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ORIGINAL ARTICLE

Molecular interactions of α-amino acids insight into aqueous β-cyclodextrin systems

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Abstract 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), and 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^0), viscosity B-coefficient and limiting apparent molar adiabatic compressibility (ϕ_K^0). 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 has been determined for the amino acids. The trends in transfer volumes, $\Delta\phi_V^0$, have been interpreted in terms of solute–cosolute interactions based on 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.

Keywords Molecular interaction · Amino acids · β-Cyclodextrin · Hydration number · Thermophysical properties

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Introduction

Cyclodextrin molecules (CD) are cyclic oligosaccharides that 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 (Li and Purdy 1992), 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) (Rafatia et al. 2005) 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, they are slightly polar having a clear affinity to encapsulate hydrophobic moiety in a largely hydrophobic internal cavity, which make the hydrophobic interaction between apolar moieties of host and guest molecules, that play an important role in the formation of inclusion complexes (Szejtli 1996; Disouza and Lipkowitz 1998) with a wide variety of molecular species (Thoma and Steward 1965) in different aqueous and non-aqueous solvent media (Ribeiro et al. 2006). 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 (Clarke et al. 1988). 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 (Szejtli 1982;

Van Etten et al. 1967a, b). The molecular structure of β-CD is shown in Scheme 1.

The stabilization of native conformations of biological macromolecules is commonly related to several non-covalent interactions including hydrogen bonding, electrostatic, and hydrophobic interactions (Kumar and Venkatesu 2012). These interactions are affected by the surrounding solutes and solvent molecules; for this reason, the physico-chemical behaviours 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 (Hippel and Schleich 1969; Jencks 1969). 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 (Enea and Jolicoeur 1982) and the hydrophobic interactions of non-polar side chains (Kauzmann 1959).

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 308.15 K, as literature survey reveals that very scarce work has been carried out in the present ternary systems.

Experimental section

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 were used as purchased. The mass fraction purity of salts was ≥0.99. The salts were dried from moisture at 373 K for 48 h, and then they were cooled and stored in a desiccator prior to use.

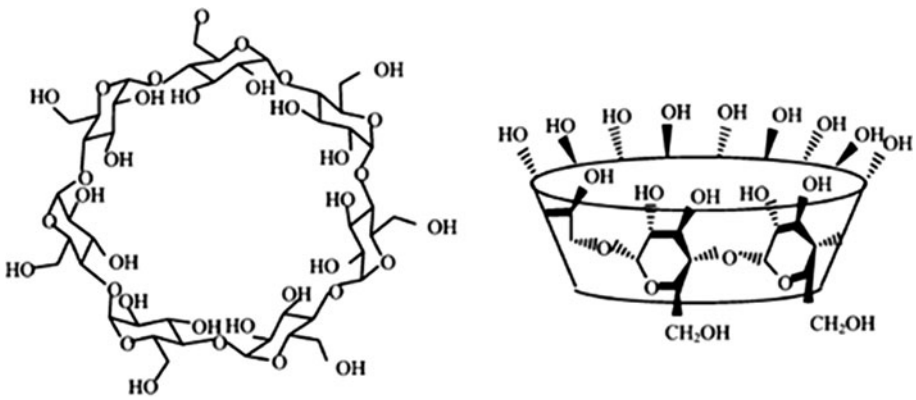
Apparatus and procedure

Aqueous binary solution of β-cyclodexrtin (β-CD) was prepared by mass (Mettler Toledo AG-285 with uncertainty ±0.0003 g), 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 4500 M) with a precision of ±0.00005 g cm^{-3} maintained at ±0.01 K 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 ±0.01 K of the desired temperature. After attaining thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to ±0.1 s. At least three repetitions of each data reproducible to ±0.1 s were taken to average the flow times.

Scheme 1 The molecular structure of β-CD



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 (Roy et al. 2012).

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. (1929) and Kiyohara et al. (1974). The obtained speeds were corrected for diffraction errors as given by Murthy and Subrahmanyam (1977). The uncertainty in the speed is ±0.2 m s^{-1}. The temperature was controlled within ±0.01 K using a Lauda thermostat during the measurement.

Results and discussion

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, and 308.15 K are reported in Table 1. The measured experimental values of densities, viscosities, and 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 293.15–308.15 K as a function of concentration (molality) are listed in Table 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, the apparent molar volumes ϕ_V were determined from the solutions densities using the following equation and the values are given in Table 3.

$$\phi_V = M/\rho - 1,000\,(\rho - \rho_0)/m\rho\rho_0 \quad (1)$$

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 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 (1929).

$$\phi_V = \phi_V^0 + S_V^*\sqrt{m} \quad (2)$$

where $\phi_V^0 (= \bar{V}_2^0)$ 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. 3. The standard deviations (σ) were determined using the following equation:

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

where N is the number of data points. The values of ϕ_V^0 and S_V^* are reported in Table 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 (Millero 1971; Marcus and Hefter 2004). The ϕ_V^0 data are often embedded with important information of solute hydrophobicity, hydration properties, and solute–solvent interactions (Marcus 1993; Millero 1972) occurred in aqueous β-CD.

