few years it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure-making or -breaking nature of any solute. Hepler[IX.43] developed a technique of examining the sign of $\left(\delta \phi_E^0 / \delta T\right)_P$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$\left(\frac{\delta \phi_E^0}{\delta T}\right)_P = \left(\frac{\delta^2 \phi_E^0}{\delta T^2}\right)_P = 2a_2 \qquad \text{(IX.16)}$$

If the sign of $\left(\delta \phi_E^0 / \delta T\right)_P$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker.[IX.44] As is evident from Table IX.9 and Figure IX.4, the $\left(\delta \phi_E^0 / \delta T\right)_P$ values for all amino acids are positive and small negative

under investigation are predominantly structure makers in all of the experimental solutions.

IX.3.2 Viscosity

The experimental viscosity data for the studied systems are listed in Table IX.2. The relative viscosity (η_r) has been analyzed using the Jones-Dole equation; [IX.45]

$$\frac{(\eta/\eta_o - 1)}{\sqrt{m}} = \frac{\eta_r - 1}{\sqrt{m}} = A + B\cdot\sqrt{m} \qquad \text{(IX.17)}$$

where $\eta_r = \eta/\eta_o$, η and η_0 are the relative viscosities, the viscosities of the ternary solutions (amino acid + aq. β-CD) and binary aqueous mixture (aq. β-CD) and m is the molality of the amino acids in ternary solutions. A and B are empirical constants known as viscosity A- and B-coefficients, which are specific to solute-solute and solute-solvent interactions, respectively. The values of A and B-coefficients are estimated by least-square method by plotting $\frac{(\eta_r - 1)}{\sqrt{m}}$ against $\sqrt{m}$, and reported in Table IX.4. The values of the A-coefficient are found to increases slightly with temperature and with the increase in mass of β-CD in the solvent mixture. These results indicate the presence of very weak solute-solute interactions. These results are in excellent agreement with those obtained from S_V^* values.

The extent of solute-solvent interaction in the solution estimated from the viscosity B-coefficient,[IX.21] gives valuable information concerning the solvation of the solvated solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules in the solutions. From Table IX.4 and Figure IX.2, it is evident that the values of the B-coefficient are positive and much higher than A-coefficient, thereby suggesting the solute-solvent interactions are dominant over the solute-solute interactions. The higher B-coefficient values for higher viscosity values is due to the solvated solutes molecule associated by the solvent molecules all round to the formation of associated molecule by solute-solvent interaction, would present greater resistance, and this type of interactions are strengthened with a rise in temperature and also increase with an increase of mass fraction (w_1) of β-CD in the solvent mixtures. These results are in good agreement with those obtained from ϕ_V^0 values discussed earlier in apparent molar volume section IX.3.1.

The Table IX.4 also shows that *B*-coefficients for all the amino acids are increase with the increase of the size of the side chains. The *B*-coefficients reflect the net structural effects of the charged groups and the hydrophobic CH_2- groups of the amino acids. As *B*-coefficients vary linearly with the number of carbon atoms of the alkyl chain (n_c), these two effects can be resolved as follows

$$B = B(NH_3^+,COO^-) + n_c\, B(CH_2) \qquad \text{(IX.18)}$$

The regression parameters, i.e., the zwitterionic group contribution $B(NH_3^+, COO^-)$, and the methylene group contribution $B(CH_2)$, to *B*-coefficients are listed in Table IX.10. It shows that both the $B(NH_3^+, COO^-)$ and $B(CH_2)$ values increases with increasing concentration (w_1) of β-CD in ternary solutions, indicating that the zwitterionic and CH_2-group enhances the structure to solute-solvent interaction in the aqueous salt solutions. The side chain contributions to *B*-coefficients, *B*(*R*), have also been derived using the same scheme as that of $\phi_V^0(R)$ and are listed in Table IX.10, which shows that *B(R)* values are positive and greater for L-valine than L-alanine in all the experimental temperatures and concentrations of solution. This order is due to the greater structure making tendency and these findings are in line with our volumetric results discussed earlier.

Table IX.4 shows that the values of the *B*-coefficients of all amino acids slight increase with increasing temperature, i.e., the $\frac{dB}{dT}$ values are positive. From Table IX.11 and Figure IX.4 small positive $\frac{dB}{dT}$ values for the present amino acids behave almost as structure-makers. Moreover, it is interesting to note that the *B*-coefficients of the studied amino acids show a linear correlation with the limiting partial molar volumes ϕ_V^0 for the amino acids in aqueous β-CD solution. This means:

$$B = A_1 + A_2\phi_V^0 \qquad \text{(IX.19)}$$

The coefficients A_1 and A_2 are included in Table X.11. This correlation is not unexpected, as both the viscosity *B*-coefficient and the partial molar volume reflect the solute–solvent interactions in the solutions. The positive slope (or A_2) shows the linear variation of *B*-coefficient with limiting apparent molar volumes ϕ_V^0. A similar correlation was also used for amino acids in different solvents.[IX.31, IX.46]

IX.3.3 Ultrasonic speed

IX.3.3.1 Apparent molar isentropic compressibility

The adiabatic compressibility, defined by the thermodynamic relation:

$$\beta_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \qquad \text{(IX.20)}$$

where V is volume, P is pressure and S is entropy, is related to the solution density ρ, and the ultrasonic speed (u), by the Newton-Laplace's equation:

$$\beta_s = \frac{1}{u^2 \rho} \qquad \text{(IX.21)}$$

providing the relation between thermodynamics and acoustics. The apparent molar adiabatic compressibility (ϕ_K), of the solutions was determined from the following relation,

$$\phi_K = \frac{M\beta_s}{\rho} + \frac{1000(\beta_s \rho_o - \beta_o \rho)}{m \rho \rho_o} \qquad \text{(IX.22)}$$

where β_0, β_s are the adiabatic compressibility of the binary mixture and ternary solution respectively and m is the molality of the ternary solution. The values of ϕ_K are reported in Table IX.3. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) or apparent molar adiabatic compressibility at infinite dilution and experimental slopes (S_K^*), were obtained by fitting ϕ_K against the square root of concentration $(\sqrt{m})$ using the least squares method;[IX.47]

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{m} \qquad \text{(IX.23)}$$

The values of ϕ_K^0 and S_K^* are presented in Table IX.4. The values of ϕ_K^0 and S_K^* are important parameter provided information about the extent of solute-solvent and solute-solute interaction respectively. The behaviour is useful in characteristic of solvation and electrostriction (the contraction of the solvent around the solute) of salt in solutions.

From Table IX.4 and Figure IX.1, IX.2, IX.3, it is observed that the value of limiting apparent molar isentropic compressibility ϕ_K^0 are positive and increases with the increase in concentration (w_1) of β-CD for all the studied solution, and

shows the stronger solute-solvent interaction. The result is good agreement with the ϕ_V^0 value discussed earlier.

At neutral pH, amino acid exists as zwitterions when dissolved in water and there is an overall decrease in the volume of water. This is due to the contraction of water near the end charged groups, termed as electrostriction. Hence the electrostricted water is much less compressible than bulk water and accounts for the apparent molar compressibilities for the amino acids in mixed ternary solutions being larger than the corresponding ones in water. It is also observed that the values of ϕ_K^0 for the studied amino acids follow the order:

$$\textit{glycine} < \textit{L-alanine} < \textit{L-valine}$$

Since the contribution of methylene group to the apparent compressibility is positive, it implies that the ions having the larger hydrophobic group may have more positive values for the partial molal expansibilities. Hence, L-valine may have largest hydrophobic group resulting higher values of ϕ_K^0.

IX.3.3.2 Hydration number from apparent molar isentropic compressibility

The limiting partial molar adiabatic compressibilities of the amino acids also can be expressed by a simple model;[IX.28]

$$\phi_K^0 = \phi_K^0(\text{int}) + \phi_K^0(\text{elect}) \qquad \text{(IX.24)}$$

where $\phi_K^0(\text{int})$ is the intrinsic partial molar adiabatic compressibility of the amino acid and $\phi_K^0(\text{elect})$ is the electrostriction partial molar adiabatic compressibility due to the hydration of the amino acid. As has been noted by Millero et al.[IX.28] as a first approximation, one can assume that $\phi_K^0(\text{int}) \approx 0$, since one would expect $\phi_K^0(\text{int})$ to very small.[IX.28] Thus ϕ_K^0 may be thought to represent $\phi_K^0(\text{elect})$. The ϕ_K^0 values of the amino acids in water are all positive; this must come from the hydration of the charged centres of the amino acids, as the hydrated water molecules are already compressed and than that in the bulk. For the amino acids, the order of increasing ϕ_K^0 values as well as hydration number n_H in aqueous β-CD is:

glycine < L-alanine < L-valine

and reported in Table IX.6. This sequence may be considered to show a decreasing order of hydration, as a first approximation, particularly for the amino acids without the -OH group of β-CD, as will be mentioned below. In Table IX.6, the observed decreasing tendency of n_H for glycine and L-alanine supports the view[IX.43] that the β-CD has a dehydration effect on these amino acids in aqueous solutions. In case of L-valine, a slight increase of n_H indicates that the increase in the interaction of hydrophobic groups of L-valine with those of the salt does not reduce the electrostriction of water molecules to it.

As has been noted by Mathieson and Conway,[IX.48] ions which a slight hydrogen-bond with water have unusual compressibility. This corresponds to the order of increasing absolute values of ϕ_K^0 in aqueous β-CD, which answers to the order of increasing hydration numbers. Thus, the less hydrated amino acids in water has the lower compressibility ratio in the mixed solvent and then loses hydrated water molecules more easily in the transfer from water to the mixed solvent.

IX.3.4 Other Thermodynamic Properties

According to Eyring and co-workers[IX.49] the free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0\#}$, can be calculated using the equation:

$$\eta_0 = \left(\frac{hN_A}{\bar{V}_1^0}\right)\exp\left(\frac{\Delta\mu_1^{0\#}}{RT}\right) \qquad \text{(IX.25)}$$

where h, N_A, and $\bar{V}_1^0 (= \phi_1^0)$ are the Planck constant, Avogadro number and partial molar volumes of the solvent, respectively. Feakins and co-workers[IX.50] applied the transition state treatment of relative viscosity to solutions and showed that the B-coefficient is given as:

$$B = \left(\frac{(\bar{V}_1^0 - \bar{V}_2^0)}{1000}\right) + \frac{\bar{V}_2^0[(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#})/RT]}{1000} \qquad \text{(IX.26)}$$

where $\bar{V}_2^0 (= \phi_V^0)$ is the partial molar volume of the solute (amino acid) and $\Delta\mu_2^{0\#}$ is the contribution per mole of the solute to the free energy of activation of viscous flow of the solution. On rearranging the equation (IX.25) and (IX.26), the values of $\Delta\mu_2^{0\#}$ and $\Delta\mu_1^{0\#}$ are obtained as:

$$\Delta\mu_1^{0\#} = RT\ln\left(\frac{\eta_0\bar{V}_1^0}{hN_A}\right) \quad \text{(IX.27)}$$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \left(\frac{RT}{\bar{V}_1^0}\right)[1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \quad \text{(IX.28)}$$

The values $\Delta\mu_2^{0\#}$ and $\Delta\mu_1^{0\#}$ for the amino acids in aqueous β-CD at 293.15, 298.15, 303.15 and 308.15K are listed in Table IX.12. The total free energy of activation of viscous flow of the solution, $\Delta\mu^{0\#}$, was calculated from the relation:

$$\Delta\mu^{0\#} = n_1\Delta\mu_1^{0\#} + n_2\Delta\mu_2^{0\#} \quad \text{(IX.29)}$$

where n_1 and n_2 are the number of moles of mixed solvent and solute, respectively. The values of $\Delta\mu^{0\#}$, also presented in Table IX.12. The thermodynamic data, ΔH^* and ΔS^* of all the amino acids in aqueous β-CD were calculated using the following equation and are listed in Table IX.12:

$$\Delta\mu^{0\#} = \Delta H^* - T\Delta S^* \quad \text{(IX.30)}$$

The ΔH^* and ΔS^* values were obtained from the intercepts and slopes of the plots of $\Delta\mu^{0\#}$ versus T. ΔH^* and ΔS^* values have proved useful in yielding structural information about solute species and about solute–solvent interactions.

