Intermolecular interaction studies of homologous α-amino acids in aqueous fructose solution at 298.15 K.

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Abstract: Values of density(ρ), ultrasonic speed(u) and viscosity(η) have been determined for four amino acids (glycine, L-alanine, L-valine and L-leucine) in aqueous fructose solutions (0.05, 0.10, 0.15, 0.20) M at T = 298.15 K. Apparent molar volume (V_φ), partial molar volumes (V_φ^0) and transfer volumes (ΔV_φ^0) are evaluated using density data. Apparent molar compressibility (K_φ), partial molar compressibility (K_φ^0) and transfer compressibility (ΔK_φ^0) have been calculated using ultrasonic speed data. Viscosity B- coefficients of Jones-Dole equation, B- coefficients transfer (ΔB), free energy of activation per mole of solvent ($\Delta\mu_1^{0*}$) and solute ($\Delta\mu_2^{0*}$) are estimated using viscosity data. The linear correlations of V_φ^0, ΔV_φ^0, K_φ^0 ,ΔK_φ^0, B, ΔB, $\Delta\mu_2^{0*}$ for a homologous series of amino acids have been used to calculate the contribution of charged end groups (NH_3^+, COO^-), CH_2 and other alkyl chain of the amino acids. Our study concludes the existence of strong solute solvent interaction in the studied systems. Furthermore, all the four amino acids behave as structure maker in aqueous fructose solutions. The thermodynamics of viscous flow has also been discussed.

Keywords: Amino acids, Fructose, Apparent molar volume, Apparent molar compressibility, B- coefficients.

Introduction

Carbohydrates located at cell surfaces are important as receptors for the bio-active structures of hormones, enzymes, viruses, antibodies, etc[1]. In living systems, interactions of carbohydrates with proteins play a pivotal role in a wide range of biochemical processes. Thus, the physico-chemical study of carbohydrate - protein interactions is very important for immunology, biosynthesis, pharmacology and medicine[2]. It is well known fact that sugars will produce remarkable effects on the stability of proteins[3]. As proteins are highly complex molecules, amino acids [AA] have been extensively used as model compounds for thermo dynamical studies[4,5]. Literature survey reveals that, there is a report available[6] regarding the volumetric, compressibility and viscometric studies of L-alanine in aqueous fructose(at higher concentrations), maltose and lactose solutions at different temperatures by A Pal and N. Chauhan. Thus in continuation of our work on ternary systems comprising Amino acids + drugs / electrolytes in water[7-14], we are reporting for the first time in literature, the volumetric, compressibility and viscometric studies of homologous amino acids in aqueous fructose at 298.15 K.

Fructose is the major component of sport drinks used by sports personalities. The purpose of sports drink is to increase the absorption of water and other essentials like carbohydrates or amino acids to maintain hydration in spite of the weather conditions. Fructose generally does not cause the insulin levels to go up. This feature is essential during training or competition. It is also much better in replacing stored glucose in the liver.

Thus the thermo dynamical study of amino acids with fructose will contribute interesting results which may be used in the field of sports medicines. In this paper, we report the data on density, ultrasonic speed and viscosity of a homologous amino acids (glycine, L-alanine, L-valine and L-leucine) in aqueous fructose solutions at T = 298.15 K. Using the above experimental data, several important thermo dynamical parameters are estimated and reported. These parameters are used to interpret the interactions taking place between solute-cosolute in ternary solution (AA + fructose + water) In addition to this ,the contribution of the charged end groups of the AAs to V_φ^0, ΔV_φ^0, K_φ^0, ΔK_φ^0, B- coefficients, ΔB and $\Delta \mu_2^{0*}$ have also been determined and reported.

Experimental

Fructose (99% assay), glycine (99.7% assay), are procured from Merck Ltd. Mumbai, L-valine (99% assay) and L-leucine (+99 % assay) are obtained from ALDRICH (U.S.A). L-alanine (99% assay) is procured from SISCO, Mumbai. The amino acids and fructose are used after drying in a desiccator over P_2O_5 for 72 hrs before use. Aqueous fructose solutions of molality 0.05M, 0.10M, 0.15M and 0.20M are prepared using doubly deionized distilled water with a conductivity of 1.5×10^{-4} $\Omega^{-1} \cdot m^{-1}$ and are used as solvents to prepare the molal concentrations of amino acids. For glycine, L-alanine, L-valine, molalities of (0.02, 0.04, 0.06, 0.08 and 0.1) M and for L-leucine, molaities of (0.02, 0.04, 0.05, 0.06 and 0.08) M are used respectively. The mass measurements are made using a high precision and electronic balance (Model HR 300, Japan) with a precision of ± 0.1 mg. The densities of the solutions are measured using a single stem Pycnometer (Pyrex glass) of bulb capacity of 15×10^{-3} dm^3 having graduated stem with 5×10^{-7} dm^3 divisions and ultrasonic speeds by a multifrequency ultrasonic interferometer (M-84, Mittal make, India) at a frequency of 2MHz.The reproducibilies of density and ultrasonic speed are within ± 2.8×10^{-4} $g \cdot cm^{-3}$ and ± 0.03% respectively[15]. Viscosity is measured by means of a suspended level Ubbelhodde viscometer and flow times have been measured using a Racer digital stopwatch having an accuracy of ±0.01s. An average of three sets of flow time reading has been taken for each solution for calculation of viscosity[16]. The overall experimental reproducibility is estimated to be within ± 2×10^{-3} m Pa·s. The temperatures of the solutions are maintained to an uncertainty of ± 0.01 K in an electronically controlled thermostatic water bath (Eurotherm, Mittal enterprises, New Delhi).