A perusal of Table 4 and Figs. 1, 2, and 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 (Belibagli and

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

Mass fraction of aq. β-CD (w_1)	Temp (K)	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		u (m s^{-1})	
		Expt	Lit	Expt	Lit	Expt	Lit
0.005	293.15	0.99999	–	1.003	–	1,484.4	–
	298.15	0.99873	–	0.893	–	1,499.5	–
	303.15	0.99747	–	0.801	–	1,508.7	–
	308.15	0.99622	–	0.723	–	1,517.2	–
0.0075	293.15	1.00120	–	1.005	–	1,485.0	–
	298.15	0.99987	–	0.895	–	1,500.3	–
	303.15	0.99854	–	0.803	–	1,509.8	–
	308.15	0.99721	–	0.725	–	1,518.6	–
0.01	293.15	1.00206	–	1.007	–	1,485.6	–
	298.15	1.00078	–	0.897	–	1,501.3	–
	303.15	0.99949	–	0.805	–	1,510.9	–
	308.15	0.99822	–	0.727	–	1,519.8	–

Table 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 293.15–308.15 K respectively

m (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})	m (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})
$w_1 = 0.005$							
Glycine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00033	1.005	1,484.9	0.0100	0.99906	0.895	1,500.8
0.0200	1.00069	1.006	1,489.1	0.0200	0.99940	0.896	1,506.0
0.0300	1.00106	1.008	1,496.8	0.0301	0.99974	0.898	1,514.7
0.0401	1.00143	1.009	1,506.2	0.0401	1.00009	0.899	1,525.6
0.0501	1.00181	1.011	1,518.0	0.0502	1.00045	0.901	1,539.8
0.0601	1.00220	1.012	1,531.4	0.0602	1.00080	0.902	1,555.9
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99779	0.803	1,512.3	0.0100	0.99653	0.725	1,522.2
0.0201	0.99812	0.804	1,517.9	0.0201	0.99684	0.727	1,529.1
0.0301	0.99845	0.806	1,527.8	0.0302	0.99716	0.728	1,540.0
0.0402	0.99878	0.807	1,540.0	0.0402	0.99747	0.730	1,553.8
0.0502	0.99912	0.809	1,555.0	0.0503	0.99778	0.731	1,571.8
0.0603	0.99946	0.810	1,573.1	0.0604	0.99810	0.733	1,592.4
Alanine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00034	1.006	1,485.1	0.0100	0.99907	0.896	1,502.8
0.0200	1.00075	1.008	1,493.5	0.0200	0.99946	0.898	1,512.5
0.0300	1.00118	1.011	1,506.5	0.0301	0.99988	0.901	1,527.4
0.0401	1.00164	1.013	1,523.6	0.0401	1.00032	0.903	1,546.5
0.0501	1.00213	1.016	1,544.5	0.0502	1.00078	0.906	1,570.1
0.0602	1.00264	1.019	1,570.0	0.0602	1.00126	0.909	1,599.8
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99780	0.804	1,514.4	0.0100	0.99654	0.726	1,524.2
0.0201	0.99817	0.807	1,525.5	0.0201	0.99689	0.728	1,536.1
0.0301	0.99857	0.809	1,542.4	0.0302	0.99726	0.731	1,553.2
0.0402	0.99899	0.812	1,564.0	0.0402	0.99765	0.734	1,576.1
0.0503	0.99942	0.815	1,590.2	0.0503	0.99806	0.737	1,604.2
0.0603	0.99987	0.818	1,621.3	0.0604	0.99848	0.740	1,639.1
Valine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00036	1.007	1,487.1	0.0100	0.99909	0.897	1,504.7
0.0200	1.00082	1.011	1,499.0	0.0201	0.99953	0.900	1,517.7
0.0301	1.00133	1.015	1,517.1	0.0301	1.00002	0.904	1,537.8
0.0401	1.00187	1.019	1,541.1	0.0402	1.00055	0.908	1,563.1
0.0502	1.00247	1.023	1,569.3	0.0502	1.00111	0.912	1,595.2
0.0602	1.00310	1.027	1,604.0	0.0603	1.00170	0.916	1,632.7
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99782	0.805	1,516.3	0.0100	0.99656	0.727	1,526.1
0.0201	0.99824	0.809	1,530.8	0.0201	0.99696	0.730	1,542.0
0.0301	0.99871	0.812	1,551.8	0.0302	0.99740	0.734	1,564.8
0.0402	0.99922	0.816	1,579.4	0.0403	0.99788	0.738	1,594.9
0.0503	0.99976	0.820	1,613.8	0.0504	0.99839	0.742	1,631.8
0.0604	1.00032	0.824	1,656.5	0.0605	0.99892	0.745	1,676.0
$w_1 = 0.0075$							
Glycine + aq. β-CD							