It is evident from the data in Table IX.12 that $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ values are positive and almost same, for all the solvent composition. This may be due to the fact that amino acid–cosolute interactions in the ground state are almost in the transition state. In other words, the solvation of amino acids in the transition state is also favourable in terms of free energy. As $\Delta\mu_2^{0\#} \cong \Delta\mu_1^{0\#}$ then according to the Feakins model,[IX.51] the solutes (amino acids) behave as structure-makers. This again supports the behavior of dB/dT for these solutes in aqueous β-CD. The $\Delta\mu_2^{0\#}$ values (Table IX.12) of the amino acids were found to increase from gly to L-valine at a given temperature. This indicates that the solvation of the amino acids in the ground state becomes increasingly favorable as the hydrophobicity (number of carbon atoms) of the side chain increases from glycine to L-valine.

The values of the activation enthalpy, ΔH^* and entropy, ΔS^*, calculated using eq. (IX.30) of the amino acids + aqueous β-CD mixtures are listed in Table IX.12. The data reveal that the ΔH^* values of the ternary mixtures are positive, thereby,

suggesting that the formation of activated species for viscous flow becomes difficult as the amount of amino acid in the mixtures increases. The negative values of $T\Delta S^*$, which increase with increasing concentration of amino acids, for all the studied mixtures, suggest that the net order of the system decreases as the concentration of amino acid in the mixture increases. Thus, the behavior of $T\Delta S^*$ supports that of ΔH^*. The ΔH^* and ΔS^* quantities contain contributions from the following processes:

(i) formation of the solute-cosolute interaction due to non-covalent interactions (H-binding, van der Waals forces, hydrophobic and electrostatic interactions and steric effects)

(ii) dehydration of the cosolutes during the molecular interactions

(iii) hydration of the complex and

(iv) conformation changes[IX.51]

The predominance of items (i) to (iii) during these processes determines the negative values for the entropy of interaction. The contribution from process (iv) can be not considerable because the β-cyclodextrin molecule is not flexible and can't change conformation upon binding with a guest molecule, it itself retain the same conformation before and after the interaction with amino acids.

IX.3.5 Structural effect of the Co-solute β-CD

The structure is a novel packing of β -CD monomers that is less compact (2300 Å^3 per β-CD) than known monomeric (≈1500-1750 Å^3) or dimeric (≈1800 Å^3) structures.

In the first X-ray crystal structure, which was determined on a crystal in contact with mother liquor, about seven disordered water molecules may be located in each β-CD cavity, and five more water molecules in interstitial sites between the β-CD macrocycles resulting in an overall composition β-CD (12 of 0.5)H_2O^6 (16 wt % H_2O). In the neutron diffraction study[IX.52] (in which not all of the weakly populated water sites were located), at room temperature, most water molecules and hydroxyl groups of β-CD are orientationally disordered and alternately form hydrogen bonds with different neighbors. This disorder is highly dynamic, i.e. associated with rapid flips of O-H groups between discrete alternative orientations ("*flip-flop*" bonds). Very

similar disorders of solvent molecules and hydroxyl groups were described for the complex β-CD-ethanol octahydrate.

Inclusion complexes are in fact energy favourable, since water molecules from the cavity are displaced by hydrophobic guest molecules to obtain an apolar-apolar interaction and decrease the cyclodextrin ring strain, thereby leading to a more stable lower energy state. The complexation strength depends on the factors such as the size of the guest molecule, the van der Waals interactions, the release of water molecules, hydrogen bonding, charge transfer interactions, hydrophobic interactions, and the release of conformational strain, etc.[IX.53] With considering the above factors, β-CD are proposed in such a way that the interaction with amino acids, the solute-solvent interaction is higher for L-valine than L-alanine which is also turn higher than glycine, this is also due to the +I effect. +I effect increases as alkyl chain group increases from glycine to L-valine, are more favourably complex, with retention of configuration of β-CD itself.

IX.4 CONCLUSION

Extensive study of thermophysical and thermodynamic properties of simple amino acids in aqueous β-CD binary mixture were done. It is evident that the association of the investigated amino acids, the L-valine is greater than L-alanine which is, in turn, greater than that glycine. The reliable values of derivative obtained from the studies of thermophysical properties suggest that the solute-solvent interaction is dominant over the solute-solute interaction in solutions. The structural effect of β-CD gives the favourable support in the molecular interaction with retention of configuration. Above all this study demands a novelty of some amino acids prevailing in the aqueous solutions of β-CD.

REFERENCES

[IX.1] Li S, Purdy WC. Cyclodextrins and Their Applications in Analytical-Chemistry. *Chem. Rev.*, **1992**, *92*, 1457-1470

[IX.2] Rafatia AA, Bagheria A, Iloukhania H, Zarinehzad M. Study of inclusion complex formation between a homologous series of n-alkyltrimethylammonium bromides and β-cyclodextrin, using conductometric technique. *J. Mol. Liquids*, **2005**, *116*, 37-47.

[IX.3] Szejtli J, Comprehensive Supramolecular Chemistry: Cyclodextrins., in Attwood J L, Davies JED, Macnicol DD, Vogtle F, Elsevier: Oxford, **1996**, vol. 3.

[IX.4] Disouza VT, Lipkowitz KB. Cyclodextrins: Introduction. *Chem. Rev.*, **1998**, *98*, 1741-1750.

[IX.5] Thoma JT, Steward L. Starch: Chemistry and Technology, in Whistler RL, Paschall EF Edn., Academic Press: New York, **1965**, Vol. 1, pp-209.

[IX.6] Ribeiro ACF, Esteso MA, Lobo VMM, Valente AJM, Simões SMN, Sobral AJFN, Ramos ML, Burrows HD, Amado AM, D'Costa A. Interactions of Copper (II) Chloride with Cyclodextrin in Aqueous Solutions at 25 and 37°C. *J. Carbohydr. Chem.*, **2006**, *25*, 173-185.

[IX.7] Clarke RJ, Coates JH, Lincoln SF. Inclusion Complexes of the Cyclomalto-Oligosaccharides (Cyclodextrins). *Advance Carbohydr. Chem. and Biochem.* **1988**, *46*: 205-211.

[IX.8] Szejtli J. The Cyclodextrins and Their Inclusion Complexes. Academiai Kiad: Budapest, Hungary, **1982**.

[IX.9] VanEtten RL, Sebastian JF, Clowes GA, Bender ML. Acceleration of Phenyl Ester Cleavage by Cycloamyloses. A Model for Enzymatic Specificity. *J. Am. Chem. Soc.* **1967**, *89*, 3242-3249.

[IX.10] Vanetten RL, Clowee GA, Sebastian JF, Bender ML. The mechanism of the cycloamylose-accelerated cleavage of phenyl esters. *J. Am. Chem. Soc.* **1967**, *89*, 3253-3260.

[IX.11] Kumar A, Venkatesu P. Overview of the Stability of α-Chymotrypsin in Different Solvent Media. *Chem. Rev.* **2012**, *112*, 4283-4289.

[IX.12] Hippel PHV, Schleich T. The effects of neutral salts on the structure and conformational stability of macromolecules in solution. In Timasheff SN, Fasman GD Edn., Structure and Stability of Biological Macromolecules. Marcel Dekker Inc: New York, **1969,** p 417-574.

[IX.13] Jencks WP. Catalysis in Chemistry and Enzymology. Dover Publications: New York, **1969**.

[IX.14] Enea O, Jolicoeur C. Heat capacities and volumes of several oligopeptides in urea-water mixtures at 25.degree.C. Some implications for protein unfolding. *J. Phys. Chem.* **1982,** *86*, 3870-3881.

[IX.15] Kauzmann W. Some factors in the interpretation of protein denaturation. *Adv Protein Chem.* **1979,** *14*, 1–63.

[IX.16] Roy MN, Ekka D, Dewan R. Ionic solvation of tetrabutylammonium hexafluorophosphate in pure nitromethane, 1,3-dioxolane and nitrobenzene: A comparative physicochemical study. *Fluid Phase Equilibria,* **2012,** *314*, 113-120.

[IX.17] Freyer EB, Hubbard JD, Andrews DH, Sonic Studies of the Physical Properties of Liquids. I. the Sonic Interferometer. The Velocity of Sound in Some Organic Liquids and Their Compressibilities. *J. Am. Chem. Soc.* **1929,** *51*, 759-770

[IX.18] Kiyohara O, Grolier JPE, Benson GC. Excess Volumes, Ultrasonic Velocities, and Adiabatic Compressibilities for Binary Cycloalkanol Mixtures at 25°C. *Can. J. Chem.* **1974,** *52*, 2287-2293.

[IX.19] Murthy NM, Subrahmanyam SV. Structure of Aqueous Isomeric Butyl Alcohols-Sound Velocity Studies. *Bull. Chem. Soc. Jpn.* **1977**, *50,* 2589-2593.

[IX.20] Masson DO. Ion-Solvent Interactions. *Phil. Mag.* **1929,** *8*, 218-226.

[IX.21] Millero FJ. The molal volumes of electrolytes. *Chem. Rev.* **1971,** *71*, 147-176.

[IX.22] Marcus Y, Hefter G. Standard Partial Molar Volumes of Electrolytes and Ions in Nonaqueous Solvents. *Chem. Rev.* **2004,** *104*, 3405-3452.

[IX.23] Marcus Y. Thermodynamics of solvation of ions: Part 6. The standard of partial volumes of aqueous ions at 298.15 K. *J. Chem. Soc. Faraday Trans,* **1993,** *89*, 713-718.

[IX.24] Millero FJ. The partial molal volumes of electrolytes in aqueous solutions, in: R.A. Horne Edn., Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes, Wiley Interscience: New York, **1972,** p 519-595.

[IX.25] Belibagli K, Agranci E. Viscosities and apparent molar volumes of some amino acids in water and 6 M Guanidine hydrochloride at 25°C. *J. Sol. Chem.* **1990,** *19,* 867-882.

[IX.26] Friedman HL, Krishnan CV, Inclusion in Water: A comprehensive Treatise. In Franks F Edn., Plenum: New York, **1973,** Vol. 3, Chapter 1.

[IX.27] Mishra AK, Prasad KP, Ahluwalia JC. Apparent molar volumes of some amino acids and peptides in aqueous urea solutions Biopolymers. **1983,** *22,* 2397-2409.

[IX.28] Millero FJ, Surdo AL, Shin C. The apparent molal volumes and adiabatic compressibilities of aqueous amino acids at 25 °C. *J. Phys. Chem.* **1978,** *82,* 784-792.

[IX.29] Xu Li, Ding C, Lin R. Transfer volumes of Glycine, L-alanine, and L-serine from water to 1,2-butanediol-water mixtures at 298.15 K. *J. Sol. Chem.* **2006,** *35,* 191-200.

[IX.30] Wadi RK, Ramasami P. Partial molal volumes and adiabatic compressibilities of transfer of Glycine and DL-alanine from water to aqueous sodium sulfate at 288.15, 298.15 and 308.15 K. *J. Chem. Soc. Faraday Trans,* **1997,** *93,* 243-247.

[IX.31] Banipal TS, Kaur D, Banipal PK. Apparent molar volumes and viscosities of some amino acids in aqueous sodium acetate solutions at 298.15 K. *J. Chem. Eng. Data.* **2004,** *49,* 1236-1246.

[IX.32] Banerjee T, Kishore N. Interactions of some amino acids with aqueous tetraethylammonium bromide at 298.15 K: A volumetric approach. *J. Sol. Chem.* **2005,** *35*: 137-153.

[IX.33] Wang J, Yan Z, Zhao Y, Cui F. Partial Molar Volumes and Viscosities of Some α-Amino Acids in Micellar Solutions of Sodium Caprylate. *J. Chem. Eng. Data.* **2004.** *49,* 1354-1358.

[IX.34] Natarajan M, Wadi RK. Apparent molar volumes and viscosities of some R- and R,ö-amino acids in aqueous ammonium chloride solutions at 298.15 K. *J. Chem. Eng. Data.* **1990,** *35,* 87-93.

[IX.35] Bhat R, Ahluwalia JC. Partial molar heat capacities and volumes of transfer of some amino acids and peptides from water to aqueous sodium chloride solutions at 298.15 K. *J. Phys. Chem.* **1985,** *89,* 1099-1105.

[IX.36] Mishra AK, Ahluwalia JC. Enthalpies, heat capacities and apparent molar volumes of transfer of some amino acids from water to aqueous t-butanol. *J. Chem. Soc. Faraday Trans I,* **1981,** *77,* 1469-1483.

[IX.37] Banipal TS, Singh G, Lark BS, Partial Molar Volumes of Transfer of Some Amino Acids from Water to Aqueous Glycerol Solutions at 25°C. *J. Sol. Chem.* **2001,** *30,* 675-670.

[IX.38] Li S, Hu X, Lin R, Sang W, Fang W. Transfer Volumes of Glycine, L-Alanine and L-Serine in Glycerol-Water Mixtures at 25°C. *J. Sol. Chem.* **2001,** *30,* 365-373.

