

## Interactions of L-arginine with maltose monohydrate in aqueous solutions at 298.15 K: A volumetric study

Ashwani Kumar and Rajinder Kumar Bamezai

**Abstract:** Density and ultrasonic speeds of L-arginine in water and in aqueous-D-maltose monohydrate (2%, 4% and 6% of maltose monohydrate, w/w in water) mixed solvents were measured at 298.15 K. From these experimental results, the apparent molar volume,  $V_\phi$ , limiting apparent molar volume,  $V_\phi^\circ$ , and the slope,  $S_v$ , transfer volume,  $V_{\phi, tr}^\circ$ , apparent molar compressibility,  $K_{s, \phi}$ , limiting apparent molar compressibility  $K_{s, \phi}^\circ$ , and the slope  $S_k$ , transfer compressibility,  $K_{s, \phi, tr}^\circ$ , and hydration number,  $n_H$ , were calculated. The results have been discussed in terms of solute-solute and solute-solvent interactions in these systems. It has been observed that there exists strong solute-solvent (hydrophilic-ionic group and hydrophilic-hydrophilic group) interactions in these systems, which increases with increase in maltose concentration. The hydrophilic-ionic and hydrophilic-hydrophilic interactions have been found to be dominating over hydrophobic-hydrophilic interactions in the solutions.

**Key words:** Density; ultrasonic speed; L-arginine; D-maltose; apparent molar volume.

### 1. Introduction

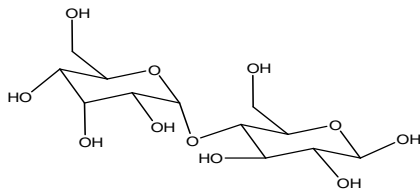
Proteins play an important role in the biological processes of nearly all living organisms. In order to understand the role played by the biological molecules in the living organism, it is necessary to study the interactions of proteins with their surrounding environment. These interactions are mainly between the protein molecules and the solvent ions. The stabilization of native conformations of proteins has been related to various non-covalent interactions like hydrogen bonding, electrostatic and hydrophobic interactions [1,2]. The study of these interactions provides important insight into the conformational stability and folding/unfolding of globular proteins [3] and are found implicated in several biochemical and physiological processes of a living cell [4-6]. Saccharides/Carbohydrates are widely distributed in various forms of life as

essential moieties of glycoproteins, glycolipids, nucleic acids and polysaccharides. Because of conformational flexibility, saccharides play significant roles in many biological processes such as signaling, cell-cell recognition, molecular and cellular communication [7-9] and stabilizing the native conformations of proteins/enzymes [10-12]. Lee and Timasheff [13] studied the thermal transitions of  $\alpha$ -chymotrypsin, chymotrypsinogen and ribonuclease in sucrose and argued that the sucrose stabilize proteins against thermal damage. The complex conformational and configurational factors determining the structure of proteins in sugar solution makes the study of protein-sugar interactions difficult. Therefore interactions of the model compounds of proteins, i.e., amino acids in aqueous saccharide solution are investigated [14-19]. Since amino acids are the model compounds of protein molecules, their thermodynamic and transport properties in aqueous solutions provide valuable information on solute-solute and solute-solvent interactions that are useful in studying the stability of proteins. Thus, the thermodynamic properties of amino acids in aqueous-saccharide solutions are important for studying the interactions in biological systems [20, 21]. Maltose a (disaccharide) is a water-soluble sugar used for immediate energy along with glucose, being basic source for all living organisms. It is also used in a number of

---

Ashwani Kumar(✉) and Rajinder K. Bamezai  
Department of Chemistry,  
University of Jammu,  
Jammu-180 006, India  
email: ashwani.kalsi@gmail.com

biological reactions as a stabilizing agent or osmolality regulator. Maltose plays an important role in changing the effect by generating a more plasticizing effect than fructose [22]. The structure of  $\alpha$ -D-maltose is:



In recent years, there have been extensive studies of thermoacoustic properties of these model components in aqueous-saccharide solutions [15–19,23-28]. But, to the best of our knowledge, very little work has been done on amino acids with positively charged side chain in aqueous-saccharide solutions [16,18,26,28] and no volumetric and ultrasonic studies have been done on L-arginine in aqueous–maltose monohydrate solutions with varying maltose monohydrate concentrations at 298.15 K. These observations led us to undertake the study of L-arginine (with positively charged R group) in aqueous-maltose monohydrate solutions.

In the present article, we report the experimentally measured values of density ( $\rho$ ) and speed of sound ( $u$ ) of L-arginine in water and aqueous-maltose monohydrate (2%, 4% and 6% maltose monohydrate, w/w in water) solvents as a function of molal concentrations of L-arginine at 298.15 K and atmospheric pressure. Using the experimentally measured density and ultrasonic data, the apparent molar volume,  $V_\phi$ , limiting apparent molar volume,  $V_\phi^\circ$ , and the slope,  $S_v$ , transfer volume,  $V_{\phi, tr}^\circ$ , apparent molar compressibility,  $K_{s, \phi}$ , limiting apparent molar compressibility  $K_{s, \phi}^\circ$ , and the slope  $S_k$ , transfer compressibility,  $K_{s, \phi, tr}^\circ$ , and hydration number,  $n_H$ , were calculated. The measured and computed parameters have been discussed in terms of ionic–hydrophilic, hydrophilic–hydrophilic and hydrophobic–hydrophilic interactions occurring in the L-arginine in water and aqueous-maltose monohydrate (2%, 4% and 6% maltose monohydrate, w/w in water).