Table 2 continued

m (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})	m (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00154	1.006	1,485.6	0.0100	1.00020	0.896	1,500.8
0.0200	1.00189	1.008	1,490.7	0.0200	1.00054	0.898	1,506.0
0.0300	1.00226	1.009	1,498.3	0.0300	1.00089	0.900	1,514.7
0.0400	1.00264	1.011	1,508.7	0.0401	1.00124	0.901	1,526.3
0.0500	1.00302	1.013	1,521.0	0.0501	1.00160	0.902	1,540.2
0.0601	1.00341	1.014	1,536.5	0.0602	1.00196	0.904	1,557.0
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99886	0.805	1,512.5	0.0100	0.99752	0.727	1,522.5
0.0200	0.99918	0.807	1,518.7	0.0201	0.99784	0.729	1,528.7
0.0301	0.99951	0.808	1,528.1	0.0301	0.99816	0.730	1,538.7
0.0401	0.99985	0.810	1,540.9	0.0402	0.99848	0.732	1,551.9
0.0502	1.00019	0.811	1,556.2	0.0502	0.99880	0.734	1,568.6
0.0602	1.00053	0.813	1,574.3	0.0603	0.99913	0.735	1,587.7
Alanine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00155	1.007	1,485.7	0.0100	1.00021	0.897	1,503.3
0.0200	1.00194	1.010	1,495.8	0.0200	1.00058	0.900	1,513.9
0.0300	1.00236	1.013	1,510.9	0.0301	1.00099	0.902	1,529.9
0.0400	1.00281	1.015	1,530.8	0.0401	1.00142	0.905	1,551.6
0.0501	1.00329	1.018	1,555.2	0.0501	1.00187	0.908	1,577.7
0.0601	1.00379	1.020	1,586.7	0.0602	1.00234	0.910	1,609.3
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99887	0.806	1,515.2	0.0100	0.99753	0.728	1,525.2
0.0201	0.99923	0.809	1,526.1	0.0201	0.99789	0.731	1,537.6
0.0301	0.99962	0.811	1,544.2	0.0301	0.99827	0.733	1,555.7
0.0401	1.00003	0.814	1,566.8	0.0402	0.99867	0.736	1,580.8
0.0502	1.00046	0.817	1,594.5	0.0503	0.99909	0.739	1,610.4
0.0603	1.00091	0.819	1,628.7	0.0604	0.99953	0.741	1,645.9
Valine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00157	1.009	1,486.9	0.0100	1.00023	0.898	1,504.7
0.0200	1.00201	1.013	1,498.9	0.0200	1.00067	0.902	1,517.6
0.0300	1.00252	1.017	1,517.0	0.0301	1.00116	0.906	1,537.5
0.0401	1.00306	1.021	1,541.7	0.0401	1.00170	0.910	1,563.1
0.0501	1.00367	1.025	1,570.8	0.0502	1.00227	0.914	1,595.6
0.0602	1.00429	1.030	1,605.4	0.0602	1.00288	0.918	1,633.8
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99889	0.807	1,516.5	0.0100	0.99755	0.729	1,526.6
0.0201	0.99931	0.811	1,530.9	0.0201	0.99796	0.733	1,541.7
0.0301	0.99979	0.815	1,551.8	0.0302	0.99841	0.737	1,563.6
0.0402	1.00030	0.819	1,579.3	0.0402	0.99890	0.740	1,592.1
0.0503	1.00085	0.822	1,613.3	0.0503	0.99942	0.744	1,629.4
0.0603	1.00143	0.826	1,656.4	0.0604	0.99997	0.748	1,673.2
$w_1 = 0.01$							
Glycine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00240	1.009	1,486.3	0.0100	1.00111	0.899	1,501.4

Table 2 continued

m (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})	m (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})
0.0200	1.00276	1.010	1,491.4	0.0200	1.00146	0.901	1,507.9
0.0300	1.00313	1.012	1,499.2	0.0300	1.00182	0.902	1,517.7
0.0400	1.00351	1.013	1,510.2	0.0400	1.00218	0.904	1,530.4
0.0500	1.00390	1.015	1,523.3	0.0501	1.00256	0.906	1,546.3
0.0600	1.00430	1.017	1,539.0	0.0601	1.00294	0.907	1,564.7
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99982	0.807	1,513.1	0.0100	0.99854	0.728	1,523.1
0.0200	1.00016	0.808	1,519.3	0.0201	0.99888	0.730	1,530.6
0.0301	1.00051	0.810	1,529.5	0.0301	0.99923	0.732	1,541.6
0.0401	1.00087	0.811	1,542.7	0.0401	0.99959	0.733	1,556.3
0.0501	1.00124	0.813	1,558.6	0.0502	0.99996	0.735	1,573.7
0.0602	1.00162	0.815	1,578.2	0.0603	1.00033	0.737	1,594.6
Alanine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00241	1.010	1,486.4	0.0100	1.00112	0.900	1,504.4
0.0200	1.00281	1.012	1,498.8	0.0200	1.00151	0.903	1,517.8
0.0300	1.00325	1.015	1,516.9	0.0300	1.00193	0.905	1,536.6
0.0400	1.00373	1.018	1,539.7	0.0400	1.00238	0.908	1,561.2
0.0500	1.00422	1.020	1,568.8	0.0501	1.00285	0.911	1,591.7
0.0600	1.00474	1.023	1,602.9	0.0601	1.00334	0.914	1,629.0
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99983	0.808	1,516.2	0.0100	0.99855	0.730	1,526.3
0.0200	1.00021	0.811	1,529.1	0.0201	0.99892	0.733	1,540.8
0.0301	1.00063	0.813	1,548.3	0.0301	0.99932	0.736	1,561.9
0.0401	1.00108	0.816	1,573.6	0.0402	0.99975	0.738	1,588.1
0.0501	1.00155	0.819	1,604.8	0.0502	1.00020	0.741	1,622.2
0.0602	1.00205	0.822	1,643.7	0.0603	1.00067	0.744	1,663.3
Valine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
0.0100	1.00243	1.011	1,486.9	0.0100	1.00114	0.902	1,505.0
0.0200	1.00289	1.015	1,499.3	0.0200	1.00158	0.906	1,518.6
0.0300	1.00340	1.020	1,518.3	0.0300	1.00208	0.910	1,538.8
0.0400	1.00397	1.024	1,542.5	0.0401	1.00262	0.914	1,565.0
0.0501	1.00458	1.029	1,572.1	0.0501	1.00320	0.918	1,597.2
0.0601	1.00522	1.033	1,608.9	0.0602	1.00382	0.922	1,637.3
T = 303.15 K				*T = 308.15 K*			
0.0100	0.99985	0.809	1,516.9	0.0100	0.99857	0.731	1,527.0
0.0200	1.00028	0.813	1,531.7	0.0201	0.99899	0.734	1,541.7
0.0301	1.00077	0.816	1,553.5	0.0301	0.99947	0.738	1,563.6
0.0401	1.00130	0.821	1,581.3	0.0402	0.99999	0.742	1,593.6
0.0502	1.00188	0.825	1,616.3	0.0503	1.00055	0.746	1,628.4
0.0603	1.00250	0.829	1,658.9	0.0604	1.00114	0.750	1,673.1