[IX.39] Berlin E, Pallansch MJ. Densities of several proteins and L-amino acids in the dry state. *J. Phys. Chem,* **1968,** *72,* 1887-1889.

[IX.40] Gucker FT, Ford WL, Moser CE. The apparent and partial molal heat capacities and volumes of Glycine and Glycolamide. *J. Phys. Chem.* **1939,** *43,* 153-168.

[IX.41] Franks F, Quickenden MA, Reid DS, Watson B. Calorimetric and volumetric studies of dilute aqueous solutions of cyclic ethers derivatives. *Trans. Faraday Soc.* **1970,** *66,* 582-589.

[IX.42] Owaga T, Mizutami K, Yasuda M. The volume, adiabatic compressibility and viscosity of amino acids in aqueous alkali chloride solutions. *Bull. Chem. Soc. Jpn.* **1984,** *57,* 2064-2068.

[IX.43] Helper LG. Studies on viscosities and densities of R4NX in ME+ water mixtures of different temperatures. *Can. J. Chem.* **1969,** *47,* 4613-4616.

[IX.44] Roy MN, Dakua VK, Sinha B, Partial Molar Volumes, Viscosity B-Coefficients, and Adiabatic Compressibilities of Sodium Molybdate in Aqueous 1,3-Dioxolane Mixtures from 303.15 to 323.15 K. *Int. J. Thermophys.* **2007,** *28,* 1275-1284.

[IX.45] Jones G, Dole D. The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.* **1929,** *51,* 2950-2964.

[IX.46] Yan Z, Wang J, Lu J. Viscosity behavior of some α-amino acids and their groups in water–sodium acetate mixtures. *Biophys. Chem.* **2002,** *99,* 199-207.

[IX.47] Roy MN, Ekka D, Dewan R. Physico-Chemical Studies of Some Bio-active Solutes in Pure Methanoic Acid. *Acta Chim. Slov.* **2011,** *58,* 792-796.

[IX.48] Mathieson JG, Conway BE. H_2O–D_2O solvent isotope effect in the apparent molal volume and compressibility of urea. *J. Sol. Chem.* **1974,** *3,* 781-788.

[IX.49] Glasstone S, Laidler K J, Eyring H. The Theory of Rate Processes. McGraw Hill: New York, **1941.**

[IX.50] Feakins D, Freemantle DJ, Lawrence KG. Transition state treatment of the relative viscosity of electrolytic solutions. Applications to aqueous, non-aqueous and methanol + water systems. *J. Chem. Soc. Faraday Trans I,* **1974,** *70,* 795-806.

[IX.51] Liu L, Guo QX. The Driving Forces in the Inclusion Complexation of Cyclodextrins. *J. Inclus. Phen. Macrocycl. Chem.* **2002,** *42,* 1-8.

[IX.52] Betzel C, Saenger W, Hingerty BE, Brown GM. Topography of cyclodextrin inclusion complexes, part 20. Circular and flip-flop hydrogen bonding in beta-cyclodextrin undecahydrate: a neutron diffraction study. *J. Am. Chem. Soc.* **1984,** *106,* 7545-7557.

[IX.53] Loftsson T. Cyclodextrins in drug delivery. *Expert Opinion Drug Delivery,* **2005,** *2(2),* 335-351.

TABLES

Table IX.1: Values of density (ρ), viscosity (η) and ultrasonic speed (u) of aqueous β-CD in different mass fraction (w_1), at 293.15K to 308.15K

Mass fraction of aq. β-CD (w_1)	Temp /K	$\rho \cdot 10^{-3}$ /kg·m^{-3}		η /mPa·s		u /m·s^{-1}	
		Expt	Lit	Expt	Lit	Expt	Lit
$w_1 = 0.005$	293.15	0.99999	-	1.003	-	1484.4	-
	298.15	0.99873	-	0.893	-	1499.5	-
	303.15	0.99747	-	0.801	-	1508.7	-
	308.15	0.99622	-	0.723	-	1517.2	-
$w_1 = 0.0075$	293.15	1.00120	-	1.005	-	1485.0	-
	298.15	0.99987	-	0.895	-	1500.3	-
	303.15	0.99854	-	0.803	-	1509.8	-
	308.15	0.99721	-	0.725	-	1518.6	-
$w_1 = 0.01$	293.15	1.00206	-	1.007	-	1485.6	-
	298.15	1.00078	-	0.897	-	1501.3	-
	303.15	0.99949	-	0.805	-	1510.9	-
	308.15	0.99822	-	0.727	-	1519.8	-

Table IX.2: Experimental values of density (ρ), viscosity (η), and ultrasonic speed (*u*) of amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15K to 308.15K respectively

m /mol·kg^{-1}	$\rho \cdot 10^{-3}$ /kg·m^{-3}	η /mPa·s	*u* /m·s^{-1}	*m* /mol·kg^{-1}	$\rho \cdot 10^{-3}$ /kg·m^{-3}	η /mPa·s	*u* /m·s^{-1}
w_1 = 0.005							
Glycine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00033	1.005	1484.9	0.0100	0.99906	0.895	1500.8
0.0200	1.00069	1.006	1489.1	0.0200	0.99940	0.896	1506.0
0.0300	1.00106	1.008	1496.8	0.0301	0.99974	0.898	1514.7
0.0401	1.00143	1.009	1506.2	0.0401	1.00009	0.899	1525.6
0.0501	1.00181	1.011	1518.0	0.0502	1.00045	0.901	1539.8
0.0601	1.00220	1.012	1531.4	0.0602	1.00080	0.902	1555.9
T = 303.15K				T = 308.15K			
0.0100	0.99779	0.803	1512.3	0.0100	0.99653	0.725	1522.2
0.0201	0.99812	0.804	1517.9	0.0201	0.99684	0.727	1529.1
0.0301	0.99845	0.806	1527.8	0.0302	0.99716	0.728	1540.0
0.0402	0.99878	0.807	1540.0	0.0402	0.99747	0.730	1553.8
0.0502	0.99912	0.809	1555.0	0.0503	0.99778	0.731	1571.8
0.0603	0.99946	0.810	1573.1	0.0604	0.99810	0.733	1592.4
Alanine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00034	1.006	1485.1	0.0100	0.99907	0.896	1502.8
0.0200	1.00075	1.008	1493.5	0.0200	0.99946	0.898	1512.5
0.0300	1.00118	1.011	1506.5	0.0301	0.99988	0.901	1527.4
0.0401	1.00164	1.013	1523.6	0.0401	1.00032	0.903	1546.5
0.0501	1.00213	1.016	1544.5	0.0502	1.00078	0.906	1570.1
0.0602	1.00264	1.019	1570.0	0.0602	1.00126	0.909	1599.8
T = 303.15K				T = 308.15K			
0.0100	0.99780	0.804	1514.4	0.0100	0.99654	0.726	1524.2

0.0201	0.99817	0.807	1525.5	0.0201	0.99689	0.728	1536.1
0.0301	0.99857	0.809	1542.4	0.0302	0.99726	0.731	1553.2
0.0402	0.99899	0.812	1564.0	0.0402	0.99765	0.734	1576.1
0.0503	0.99942	0.815	1590.2	0.0503	0.99806	0.737	1604.2
0.0603	0.99987	0.818	1621.3	0.0604	0.99848	0.740	1639.1
Valine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00036	1.007	1487.1	0.0100	0.99909	0.897	1504.7
0.0200	1.00082	1.011	1499.0	0.0201	0.99953	0.900	1517.7
0.0301	1.00133	1.015	1517.1	0.0301	1.00002	0.904	1537.8
0.0401	1.00187	1.019	1541.1	0.0402	1.00055	0.908	1563.1
0.0502	1.00247	1.023	1569.3	0.0502	1.00111	0.912	1595.2
0.0602	1.00310	1.027	1604.0	0.0603	1.00170	0.916	1632.7
T = 303.15K				T = 308.15K			
0.0100	0.99782	0.805	1516.3	0.0100	0.99656	0.727	1526.1
0.0201	0.99824	0.809	1530.8	0.0201	0.99696	0.730	1542.0
0.0301	0.99871	0.812	1551.8	0.0302	0.99740	0.734	1564.8
0.0402	0.99922	0.816	1579.4	0.0403	0.99788	0.738	1594.9
0.0503	0.99976	0.820	1613.8	0.0504	0.99839	0.742	1631.8
0.0604	1.00032	0.824	1656.5	0.0605	0.99892	0.745	1676.0
w_1 = 0.0075							
Glycine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00154	1.006	1485.6	0.0100	1.00020	0.896	1500.8
0.0200	1.00189	1.008	1490.7	0.0200	1.00054	0.898	1506.0
0.0300	1.00226	1.009	1498.3	0.0300	1.00089	0.900	1514.7
0.0400	1.00264	1.011	1508.7	0.0401	1.00124	0.901	1526.3
0.0500	1.00302	1.013	1521.0	0.0501	1.00160	0.902	1540.2
0.0601	1.00341	1.014	1536.5	0.0602	1.00196	0.904	1557.0
T = 303.15K				T = 308.15K			
0.0100	0.99886	0.805	1512.5	0.0100	0.99752	0.727	1522.5
0.0200	0.99918	0.807	1518.7	0.0201	0.99784	0.729	1528.7

0.0301	0.99951	0.808	1528.1	0.0301	0.99816	0.730	1538.7
0.0401	0.99985	0.810	1540.9	0.0402	0.99848	0.732	1551.9
0.0502	1.00019	0.811	1556.2	0.0502	0.99880	0.734	1568.6
0.0602	1.00053	0.813	1574.3	0.0603	0.99913	0.735	1587.7
Alanine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00155	1.007	1485.7	0.0100	1.00021	0.897	1503.3
0.0200	1.00194	1.010	1495.8	0.0200	1.00058	0.900	1513.9
0.0300	1.00236	1.013	1510.9	0.0301	1.00099	0.902	1529.9
0.0400	1.00281	1.015	1530.8	0.0401	1.00142	0.905	1551.6
0.0501	1.00329	1.018	1555.2	0.0501	1.00187	0.908	1577.7
0.0601	1.00379	1.020	1586.7	0.0602	1.00234	0.910	1609.3
T = 303.15K				T = 308.15K			
0.0100	0.99887	0.806	1515.2	0.0100	0.99753	0.728	1525.2
0.0201	0.99923	0.809	1526.1	0.0201	0.99789	0.731	1537.6
0.0301	0.99962	0.811	1544.2	0.0301	0.99827	0.733	1555.7
0.0401	1.00003	0.814	1566.8	0.0402	0.99867	0.736	1580.8
0.0502	1.00046	0.817	1594.5	0.0503	0.99909	0.739	1610.4
0.0603	1.00091	0.819	1628.7	0.0604	0.99953	0.741	1645.9
Valine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00157	1.009	1486.9	0.0100	1.00023	0.898	1504.7
0.0200	1.00201	1.013	1498.9	0.0200	1.00067	0.902	1517.6
0.0300	1.00252	1.017	1517.0	0.0301	1.00116	0.906	1537.5
0.0401	1.00306	1.021	1541.7	0.0401	1.00170	0.910	1563.1
0.0501	1.00367	1.025	1570.8	0.0502	1.00227	0.914	1595.6
0.0602	1.00429	1.030	1605.4	0.0602	1.00288	0.918	1633.8
T = 303.15K				T = 308.15K			
0.0100	0.99889	0.807	1516.5	0.0100	0.99755	0.729	1526.6
0.0201	0.99931	0.811	1530.9	0.0201	0.99796	0.733	1541.7
0.0301	0.99979	0.815	1551.8	0.0302	0.99841	0.737	1563.6
0.0402	1.00030	0.819	1579.3	0.0402	0.99890	0.740	1592.1