## 2. Experimental

L-Arginine and D-Maltose monohydrate, herein abbreviated as MM, was used as such (Table 1) without further purification, except

drying in an oven for 24 h. The aqueous-saccharide solutions (2%, 4% and 6% of MM, w/w in water) were prepared using triple distilled water with specific conductance less than  $1 \times 10^{-6} \text{ S cm}^{-1}$ . The saccharide solution was used as solvent to prepare L-arginine solution of eight different molal concentrations (ranging from 0.0 m to 0.2 m).

**Table 1.** Provenance and purity of the chemical samples studied.

Chemical name	Provenance	Purification method	Final mass fraction purity
L-Arginine	Sigma Aldrich, India	Used as received	>0.998
D-Maltose monohydrate	Sigma Aldrich, India	Used as received	>0.998

An electronic single pan five digit analytical balance (Mettler; Model AE-240) with a precision of  $\pm 0.00001 \text{ g}$  was used for weighing. All the solutions were prepared with care and stored in special airtight bottles to avoid the exposure of solution to air and evaporation. The possible error in the mole fraction is calculated to be less than  $\pm 1 \times 10^{-4}$ . The densities of solutions were measured using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of  $\sim 10 \text{ mL}$ . The capillary, with graduated marks had a uniform bore which could be closed by a well-fitted glass cap. The pycnometer was calibrated by measuring the density of triply distilled water at 298.15 K. The uncertainty in density measurements was within  $\pm 0.03 \text{ kg m}^{-3}$ . The speed of sound in the solutions were measured using a single-crystal variable-path multi-frequency ultrasonic interferometer (Model: M-82S, Mittal Enterprises, India) having stainless steel sample cell (with digital micrometer) operating at a fixed frequency of 2 MHz. The uncertainty in speed measurement was found to be within  $\pm 0.5 \text{ m s}^{-1}$ . The temperature of the sample solution was maintained to an accuracy of  $\pm 0.02 \text{ K}$  using an electronic controlled thermostatic water bath (Model: TIC-4000N, Thermotech, India).

## 3. Results and discussion

The experimental values of density ( $\rho$ ) and speed of sound ( $u$ ) of L-arginine in water and aqueous-MM (2%, 4% and 6% MM) as a function of molal concentration of L-arginine at 298.15 K are listed in Tables 2 and 3, respectively.

**Table 2.** Densities ( $\rho/\text{kg m}^{-3}$ ) of solutions of L-arginine in water, aqueous-MM (2%, 4% and 6%) as function of molality ( $\text{m}/\text{mol kg}^{-1}$ ) of L-arginine at 298.15 K.

Molality ( $\text{m}/\text{mol kg}^{-1}$ )	L-Arginine in water	L-Arginine in 2% MM	L-Arginine in 4% MM	L-Arginine in 6% MM
0.0000	997.07	1004.26	1011.64	1020.59
0.0250	998.35	1005.50	1012.86	1021.78
0.0500	999.63	1006.74	1014.08	1022.97
0.0750	1000.91	1007.98	1015.30	1024.16
0.1000	1002.19	1009.22	1016.52	1025.35
0.1250	1003.47	1010.46	1017.74	1026.54
0.1500	1004.75	1011.70	1018.96	1027.73
0.1750	1006.03	1012.94	1020.18	1028.92
0.2000	1007.31	1014.18	1021.40	1030.11

**Table 3.** Viscosities ( $\eta \times 10^3/\text{N s m}^{-2}$ ) of solutions of L-arginine in water, aqueous-MM (2%, 4% and 6%) as functions of molality ( $\text{m}/\text{mol kg}^{-1}$ ) of L-arginine at 298.15 K.

Molality ( $\text{m}/\text{mol kg}^{-1}$ )	L-Arginine in water	L-Arginine in 2% MM	L-Arginine in 4% MM	L-Arginine in 6% MM
0.0000	1497.60	1506.33	1512.27	1516.80
0.0250	1499.60	1508.40	1514.38	1518.92
0.0500	1501.58	1510.47	1516.47	1521.02
0.0750	1503.54	1512.51	1518.54	1523.10
0.1000	1505.48	1514.53	1520.59	1525.16
0.1250	1507.40	1516.53	1522.62	1527.20
0.1500	1509.30	1518.51	1524.63	1529.22
0.1750	1511.18	1520.47	1526.62	1531.22
0.2000	1513.04	1522.41	1528.59	1533.20

**Apparent molar volume and apparent molar compressibility**

The apparent molar volume ( $V_\phi$ ) and apparent molar compressibility ( $K_{s,\phi}$ ) of the solutions were calculated using relations 1 and 2.

$$V_\phi = \frac{1000(\rho_o - \rho)}{m\rho\rho_o} + \frac{M}{\rho} \dots\dots\dots 1$$

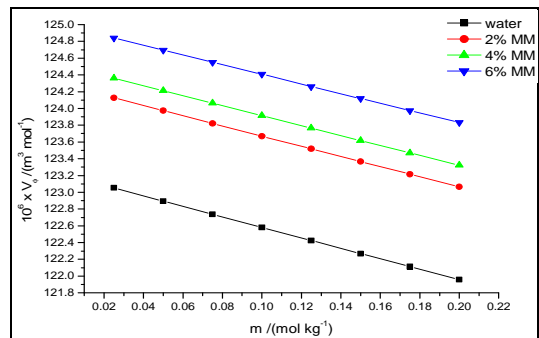
$$K_{s,\phi} = \frac{1000(\kappa_s\rho_o - \kappa_s^o\rho)}{m\rho\rho_o} + \frac{M}{\rho} \dots\dots\dots 2$$

where  $m$  is the molality of L-arginine in solution,  $\rho$  and  $\rho_o$  are densities of the solution and the solvent (aqueous-MM), respectively;  $M$  is the molar mass of the solute (L-arginine).  $\kappa_s$  and  $\kappa_s^o$  are isentropic compressibilities of the solution and the solvent, respectively.