Agranci 1990). 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. (2001). The behaviour of ϕ_V^0 for the present systems can be explained employing the co-sphere model, proposed by Friedman and Krishnan (1973) according to which the effect of overlap of hydration co-spheres is destructive. Mishra et al. (1983) using this model

Table 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 293.15–308.15 K respectively

m (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	$(\eta_r - 1)/\sqrt{m}$ (kg$^{1/2}$ mol$^{-1/2}$)	$\phi_K \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})	m (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	$(\eta_r - 1)/\sqrt{m}$ (kg$^{1/2}$ mol$^{-1/2}$)	$\phi_K \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})
$w_1 = 0.005$							
Glycine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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
$w_1 = 0.0075$							

Table 3 continued

m (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	$(\eta_r - 1)/\sqrt{m}$ (kg$^{1/2}$ mol$^{-1/2}$)	$\phi_K \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})	m (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	$(\eta_r - 1)/\sqrt{m}$ (kg$^{1/2}$ mol$^{-1/2}$)	$\phi_K \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})
Glycine + aq. β-CD							
T = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			

Table 3 continued

m (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	$(\eta_r - 1)/\sqrt{m}$ (kg$^{1/2}$ mol$^{-1/2}$)	$\phi_K \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})	m (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	$(\eta_r - 1)/\sqrt{m}$ (kg$^{1/2}$ mol$^{-1/2}$)	$\phi_K \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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 = 293.15 K				*T = 298.15 K*			
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 = 303.15 K				*T = 308.15 K*			
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

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 4) are due to the effect of ion–hydrophilic interactions (between zwitterionic

Table 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 293.15–308.15 K respectively

Temp /K	$\phi_V^0 \times 10^6$ (m^3 mol^{-1})	$S_V^* \times 10^6$ (m^3 $mol^{-3/2}$ $kg^{1/2}$)	B ($kg^{1/2}$ $mol^{-1/2}$)	A ($kg^{1/2}$ $mol^{-1/2}$)	$\phi_K^0 \times 10^{11}$ (m^3 mol^{-1} Pa^{-1})	$S_K^* \times 10^{11}$ (m^3 mol^{-1} Pa^{-1} $kg^{1/2}$)
$w_1 = 0.0050$						
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

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 2.

The values of ϕ_V^0 and S_V^* for the amino acids in pure water are adopted from the literature (Millero et al. 1978; Xu et al. 2006). The parameter S_V^* is the volumetric virial coefficient, and it characterizes the pair-wise interaction of solute species in solution (Wadi and Ramasami 1997; Banipal et al. 2004). 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 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 slightly 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.

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 (Millero et al. 1978; Xu et al. 2006) and this linear variation can be represented as follows:

$$\phi_V^0 = \phi_V^0(NH_3^+, COO^-) + n_c\phi_V^0(CH_2) \quad (4)$$

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 5, where those values in pure water are also provided from the literature (Banerjee and Kishore 2005) It is well described in the literature (Banerjee and Kishore 2005) 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.

$$\phi_V^0(CH) = 0.5\,\phi_V^0(CH_2) \quad (5)$$

$$\phi_V^0(CH_3) = 1.5\,\phi_V^0(CH_2) \quad (6)$$

and are listed in Table 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 (Wang et al. 2004) for some α-amino acids in aqueous sodium caprylate solutions.

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

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

The results are illustrated in Table 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 (Belibagli and Agranci 1990). This agreement among the amino acids can be explained by the co-sphere model, as developed by Friedman and Krishnan (1973) 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), 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

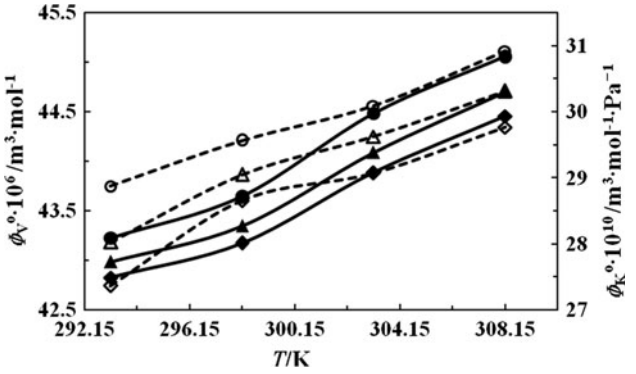


Fig. 1 Plot of limiting apparent molar volume (ϕ_V^0) for glycine (*filled diamond*), alanine (*filled triangle*), valine (*filled circle*), and limiting molar isentropic compressibility (ϕ_K^0) for glycine (*open diamond*), alanine (*open triangle*), valine (*open circle*), against studied temp (T) in $w_1 = 0.005$ mass fraction of aq. β-CD