0.0503	1.00085	0.822	1613.3	0.0503	0.99942	0.744	1629.4
0.0603	1.00143	0.826	1656.4	0.0604	0.99997	0.748	1673.2
$w_1 = 0.01$							
Glycine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00240	1.009	1486.3	0.0100	1.00111	0.899	1501.4
0.0200	1.00276	1.010	1491.4	0.0200	1.00146	0.901	1507.9
0.0300	1.00313	1.012	1499.2	0.0300	1.00182	0.902	1517.7
0.0400	1.00351	1.013	1510.2	0.0400	1.00218	0.904	1530.4
0.0500	1.00390	1.015	1523.3	0.0501	1.00256	0.906	1546.3
0.0600	1.00430	1.017	1539.0	0.0601	1.00294	0.907	1564.7
T = 303.15K				T = 308.15K			
0.0100	0.99982	0.807	1513.1	0.0100	0.99854	0.728	1523.1
0.0200	1.00016	0.808	1519.3	0.0201	0.99888	0.730	1530.6
0.0301	1.00051	0.810	1529.5	0.0301	0.99923	0.732	1541.6
0.0401	1.00087	0.811	1542.7	0.0401	0.99959	0.733	1556.3
0.0501	1.00124	0.813	1558.6	0.0502	0.99996	0.735	1573.7
0.0602	1.00162	0.815	1578.2	0.0603	1.00033	0.737	1594.6
Alanine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00241	1.010	1486.4	0.0100	1.00112	0.900	1504.4
0.0200	1.00281	1.012	1498.8	0.0200	1.00151	0.903	1517.8
0.0300	1.00325	1.015	1516.9	0.0300	1.00193	0.905	1536.6
0.0400	1.00373	1.018	1539.7	0.0400	1.00238	0.908	1561.2
0.0500	1.00422	1.020	1568.8	0.0501	1.00285	0.911	1591.7
0.0600	1.00474	1.023	1602.9	0.0601	1.00334	0.914	1629.0
T = 303.15K				T = 308.15K			
0.0100	0.99983	0.808	1516.2	0.0100	0.99855	0.730	1526.3
0.0200	1.00021	0.811	1529.1	0.0201	0.99892	0.733	1540.8
0.0301	1.00063	0.813	1548.3	0.0301	0.99932	0.736	1561.9
0.0401	1.00108	0.816	1573.6	0.0402	0.99975	0.738	1588.1
0.0501	1.00155	0.819	1604.8	0.0502	1.00020	0.741	1622.2

0.0602	1.00205	0.822	1643.7	0.0603	1.00067	0.744	1663.3
Valine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	1.00243	1.011	1486.9	0.0100	1.00114	0.902	1505.0
0.0200	1.00289	1.015	1499.3	0.0200	1.00158	0.906	1518.6
0.0300	1.00340	1.020	1518.3	0.0300	1.00208	0.910	1538.8
0.0400	1.00397	1.024	1542.5	0.0401	1.00262	0.914	1565.0
0.0501	1.00458	1.029	1572.1	0.0501	1.00320	0.918	1597.2
0.0601	1.00522	1.033	1608.9	0.0602	1.00382	0.922	1637.3
T = 303.15K				T = 308.15K			
0.0100	0.99985	0.809	1516.9	0.0100	0.99857	0.731	1527.0
0.0200	1.00028	0.813	1531.7	0.0201	0.99899	0.734	1541.7
0.0301	1.00077	0.816	1553.5	0.0301	0.99947	0.738	1563.6
0.0401	1.00130	0.821	1581.3	0.0402	0.99999	0.742	1593.6
0.0502	1.00188	0.825	1616.3	0.0503	1.00055	0.746	1628.4
0.0603	1.00250	0.829	1658.9	0.0604	1.00114	0.750	1673.1

Table IX.3: Molality (m), apparent molar volume (ϕ_V), $(\eta_r-1)/\sqrt{m}$, and apparent molar adiabatic compressibility (ϕ_K) of amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15K to 308.15K respectively

m /mol·kg^{-1}	$\phi_V \cdot 10^6$ /m^3·mol^{-1}	$(\eta_r-1)/\sqrt{m}$ /kg$^{1/2}$·mol$^{-1/2}$	$\phi_K \cdot 10^{11}$ /m^3·mol^{-1}·Pa^{-1}	m /mol·kg^{-1}	$\phi_V \cdot 10^6$ /m^3·mol^{-1}	$(\eta_r-1)/\sqrt{m}$ /kg$^{1/2}$·mol$^{-1/2}$	$\phi_K \cdot 10^{11}$ /m^3·mol^{-1}·Pa^{-1}
$w_1 = 0.005$							
Glycine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	41.07	0.015	-2.73	0.0100	42.12	0.019	-4.50
0.0200	40.07	0.022	-14.06	0.0200	41.67	0.025	-17.40
0.0300	39.40	0.025	-24.76	0.0301	41.32	0.030	-28.34
0.0401	39.07	0.030	-32.42	0.0401	41.05	0.034	-36.70
0.0501	38.67	0.033	-39.56	0.0502	40.80	0.038	-45.08
0.0601	38.24	0.036	-45.55	0.0602	40.57	0.042	-51.99
T = 303.15K				T = 308.15K			
0.0100	43.18	0.024	-6.06	0.0100	44.24	0.029	-8.33
0.0201	42.83	0.031	-18.95	0.0201	44.14	0.038	-23.38
0.0301	42.61	0.036	-31.21	0.0302	44.07	0.044	-35.57

0.0402	42.43	0.041	-40.23	0.0402	44.01	0.049	-45.22
0.0502	42.26	0.045	-48.31	0.0503	43.96	0.054	-54.97
0.0603	42.09	0.048	-55.97	0.0604	43.90	0.059	-63.08
Alanine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	54.09	0.025	-13.14	0.0100	55.16	0.030	-15.78
0.0200	51.09	0.035	-31.81	0.0200	52.66	0.042	-35.96
0.0300	49.42	0.043	-46.80	0.0301	50.82	0.051	-52.18
0.0401	47.84	0.049	-59.66	0.0401	49.48	0.059	-65.40
0.0501	46.29	0.056	-70.90	0.0502	48.15	0.066	-77.25
0.0602	44.92	0.062	-81.60	0.0602	46.98	0.073	-89.23
T = 303.15K				T = 308.15K			
0.0100	56.23	0.038	-17.68	0.0100	57.31	0.042	-19.17
0.0201	54.23	0.052	-40.17	0.0201	55.80	0.057	-42.48
0.0301	52.56	0.062	-57.90	0.0302	54.63	0.069	-59.11
0.0402	51.22	0.072	-72.20	0.0402	53.54	0.079	-74.16
0.0503	50.22	0.079	-84.44	0.0503	52.49	0.087	-87.25
0.0603	49.21	0.086	-95.39	0.0604	51.62	0.095	-99.97

Valine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	80.15	0.037	-24.23	0.0100	81.25	0.043	-25.90
0.0200	75.65	0.054	-47.26	0.0201	77.25	0.059	-49.98
0.0301	72.48	0.067	-66.40	0.0301	74.24	0.074	-70.60
0.0401	70.15	0.078	-83.17	0.0402	71.74	0.085	-86.72
0.0502	67.55	0.089	-96.44	0.0502	69.64	0.096	-101.87
0.0602	65.32	0.097	-109.25	0.0603	67.74	0.108	-114.53
T = 303.15K				T = 308.15K			
0.0100	82.36	0.050	-27.56	0.0100	83.47	0.055	-28.87
0.0201	78.85	0.069	-54.12	0.0201	80.45	0.075	-57.80
0.0301	76.01	0.084	-74.01	0.0302	78.11	0.092	-78.75
0.0402	73.59	0.097	-91.31	0.0403	75.94	0.104	-97.06
0.0503	71.53	0.108	-106.75	0.0504	74.03	0.117	-112.68
0.0604	69.83	0.119	-121.42	0.0605	72.42	0.129	-126.38
w_1 = 0.0075							
Glycine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	41.02	0.017	-3.34	0.0100	42.08	0.019	-4.82

0.0200	40.32	0.023	-17.02	0.0200	41.58	0.027	-17.54
0.0300	39.72	0.028	-26.45	0.0300	41.08	0.032	-28.43
0.0400	39.15	0.032	-35.09	0.0401	40.82	0.036	-37.73
0.0500	38.70	0.035	-42.18	0.0501	40.47	0.039	-45.54
0.0601	38.26	0.039	-49.57	0.0602	40.24	0.043	-52.97
	T = 303.15K				T = 308.15K		
0.0100	43.23	0.021	-5.52	0.0100	44.09	0.025	-6.35
0.0200	42.93	0.029	-20.36	0.0201	43.84	0.034	-20.41
0.0301	42.66	0.034	-31.17	0.0301	43.62	0.040	-31.96
0.0401	42.46	0.038	-40.99	0.0402	43.47	0.046	-41.76
0.0502	42.23	0.044	-49.19	0.0502	43.33	0.050	-50.91
0.0602	42.01	0.047	-56.66	0.0603	43.21	0.055	-58.56
			Alanine + aq. β-CD				
	T = 293.15K				T = 298.15K		
0.0100	54.42	0.027	-18.56	0.0100	55.50	0.030	-19.00
0.0200	52.03	0.037	-39.45	0.0200	53.60	0.040	-40.03
0.0300	50.36	0.046	-55.76	0.0301	51.76	0.050	-56.79
0.0400	48.78	0.053	-70.00	0.0401	50.35	0.058	-72.15

0.0501	47.23	0.059	-82.51	0.0501	49.10	0.066	-84.90
0.0601	45.87	0.064	-95.78	0.0602	47.93	0.072	-96.72
	T = 303.15K				T = 308.15K		
0.0100	56.57	0.032	-20.54	0.0100	57.25	0.035	-21.12
0.0201	54.67	0.046	-40.93	0.0201	55.24	0.050	-44.78
0.0301	53.17	0.057	-60.48	0.0301	53.91	0.061	-62.33
0.0401	51.92	0.064	-75.29	0.0402	52.74	0.071	-79.21
0.0502	50.76	0.074	-88.23	0.0503	51.63	0.081	-92.47
0.0603	49.66	0.081	-100.71	0.0604	50.56	0.089	-104.46
			Valine + aq. β-CD				
	T = 293.15K				T = 298.15K		
0.0100	80.05	0.041	-24.80	0.0100	81.16	0.043	-26.20
0.0200	76.56	0.057	-47.71	0.0200	77.16	0.059	-49.80
0.0300	73.06	0.071	-66.65	0.0301	74.16	0.074	-70.08
0.0401	70.56	0.082	-84.27	0.0401	71.41	0.087	-86.73
0.0501	67.67	0.093	-98.19	0.0502	69.16	0.096	-102.24
0.0602	65.57	0.102	-110.51	0.0602	66.99	0.109	-115.35
	T = 303.15K				T = 308.15K		
0.0100	82.27	0.047	-27.00	0.0100	83.38	0.051	-27.97

0.0201	78.76	0.067	-53.50	0.0201	79.88	0.073	-55.12
0.0301	75.59	0.081	-73.40	0.0302	77.36	0.090	-75.41
0.0402	73.25	0.094	-90.68	0.0402	75.11	0.103	-92.64
0.0503	71.05	0.105	-105.85	0.0503	73.15	0.116	-109.69
0.0603	69.08	0.116	-120.99	0.0604	71.35	0.126	-123.74
			w_1 = 0.0100				
			Glycine + aq. β-CD				
		T = 293.15K				T = 298.15K	
0.0100	40.99	0.020	-3.94	0.0100	41.74	0.022	-6.51
0.0200	39.99	0.027	-17.30	0.0200	41.04	0.027	-22.18
0.0300	39.32	0.031	-27.01	0.0300	40.51	0.033	-33.56
0.0400	38.74	0.034	-36.35	0.0400	39.94	0.037	-43.04
0.0500	38.19	0.039	-44.06	0.0501	39.50	0.042	-51.84
0.0600	37.66	0.042	-51.27	0.0601	39.04	0.045	-59.45
		T = 303.15K				T = 308.15K	
0.0100	42.49	0.024	-6.83	0.0100	42.95	0.026	-7.39
0.0200	41.69	0.031	-21.05	0.0201	42.15	0.034	-24.62
0.0301	41.09	0.036	-33.15	0.0301	41.48	0.041	-36.58

0.0401	40.59	0.042	-43.01	0.0401	40.89	0.047	-47.18
0.0501	40.09	0.045	-51.42	0.0502	40.34	0.051	-55.88
0.0602	39.59	0.051	-59.75	0.0603	39.97	0.056	-64.06
Alanine + aq. β-CD							
T = 293.15K				T = 298.15K			
0.0100	53.98	0.029	-23.06	0.0100	55.05	0.030	-23.61
0.0200	51.48	0.040	-48.49	0.0200	52.55	0.042	-50.33
0.0300	49.32	0.048	-67.37	0.0300	50.72	0.052	-68.58
0.0400	47.24	0.055	-82.40	0.0400	49.05	0.060	-84.45
0.0500	45.80	0.061	-96.85	0.0501	47.65	0.068	-98.63
0.0600	44.33	0.068	-109.17	0.0601	46.39	0.075	-111.90
T = 303.15K				T = 308.15K			
0.0100	55.42	0.038	-24.15	0.0100	56.39	0.042	-24.91
0.0200	53.12	0.052	-48.33	0.0201	54.19	0.059	-52.38
0.0301	51.12	0.062	-67.25	0.0301	52.52	0.071	-72.48
0.0401	49.37	0.072	-83.65	0.0402	50.93	0.081	-87.84
0.0501	47.91	0.081	-97.98	0.0502	49.58	0.090	-103.23
0.0602	46.45	0.089	-111.90	0.0603	48.34	0.099	-116.91
Valine + aq. β-CD							