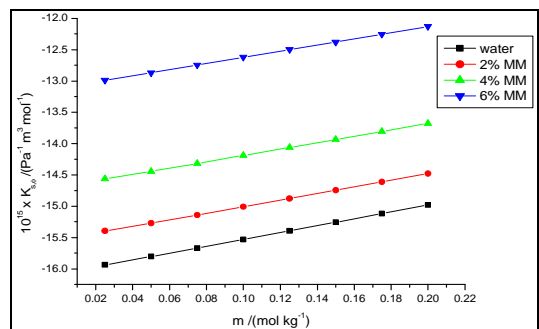
The variation of  $V_\phi$  (Fig. 1) and  $K_{s,\phi}$  (Fig. 2) as function of molality of L-arginine has been found to be linear in the studied concentration range at 298.15 K for L-arginine in water, and in all the three aqueous-MM solvents.

The isentropic compressibility ( $\kappa_s$ ) has been calculated using the relation:

$$\kappa_s = 1/u^2\rho \dots\dots\dots 3$$

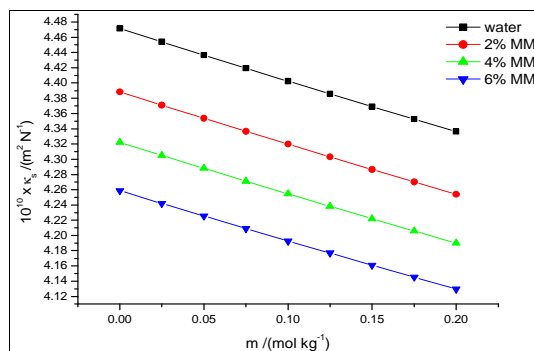


**Fig. 1.** Variations of apparent molar volume,  $V_\phi$  vs. molality,  $m$  of L-arginine in water and MM + water (w/w) solutions at 298.15 K.



**Fig. 2.** Variations of apparent molar compressibility,  $K_{s,\phi}$  vs. molality,  $m$  of L-arginine in water and MM + water (w/w) solutions at 298.15 K.

The isentropic compressibility of L-arginine in water and aqueous-MM plotted in Fig. 3 show a decrease with increase in molal concentration of L-arginine. The decreasing  $\kappa_s$  values in aqueous-MM, on increasing the amount of L-arginine, indicate that the water molecules associated with ionic groups of zwitterion/hydrophilic groups of L-arginine are less compressible than those of the water molecules in the bulk solution [29, 30].



**Fig. 3.** Variations of isentropic compressibility,  $\kappa_s$ , vs. molality,  $m$  of L-arginine in water and MM + water (w/w) solutions at 298.15 K.

### Limiting apparent molar volume and apparent molar compressibility

The values of limiting apparent molar volume ( $V_\phi^0$ ) and limiting apparent molar compressibility ( $K_{s,\phi}^0$ ) were estimated by the least square fit of the apparent molar volume and apparent molar compressibility values using the following equations [31].

$$V_\phi = V_\phi^0 + S_v m \dots\dots\dots 4$$

$$K_{s,\phi} = K_{s,\phi}^0 + S_k m \dots\dots\dots 5$$

Here, the intercepts,  $V_\phi^0$  and  $K_{s,\phi}^0$  are limiting apparent molar volume and limiting apparent molar compressibility at infinite dilution, respectively, whereas  $S_v$  or  $S_k$  is their corresponding slopes. The values of  $V_\phi^0$ ,  $K_{s,\phi}^0$ ,  $S_v$  and  $S_k$  along with the standard deviation,  $\sigma$ , for L-arginine in aqueous-MM at 298.15 K are summarized in Tables 4 and 5 and shown graphically in the Figs. S1 and S2 as supplementary material.

**Table 4.** Limiting apparent molar volume ( $V_\phi^0$ ), standard deviation of linear regression ( $\sigma$ , using Equation 4), slope ( $S_v$ ) and transfer volume ( $V_{\phi,tr}^0$ ) for L-arginine in aqueous-MM at 298.15 K.

Property	T/K (298.15 K)
<b>L-Arginine in water</b>	
$10^6 \cdot V_\phi^0 / \text{m}^3 \text{mol}^{-1}$	123.208
$\sigma$ for equation (4)	0.001
$10^6 \cdot S_v / \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	-6.256
<b>L-Arginine in 2% aqueous-MM</b>	
$10^6 \cdot V_\phi^0 / \text{m}^3 \text{mol}^{-1}$	124.278
$\sigma$ for equation (4)	0.001
$10^6 \cdot S_v / \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	-6.073
$10^6 \cdot V_{\phi,tr}^0 / \text{m}^3 \text{mol}^{-1}$	1.070
<b>L-Arginine in 4% aqueous-MM</b>	
$10^6 \cdot V_\phi^0 / \text{m}^3 \text{mol}^{-1}$	124.509
$\sigma$ for equation (4)	0.001
$10^6 \cdot S_v / \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	-5.942
$10^6 \cdot V_{\phi,tr}^0 / \text{m}^3 \text{mol}^{-1}$	1.301
<b>L-Arginine in 6% aqueous-MM</b>	
$10^6 \cdot V_\phi^0 / \text{m}^3 \text{mol}^{-1}$	124.984
$\sigma$ for equation (4)	0.001
$10^6 \cdot S_v / \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	-5.766
$10^6 \cdot V_{\phi,tr}^0 / \text{m}^3 \text{mol}^{-1}$	1.776