Results

The densities (ρ) and ultrasonic speed (u) of amino acids in aqueous fructose solutions at the studied temperature are used to evaluate apparent molar volumes (V_φ) and apparent molar compressibility (K_φ) using the following equations (1) and (2) and are reported in Table 1 and 2.

$$V_\varphi = (M/\rho)\text{-}1000 \, (\rho - \rho_0) \,/m \, \rho \, \rho_0 \qquad (1)$$
$$K_\varphi = \beta_s \, M/\rho + 1000 \, (\beta_s \, \rho_0 - \beta_0 \, \rho)/ \, m \, \rho \, \rho_0 \qquad (2)$$

Where M is the molar mass of the solute, m is the solution molality and ρ , ρ_0, β_s and β_0 are the densities and coefficients of adiabatic compressibilities of the solution and solvent(aqueous fructose) respectively. The adiabatic compressibilities β_s and β_0 of the solution and solvent are determined from the experimental values of the ultrasonic speed and density using the Newton-Laplace equation

$$\beta_= 1/\rho \, u^2$$

The partial molar quantities (Y_φ^0) are obtained using the equation (3)

$$Y_\varphi = Y_\varphi^0 + S_y \, m \qquad (3)$$

Where Y_φ^0 (Y_φ^0 denotes V_φ^0 or K_φ^0) is the infinite dilution value that is equal to the partial molar property at infinite dilution and S_y (S_y denotes S_v or S_k) is the experimental slope [17].

Equation (3) is fitted to Y_φ (Y_φ denotes V_φ or K_φ) values by the method of least squares to evaluate V_φ^0 and K_φ^0 values. The evaluated values of partial molar volumes V_φ^0 and partial molar compressibility K_φ^0 along with standard deviations of linear regression , σ , are given in tables 3 and 4 respectively. The values of V_φ^0 and K_φ^0 of the four amino acids in water at T= 298.15 K agrees (see tables 3 and 4) fairly well with literature values [18-25], thus validating our experimental procedures.

The partial molar volumes of transfer ΔV_φ^0 and partial molar compressibility of transfer ΔK_φ^0 of amino acids from pure water to fructose water mixtures are calculated using equation (4).

$$\Delta Y_\varphi^0 = Y_\varphi^0 \text{ (in aqueous fructose) - } Y_\varphi^0 \text{ (in pure water)} \tag{4}$$

Where ΔY_φ^0 denotes ΔV_φ^0 and ΔK_φ^0 and the results are given in tables 3 and 4 respectively

The relative viscosities of amino acids in various concentrations of aqueous fructose solutions are calculated using the following equation (5) and are given in table 5.

$$\eta_r = \eta / \eta_0 \tag{5}$$

Where η and η_0 are the viscosities of the solution and solvent (Fructose + Water). The B-coefficients values are evaluated by fitting the η_r values to the Jones-Dole equation (6) by a least squares method[26] as follows.

$$\eta_r = \eta / \eta_0 = 1 + B \cdot c \tag{6}$$

Where 'c' is the molarity (calculated from molality data). The values of B-coefficients are summarized in table 6. It is seen from the table 6 that, the values of B- coefficients for amino acids in water agree very well with available literature values [27-29].

The B-coefficients data in aqueous fructose solutions have been used to calculate the corresponding (ΔB) transfer function as follows:

$$\Delta B = \Delta B \text{ (in W + F) - } \Delta B \text{ (in W)} \tag{7}$$

Where W stands for water and F stands for fructose. The ΔB values as a function of molality of the solute amino acid at a studied temperature are given in table 6

The viscosity data are used to estimate the free energy of activation per mole of the solvent ($\Delta\mu_1^{0*}$) and solute ($\Delta\mu_2^{0*}$) as suggested by Feakins et al.[30] and Eyring et al.[31] using the following equations (8-10).

$$B = (\overline{V}_1^0 - \overline{V}_2^0)/1000 + \overline{V}_1^0/1000RT(\Delta\mu_2^{0*} - \Delta\mu_1^{0*}) \tag{8}$$

$$\Delta\mu_1^{0*} = RT \ln\left(\eta_0 \overline{V}_1^0 / hN\right) \tag{9}$$

Equation (8) can be rearranged as

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + RT/\overline{V}_1^0[1000B - (\overline{V}_1^0 - \overline{V}_2^0)] \tag{10}$$

Where $\overline{V}_1^0 = (\Sigma x_i m_i / \rho)$ is the mean volume of the solvent and $\overline{V}_2^0 = V_\phi^0$ is the partial molar volume at infinite dilution. The terms x_i and m_i denote the mole fractions and molecular weights of water (1) and fructose (2) and ρ is the density of the solvent mixture (fructose + water), 'h' is the Planck's constant, 'N' is the Avogadro's number, η_0 is the viscosity of the solvent and 'R' is the gas constant. The reported values of $\Delta\mu_1^{0*}$, $\overline{V}_1^0$ and $\Delta\mu_2^{0*}$ (See table 7) for the studied amino acids in water, at $T = 298.15$ K, agree fairly well with the literature values [28,29,32].

According to transition state theory [30], every solvent molecule in one mole of solution must pass through the transition state and also interact more or less strongly with solute molecules. Thus, the activation free energy $\Delta\mu_2^{0*}$ include the free energy transfer of solute from ground state to transition state solvents [$\Delta G_2°$ (1→1')] and the free energy of solute through its own viscous transition state [$\Delta G_2°$ (2→2')]. The [$\Delta G_2°$ (1→1')] values, calculated by using methods similar to those reported elsewhere [24, 30] are also given in Table 7.

The solvation of any solute can be judged from the magnitude of B/V_φ^0 [18]. A value between 0 and 2.5 indicates an unsolvated spherical species, and any higher value is an indication of solvated ones[33]. The evaluated B/V_φ^0 values are also listed in Table 7.

Thermodynamic transfer functions of amino acids may be expressed by the McMillan-Mayer Theory[34] of solutions that permits the formal separation of the effects due to interactions involving two or more solute molecules. This approach has been further discussed by Friedman and Krishnan[35] and Frank et al.[36] in order to include solute - cosolute interactions in the solvation spheres. According to this treatment, a thermodynamic transfer function at infinite dilution can be expressed as

$$\Delta Y_\varphi^0 = 2Y_{AB}m_B + 3Y_{ABB}m_B^2 + ---- \tag{11}$$

Where Y_{AB} is $V_{AB}/K_{AB}/\eta_{AB}$ and Y_{ABB} is $V_{ABB}/K_{ABB}/\eta_{ABB}$, A stands for aminoacid and B stands for Fructose and m_B is the molality of fructose (cosolute). The constants Y_{AB} and Y_{ABB} are pair and triplet interaction parameters, obtained by fitting ΔY_φ^0 data to equation (11). The parameters V_{AB} and V_{ABB} for volumes, K_{AB} and K_{ABB} for adiabatic compressibilities and η_{AB} *and* η_{ABB} for viscosity are listed in Table 8.