	T = 293.15K				T = 298.15K		
0.0100	79.99	0.044	-25.01	0.0100	81.09	0.048	-26.06
0.0200	75.49	0.061	-49.06	0.0200	77.09	0.067	-51.67
0.0300	72.33	0.074	-69.20	0.0300	73.76	0.080	-71.80
0.0400	69.26	0.087	-85.45	0.0401	71.09	0.093	-88.68
0.0501	66.61	0.097	-99.58	0.0501	68.70	0.103	-103.38
0.0601	64.35	0.106	-113.36	0.0602	66.43	0.114	-117.63
	T = 303.15K				T = 308.15K		
0.0100	81.69	0.050	-27.10	0.0100	82.30	0.055	-27.83
0.0200	77.69	0.069	-54.66	0.0201	78.79	0.075	-53.93
0.0301	74.52	0.084	-75.71	0.0301	75.62	0.092	-74.66
0.0401	71.94	0.099	-92.68	0.0402	73.03	0.108	-93.96
0.0502	69.39	0.111	-108.29	0.0503	70.68	0.120	-108.36
0.0603	67.10	0.121	-122.49	0.0604	68.61	0.132	-123.35

Table IX.4: Limiting apparent molal volumes (ϕ_V^0), experimental slopes (S_V^*), viscosity *A*, *B*-coefficients, limiting partial molal adiabatic compressibilities (ϕ_K^0), and experimental slopes (S_K^*) of amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15K to 308.15K respectively

Temp /K	$\phi_V^0 \cdot 10^6$ /$m^3 \cdot mol^{-1}$	$S_V^* \cdot 10^6$ /$m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$	*B* /$kg^{1/2} \cdot mol^{-1/2}$	*A* /$kg \cdot mol^{-1}$	$\phi_K^0 \cdot 10^{11}$ /$m^3 \cdot mol^{-1} \cdot Pa^{-1}$	$S_K^* \cdot 10^{11}$ /$m^3 \cdot mol^{-3/2} \cdot Pa^{-1} \cdot kg^{1/2}$
w_1 = 0.0050						
Glycine + aq. β-CD						
293.15	42.83±0.03	-18.89±0.01	0.143±0.009	0.0009±0.0003	27.37±0.02	-298.23±0.02
298.15	43.18±0.02	-10.65±0.03	0.156±0.006	0.0032±0.0000	28.66±0.03	-328.18±0.01
303.15	43.89±0.03	-7.34±0.02	0.172±0.008	0.0066±0.0000	29.08±0.03	-345.64±0.03
308.15	44.46±0.02	-2.27±0.02	0.203±0.006	0.0089±0.0000	29.77±0.02	-376.68±0.03
Alanine + aq. β-CD						
293.15	60.13±0.01	-61.91±0.02	0.253±0.010	-0.0006±0.0001	34.53±0.02	-471.39±0.02
298.15	60.64±0.02	-55.86±0.01	0.292±0.006	0.0004±0.0000	34.98±0.02	-502.96±0.03
303.15	61.05±0.03	-48.50±0.02	0.328±0.004	0.0054±0.0000	35.62±0.03	-535.66±0.03
308.15	61.33±0.03	-39.19±0.03	0.370±0.008	0.0045±0.0000	36.16±0.03	-551.45±0.02
Valine + aq. β-CD						

293.15	90.10±0.02	-100.77±0.02	0.417±0.006	-0.0051±0.0001	35.19±0.04	-588.13±0.03
298.15	90.46±0.03	-92.94±0.03	0.442±0.004	-0.0023±0.0000	36.01±0.02	-613.29±0.03
303.15	91.08±0.01	-86.84±0.02	0.470±0.009	0.0028±0.0000	37.00±0.03	-641.92±0.03
308.15	91.21±0.01	-76.22±0.03	0.506±0.008	0.0037±0.0000	37.64±0.02	-669.23±0.03
			$w_1 = 0.0075$			
			Glycine + aq. β-CD			
293.15	42.99±0.01	-19.17±0.03	0.147±0.006	0.0026±0.0000	28.03±0.02	-315.54±0.01
298.15	43.35±0.02	-12.74±0.01	0.161±0.002	0.0035±0.0000	29.05±0.02	-333.25±0.02
303.15	44.09±0.04	-8.34±0.02	0.181±0.001	0.0028±0.0000	29.63±0.02	-351.79±0.03
308.15	44.70±0.02	-6.13±0.02	0.201±0.004	0.0054±0.0000	30.32±0.02	-360.95±0.02
			Alanine + aq. β-CD			
293.15	60.35±0.03	-58.54±0.01	0.259±0.009	0.0008±0.0000	34.98±0.03	-527.74±0.01
298.15	60.88±0.03	-52.59±0.02	0.298±0.006	-0.0010±0.0000	35.46±0.04	-536.96±0.01
303.15	61.36±0.02	-47.37±0.03	0.332±0.006	-0.0012±0.0000	36.13±0.02	-555.68±0.02
308.15	61.76±0.02	-45.32±0.02	0.371±0.010	-0.0026±0.0000	36.72±0.01	-575.32±0.03
			Valine + aq. β-CD			
293.15	90.49±0.03	-100.99±0.04	0.420±0.004	-0.0014±0.0000	35.70±0.01	-596.16±0.02
298.15	90.94±0.03	-97.37±0.03	0.449±0.011	-0.0033±0.0000	36.57±0.02	-617.49±0.03

303.15	91.49±0.02	-91.12±0.03	0.472±0.004	-0.0003±0.0000	37.58±0.03	-642.03±0.03
308.15	91.61±0.02	-82.33±0.01	0.513±0.009	0.0001±0.0000	38.17±0.03	-656.92±0.02
			$w_1 = 0.0100$			
			Glycine + aq. β-CD			
293.15	43.23±0.01	-22.62±0.00	0.149±0.011	0.0049±0.0000	28.88±0.04	-326.19±0.02
298.15	43.65±0.02	-18.57±0.03	0.165±0.010	0.0045±0.0000	29.57±0.03	-363.63±0.01
303.15	44.49±0.01	-19.73±0.02	0.186±0.006	0.0047±0.0000	30.09±0.02	-364.95±0.02
308.15	45.06±0.02	-20.81±0.03	0.206±0.006	0.0050±0.0000	30.92±0.01	-388.23±0.01
			Alanine + aq. β-CD			
293.15	60.84±0.02	-67.28±0.02	0.261±0.009	0.0030±0.0000	35.62±0.03	-591.88±0.03
298.15	61.01±0.01	-59.65±0.03	0.310±0.009	-0.0016±0.0000	35.99±0.02	-602.90±0.03
303.15	61.76±0.01	-61.95±0.01	0.346±0.006	0.0030±0.0000	36.70±0.02	-602.56±0.02
308.15	62.02±0.03	-55.43±0.02	0.389±0.010	0.0031±0.0000	37.26±0.03	-627.84±0.03
			Valine + aq. β-CD			
293.15	90.80±0.02	-107.75±0.03	0.434±0.009	-0.0003±0.0000	36.34±0.03	-608.79±0.03
298.15	91.26±0.02	-100.91±0.01	0.451±0.010	0.0027±0.0000	37.09±0.01	-628.78±0.01
303.15	91.81±0.03	-100.05±0.02	0.494±0.006	-0.0002±0.0000	38.13±0.03	-654.09±0.04
308.15	92.00±0.03	-94.88±0.02	0.535±0.009	0.0001±0.0000	38.68±0.03	-657.81±0.01

Table IX.5: Contributions of zwitter ionic group (NH_3^+, COO^-), CH_2 group, and the other alkyl chains to the limiting apparent molar volume, ϕ_V^0, for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15 to 308.15K respectively

$\phi_V^0 \cdot 10^6$ /$m^3 \cdot mol^{-1}$									
	w_1 = 0.0000					w_1 = 0.005			
Temp/K	293.15	298.15	303.15	308.15	Temp/K	293.15	298.15	303.15	308.15
NH_3^+, COO^-	27.71	27.98	28.26	28.45	NH_3^+, COO^-	27.88	28.30	28.90	29.55
(CH)	7.60	7.61	7.62	7.62	(CH)	7.48	7.44	7.50	7.46
Gly (CH_2)	15.20	15.22	15.23	15.24	Gly (CH_2)	14.95	14.88	14.99	14.91
(CH_3)	22.80	22.83	22.85	22.86	(CH_3)	22.43	22.32	22.49	22.37
Ala (CH_3CH-)	32.53	32.51	32.49	32.56	Ala (CH_3CH-)	32.25	32.34	32.15	31.78
Val (CH_3CH_2CH-)	62.98	63.00	63.00	63.10	Val (CH_3CH_2CH-)	62.22	62.16	62.18	61.66
	w_1 = 0.0075					w_1 = 0.01			
Temp/K	293.15	298.15	303.15	308.15	Temp/K	293.15	298.15	303.15	308.15
NH_3^+, COO^-	27.95	28.35	29.24	29.80	NH_3^+, COO^-	28.29	28.56	29.50	30.10
(CH)	7.52	7.50	7.43	7.45	(CH)	7.47	7.55	7.50	7.48
Gly (CH_2)	15.04	15.00	14.85	14.90	Gly (CH_2)	14.94	15.09	14.99	14.96
(CH_3)	22.56	22.50	22.28	22.35	(CH_3)	22.41	22.64	22.49	22.44
Ala (CH_3CH-)	32.40	32.53	32.12	31.96	Ala (CH_3CH-)	32.55	32.45	32.26	31.92
Val (CH_3CH_2CH-)	62.54	62.59	61.88	61.81	Val (CH_3CH_2CH-)	62.51	62.70	62.31	61.90

Table IX.6: Values of ϕ_V^0(aqueous), $\Delta\phi_V^0$, ϕ_V^0(elect), ϕ_K^0(elect), and hydration number (n_H) for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15 to 308.15K respectively

	$\phi_V^0 \cdot 10^6$(aqueous)	$\Delta\phi_V^0 \cdot 10^6$	$\phi_V^0 \cdot 10^6$(elect)	$\phi_K^0 \cdot 10^{10}$(elect)	n_H	
	/m³·mol⁻¹	/m³·mol⁻¹	/m³·mol⁻¹	/m³·mol⁻¹·Pa⁻¹	From volume	From compressibility
Temp/K				w_1 = 0.005		
	Glycine					
293.15	42.91	-0.08	9.02	24.67	3.01	3.07
298.15	43.20	-0.02	8.67	25.96	2.89	3.23
303.15	43.49	0.40	7.96	26.38	2.65	3.28
308.15	43.69	0.77	7.39	27.07	2.46	3.36
	Alanine					
293.15	60.24	-0.11	11.62	31.83	3.87	3.95
298.15	60.49	0.15	11.10	32.28	3.70	4.01
303.15	60.75	0.30	10.69	32.92	3.56	4.09
308.15	61.01	0.32	10.42	33.46	3.47	4.16
	Valine					
293.15	90.69	-0.59	11.99	32.49	4.00	4.04

298.15	90.98	-0.52	11.63	33.31	3.88	4.14
303.15	91.26	-0.18	11.01	34.30	3.67	4.26
308.15	91.55	-0.34	10.88	34.94	3.63	4.34
Temp/K				$w_1 = 0.0075$		
	Glycine					
293.15	42.91	0.08	8.86	25.33	2.95	3.15
298.15	43.20	0.15	8.50	26.35	2.83	3.27
303.15	43.49	0.60	7.76	26.93	2.59	3.35
308.15	43.69	0.91	7.15	27.62	2.38	3.43
	Alanine					
293.15	60.24	0.11	11.40	32.28	3.80	4.01
298.15	60.49	0.39	10.87	32.76	3.62	4.07
303.15	60.75	0.61	10.39	33.43	3.46	4.15
308.15	61.01	0.75	9.99	34.02	3.33	4.23
	Valine					
293.15	90.69	-0.20	11.60	33.00	3.87	4.10
298.15	90.98	-0.04	11.15	33.87	3.72	4.21
303.15	91.26	-0.04	10.97	34.88	3.66	4.33