The intercept,  $V_\phi^0$ , is free from solute-solute interactions and, therefore, provides a measure of solute-solvent interactions and  $S_v$  is the experimental slope; an indicative of solute-solute interactions. An evaluation of Table 4 reveals that the  $V_\phi^0$  values are positive and  $S_v$  values are negative for L-arginine in aqueous as well as aqueous-MM indicating the presence of strong solute-solvent interactions and weak solute-solute interactions. This trend of  $V_\phi^0$  values may be due to their hydration behaviour that depends on the nature of solute species which comprises of following interactions [20, 32-34]: (i) the terminal groups of zwitterions of amino acids,  $\text{NH}_3^+$  and  $\text{COO}^-$  are hydrated in an electrostatic manner; whereas hydration of R group depends on its nature, which may be hydrophilic, hydrophobic or amphiphilic; (ii) electrostriction of  $\text{NH}_3^+$  end is ten times greater than  $\text{COO}^-$  end of the zwitterion; and (iii) the overlapping of hydration co-spheres of terminal groups, i.e.,  $\text{NH}_3^+$  and  $\text{COO}^-$  groups and of adjacent groups results in volume change. The  $V_\phi^0$  value increases due to reduction in the electrostriction at terminals, whereas it decreases due to disruption of side group hydration by that of the charged end. A similar behaviour with glucose/sucrose concentration

was observed by Zhao et al. [28] for arginine in aqueous-carbohydrate solution and by Nain et al. [16,26] for L-histidine in aqueous-glucose, and aqueous-sucrose solutions.

The  $K_{s,\phi}^\circ$  and  $S_k$  values (Table 5) are found to be negative and positive, respectively in the studied concentration region. The former values are negative (Fig. S2 of supplementary material), indicating that there occurs strong solute-solvent interactions and weak solute-solute interactions in these systems. This further supports the observation that the hydrophilic-ionic and hydrophilic-hydrophilic groups interaction between OH groups of maltose monohydrate with L-arginine zwitterions dominate in these systems. The negative values of  $K_{s,\phi}^\circ$  (loss of compressibility of medium) reindicates that the water molecules surrounding the amino acid molecules provide great resistance to compression than water molecules present in bulk.

**Table 5.** Limiting apparent molar compressibility ( $K_{s,\phi}^\circ$ ), standard deviation of linear regression ( $\sigma$ , using Equation 5) slope ( $S_k$ ) and transfer compressibility, ( $K_{s,\phi, tr}^\circ$ ) for L-arginine in aqueous-MM at 298.15 K.

Property	T/K (298.15)
<b>L-Arginine in water</b>	
$10^{15} \cdot K_{s,\phi}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	-16.079
$\sigma$ for equation (5)	0.002
$10^{15} \cdot S_k / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	5.490
<b>L-Arginine in 2% aqueous-MM</b>	
$10^{15} \cdot K_{s,\phi}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	-15.532
$\sigma$ for equation (5)	0.003
$10^{15} \cdot S_k / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	5.261
$10^6 \cdot K_{s,\phi, tr}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	0.547
<b>L-Arginine in 4% aqueous-MM</b>	
$10^{15} \cdot K_{s,\phi}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	-14.695
$\sigma$ for equation (5)	0.003
$10^{15} \cdot S_k / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	5.079
$10^6 \cdot K_{s,\phi, tr}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	1.384
<b>L-Arginine in 6% aqueous-MM</b>	
$10^{15} \cdot K_{s,\phi}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	-13.112
$\sigma$ for equation (5)	0.001
$10^{15} \cdot S_k / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1} \text{kg}^{-1}$	4.906
$10^6 \cdot K_{s,\phi, tr}^\circ / \text{Pa}^{-1} \text{m}^3 \text{mol}^{-1}$	2.967

**Transfer volume**

The limiting apparent molar transfer volume ( $V_{\phi, tr}^\circ$ ) of L-arginine from water to aqueous-MM was calculated using the following expression.

$$V_{\phi, tr}^\circ = V_{\phi, \text{aq-MM}}^\circ - V_{\phi, \text{water}}^\circ \dots\dots\dots 6$$

where  $V_{\phi, \text{water}}^\circ$  is the limiting apparent molar volume of L-arginine in water (Table 4). The  $V_{\phi, tr}^\circ$  value for L-arginine from water to aqueous-MM is shown in Table 4. The values of  $V_{\phi}^\circ$  of L-arginine in aqueous - MM are more than those in pure water, i.e.,  $V_{\phi, tr}^\circ$  value of L-arginine is positive and increases with increase in mass % of MM. The different types of interactions occurring between L-arginine and MM may be classified as follows [20,27,33,34].