Discussion

From table-1, it is seen that, the values of V_φ increase with increase in concentration of fructose solution at T= 298.15 K for all the amino acids reported, thereby showing the presence of strong solute solvent interaction[7]. The volumetric behavior of solute at infinite dilution represented by V_φ^0 (see table 3) are large positive values for all the ternary mixtures at T=298.15 K investigated, suggesting the presence of strong solute –solvent interactions in the medium.

Further, V_φ^0 value increases as the size of alkyl group in the amino acids increases from glycine to leucine. This is due to the reduction in the electrostriction at the terminal charged groups [10].

In the currently studied ternary system (amino acid + water+ fructose the value of ΔV_φ^0 is of the order of Leucine > Valine > Alanine> Glycine at a particular concentration of fructose.The introduction of CH_3- group of L-alanine provides an additional tendency for ion- hydrophilic and hydrophilic- hydrophilic group interactions and as a result smaller electrostriction of water is produced leading to larger values of ΔV_φ^0 . Similarly when the H- atom of glycine is replaced by the $(CH_3)_2CH$- group in L- valine the additional propensity for ion – hydrophophilic and hydrophilic – hydrophilic grouip interactions increases further that might leads to increase in ΔV_φ^0 values[37].Similar arguments made also be advanced for the increase of ΔV_φ^0 in L-Leucine system.

The values of the transfer volumes ΔV_φ^0 (see table 3) for the four amino acids are negative and increase monotonically with the mass fractions of fructose in aqueous fructose solutions. These results can be further explained by the cosphere overlap model, as developed by Friedman and Krishnan[38]. Two types of interaction are possible between solute and co solute namely hydrophilic-ionic interactions and hydrophobic – ionic interactions. Applying the co sphere overlap model[39] the observed negative ΔV_φ^0 values suggest the dominance of hydrophobic-ionic interactions over hydrophilic–ionic interactions in all the systems at different concentration studies. Our observations of the presence of hydrophobic-ionic interactions in the studied system have been supplemented from Enthalphic studies by Liu et al [40] and volumetric and viscometric studies by A Pal et al [6] in L-alanine in aqueous fructose solutions. Similar results of negative ΔV_φ^0 values are available in literature for methyl α-D-xylo- and methyl β-D-xylo pyranosides at the lower concentrations of Kcl[41] and for D-xylose, L-sorbose and D-fructose at a lower temperature and concentration of sodium acetate[42]. The systematic increase in ΔV_φ^0 values with an increasing concentration of fructose indicates the strengthening of hydrophilic-ionic interactions over the range of concentration studied.

Infinite dilution standard partial molar volume of the fructose molecule could be explained using Shahidis equations [43] as follows.

$$\Delta V_\varphi^0 = V_{v.w} + V_{void} - V_{shrinkage} \tag{12}$$

It has been assumed that $V_{v.w}$ (vanderwall's volume) and V_{void} (associated void volume) have the same magnitude in water and aqueous fructose solutions. The negative ΔV_φ^0 values accompanying the transfer of fructose may be attributed to the increase in the volume of shrinkage $V_{shrinkage}$ in aqueous fructose solutions[44].

It is further seen from table 2 that, the K_φ values of the amino acid in aqueous fructose solutions are negative, indicating the water molecules around ionic charged groups of amino acids are less compressible than the water molecules in the bulk solution [45]. From table 4, it is found that K_φ^0 values are negative and increase linearly with the increase in concentration of fructose solutions. This indicates that the solute– solvent interactions increase on increasing concentration of fructose solutions. The values of K_φ^0 are negative for all the amino acids studied in aqueous fructose solutions indicating that the water molecules around ionic charged groups of amino acids are less compressible than the water molecules in the bulk solutions.[45, 46]. This further supports the conclusions that their exists strong solute – solvent interactions in the studied systems

The apparent molar compressibilities of transfer (ΔK_φ^0) from water to fructose at infinite dilutions are given in Table 4 and are found to be negative at lower concentrations indicating the dominance of hydrophilic – ionic interactions. However at higher concentrations ΔK_φ^0 values become positive indicating the dominance of hydrophobic –ionic interactions over hydrophilic – ionic interactions and there by complementing the volumetric results. It must be noted that , the interaction between solute and co solute are mainly reflected in transfer volume ΔV_φ^0 values and less manifested in ΔK_φ^0 values due to the fact that ΔV_φ^0 reflects directly the change in volume af amino acids in going from aqueous solution to fructose solution while ΔK_φ^0 reflects only the change in this ΔV_φ^0 with pressure which expected to be less significant than ΔV_φ^0 itself [47]

Table-1 - Density, ρ , and apparent molal volume ,V_φ , of amino acids in aqueous fructose solution at T = 298.15 K