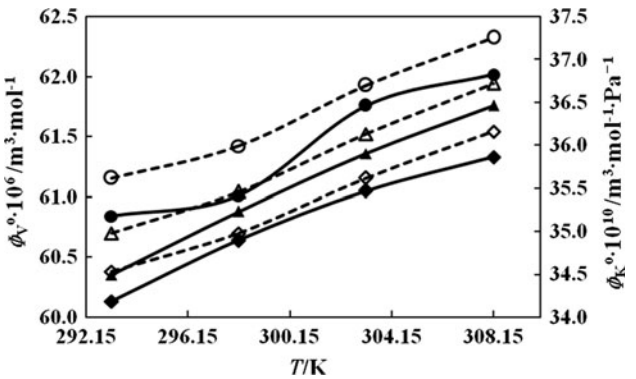


Fig. 2 Plot of limiting apparent molar volume (ϕ_V^0) for glycine (*filled diamond*), alanine (*filled triangle*), valine (*filled circle*), and limiting molar isentropic compressibility (ϕ_K^0) for glycine (*open diamond*), alanine (*open triangle*), valine (*open circle*), against studied temp (T) in $w_1 = 0.0075$ mass fraction of aq. β-CD

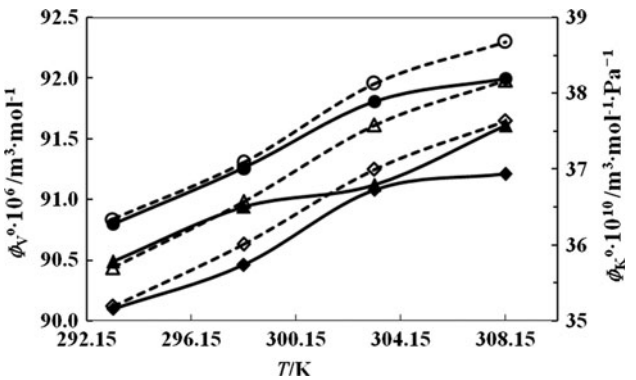


Fig. 3 Plot of limiting apparent molar volume (ϕ_V^0) for glycine (*filled diamond*), alanine (*filled triangle*), valine (*filled circle*), and limiting molar isentropic compressibility (ϕ_K^0) for glycine (*open diamond*), alanine (*open triangle*), valine (*open circle*), against studied temp (T) in $w_1 = 0.01$ mass fraction of aq. β-CD

hydrophobic–hydrophobic interactions predominate over the ion–hydrophilic and hydrophilic–hydrophilic interactions. The observed trend can also be explained based on the following equation (Natarajan and Wadi 1990; Bhat and Ahluwalia 1985)

$$\phi_V^0 = \phi_{VW} + \phi_V - \phi_S \tag{8}$$

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 (Mishra and Ahluwalia 1981), 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 et al. (2001) 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. (2001) 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

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

and are included in Table 7 and illustrated in Fig. 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 has 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

Scheme 2 Plausible mechanism of interaction of glycine, L-alanine, L-valine with β-CD

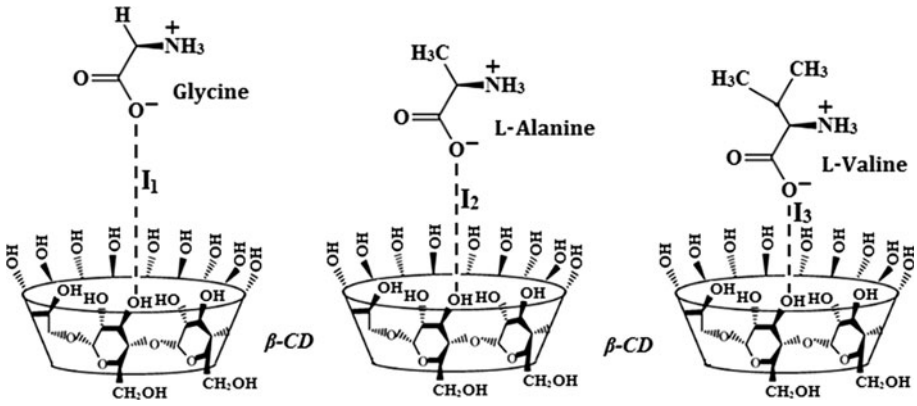


Table 5 Contributions of zwitter ionic group (NH_3^+, COO^-), CH_2 group, and the other alkyl chains to the limiting apparent molar volume, ϕ_V^0, for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15–308.15 K respectively

	$\phi_V^0 \times 10^6$ (m^3 mol^{-1})								
Temp (K):	293.15	298.15	303.15	308.15		293.15	298.15	303.15	308.15
w_1 = 0.0000					*w_1 = 0.005*				
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*				
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

$$\Delta\phi_V^0(R) = \phi_V^0(\text{amino acid}) - \phi_V^0(\text{glycine}) \quad (10)$$

where $\Delta\phi_V^0(R)$ 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 7. The table shows that the $\Delta\phi_V^0(R)$ values for L-alanine (CH_3CH–) and L-valine (CH_3CH_2CH–) are positive, which suggests that the contribution of alkyl chain is greater than relative to the H-atom of glycine in solute–solvent interaction in solution.