- (a) Hydrophilic-ionic interaction between OH groups of MM and  $(\text{NH}_3^+$  and  $\text{COO}^-)$  zwitterionic centers of L-arginine molecules.
- (b) Hydrophilic-hydrophilic interaction between the OH groups of MM and  $\text{NH}_3^+$  groups of L-arginine molecules mediated through hydrogen bonding.
- (c) Hydrophilic-hydrophobic interaction between the OH groups of MM and non-polar ( $-\text{CH}_2$ ) groups of L-arginine molecules.
- (d) Hydrophobic-hydrophobic interaction between the non-polar groups of MM molecules and non-polar ( $-\text{CH}_2$ ) in side chain of L-arginine molecules.

The interactions occurring between MM and L-arginine molecules can be explained by the co-sphere overlap model, as proposed by Friedman and Krishnan model [35], according to which the effect of overlap of hydration co-sphere is decisive in determining the nature of interaction between the solute species. It has been observed [33] that the overlap of co-spheres of two ionic species produces an increase in volume, whereas the overlap of hydrophobic-hydrophobic groups and ionic-hydrophobic groups results in a decrease in volume. Since amino acids exist predominantly as zwitterions in pure water, there is an overall decrease in volume of the water due to the electrostriction of water near the end group. Interaction of type (a) leads to a positive contribution to the transfer volume owing to the overlap of the hydration co-sphere of the ion ( $\text{COO}^-$  and  $\text{NH}_3^+$ ) and hydrophilic OH group, which leads to the reduction in electrostriction of the water caused by these ions. The interaction of type (b) also makes a positive contribution to the transfer volume, since the overlap of the hydration co-sphere of  $\text{NH}_2$  and OH groups leads to increase in the magnitude

of hydrogen bonding interaction. On the other hand, interaction of type (c) makes a negative contribution to the transfer volume because of their co-sphere overlap. Interaction of type (d) also leads to a negative contribution to the transfer volume due to disruption of side group hydration by that of charged end. The observed positive  $V_{\phi, tr}^{\circ}$  values for these systems suggest that the ionic-hydrophilic and hydrophilic-hydrophilic group interactions dominate in these systems. The  $V_{\phi, tr}^{\circ}$  values increase with increase MM concentration in the solutions (Table 4). This may be due to greater ionic-hydrophilic group and hydrophilic-hydrophilic group interactions with increased concentrations of MM.

**Transfer compressibility**

The limiting apparent molar transfer compressibility ( $K_{s, \phi, tr}^{\circ}$ ) of L-arginine from water to aqueous-MM were calculated by using the following relation.

$$K_{s, \phi, tr}^{\circ} = K_{s, \phi, aq-MM}^{\circ} - K_{s, \phi, water}^{\circ} \dots\dots\dots 7$$

$K_{s, \phi, water}^{\circ}$  is the limiting apparent molar compressibility of L-arginine in water (Table 5). The  $K_{s, \phi, tr}^{\circ}$  value for L-arginine from water to aqueous-MM is given in Table 5. The  $K_{s, \phi}^{\circ}$  values of L-arginine in aqueous-MM are more than that in pure water, i.e.,  $K_{s, \phi, tr}^{\circ}$  values are positive which indicates that the ionic-hydrophilic group and hydrophilic-hydrophilic group interactions dominate in the system. The increase of  $K_{s, \phi, tr}^{\circ}$  values with increase in aqueous - MM concentration may be due to greater ionic-hydrophilic group and hydrophilic-hydrophilic group interactions. The observed trends in  $K_{s, \phi}^{\circ}$  and  $K_{s, \phi, tr}^{\circ}$  further support the conclusions obtained from  $V_{\phi}^{\circ}$  and  $V_{\phi, tr}^{\circ}$ .

**Hydration number**

The hydration number is evaluated using electrostriction partial molar volume, ( $V_{\phi}^{\circ}$  (elect.)), of L-arginine which can be explained using a simple model [36].

$$V_{\phi}^{\circ} \text{ (elect.)} = V_{\phi}^{\circ} - V_{\phi}^{\circ} \text{ (int.)} \dots\dots\dots 8$$

$V_{\phi}^{\circ}$  (elect.) is the electrostriction partial molar volume due to the hydration of L-arginine and  $V_{\phi}^{\circ}$  (int.) is the intrinsic partial molar volume of L-arginine. The term  $V_{\phi}^{\circ}$  (int.) comprises of the van der Waals volume and the volume due to packing effects. The

values  $V_{\phi}^{\circ}$  (int.) for L-arginine has been calculated from equation [36]

$$V_{\phi}^{\circ} \text{ (int.)} = (0.7/0.634)V_{\phi}^{\circ} \text{ (cryst.)} \dots\dots\dots 9$$

where 0.7 is the packing density for molecules in organic crystals, 0.634 is the packing density for random packing spheres and  $V_{\phi}^{\circ}$  (cryst.) is the crystal molar volume [36], which can be evaluated by the following equation

$$V_{\phi}^{\circ} \text{ (cryst.)} = /\rho \text{ (cryst.)} \dots\dots\dots 10$$

where  $\rho$ (cryst.) is the crystal density of L-arginine and its value can be taken from the work of Berlin and Pallansch [37]. The decrease in volume due to electrostriction can be related to the number of water molecules hydrated to L-arginine [38], i.e., hydration number,  $n_H$ , can be given as:

$$n_H = V_{\phi}^{\circ} \text{ (elect.)} / (V_E^{\circ} - V_B^{\circ}) \dots\dots\dots 11$$

where  $V_E^{\circ}$  is the molar volume of electrostricted water and  $V_B^{\circ}$  is the molar volume of bulk water at  $T = 298.15$  K. According to Millero et al. [38].

$$V_E^{\circ} - V_B^{\circ} = -3.3 \text{ cm}^3 \cdot \text{mol}^{-1} \dots\dots\dots 12$$

Therefore, hydration number,  $n_H$  can be obtained as

$$n_H = V_{\phi}^{\circ} \text{ (elect.)} / (-3.3) \dots\dots\dots 13$$

The  $n_H$  value (volumetric method) for L-arginine in aqueous - MM is presented in Table 6 and Fig. S3. The  $n_H$  values for L-arginine decrease with increase in the concentration of D-maltose in the solution. This indicates the increase in solute-co-solute interactions. The hydration numbers mainly come from the electrostriction effect of the charged end/polar groups of amino acids on water.