m_A (mol·kg^{-1})	$10^3\rho/$ (kg·m^{-3})	$10^6 V_\varphi/$ (m^3·mol^{-1})	$10^3\rho/$ (kg·m^{-3})	$10^6 V_\varphi/$ (m^3·mol^{-1})	$10^3\rho/$ (kg·m^{-3})	$10^6 V_\varphi/$ (m^3·mol^{-1})
			Glycine			
	$m_S = 0$ mol·kg^{-1}		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
0	0.99704		1.00051		1.00398	
0.02	0.99768	43.07	1.00124	38.54	1.00470	39.03
0.04	0.99831	43.30	1.00195	39.01	1.00540	39.50
0.06	0.99894	43.36	1.00264	39.48	1.00609	39.80
0.08	0.99956	43.50	1.00331	39.96	1.00676	40.19
0.1	1.00018	43.57	1.00397	40.33	1.00742	40.51
	$m_S = 0.15$ mol·kg^{-1}		$m_S = 0.20$ mol·kg^{-1}			
0	1.00746		1.01094			
0.02	1.00816	40.00	1.01162	40.96		
0.04	1.00884	40.47	1.01227	41.67		
0.06	1.00949	41.10	1.01287	42.70		
0.08	1.01011	41.77	1.01344	43.57		
0.1	1.01071	42.36	1.01397	44.48		
			Alanine			
	$m_S = 0$ mol·kg^{-1}		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
0	0.99704		1.00051		1.00398	
0.02	0.99761	60.65	1.00114	57.54	1.00460	57.95
0.04	0.99816	61.12	1.00173	58.50	1.00518	58.90
0.06	0.99870	61.42	1.00229	59.30	1.00573	59.70
0.08	0.99921	61.93	1.00280	60.31	1.00624	60.57
0.1	0.99972	62.23	1.00329	61.10	1.00673	61.29
	$m_S = 0.15$ mol·kg^{-1}		$m_S = 0.20$ mol·kg^{-1}			
0	1.00746		1.01094			
0.02	1.00807	58.35	1.01154	58.74		
0.04	1.00865	59.05	1.01211	59.44		
0.06	1.00921	59.59	1.01266	59.97		
0.08	1.00971	60.58	1.01317	60.72		
0.1	1.01023	60.97	1.01368	61.15		
			Valine			
	$m_S = 0$ mol·kg^{-1}		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
0	0.99704		1.00051		1.00398	
0.02	0.99756	91.30	1.00108	88.57	1.00454	88.86
0.04	0.99805	92.00	1.00164	88.77	1.00508	89.31
0.06	0.99851	92.72	1.00217	89.30	1.00560	89.75
0.08	0.99894	93.43	1.00269	89.67	1.00609	90.33
0.1	0.99934	94.14	1.00316	90.38	1.00658	90.66
	$m_S = 0.15$ mol·kg^{-1}		$m_S = 0.20$ mol·kg^{-1}			
0	1.00746		1.01094			
0.02	1.00801	89.14	1.01147	89.91		

0.04	1.00854	89.58	1.01197	90.59		
0.06	1.00905	90.03	1.01245	91.12		
0.08	1.00953	90.60	1.01290	91.73		
0.1	1.01000	91.03	1.01334	92.18		
	Leucine					
	$m_S = 0$ mol·kg^{-1}		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
0	0.99704		1.00051		1.00398	
0.02	0.99748	109.38	1.00101	106.08	1.00446	106.79
0.04	0.99785	111.10	1.00149	106.52	1.00491	107.48
0.05	0.99813	109.51	1.00173	106.60	1.00513	107.71
0.06	0.99835	109.45	1.00196	106.81	1.00534	108.02
0.08	0.99850	113.04	1.00242	107.05	1.00572	108.88
	$m_S = 0.15$ mol·kg^{-1}		$m_S = 0.20$ mol·kg^{-1}			
0	1.00746		1.01094			
0.02	1.00793	107.00	1.01139	107.69		
0.04	1.00837	107.69	1.01182	108.13		
0.05	1.00858	108.01	1.01202	108.50		
0.06	1.00878	108.38	1.01221	108.90		
0.08	1.00915	109.20	1.01256	109.76		

Table 2   Ultrasonic speed, u, and apparent molar compressibility, K$_\varphi$, of amino acids in aqueous fructose solution at T = 298.15 K.

m_A (mol·kg^{-1})	Glycine					
	u / (m·s^{-1})	10^{15} K_φ/ (m^3·mol^{-1}·Pa^{-1})	u / (m·s^{-1})	10^{15} K_φ/ (m^3·mol^{-1}·Pa^{-1})	u / (m·s^{-1})	10^{15} K_φ/ (m^3·mol^{-1}·Pa^{-1})
	$m_S = 0$ mol·kg^{-1}		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
0	1496.6		1499.6		1502.0	
0.02	1497.6	-25.11	1500.5	-25.72	1502.9	-24.87
0.04	1498.5	-23.39	1501.2	-22.31	1503.7	-22.96
0.06	1499.3	-21.81	1501.9	-20.88	1504.3	-20.24
0.08	1500.1	-20.92	1502.3	-17.74	1504.8	-17.93
0.1	1500.6	-18.59	1502.4	-14.00	1505.2	-15.88
	$m_S = 0.15$ mol·kg^{-1}		$m_S = 0.20$ mol·kg^{-1}			
0	1503.8		1505.0			
0.02	1504.7	-23.63	1505.9	-22.46		
0.04	1505.5	-21.75	1506.7	-20.38		
0.06	1506.2	-19.73	1507.5	-18.98		
0.08	1506.6	-16.24	1508.0	-15.82		
0.1	1507.2	-15.13	1508.5	-13.60		
	Alanine					
	$m_S = 0$ mol·kg^{-1}		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
0	1496.6		1499.6		1502.0	
0.02	1497.9	-24.67	1500.8	-23.94	1503.2	-23.11

0.04	1499.0	-21.23	1501.9	-21.58	1504.3	-20.78
0.06	1500.2	-20.94	1502.9	-19.37	1505.3	-18.60
0.08	1501.3	-19.71	1503.8	-16.99	1506.2	-16.36
0.1	1502.5	-19.58	1504.5	-14.21	1507.1	-14.84
	m_S = 0.15 mol·kg^{-1}		m_S = 0.20 mol·kg^{-1}			
0	1503.8		1505.0			
0.02	1505.0	-22.33	1506.2	-21.60		
0.04	1506.1	-20.24	1507.2	-18.10		
0.06	1507	-17.34	1508.3	-17.61		
0.08	1508.1	-16.70	1509.3	-16.24		
0.1	1508.9	-14.76	1510.1	-14.27		
	Valine					
	m_S = 0 mol·kg^{-1}		m_S = 0.05 mol·kg^{-1}		m_S = 0.10 mol·kg^{-1}	
0	1496.6		1499.6		1502.0	
0.02	1498.5	-27.83	1501.5	-29.55	1503.9	-28.64
0.04	1500.3	-25.66	1503.3	-27.85	1505.7	-26.75
0.06	1501.9	-22.51	1504.9	-24.89	1507.4	-24.86
0.08	1503.5	-20.62	1506.4	-22.57	1509.0	-22.87
0.1	1505.0	-18.62	1507.8	-20.17	1510.5	-21.11
	m_S = 0.15 mol·kg^{-1}		m_S = 0.20 mol·kg^{-1}			
0	1503.8		1505.0			
0.02	1505.7	-27.79	1506.9	-26.58		
0.04	1507.4	-24.48	1508.6	-23.09		
0.06	1509.2	-24.06	1510.3	-21.65		
0.08	1510.7	-21.37	1512	-20.62		
0.1	1512.4	-20.84	1513.7	-19.93		
	Leucine					
	m_S = 0 mol·kg^{-1}		m_S = 0.05 mol·kg^{-1}		m_S = 0.10 mol·kg^{-1}	
0	1496.6		1499.6		1502.0	
0.02	1498.9	-29.93	1501.8	-29.11	1504.2	-27.76
0.04	1501.2	-28.36	1503.9	-27.19	1506.2	-24.20
0.05	1502.2	-27.96	1504.9	-26.23	1507.1	-22.24
0.06	1503.2	-26.80	1505.6	-22.50	1508.0	-20.80
0.08	1505.7	-25.83	1507.1	-18.59	1509.5	-16.39
	m_S = 0.15 mol·kg^{-1}		m_S = 0.20 mol·kg^{-1}			
0	1503.8		1505.0			
0.02	1506	-26.92	1507.2	-25.72		
0.04	1507.9	-21.96	1509.1	-21.02		
0.05	1508.9	-21.38	1510.0	-19.26		
0.06	1509.6	-17.97	1510.9	-17.95		
0.08	1511.5	-17.01	1512.9	-17.44		