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 (Millero et al. 1978)

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

where ϕ_V^0(int) is the intrinsic partial molar volumes of the amino acids and ϕ_V^0(elect) is the electrostriction partial molar volume as a result of hydration of the amino acids. The ϕ_V^0(int) consists of two terms: the van der Waals volume and the volume due to packing effects. The values of ϕ_V^0(int) for the amino acids were calculated from their crystal molar volume (Millero et al. 1978) using the following relationship,

$$\phi_V^0(\text{int}) = (0.7/0.634)\phi_V^0(\text{cryst}) \quad (12)$$

where, 0.7 is the packing density in an organic crystal and 0.634 is the packing density of randomly packed spheres.

Table 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 293.15–308.15 K respectively

Temp (K)	$\phi_V^0 \times 10^6$(aqueous) (m^3 mol^{-1})	$\Delta\phi_V^0 \times 10^6$ (m^3 mol^{-1})	$\phi_V^0 \times 10^6$(elect) (m^3 mol^{-1})	$\phi_K^0 \times 10^{10}$(elect) (m^3 mol^{-1} Pa^{-1})	n_H	
					From volume	From compressibility
$w_1 = 0.005$						
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
$w_1 = 0.0075$						
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
$w_1 = 0.01$						
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 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 293.15–308.15 K respectively

$\Delta\phi_V^0 \times 10^6$ (m^3 mol^{-1})					$\Delta\phi_V^0(R) \times 10^6$ (m^3 mol^{-1})			
Temp (K):	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
w_1 = 0.005								
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								
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								
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

The molar volume of crystals ϕ_V^0(cryst) was calculated using the crystal densities of the amino acids represented by Berlin and Pallansch (1968) at 298.15 K (Gucker et al. 1939). The ϕ_V^0(elect) values can be calculated (Franks et al. 1970) from the intrinsic partial molar volumes of the amino acids ϕ_V^0(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 (Millero et al. 1978) which is estimated using the following relation

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

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 (Millero et al. 1978) 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 average value is −3.5 cm^3 mol^{-1} at 303.15 K. The obtained n_H values are listed in Table 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 (Owaga et al. 1984) 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)

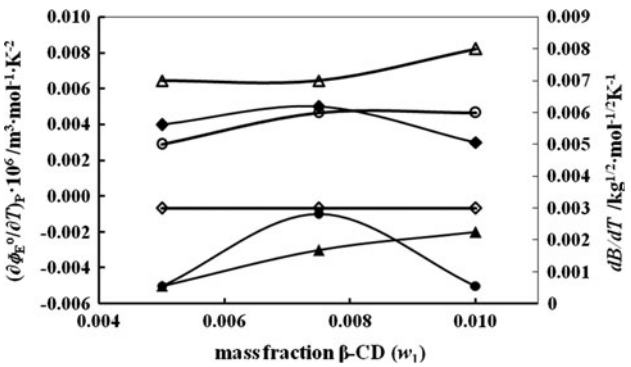


Fig. 4 Plot of $\left(\partial\phi_E^0/\partial T\right)_P$ for glycine (*filled diamond*), alanine (*filled triangle*), valine (*filled circle*), and dB/dT for glycine (*open diamond*), alanine (*open triangle*), valine (*open circle*), against studied temp (T) in w_1 = 0.01 mass fraction of aq. β-CD

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 to 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 3, where w_1 is the mass fraction of β-CD in aqueous solution.

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,

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \tag{14}$$

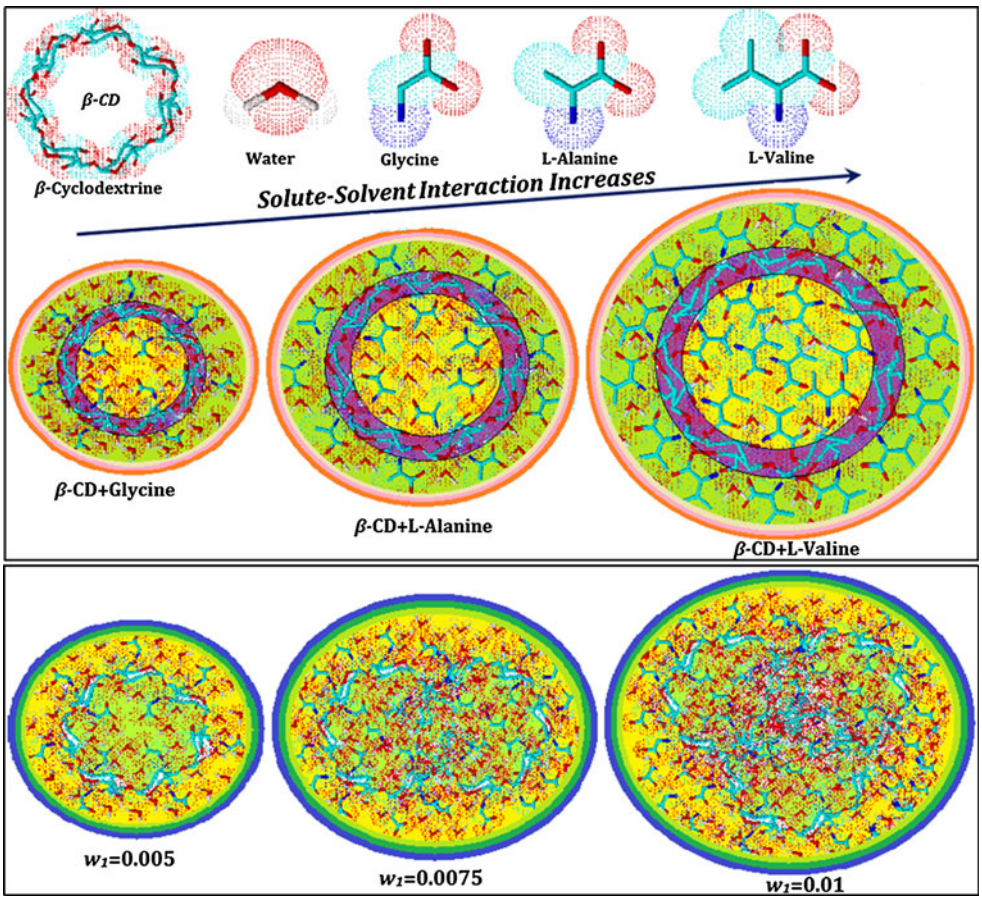
where a_0, a_1, a_2 are the empirical coefficients depending on the solute, mass fraction (w_1) of the cosolute β-CD, and T is the temperature range under study in Kelvin. The values of these coefficients of the above equation for the amino acids in aqueous β-CD mixtures are reported in Table 8.