**Table 6.** Hydration number ( $n_H$ ) for L-arginine in water and aqueous-MM at  $T = 298.15$  K

System	Volumetric method	Compressibility method
L-Arginine + water	6.65	1.99
L-Arginine + 2% aqueous-MM	6.33	1.92
L-Arginine + 4% aqueous-MM	6.26	1.81
L-Arginine + 6% aqueous-MM	6.11	1.62

This shows that D-maltose have a dehydration effect on the L-arginine, i.e., water

molecules are replaced by maltose molecules with increasing concentration of maltose in solution. Similar trends in  $n_H$  values were also observed by Nain et. al. [18, 39] for L-arginine in water + xylose/arabinose and L-phenylalanine in water + arabinose/glucose/sucrose solutions.

Further, the number of water molecules hydrated to the amino acids,  $n_H$  was estimated by from the electrostriction partial molar compressibility  $K_{s,\phi}^{\circ}(\text{elect.})$  using the method given by Millero et al. [36],

$$n_H = - K_{s,\phi}^{\circ}(\text{elect.}) / (V_{\phi,b}^{\circ} \cdot K_{s,\phi,b}^{\circ}) \dots \dots \dots 14$$

where  $K_{s,\phi,b}^{\circ}$  is the isothermal compressibility of bulk water. Value of  $(V_{\phi,b}^{\circ} \cdot K_{s,\phi,b}^{\circ})$  is  $8.1 \times 10^{-15} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$ . The electrostriction partial molar compressibility  $K_{s,\phi}^{\circ}(\text{elect.})$  can be calculated from the experimentally measured values of  $K_{s,\phi}^{\circ}$  using the following relation:

$$K_{s,\phi}^{\circ}(\text{elect.}) = K_{s,\phi}^{\circ} - K_{s,\phi}^{\circ}(\text{int.}) \dots \dots \dots 15$$

where  $K_{s,\phi}^{\circ}(\text{int.})$  is  $K_{s,\phi}^{\circ}$  (isomer) for L-arginine.  $K_{s,\phi}^{\circ}(\text{int.})$  is less than  $5 \times 10^{-15} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$  for ionic crystals and many organic solutes in water. So, we can assume  $K_{s,\phi}^{\circ}(\text{int.}) = 0$ . Therefore, for  $K_{s,\phi}^{\circ}(\text{int.}) = 0$ , equation (15) becomes

$$K_{s,\phi}^{\circ}(\text{elect.}) = K_{s,\phi}^{\circ} \dots \dots \dots 16$$

The value of  $n_H$  (compressibility method) for L-arginine in aqueous-MM is given in Table 6 and shown in Fig. S3.

#### 4. Conclusions

The densities,  $\rho$  and ultrasonic speeds,  $u$  of solutions of L-arginine in aqueous-maltose monohydrate solvents 2%, 4% and 6% of maltose monohydrate, w/w in water, were measured at 298.15 K. From the experimental results, various parameters, viz.,  $V_{\phi}$ ,  $V_{\phi}^{\circ}$ ,  $V_{\phi,\text{tr}}^{\circ}$ ,  $K_{s,\phi}$ ,  $K_{s,\phi}^{\circ}$ ,  $K_{s,\phi,\text{tr}}^{\circ}$  and hydration number,  $n_H$ , were calculated. The results indicate that there exist strong solute-solvent (ionic-hydrophilic group and hydrophilic-hydrophilic group) interactions in these systems, which increase with increase in maltose concentration. The ionic-hydrophilic and hydrophilic-hydrophilic interactions have been found to be dominating over hydrophobic-hydrophilic interactions in the solutions.

#### Acknowledgements

The authors are thankful to the Head Department of Chemistry, University of Jammu, Jammu for providing the necessary facilities for the completion of this work.