Table-3 - Partial molar volume, V_φ^0, and transfer partial molar volume, ΔV_φ^0, of amino acids in aqueous Fructose solution at T = 298.15 K.

Amino acids	$10^6\,V_\varphi^0/$ $(m^3 \cdot mol^{-1})$ $m_S = 0$ mol·kg^{-1}	$10^6\,V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	$10^6\,\Delta V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	$10^6\,V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	$10^6\,\Delta V_\varphi^0/$ $(m^3 \cdot mol^{-1})$
		$m_S = 0.05$ mol·kg^{-1}		$m_S = 0.10$ mol·kg^{-1}	
Glycine	43.003(0.09) 43.14[a], 43.19[b], 43.30[c], 42.89[d]	38.109(0.09)	-4.894	38.711(0.09)	-4.292
Alanine	60.280(0.09) 60.23[a], 60.52[b], 60.40[c], 60.23[d]	56.673(0.09)	-3.607	57.176(0.09)	-3.104
Valine	90.581(0.10) 90.65[a], 90.81[b]	87.982(0.09)	-2.599	88.394(0.09)	-2.187
Leucine	108.166(0.04) 107.48[a], 107.76[b]	105.810(0.09)	-2.356	106.072(0.09)	-2.094
	$10^6\,V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	$10^6\,\Delta V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	$10^6\,V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	$10^6\,\Delta V_\varphi^0/$ $(m^3 \cdot mol^{-1})$	
	$m_S = 0.15$ mol·kg^{-1}		$m_S = 0.20$ mol·kg^{-1}		
Glycine	39.336(0.09)	-3.667	39.996(0.09)	-3.007	
Alanine	57.672(0.09)	-2.608	58.171(0.09)	-2.109	
Valine	88.639(0.09)	-1.942	89.401(0.09)	-1.180	
Leucine	106.227(0.09)	-1.939	106.848(0.09)	-1.318	

[a]Ref 19, [b] Ref 20, [c] Ref 21, [d] Ref 22

The Viscosity B- coefficients are important for many reasons [48] and their important applications are in two research areas. That is, B-coefficients provide information about the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. In addition to that, some activation parameters of viscous flow can also be obtained using B-coefficients.

We see from table 6 that, the B-coefficients are positive, indicating [14] the presence of strong solute-solvent interactions. Further, table 6 shows that the *B* values of the amino acids increases with increase in molality of aqueous fructose solution, which shows that the ion solvent interactions become stronger with the increase in concentration of fructose. The viscosity *B* coefficient values for amino acids in aqueous fructose solutions at a particular concentration show the following order: glycine < L-alanine < L-valine < L-leucine.

Generally it is given in literature that the positive values of the B- coefficient correspond to the structure – making behavior and negative values corresponds to the structure breaking behavior.

Table-4 - Partial molal compressibility, K_φ^0, experimental slope, S_k, and transfer partial molar compressibility, ΔK_φ^0, of amino acids in aqueous Fructose solution at T = 298.15 K.

Amino acids	$10^{15} K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{18} S_k$ / (kg·m³·mol⁻²·Pa⁻¹)	$10^{15} K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{18} S_k$ / (kg·m³·mol⁻²·Pa⁻¹)	$10^{15} \Delta K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{15} K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{18} S_k$ / (kg·m³·mol⁻²·Pa⁻¹)	$10^{15} \Delta K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)
	m_S = 0 mol·kg⁻¹		m_S = 0.05 mol·kg⁻¹			m_S = 0.10 mol·kg⁻¹		
Glycine	-26.62(0.05) -26.50[a], -26.95[e], -27.00[f], -26.60[h]	7.759	-28.53(0.10)	14.002	-0.191	-27.27(0.03)	11.497	-0.065
Alanine	-24.74((0.16) -25.16a, -25.03[f], -25.69[g], -25.10h	5.859	-26.44(0.02)	12.027	-0.170	-25.03(0.04)	10.484	-0.029
Valine	-30.09(0.06) -29.82[a], -30.00[g], -28.80[h]	11.729	-32.22(0.04)	12.023	-0.213	-30.52(0.01)	9.465	-0.043
Leunine	-31.24(0.05) -31.59[a], -31.30[g], -30.50[h]	6.927	-33.78(0.27)	18.123	-0.254	-31.65(0.06)	18.755	-0.041

Amino acids	$10^{15} K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{18} S_k$ / (kg·m³·mol⁻²·Pa⁻¹)	$10^{15} \Delta K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{15} K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)	$10^{18} S_k$ / (kg·m³·mol⁻²·Pa⁻¹)	$10^{15} \Delta K_\varphi^0$ / (m³·mol⁻¹·Pa⁻¹)
	m_S = 0.15 mol·kg⁻¹			m_S = 0.20 mol·kg⁻¹		
Glycine	-26.05(0.09)	11.257	0.057	-24.93(0.07)	11.139	0.169
Alanine	-23.88(0.09)	9.348	0.086	-22.52(0.12)	8.259	0.222
Valine	-28.81(0.13)	8.507	0.128	-27.10(0.15)	7.884	0.299
Leunine	-29.48(0.26)	16.865	0.176	-27.26(0.30)	13.96	0.398

[a]Ref20, [e]Ref 23, [f]Ref 24; [g] Ref 25, [h] Ref 26.