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

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T\right)_P = a_1 + 2a_2 T \tag{15}$$

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 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 (Millero 1972) 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 (1969) 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,



Scheme 3 The schematic representation of solute–solvent interaction, for the studied amino acids in aqueous β-cyclodextrine binary mixtures, where w_1 is the mass fraction of β-CD in aqueous solution

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

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

$$\left(\delta\phi_{\mathrm{E}}^{0}/\delta T\right)_{P} = \left(\delta^{2}\phi_{\mathrm{V}}^{0}/\delta T^{2}\right)_{P} = 2a_2 \tag{16}$$

If the sign of $\left(\delta\phi_{\mathrm{E}}^{0}/\delta T\right)_{P}$ is positive or a small negative, the molecule is a structure-maker; otherwise, it is a structure breaker (Roy et al. 2007). As is evident from Table 9 and Fig. 4, the $\left(\delta\phi_{\mathrm{E}}^{0}/\delta T\right)_{P}$ values for all amino acids are positive and small negative under investigation are predominantly structure-makers in all of the experimental solutions.

Viscosity

The experimental viscosity data for the studied systems are listed in Table 2. The relative viscosity (η_r) has been analyzed using the Jones–Dole (1929) equation

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B\sqrt{m} \tag{17}$$

where $\eta_r = \eta/\eta_0$, 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 $(\eta_r - 1)/\sqrt{m}$ against $\sqrt{m}$, and reported in Table 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 (Millero 1971)

Table 9 Limiting apparent molal expansibilities (ϕ_{E}^{0}) for amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15–308.15 K respectively

Solvent mixture (w_1)	$\phi_{\mathrm{E}}^{0} \times 10^6$ (m^3 mol^{-1} K^{-1})				$\left(\partial\phi_{\mathrm{E}}^{0}/\partial T\right)_P \times 10^6$ (m^3 mol^{-1} K^{-2})
T (K):	293.15	298.15	303.15	308.15	
Glycine + aq. β-CD					
0.0050	0.079	0.101	0.123	0.145	0.004
0.0075	0.080	0.105	0.130	0.155	0.005
0.0100	0.104	0.119	0.134	0.149	0.003
Alanine + aq. β-CD					
0.0050	0.115	0.092	0.069	0.046	−0.005
0.0075	0.114	0.101	0.088	0.075	−0.003
0.0100	0.072	0.081	0.090	0.099	−0.002
Valine + aq. β-CD					
0.0050	0.114	0.091	0.068	0.045	−0.005
0.0075	0.065	0.069	0.073	0.077	−0.001
0.0100	0.124	0.097	0.070	0.043	−0.005

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 4 and Fig. 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 are due to the solvated solute molecules associated with the solvent molecules, all round the formation of associated molecule by solute–solvent interaction would present greater resistance, and this type of interactions is strengthened with a rise in temperature and also increases 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.

The Table 4 also shows that B-coefficients for all the amino acids 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

$$B = B\left(NH_3^{+}, COO^{-}\right) + n_c B(CH_2) \tag{18}$$

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 10. It shows that both the $B(NH_3^{+}, COO^{-})$ and $B(CH_2)$ values increase 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 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 4 shows that the values of the *B* coefficients of all amino acids slightly increase with increasing temperature, i.e., the d*B*/d*T* values are positive. From Table 11 and Fig. 4, small positive d*B*/d*T* 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

$$B = A_1 + A_2\phi_V^0. \tag{19}$$

The coefficients A_1 and A_2 are included in Table 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 (Banipal et al. 2004; Yan et al. 2002).