308.15	91.55	0.06	10.48	35.47	3.49	4.41
Temp/K			w_1 = 0.01			
				Glycine		
293.15	42.91	0.32	8.62	26.18	2.87	3.25
298.15	43.20	0.45	8.20	26.87	2.73	3.34
303.15	43.49	1.00	7.36	27.39	2.45	3.40
308.15	43.69	1.27	6.79	28.22	2.26	3.51
				Alanine		
293.15	60.24	0.60	10.91	32.92	3.64	4.09
298.15	60.49	0.52	10.74	33.29	3.58	4.14
303.15	60.75	1.01	9.99	34.00	3.33	4.22
308.15	61.01	1.01	9.73	34.56	3.24	4.29
				Valine		
293.15	90.69	0.11	11.29	33.64	3.76	4.18
298.15	90.98	0.28	10.83	34.39	3.61	4.27
303.15	91.26	0.55	10.28	35.43	3.43	4.40
308.15	91.55	0.45	10.09	35.98	3.36	4.47

Table IX.7. Contributions of zwitter ionic group (NH_3^+, COO^-), CH_2 group, and the other alkyl chains to the limiting apparent molar volume transfer $\Delta\phi_V^0$, in different mass fraction of aqueous β-CD (w_1) at 293.15 to 308.15K respectively

	$\Delta\phi_V^0 \cdot 10^6$ /$m^3 \cdot mol^{-1}$				$\Delta\phi_V^0(R) \cdot 10^6$ /$m^3 \cdot mol^{-1}$			
	w_1 = 0.005							
Temp/K	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
NH_3^+, COO^-	0.17	0.32	0.64	1.10	-	-	-	-
(CH)	-0.12	-0.17	-0.12	-0.16	-	-	-	-
Gly (CH_2)	-0.25	-0.34	-0.24	-0.33	-	-	-	-
(CH_3)	-0.37	-0.51	-0.36	-0.49	-	-	-	-
Ala (CH_3CH-)	-0.28	-0.17	-0.34	-0.78	17.30	17.46	17.16	16.87
Val (CH_3CH_2CH-)	-0.76	-0.84	-0.82	-1.44	47.27	47.28	47.19	46.75
	w_1 = 0.0075							
Temp/K	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
NH_3^+, COO^-	0.24	1.26	-0.31	1.53	-	-	-	-
(CH)	-0.08	-0.18	-0.10	-0.17	-	-	-	-
Gly (CH_2)	-0.16	-0.37	-0.19	-0.35	-	-	-	-
(CH_3)	-0.24	-0.55	-0.29	-0.52	-	-	-	-
Ala (CH_3CH-)	-0.13	-0.39	-0.09	-0.41	17.36	17.53	17.27	17.06

Val (CH_3CH_2CH-)	-0.44	-1.12	-0.46	-1.10	47.50	47.59	47.03	46.91
	w_1 = 0.01							
Temp/K	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
NH_3^+, COO^-	0.58	0.58	1.24	1.65	-	-	-	-
(CH)	-0.13	-0.06	-0.12	-0.14	-	-	-	-
Gly (CH_2)	-0.26	-0.13	-0.24	-0.28	-	-	-	-
(CH_3)	-0.39	-0.19	-0.36	-0.42	-	-	-	-
Ala (CH_3CH-)	0.02	-0.06	-0.23	-0.64	17.61	17.36	17.27	16.96
Val (CH_3CH_2CH-)	-0.47	-0.30	-0.69	-1.20	47.57	47.61	47.32	46.94

Table IX.8: Values of empirical coefficients (a_0, a_1, and a_2) of Equation IX.14 for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15K to 308.15K respectively

solvent mixture	$a_0 \cdot 10^6$ /$m^3 \cdot mol^{-1}$	$a_1 \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-1}$	$a_2 \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-2}$
	Glycine + aq. β-CD		
w_1 = 0.0050	208.71	-1.211	0.0022
w_1 = 0.0075	234.38	-1.386	0.0025
w_1 = 0.0100	141.58	-0.775	0.0015
	Alanine + aq. β-CD		
w_1 = 0.0050	-171.15	1.463	-0.0023
w_1 = 0.0075	-84.70	0.876	-0.0013
w_1 = 0.0100	116.93	-0.455	0.0009
	Valine + aq. β-CD		
w_1 = 0.0050	-140.86	1.462	-0.0023
w_1 = 0.0075	105.90	-0.170	0.0004
w_1 = 0.0100	-177.46	1.707	-0.0027

Table IX.9. Limiting apparent molal expansibilities (ϕ_E^{θ}) for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15K to 308.15K respectively

Solvent mixture	$\phi_E^0 \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-1}$				$\left(\partial\phi_E^0/\partial T\right)_P \cdot 10^6$ /$m^3 \cdot mol^{-1} \cdot K^{-2}$
	Glycine + aq. β-CD				
T/K	293.15	298.15	303.15	308.15	
w_1 = 0.0050	0.079	0.101	0.123	0.145	0.004
w_1 = 0.0075	0.080	0.105	0.130	0.155	0.005
w_1 = 0.0100	0.104	0.119	0.134	0.149	0.003

Alanine + aq. β-CD					
T/K	293.15	298.15	303.15	308.15	
w_1 = 0.0050	0.115	0.092	0.069	0.046	-0.005
w_1 = 0.0075	0.114	0.101	0.088	0.075	-0.003
w_1 = 0.0100	0.072	0.081	0.090	0.099	-0.002
Valine + aq. β-CD					
T/K	293.15	298.15	303.15	308.15	
w_1 = 0.0050	0.114	0.091	0.068	0.045	-0.005
w_1 = 0.0075	0.065	0.069	0.073	0.077	-0.001
w_1 = 0.0100	0.124	0.097	0.070	0.043	-0.005

Table IX.10: Contributions of zwitter ionic group (NH_3^+, COO^-), CH_2 group, and the other alkyl chains to the *B*-coefficient in different mass fraction of aqueous β-CD (w_1) at 293.15 to 308.15K respectively

	B /kg$^{1/2}$·mol$^{-1/2}$				B(R) /kg$^{1/2}$·mol$^{-1/2}$			
				w_1 = 0.005				
Temp/K	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
NH_3^+, COO^-	0.317	0.395	0.477	0.575	-	-	-	-
(CH)	0.102	0.110	0.119	0.121	-	-	-	-
Gly (CH_2)	0.205	0.221	0.237	0.242	-	-	-	-
(CH_3)	0.307	0.331	0.356	0.362	-	-	-	-
Ala (CH_3CH-)	0.476	0.507	0.536	0.563	0.272	0.286	0.299	0.321
Val (CH_3CH_2CH-)	0.886	0.948	1.011	1.048	0.681	0.728	0.774	0.806
				w_1 = 0.0075				
Temp/K	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
NH_3^+, COO^-	0.386	0.480	0.548	0.650	-	-	-	-
(CH)	0.091	0.094	0.105	0.109	-	-	-	-
Gly (CH_2)	0.181	0.188	0.210	0.219	-	-	-	-
(CH_3)	0.272	0.283	0.316	0.328	-	-	-	-

Ala (CH_3CH-)	0.480	0.491	0.523	0.554	0.299	0.302	0.313	0.335
Val (CH_3CH_2CH-)	0.844	0.870	0.945	0.994	0.663	0.682	0.735	0.775
				$w_1 = 0.01$				
Temp/K	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
NH_3^+, COO^-	0.426	0.552	0.651	0.727	-	-	-	-
(CH)	0.099	0.097	0.093	0.100	-	-	-	-
Gly (CH_2)	0.198	0.194	0.185	0.199	-	-	-	-
(CH_3)	0.296	0.290	0.278	0.299	-	-	-	-
Ala (CH_3CH-)	0.504	0.484	0.503	0.524	0.306	0.291	0.317	0.324
Val (CH_3CH_2CH-)	0.900	0.872	0.875	0.924	0.702	0.678	0.690	0.724

Table IX.11: Values of $\frac{dB}{dT}$, A_1, and A_2 coefficient for the amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15 to 308.15K respectively

solvent mixture	$\frac{dB}{dT}$	A_1	A_2
	Glycine + aq. β-CD		
$w_1 = 0.0050$	0.003	-1.352	0.034
$w_1 = 0.0075$	0.003	-5.446	0.094
$w_1 = 0.0100$	0.003	-5.884	0.069
	Alanine + aq. β-CD		
$w_1 = 0.0050$	0.007	-1.176	0.030
$w_1 = 0.0075$	0.007	-4.464	0.078
$w_1 = 0.0100$	0.008	-7.210	0.084
	Valine + aq. β-CD		
$w_1 = 0.0050$	0.005	-1.149	0.030
$w_1 = 0.0075$	0.006	-5.246	0.090
$w_1 = 0.0100$	0.006	-6.802	0.079

Table IX.12: Values of ϕ_1^0, ϕ_V^0(aqueous), $\mu^{0\#}$, $T\Delta S^{\#}$, $\Delta H^{\#}$, for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15 to 308.15K respectively

Parameters	$\phi_1^0 \cdot 10^6$ /m^3·mol^{-1}	$\Delta\mu_1^{0\#}$ /kJ·mol^{-1}	$\Delta\mu_2^{0\#}$ /kJ·mol^{-1}	$\Delta\mu^{0\#}$ /kJ·mol^{-1}	$T\Delta S^{\#}$ /kJ·mol^{-1}	$\Delta H^{\#}$ /kJ·mol^{-1}
			w_1= 0.005			
Temp/K			Glycine			
293.15	18.016	62.97	62.98	62.97	-14.66	48.31
298.15	18.039	62.70	62.72	62.70	-14.91	47.79
303.15	18.062	62.45	62.45	62.45	-15.16	47.29
308.15	18.084	62.21	62.20	62.21	-15.41	46.80
Temp/K			Alanine			
293.15	18.016	63.81	63.82	63.81	-15.24	48.57
298.15	18.039	63.54	63.53	63.53	-15.50	48.03
303.15	18.062	63.28	63.27	63.28	-15.76	47.51
308.15	18.084	63.03	63.03	63.03	-16.02	47.01
Temp/K			Valine			
293.15	18.016	64.83	64.83	64.83	-15.24	49.58
298.15	18.039	64.55	64.55	64.55	-15.50	49.04
303.15	18.062	64.28	64.29	64.28	-15.76	48.52
308.15	18.084	64.04	64.04	64.04	-16.02	48.01
			w_1= 0.0075			
Temp/K			Glycine			
293.15	18.016	62.98	62.98	62.98	-14.66	48.32
298.15	18.039	62.71	62.71	62.71	-14.91	47.80
303.15	18.062	62.45	62.45	62.45	-15.16	47.30
308.15	18.084	62.22	62.22	62.22	-15.41	46.81
Temp/K			Alanine			
293.15	18.016	63.82	63.82	63.82	-14.95	48.87
298.15	18.039	63.54	63.54	63.54	-15.21	48.34
303.15	18.062	63.28	63.28	63.28	-15.46	47.82

308.15	18.084	63.04	63.04	63.04	-15.72	47.33
Temp/K			Valine			
293.15	18.016	64.83	64.83	64.83	-14.95	49.88
298.15	18.039	64.55	64.52	64.52	-15.21	49.32
303.15	18.062	64.29	64.26	64.26	-15.46	48.80
308.15	18.084	64.05	64.07	64.07	-15.72	48.35
			w_1= 0.01			
Temp/K			Glycine			
293.15	18.016	62.98	62.98	62.98	-14.66	48.33
298.15	18.039	62.71	62.71	62.71	-14.91	47.81
303.15	18.062	62.46	62.46	62.46	-15.16	47.30
308.15	18.084	62.22	62.22	62.22	-15.41	46.82
Temp/K			Alanine			
293.15	18.016	63.82	63.82	63.82	-14.95	48.87
298.15	18.039	63.55	63.55	63.55	-15.21	48.34
303.15	18.062	63.29	63.29	63.29	-15.46	47.83
308.15	18.084	63.05	63.05	63.05	-15.72	47.33
Temp/K			Valine			
293.15	18.016	64.84	64.85	64.85	-14.95	49.90
298.15	18.039	64.56	64.56	64.56	-15.21	49.36
303.15	18.062	64.30	64.30	64.30	-15.46	48.84
308.15	18.084	64.05	64.06	64.06	-15.72	48.34