#### References

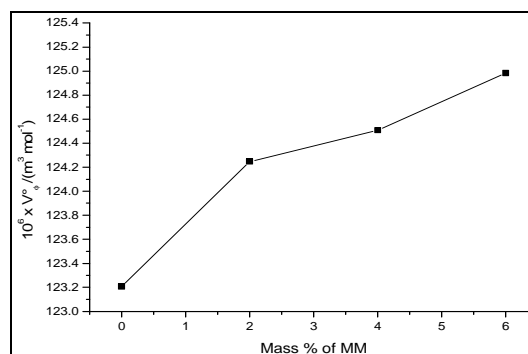
- [1] P.H. Von Hippel, T. Schleich, Ion effects on the solution structure of biological macromolecules, *Accounts Chem. Res.* 2 (1969) 257–265.
- [2] F. Franks, Proteins stability: the value of old literature, *Biophys. Chem.* 96 (2002) 117–127.
- [3] Z. Yan, J. Wang, W. Kong, J. Lu, Effect of temperature on volumetric and viscosity properties of some  $\alpha$ -amino acids in aqueous calcium chloride solutions, *Fluid Phase Equilib.* 215 (2004) 143–150.
- [4] C.M. Romero, E. Moreno, J.L. Rojas, Apparent molal volumes and viscosities of DL-  $\alpha$ - alanine in water-alcohol mixtures, *Thermochim. Acta* 328 (1999) 33–38.
- [5] A. Taravati, M. Shokrzadeh, A.G. Ebadi, P. Valipour, A.T.M. Hassan, F. Farrokhi, Various effects of sugar and polyols on the protein structure and function: role as osmolyte on protein stability, *World Appl. Sci. J.* 2 (2007) 353–362.
- [6] K. Gekko, Mechanism of polyol-induced protein stabilization: solubility of amino acids and diglycine in aqueous polyol solutions, *J. Biochem.* 90 (1981) 1633–1641.
- [7] D.P. Miller, J.J. de Pablo, Calorimetric solution properties of simple saccharides and their significance for the stabilization of biological structure and function, *J. Phys. Chem. B*, 104 (2000) 8876–8883.
- [8] K. Zhuo, H. Liu, H. Zhang, Y. Liu, J. Wang, Activity coefficients and volumetric properties for the NaI + maltose + water system at 298.15 K, *J. Chem. Eng. Data*, 53 (2008) 57–62.
- [9] G.O. Hernandez-Segura, M. Campos, M. Costas, L.A. Torres, Temperature dependence of the heat capacities in the solid state of 18 mono-, di-, and poly-saccharides, *J. Chem. Thermodyn.* 41 (2009) 17–20.
- [10] J.F. Back, D. Oakenfull, M.B. Smith, Increased thermal stability of proteins in the presence of sugars and polyols, *Biochemistry*, 18 (1979) 5191–5196.
- [11] H. Uedaira, H. Uedaira, The effect of sugars on the thermal denaturation of

- lysozyme, *Bull. Chem. Soc. Jpn.* 53 (1980) 2451-2455.
- [12] S. Li, W. Sang, R. Lin, Partial molar volumes of glycine, L-alanine and L-serine in aqueous glucose solutions at T = 298.15 K, *J. Chem. Thermodyn.* 34 (2002) 1761-1768.
- [13] J.C. Lee, S.N. Timasheff, The stabilization of proteins by sucrose, *J. Biol. Chem.* 256 (1981) 7193-7201.
- [14] T.S. Banipal, G. Sehgal, Partial molal adiabatic compressibilities of transfer of some amino acids and peptides from water to aqueous sodium chloride and aqueous glucose solutions, *Thermochim. Acta* 262 (1995) 175-183.
- [15] Riyazuddeen, M.A. Usmani, Interactions in (L-alanine/L-threonine + aqueous glucose/aqueous sucrose) systems at (298.15-323.15) K, *Thermochim. Acta* 527 (2012) 112-117.
- [16] A.K. Nain, R. Pal, R.K. Sharma, Volumetric, ultrasonic, and viscometric behaviour of L-histidine in aqueous-glucose solutions at different temperatures, *J. Chem. Thermodyn.* 43 (2011) 603-612.
- [17] A.K. Nain, R. Pal, Study of solute-solute and solute-solvent interactions of L-threonine in aqueous-glucose solutions at different temperatures by using volumetric and viscometric methods, *J. Chem. Thermodyn.* 60 (2013) 98-104.
- [18] A.K. Nain, M. Lather, Nettu, Probing solute-solute and solute-solvent interactions in (L-arginine + D-xylose/ L-arabinose + water) solutions at different temperatures by using volumetric and viscometric methods, *J. Chem. Thermodyn.* 63 (2013) 67-73.
- [19] A. Pal, N. Chauhan, Interactions of diglycine in aqueous saccharide solutions at varying temperatures: a volumetric, ultrasonic and viscometric study, *J. Solut. Chem.* 39 (2010) 1636-1652.
- [20] G.R. Hedwig, H. Hoiland, Thermodynamic properties of peptide solutions. 9. Partial molar isentropic pressure coefficients in aqueous solutions of sequence isomeric tripeptides with a single -CH<sub>3</sub> side-chain, *J. Chem. Thermodyn.* 25 (1993) 349-354.
- [21] R. Palani, A. Geetha, Acoustical and thermodynamical studies of L-serine, L-glutamine and L-asparagine in aqueous D-glucose solutions at 298.15 K, *Res. J. Phys.* 1 (2007) 82-89.
- [22] C.M. Villablanca, N.R. Velasquez, Sugar-lignocellulosic composites: The incorporation of two simple saccharides into moulding as additives, *J. Chil. Chem. Soc.* 48 (2003) 55-61.
- [23] A. Pal, N. Chauhan, Densities, speeds of sound and viscosities of L-alanine in aqueous fructose, maltose and lactose solutions at different temperatures, *Ind. J. Chem.* 48A (2009) 1069-1077.
- [24] G.A. Kulikova, E.V. Parfenyuk, Influence of side chain of L- $\alpha$ -amino acids on their interaction with D-glucose in dilute aqueous solutions, *J. Solut. Chem.* 37 (2008) 835-840.
- [25] A. Ali, S. Hyder, S. Sabir, D. Chand, A.K. Nain, Volumetric, viscometric, and refractive index behaviour of  $\alpha$ -amino acids and their groups contribution in aqueous D-glucose solution at different temperatures, *J. Chem. Thermodyn.* 38 (2006) 136-143.
- [26] A.K. Nain, R. Pal, R.K. Sharma, Physicochemical study of solute-solute and solute-solvent interactions of L-histidine in water + sucrose solutions at different temperatures, *J. Mol. Liq.* 165 (2012) 154-160.
- [27] Riyazuddeen, M.A. Usmani, Densities, speeds of sound, and viscosities of (L-proline + aqueous glucose) and (L-proline + aqueous sucrose) solutions in the temperature range (298.15 to 323.15K), *J. Chem. Eng. Data.* 56 (2011) 3504-3509.
- [28] C. Zhao, P. Ma, J. Li, Partial molar volumes and viscosity B-coefficients of arginine in aqueous glucose, sucrose and L-ascorbic acid solutions at T = 298.15 K, *J. Chem. Thermodyn.* 37 (2005) 37-42.
- [29] H. Rodriguez, A. Soto, A. Arce, M.K. Khoshkbarchi, Apparent molar volume, isentropic compressibility, refractive index, and viscosity of DL-alanine in aqueous NaCl Solutions, *J. Solut. Chem.* 32 (2003) 53-63.
- [30] A. Soto, A. Arce, M.K. Khoshkbarchi, Thermodynamics of diglycine and triglycine in aqueous NaCl solutions: apparent molar volume, isentropic compressibility, and refractive index, *J. Solut. Chem.* 33 (2004) 11-21.
- [31] D.O. Masson, Solute molecular volumes in relation to solvation and ionization, *Philos. Mag.* 8 (1929) 218-235.