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Table 5 Relative viscosity, η_r, of some amino acids in aqueous fructose solution as a function of concentration of amino acids, c , at T = 298.15 K.

c (mol·dm⁻³)	η_r	c (mol·dm⁻³)	η_r	c (mol·dm⁻³)	η_r	c (mol·dm⁻³)	η_r	c (mol·dm⁻³)	η_r
$m_S = 0$ mol·kg⁻¹		$m_S = 0.05$ mol·kg⁻¹		$m_S = 0.10$ mol·kg⁻¹		$m_S = 0.15$ mol·kg⁻¹		$m_S = 0.20$ mol·kg⁻¹	
Glycine									
0.0199	1.0043	0.0200	1.0035	0.0201	1.0039	0.0201	1.0046	0.0202	1.0049
0.0397	1.0071	0.0400	1.0069	0.0401	1.0075	0.0402	1.0083	0.0404	1.0089
0.0595	1.0104	0.0599	1.0103	0.0601	1.0111	0.0603	1.0121	0.0605	1.0129
0.0791	1.0136	0.0798	1.0135	0.0801	1.0147	0.0803	1.0159	0.0806	1.0170
0.0987	1.0167	0.0996	1.0170	0.1000	1.0182	0.1003	1.0196	0.1006	1.0208
Alanine									
0.0199	1.0060	0.0200	1.0061	0.0201	1.0065	0.0201	1.0068	0.0202	1.0071
0.0397	1.0110	0.0399	1.0116	0.0401	1.0121	0.0402	1.0127	0.0403	1.0131
0.0595	1.0164	0.0598	1.0170	0.0600	1.0178	0.0602	1.0188	0.0604	1.0193
0.0791	1.0214	0.0797	1.0225	0.0799	1.0234	0.0802	1.0247	0.0805	1.0254
0.0987	1.0263	0.0994	1.0279	0.0998	1.0292	0.1001	1.0304	0.1005	1.0315
Valine									
0.0199	1.0090	0.0200	1.0098	0.0200	1.0102	0.0201	1.0105	0.0202	1.0108
0.0397	1.0174	0.0399	1.0188	0.0400	1.0194	0.0402	1.0200	0.0403	1.0205
0.0595	1.0261	0.0597	1.0278	0.0599	1.0288	0.0601	1.0295	0.0603	1.0301
0.0791	1.0348	0.0795	1.0370	0.0797	1.0379	0.0800	1.0390	0.0803	1.0400
0.0987	1.0430	0.0992	1.0455	0.0995	1.0471	0.0998	1.0485	0.1002	1.0496
Leucine									
0.0199	1.0107	0.0200	1.0108	0.0200	1.0112	0.0201	1.0117	0.0202	1.0120
0.0397	1.0204	0.0399	1.0211	0.0400	1.0216	0.0401	1.0222	0.0403	1.0231
0.0496	1.0250	0.0498	1.0260	0.0499	1.0269	0.0501	1.0278	0.0503	1.0284
0.0594	1.0302	0.0596	1.0311	0.0598	1.0319	0.0601	1.0332	0.0603	1.0339
0.0791	1.0399	0.0794	1.0410	0.0796	1.0424	0.0799	1.0437	0.0802	1.0450

Table 6 Viscosity B coefficients, B, and Transfer B coefficients, ΔB, of amino acids in aqueous fructose solution at T = 298.15 K.

Amino acids	$10^3 B$ (m³·mol⁻¹)	$10^3 B$ (m³·mol⁻¹)	$10^3 \Delta B$	$10^3 B$ (m³·mol⁻¹)	$10^3 \Delta B$	$10^3 B$ (m³·mol⁻¹)	$10^3 \Delta B$
	$m_S = 0$ mol·kg⁻¹	$m_S = 0.05$ mol·kg⁻¹		$m_S = 0.10$ mol·kg⁻¹		$m_S = 0.15$ mol·kg⁻¹	
Glycine	0.159(0.02) 0.153[i]	0.168(0.01)	0.009	0.168(0.01)	0.02	0.187(0.01)	0.028

Alanine	0.259(0.02) 0.259[j]	0.273(0.01)	0.014	0.285(0.01)	0.026	0.295(0.01)	0.036
Valine	0.433(0.02) 0.447[k]	0.453(0.02)	0.020	0.464(0.01)	0.031	0.475(0.01)	0.042
Leucine	0.493(0.03) 0.487[j]	0.509(0.01)	0.016	0.522(0.01)	0.029	0.522(0.02)	0.029
	$10^3 B$ ($m^3 \cdot mol^{-1}$)	$10^3 \Delta B$					
	$m_S = 0.20$ mol·kg^{-1}						
Glycine	0.198(0.01)	0.039					
Alanine	0.304(0.01)	0.045					
Valine	0.486(0.01)	0.053					
Leucine	0.549(0.01)	0.056					

[i]Ref 27, [j]Ref 28, [k]Ref 29

of the solute[49]. Thus , the Positive B values shown by all the amino acids in aqueous fructose solution indicate that they act as   structure maker in aqueous fructose solution.

It is clear from Table 6 ΔB is positive in all cases. The positive ΔB values could be accounted to the more structured medium in the presence of aqueous fructose solutions[27]. Similar conclusions have been availed by others in literature [50].