Ultrasonic speed

Apparent molar isentropic compressibility

The adiabatic compressibility, defined by the thermodynamic relation

$$\beta_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{20}$$

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:

$$\beta_s = 1/u^2\rho \tag{21}$$

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

$$\phi_K = M\beta_s/\rho + 1,000(\beta_s\rho_0 - \beta_0\rho)/m\rho\rho_0 \tag{22}$$

where β_0 and 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

Table 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 293.15–308.15 K respectively

B ($kg^{1/2}$ $mol^{-1/2}$)					*B*(R) ($kg^{1/2}$ $mol^{-1/2}$)			
Temp (K):	293.15	298.15	303.15	308.15	293.15	298.15	303.15	308.15
w_1 = 0.005								
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								
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								
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 11 Values of dB/dT, A_1, and A_2 coefficients for the amino acids in different mass fraction of aqueous β-CD (w_1) at 293.15–308.15 K respectively

Solvent mixture (w_1)	dB/dT	A_1	A_2
Glycine + aq. β-CD			
0.0050	0.003	−1.352	0.034
0.0075	0.003	−5.446	0.094
0.0100	0.003	−5.884	0.069
Alanine + aq. β-CD			
0.0050	0.007	−1.176	0.030
0.0075	0.007	−4.464	0.078
0.0100	0.008	−7.210	0.084
Valine + aq. β-CD			
0.0050	0.005	−1.149	0.030
0.0075	0.006	−5.246	0.090
0.0100	0.006	−6.802	0.079

reported in Table 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 (Roy et al. 2011)

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m}. \tag{23}$$

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

From Table 4 and Figs. 1, 2, and 3, it is observed that the value of limiting apparent molar isentropic compressibility ϕ_K^0 is 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:

glycine < L-alanine < 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.

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 (Millero et al. 1978)

$$\phi_K^0 = \phi_K^0(\text{int}) + \phi_K^0(\text{elect}) \tag{24}$$

where ϕ_K^0(int) is the intrinsic partial molar adiabatic compressibility of the amino acid and ϕ_K^0(elect) is the electrostriction partial molar adiabatic compressibility due to the hydration of the amino acid. As has been noted by Millero et al. (1978), as a first approximation, one can assume that ϕ_K^0(int) ≈ 0, since one would expect ϕ_K^0(int) to very small (Millero et al. 1978). Thus ϕ_K^0 may be thought to represent ϕ_K^0(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 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 6, the observed decreasing tendency of n_H for glycine and L-alanine supports the view (Owaga et al. 1984) 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 (1974), ions with 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.

Table 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 293.15–308.15 K respectively

Temp (K)	Parameters					
	$\phi_1^0 \times 10^6$ (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})
$w_1 = 0.005$						
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
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
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
$w_1 = 0.0075$						
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
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
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
$w_1 = 0.01$						
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
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
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

Table 12 continued

Temp (K)	Parameters					
	$\phi_1^0 \times 10^6$ (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})
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

Other thermodynamic properties

According to Glasstone et al. (1941), the free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0\#}$, can be calculated using the equation:

$$\eta_0 = (hN_A/\bar{V}_1^0)\ \exp(\Delta\mu_1^{0\#}/RT) \tag{25}$$

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 et al. (1974) applied the transition state treatment of relative viscosity to solutions and showed that the B-coefficient is given as:

$$B = (\bar{V}_1^0 - \bar{V}_2^0)/1,000 + \bar{V}_2^0[(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#})/RT]/1,000 \tag{26}$$

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 Eqs. (25) and (26), the values of $\Delta\mu_2^{0\#}$ and $\Delta\mu_1^{0\#}$ are obtained as:

$$\Delta\mu_1^{0\#} = RT\ln(\eta_0\bar{V}_1^0/hN_A) \tag{27}$$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + (RT/\bar{V}_1^0)\ [1,000B - (\bar{V}_1^0 - \bar{V}_2^0)] \tag{28}$$

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 308.15 K are listed in Table 12. The total free energy of activation of viscous flow of the solution, $\Delta\mu^{0\#}$, was calculated from the relation:

$$\Delta\mu^{0\#} = n_1\Delta\mu_1^{0\#} + n_2\Delta\mu_2^{0\#} \tag{29}$$

where n_1 and n_2 are the number of moles of mixed solvent and solute, respectively. The values of $\Delta\mu^{0\#}$ are presented in Table 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 12:

$$\Delta\mu^{0\#} = \Delta H^* - T\Delta S^* \tag{30}$$

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 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 (1974), the solutes (amino acids) behave as structure-makers. This again supports the behaviour of dB/dT for these solutes in aqueous β-CD. The $\Delta\mu_2^{0\#}$ values (Table 12) of the amino acids were found to increase from glycine to L-valine at a given temperature. This indicates that the solvation of the amino acids in the ground state becomes increasingly favourable 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. (30) of the amino acids + aqueous β-CD mixtures are listed in Table 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 behaviour 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 (Liu and Guo 2002).

The predominance of items (i)–(iii) during these processes determines the negative values for the entropy of interaction. The contribution from process (iv) cannot be considerable because the β-cyclodextrin molecule is not flexible and cannot change conformation upon binding

with a guest molecule, it itself retain the same conformation before and after the interaction with amino acids.

Structural effect of the cosolute β-CD

The structure is a novel packing of β-CD monomers that is less compact (2,300 $Å^3$ per β-CD) than known monomeric ($\approx$1,500–1,750 $Å^3$) or dimeric ($\approx$1,800 $Å^3$) 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 (Betzel et al. 1984) (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 neighbours. 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, the release of conformational strain, etc. (Loftsson et al. 2005). 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, is more favourably complex, with retention of configuration of β-CD itself.

Conclusion

Extensive study of thermophysical and thermodynamic properties of simple amino acids in aqueous β-CD binary mixture was done. It is evident that in 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.

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Conflict of interest The authors declare that they have no conflict of interest.

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