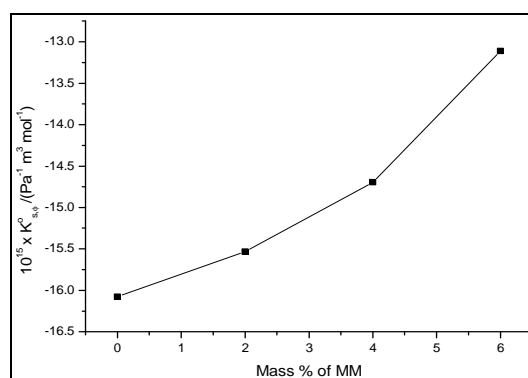


- [32] D.P. Kharakoz, Volumetric properties of proteins and their analogues in diluted water solutions. 1. Partial volumes of amino acids at 15-55 degrees C, *Biophys. Chem.* 34 (1989) 115–125; Volumetric properties of proteins and their analogues in diluted water solutions. 2. Partial adiabatic compressibilities of amino acids at 15-70 °C, *J. Phys. Chem.* 95 (1991) 5634–5642.
- [33] R. Bhat, N. Kishore, J.C. Ahluwalia, Thermodynamic studies of transfer of some amino acids and peptides from water to aqueous glucose and sucrose solutions at 298.15 K, *J. Chem. Soc. Faraday Trans. I*, 84 (1988) 2651–2665.
- [34] A.K. Mishra, J.C. Ahluwalia, Apparent molal volumes of amino acids, N-acetylamino acids, and peptides in aqueous solution, *J. Phys. Chem.* 88 (1984) 86–92.
- [35] H.L. Friedman, C.V. Krishnan, in: F. Franks (Ed.), *Water: A Comprehensive Treatise*, vol. 3, Plenum Press, New York, 1973 (Chapter 1).
- [36] F.J. Millero, A. Losurdo, C. Shin, The apparent molal and adiabatic compressibilities of aqueous amino acids at 25°C, *J. Phys. Chem.* 82 (1978) 784–792.
- [37] E. Berlin, M.J. Pallansch, Densities of several proteins and L-amino acids in the dry state, *J. Phys. Chem.* 72 (1968) 1887–1889.
- [38] F.J. Millero, G.K. Lepple, E.V. Haff, Isothermal compressibility of aqueous sodium chloride, magnesium chloride, sodium sulfate, and magnesium sulfate solutions from 0 to 45°C at 1atm, *J. Phys. Chem.* 78 (1974) 1636–1643.
- [39] A.K. Nain, R. Pal, Neetu, Physicochemical study of solute–solute and solute–solvent interactions of L-phenylalanine in (water + arabinose/glucose/sucrose) solutions at different temperatures, *J. Chem. Thermodyn.* 68 (2014) 169–182.

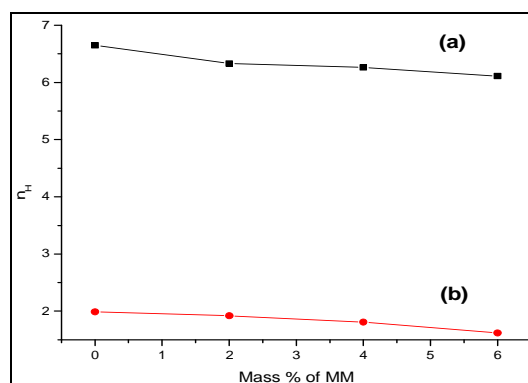
### Supplementary material:



**Fig. S1.** Variations of limiting apparent molar volume,  $V_\phi^0$  vs. mass % of MM for L-arginine in water + MM solutions at 298.15 K.



**Fig. S2.** Variations of limiting apparent molar compressibility,  $K_{s,\phi}^0$  vs. mass % of MM for L-arginine in water + MM solutions at 298.15 K.



**Fig. S3.** Variation of hydration number,  $n_H$  with mass % of MM for L-arginine in aqueous -MM by (a) volumetric method, (b) compressibility method, at 298.15 K.