Table 7 Free energy of activation of solvent, $\Delta\mu_1^{0*}$, and mean volume of solvent,   Free energy $\overline{V}_1^0$ of activation of solute, $\Delta\mu_2^{0*}$, and mean volume of solute, Thermodynamic   activation parameter of transfer, $G_2°(1\rightarrow1')$, Ratio of B coefficient to partial molar   volume, B/V_φ^0, of aqueous fructose solution at T = 298.15 K.

m_A mol·kg^{-1}	$\Delta\mu_1^{0*}$ (kJ·mol^{-1})	$10^6 \overline{V}_1^0$ (m^3·mol^{-1})	$\Delta\mu_2^{0*}$ (kJ·mol^{-1})	$10^6 \overline{V}_2^0$ (m^3·mol^{-1})	$\Delta G_2°(1\rightarrow1')$ (kJ·mol^{-1})	B/V_φ^0
Glycine						
0	9.16	18.07	34.40	43.00	25.24	3.70
	9.16[j]	18.02[j]	32.70 [k]			
0.05	9.23	18.15	34.90	38.11	25.67	4.41
0.10	9.29	18.23	36.41	38.71	27.12	4.62
0.15	9.36	18.32	37.51	39.34	28.16	4.75
0.02	9.41	18.40	39.01	40.00	29.59	4.95
Alanine						
0	9.16	18.07	50.49	60.28	41.33	4.30
			50.40 [k]		41.38 [l]	
0.05	9.23	18.15	51.78	56.67	42.54	4.82
0.10	9.29	18.23	53.34	57.18	44.04	4.98
0.15	9.36	18.32	54.61	57.67	45.25	5.12
0.02	9.41	18.40	55.74	58.17	46.33	5.23
Valine						
0	9.16	18.07	78.52	90.58	69.36	4.78
			80.60 [k]			
0.05	9.23	18.15	80.64	87.98	71.40	5.15
0.10	9.29	18.23	81.92	88.39	72.62	5.25
0.15	9.36	18.32	83.17	88.64	73.81	5.36
0.02	9.41	18.40	84.47	89.40	75.06	5.44
Leucine						
0	9.16	18.07	89.16	108.17	80.00	4.56
			88.30[k]			
0.05	9.23	18.15	90.72	105.81	81.49	4.81

0.10	9.29	18.23	92.20	106.07	82.91	4.92
0.15	9.36	18.32	93.94	106.23	84.58	5.06
0.02	9.41	18.40	95.31	106.85	85.90	5.14

[J] Ref 28, [k] Ref 29, [l] Ref 32

It is available in literature that the solvation effect of the solutes may be estimated from B /V_φ^0 values. Table 7 shows that values of B /V_φ^0 are greater than 2.5 in all the cases and hence all amino acids studied are highly solvated.

Free energy of activation of viscous flow $(\Delta\mu_2^{0*})$ is another useful parameter to assess the complexity of liquid structure. It is evident from table 7, that $\Delta\mu_2^{0*}$ values are positive and much larger than $\Delta\mu_1^{0*}$ which indicate that solute-solvent interactions are stronger and also indicating the structure making ability of the solute [30] in aqueous fructose solution. It further suggests that the interactions between solute and solvent molecules in the ground state are stronger than in the transition state. Thus, the solvation of the solute in the transition state is unfavourable in free energy terms. Similar results are obtained for glycine in aqueous solutions of transition metal chlorides by Mishra et al [51]. Further, $\Delta\mu_2^{0*}$ varies in the order glycine < L-alanine < L-valine < L-leucine at a given temperature, indicating that the solvation of amino acid molecules becomes increasingly unfavorable as the hydrophobicity or the number of carbon atoms of the side chain increases from glycine to L-leucine. Similar results are available in literature for α-amino acids in aqueous and mixed aqueous solutions [52,53].

Table 7 shows that, the $[\Delta G_2^\circ\ (1\rightarrow1')]$ values increase from glycine to L-leucine, that indicates the requirement of more energy for the amino acids with longer alkyl side chains for the transfer from ground state solvent to transition state solvent. This effectively means that more solute solvent bonds must be broken to form transition state.

From the table 8, it is seen that the V_{AB} and K_{AB} values are negative and V_{ABB} and K_{ABB} are positive. The change in V_{AB} and K_{AB} values from glycine to L-leucine comes from the difference in the interactions of the alkyl side chains of the amino acids with fructose. Similar results are available in literature for amino acids in aqueous KCl solutions at 310.15 K[54].

Table 8 shows that the values of viscosity pair interaction coefficient η_{AB} are positive and that of the triplet η_{ABB} interaction coefficient are negative. The positive η_{AB} values suggest the dominance of pair interaction that occur due to the overlap of hydration spheres of amino acids and fructose molecules, which supports the conclusion drawn earlier from the cosphere overlap model using volumetric data[7]. Similar results are also available in literature[32].

Table 8   Values of pair (V_{AB} and K_{AB}) , triplet (V_{ABB} and K_{ABB}) and Pair (η_{AB}) and triplet (η_{ABB}) of amino acids in aqueous fructose solution at T = 298.15 K.

Amino acids	From volume		From compressibility		From viscosity	
	$V_{AB} \times 10^6$ / $m^3 \cdot mol^{-2} \cdot kg$	$V_{ABB} \times 10^6$ / $m^3 \cdot mol^{-3} \cdot kg^2$	$K_{AB} \times 10^{15}$ / $m^3 \cdot mol^{-1} \cdot kg \cdot Pa^{-1}$	$K_{ABB} \times 10^{15}$ / $m^3 \cdot mol^{-1} \cdot kg^2 \cdot Pa^{-1}$	$10^3\ \eta_{AB}$/ $m^3 \cdot mol^{-2} \cdot kg$	$10^3\ \eta_{ABB}$/ $m^3 \cdot mol^{-3} \cdot kg^2$
Glycine	-55.900	178.000	-2.284	10.017	0.091	0.021
Alanine	-41.190	132.267	-2.050	9.593	0.149	-0.123
Valine	-29.980	98.100	-2.611	12.363	0.211	-0.290
Leucine	-27.145	86.400	-3.140	15.193	0.163	-0.078

Amino Acid Group Contribution

The linear regression analysis of D_φ^0 values as a function of number of carbon atoms (n_c) in the alkyl chain of the amino acids can be represented as [7,55]

$$D_\varphi^0 = D_\varphi^0 (NH_3^+, COO^-) + n_c\, D_\varphi^0 (CH_2) \tag{13}$$

Where D_φ^0 (NH$_3^+$, COO$^-$) and D_φ^0 (CH$_2$) are the zwitterionic end groups and the methylene group contribution to D_φ^0, respectively. Here D_φ^0 stands for V_φ^0/ ΔV_φ^0 /K_φ^0 / ΔK_φ^0 / B/ΔB and $\Delta\mu_2^{0*}$. As suggested by Hakin et al. [56, 57], the contributions of the other alkyl chain of the α-amino acids are calculated as follows:

$$D_\varphi^0 (CH_3) = 1.5 \, D_\varphi^0 (CH_2) \qquad\qquad (14)$$
$$D_\varphi^0 (CH) = 0.5 \, D_\varphi^0 (CH_2) \qquad\qquad (15)$$

The alkyl chains of homologous series of the α-amino acids studied in this work are CH$_2$-(gly), CH$_3$CH-(Ala), CH$_3$CH$_3$CHCH-(Val) and CH$_3$CH$_3$CHCH$_2$CH-(Leu), the values of D_φ^0 (CH$_2$) obtained by this procedure characterize the mean contribution of CH- and CH$_3$- groups to D_φ^0 of the α-amino acids[58]. The results are given in Tables 9-12.