FIGURES

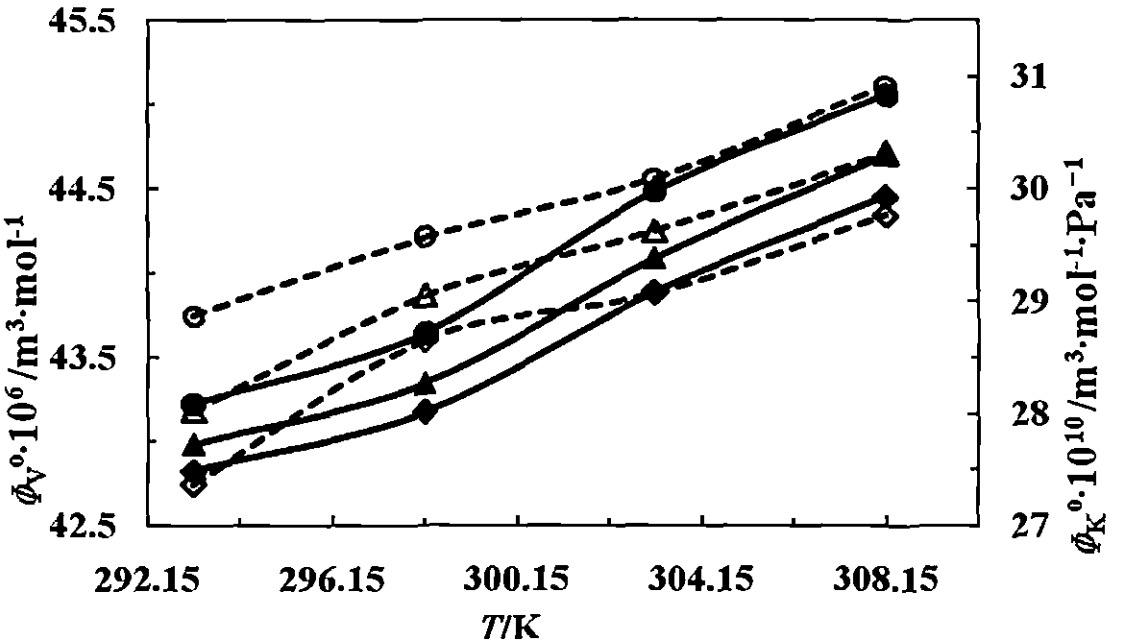


Figure IX.1: Plot of limiting apparent molar volume (ϕ_V^0) for glycine (♦), alanine (▲), valine (●), and limiting molar isentropic compressibility (ϕ_K^0) for glycine (◊), alanine (Δ), valine (○), against studied temp (*T*) in w_1=0.005 mass fraction of aq. β-CD.

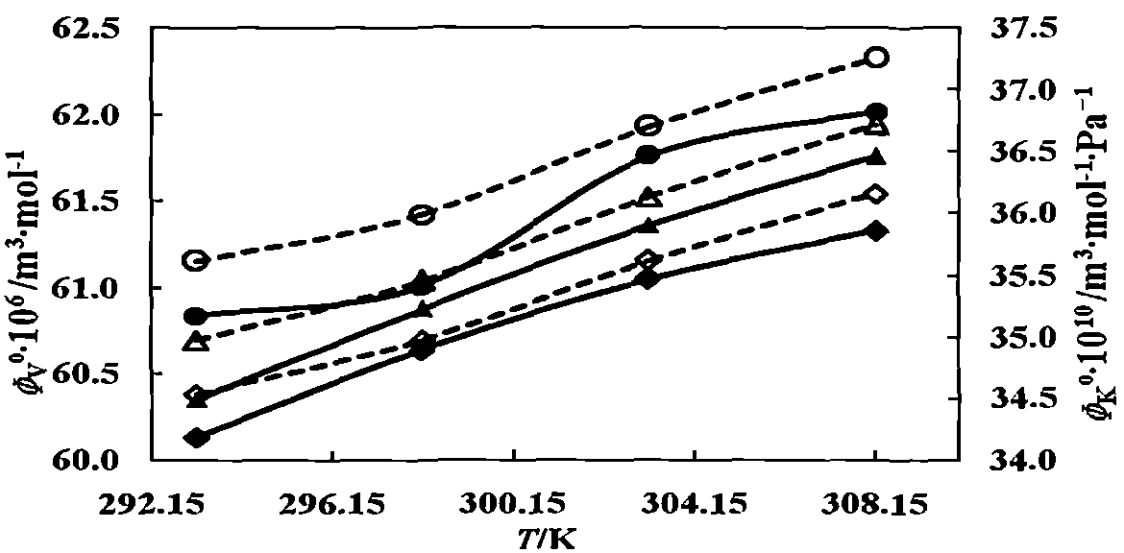


Figure IX.2: Plot of limiting apparent molar volume (ϕ_V^0) for glycine (♦), alanine (▲), valine (●), and limiting molar isentropic compressibility (ϕ_K^0) for glycine (◊), alanine (Δ), valine (○), against studied temp (*T*) in w_1=0.0075 mass fraction of aq. β-CD.

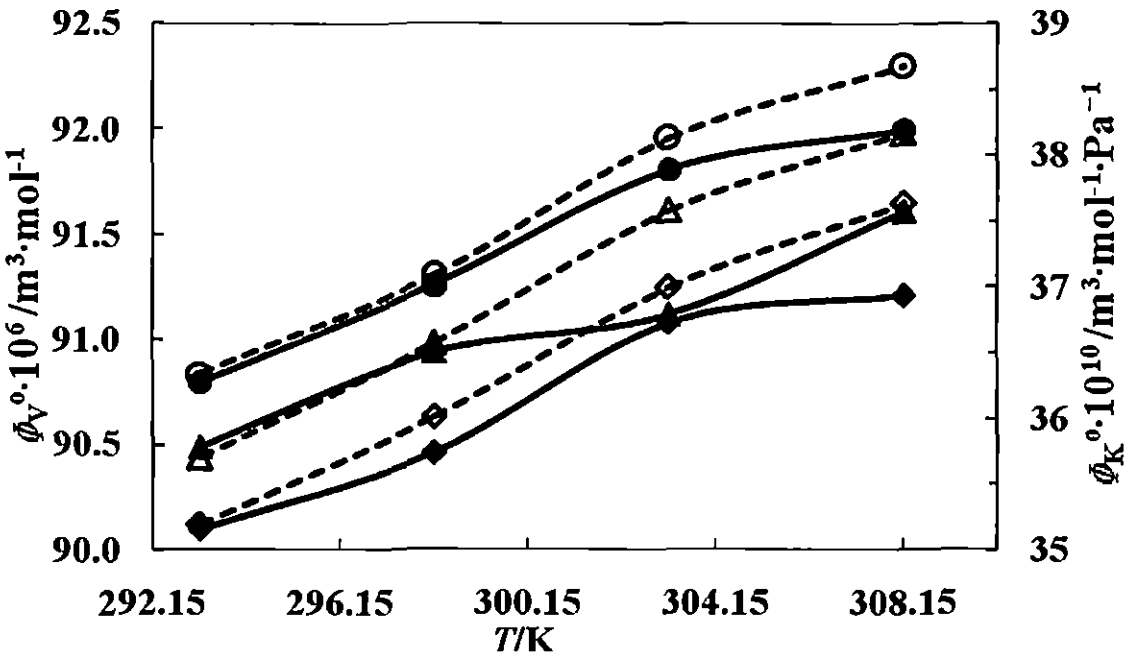


Figure IX.3: Plot of limiting apparent molar volume (ϕ_V^o) for glycine (♦), alanine (▲), valine (●), and limiting molar isentropic compressibility (ϕ_K^o) for glycine (◊), alanine (Δ), valine (○), against studied temp (T) in w_1=0.01 mass fraction of aq. β-CD.

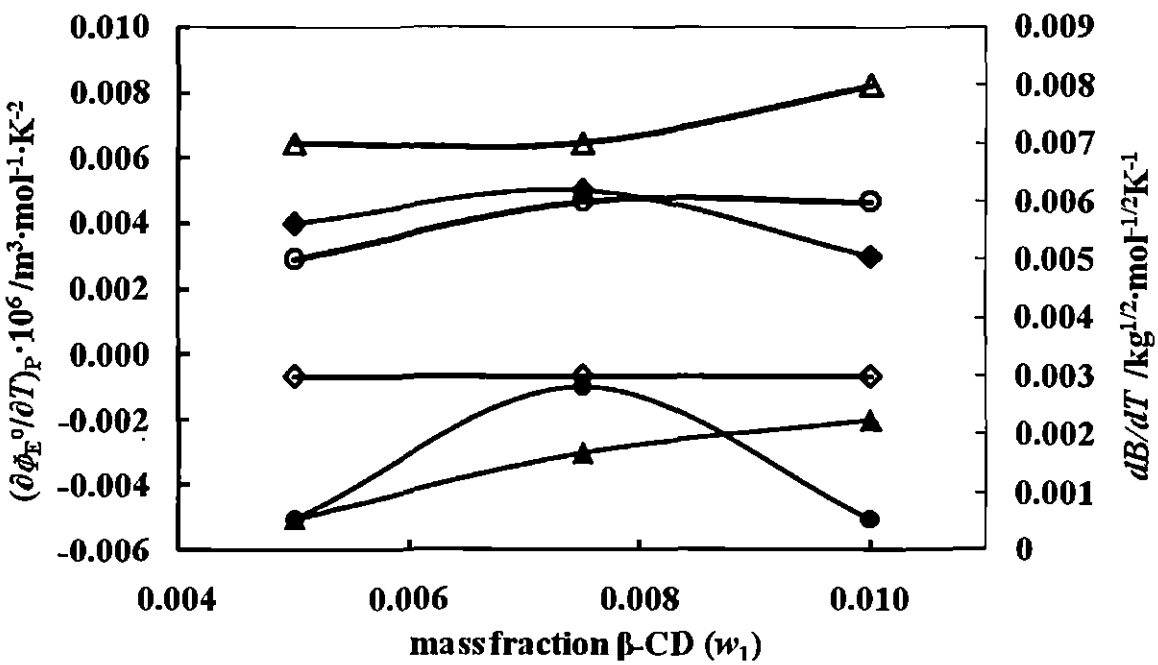
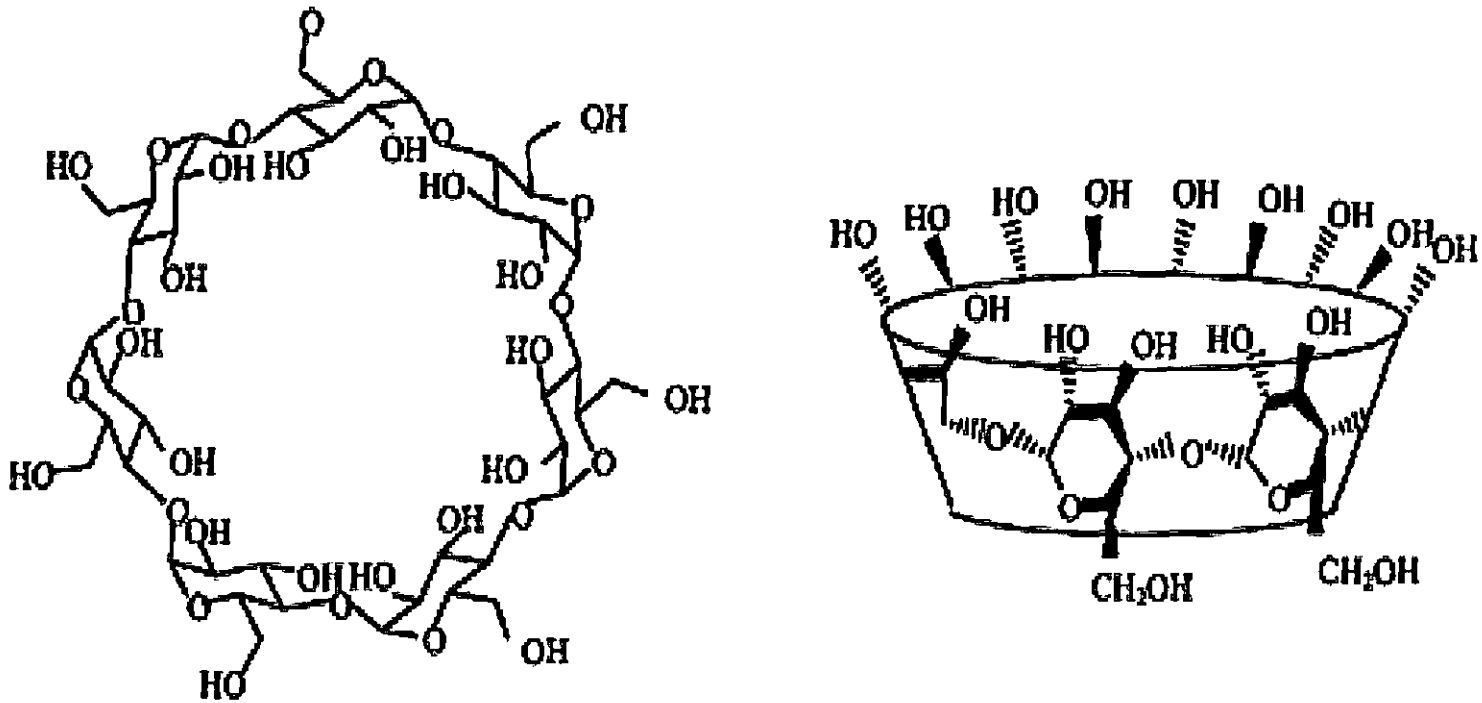


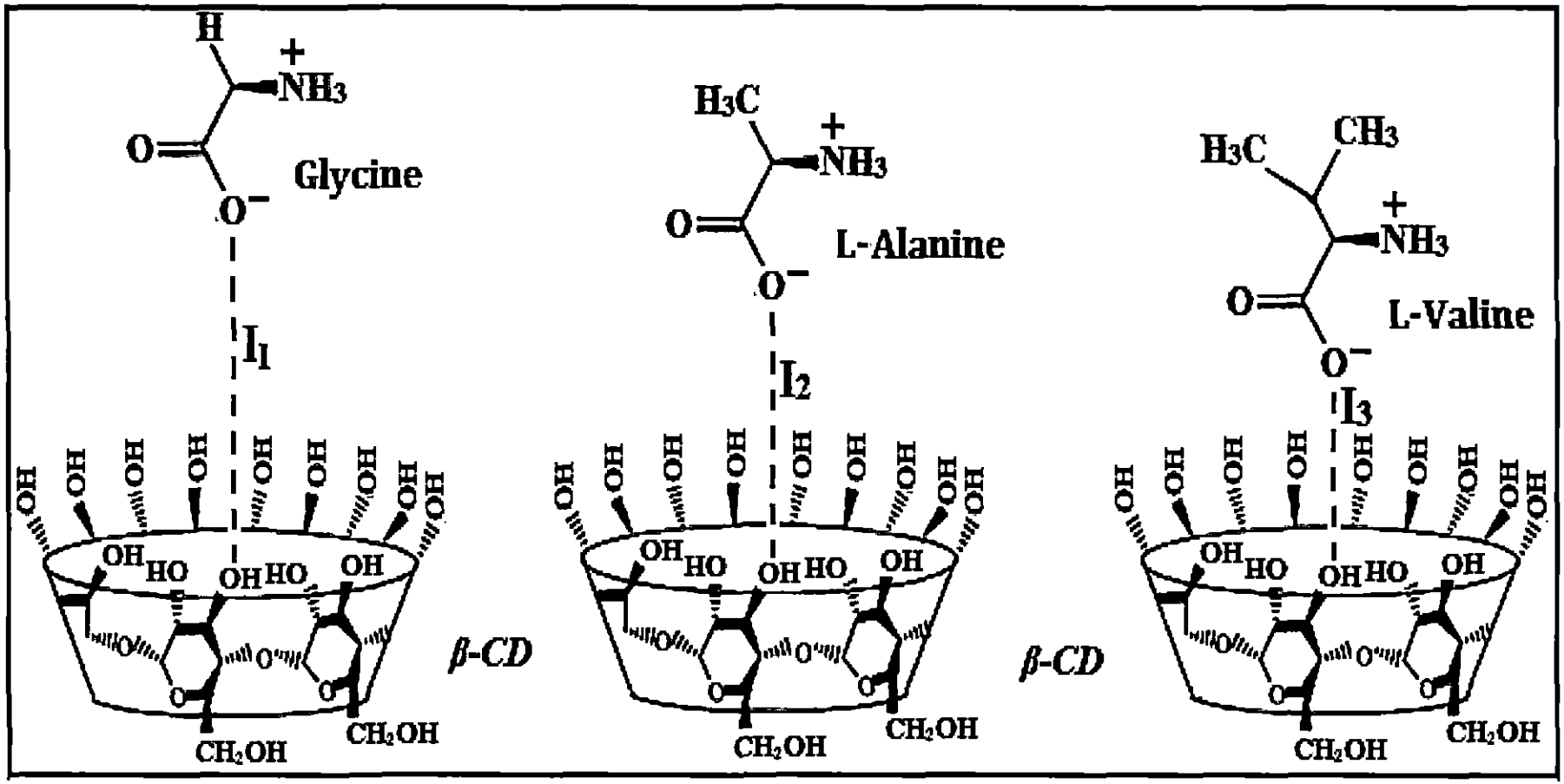
Figure IX.4: Plot of $\left(\partial\phi_E^0/\partial T\right)_P$ for glycine (♦), alanine (▲), valine (●), and dB/dT for glycine (◊), alanine (Δ), valine (○), against studied temp (T) in w_1=0.01 mass fraction of aq. β-CD.

SCHEMES

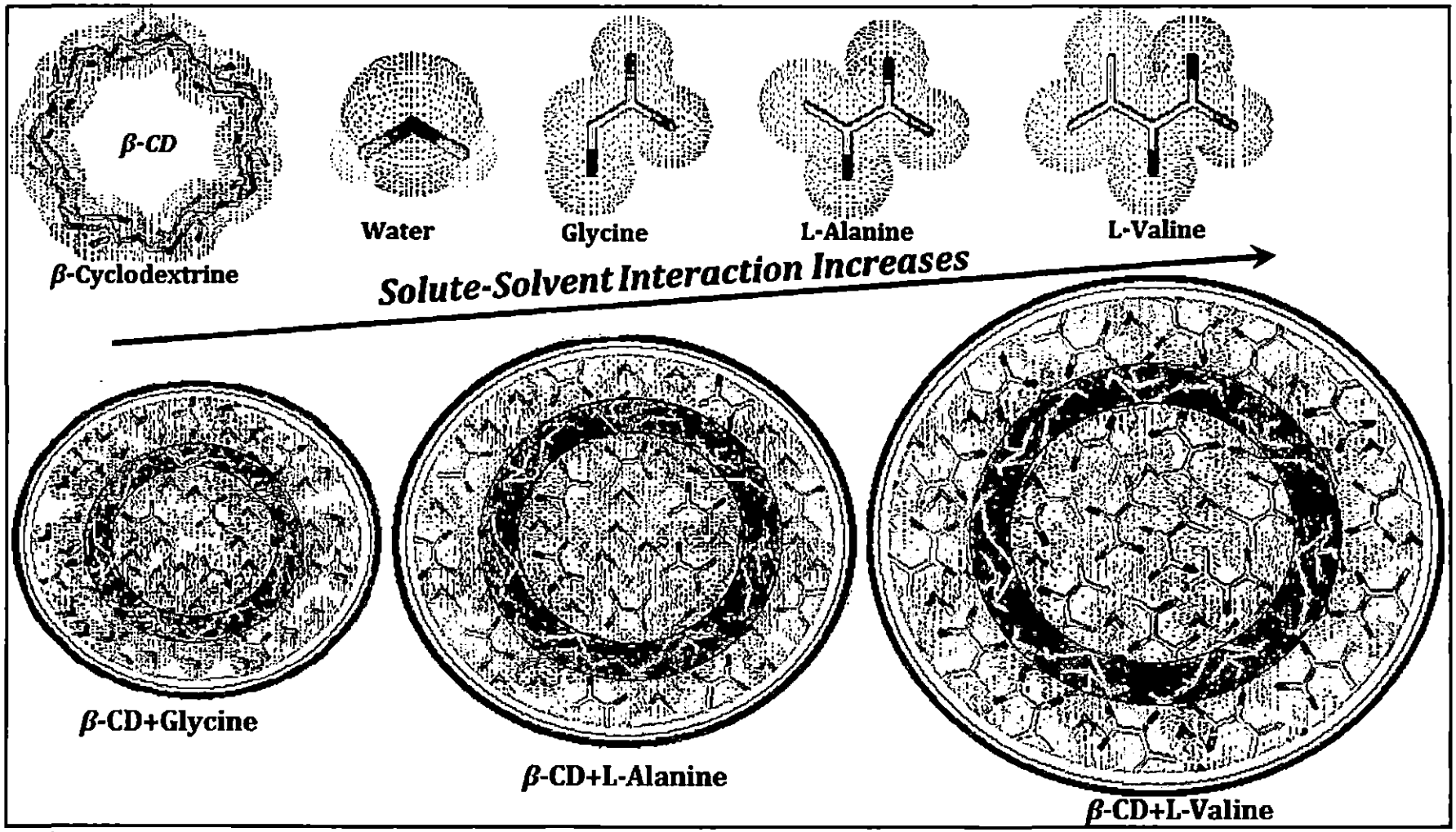


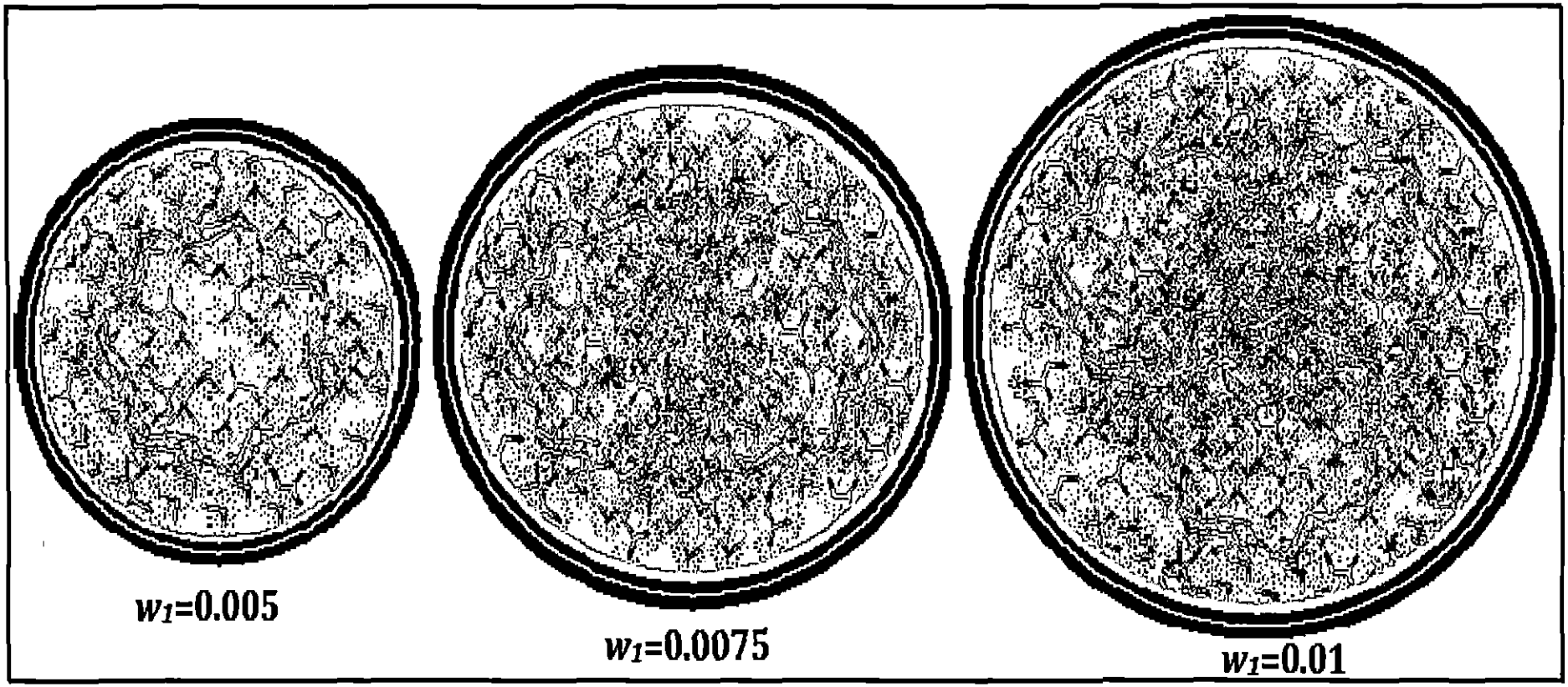
Top view **Side view**

Scheme IX.1: The molecular structure of β-CD.



Scheme IX.2: A plausible mechanism of interaction between β-CD and different amino acids as evident from the experimental observation


β-CD
β-Cyclodextrine
Water
Glycine
L-Alanine
L-Valine
Solute-Solvent Interaction Increases
β-CD+Glycine
β-CD+L-Alanine
β-CD+L-Valine



Scheme IX.3: The schematic representation of solute-solvent interaction, for the studied amino acids in aqueous β-cyclodextrine binary mixtures, in view of various derived parameters; where w_1 is the mass fraction of β-CD in aqueous solution.