It is seen from table 9 that the values of V_φ^0 (NH$_3^+$, COO$^-$) increases with increasing concentration of fructose while no regular trend is noted with V_φ^0 (CH$_2$). This indicates that the interactions between co solute and charged end groups (NH$_3^+$, COO$^-$) of amino acids are much stronger than those between the co solute and (CH$_2$). Similar results on group contribution to V_φ^0 are available in literature[29,59]. This leads to the reduction in the electrostriction of the

Table 9 Contribution to the partial molar volume V_φ^0 from zwitterionic groups, CH_2, the partial molar transfer volume, ΔV_φ^0 and other alkyl side chains of amino acids in aqueous fructose solution at T = 298.15 K.

Group	$10^6 V_\varphi^0 / (m^3 \cdot mol^{-1})$					$10^6 \Delta V_\varphi^0 / (m^3 \cdot mol^{-1})$			
	$m_S = 0$	$m_S = 0.05$	$m_S = 0.10$	$m_S = 0.15$	$m_S = 0.20$	$m_S = 0.05$	$m_S = 0.10$	$m_S = 0.15$	$m_S = 0.20$
	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}
NH_3^+, COO^-	27.31 28.30 [k] 27.72 [m]	22.13	22.80	23.54	24.12	-5.189	-4.513	-3.775	-3.195
CH_2-	16.06 15.80 [k] 15.99 [m]	16.67	16.59	16.47	16.49	0.608	0.531	0.412	0.430
CH_3CH-	32.12 31.60 [k] 31.98 [m]	33.34	33.18	32.94	32.98	1.216	1.062	0.824	0.86
$(CH_3)_2CHCH$-	64.24 63.30 [k]	66.68	66.36	65.88	65.96	2.432	2.124	1.648	1.72
$(CH_3)_2CH\ CH_2\ CH$ -	80.30 79.10 [k] 79.95 [m]	83.35	82.95	82.35	82.45	3.040	2.655	2.060	2.150

[k] **Ref 29,** [m] **Ref 59**

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Table 10 Contribution from zwitterionic groups, CH$_2$ and other alkyl side chains to the partial molar compressibility, K_φ^0 , partial molar transfer compressibility, ΔK_φ^0, of amino acids in aqueous fructose solution at T = 298.15 K.

Group	$10^{15} K_\varphi^0$ / (m^3·mol^{-1}·Pa^{-1})					$10^{15} \Delta K_\varphi^0$ / (m^3·mol^{-1}·Pa^{-1})			
	$m_S = 0$ mol·kg^{-1}	$m_S = 0.05$ mol·kg^{-1}	$m_S = 0.10$ mol·kg^{-1}	$m_S = 0.15$ mol·kg^{-1}	$m_S = 0.20$ mol·kg^{-1}	$m_S = 0.05$ mol·kg^{-1}	$m_S = 0.10$ mol·kg^{-1}	$m_S = 0.15$ mol·kg^{-1}	$m_S = 0.20$ mol·kg^{-1}
NH$_3^+$, COO$^-$	-23.79	-25.35	-24.34	-23.51	-22.68	-1.563	-0.547	0.277	1.115
CH$_2$-	-1.459	-1.628	-1.425	-1.179	-0.924	-0.169	0.034	0.280	0.535
CH$_3$CH-	-2.918	-3.256	-2.850	-2.358	-1.848	-0.338	0.068	0.560	1.070
(CH$_3$)$_2$CHCH-	-5.836	-6.512	-5.700	-4.716	-3.696	-0.676	0.136	1.120	2.140
(CH$_3$)$_2$CH CH$_2$ CH -	-7.295	-8.140	-7.125	-5.895	-4.620	-0.845	0.170	1.400	2.675

Table 11 Contribution to the viscosity *B* coefficient , the transfer B coefficient , ΔB from zwitterionic groups, CH$_2$ and other alkyl side chains of amino acids in aqueous fructose solution at T = 298.15 K.

Group	$10^3 B$ (m^3·mol^{-1})					$10^3 \Delta B$ (m^3·mol^{-1})			
	$m_S = 0$ mol·kg^{-1}	$m_S = 0.05$ mol·kg^{-1}	$m_S = 0.10$ mol·kg^{-1}	$m_S = 0.15$ mol·kg^{-1}	$m_S = 0.20$ mol·kg^{-1}	$m_S = 0.05$ mol·kg^{-1}	$m_S = 0.10$ mol·kg^{-1}	$m_S = 0.15$ mol·kg^{-1}	$m_S = 0.20$ mol·kg^{-1}
NH$_3^+$, COO$^-$	0.083 0.073[j] 0.074[k]	0.092	0.103	0.109	0.119	0.008	0.019	0.026	0.035
CH$_2$-	0.084 0.084[j] 0.088[k]	0.086	0.086	0.088	0.088	0.002	0.002	0.003	0.004
CH$_3$CH-	0.168	0.172	0.172	0.176	0.176	0.004	0.004	0.006	0.008
(CH$_3$)$_2$CHCH- (CH$_3$)$_2$CH CH$_2$ CH	0.336	0.344	0.344	0.352	0.352	0.008	0.008	0.012	0.016
-	0.420	0.430	0.430	0.440	0.440	0.010	0.010	0.015	0.020

[j] **Ref 28,** [k] **Ref 29**

Table 12 Contribution to the free energy of activation of solute, $\Delta\mu_2^{0*}$, from Zwitterionic groups, CH2 and other alkyl side chains of amino acids in aqueous fructose solution T = 298.15 K.

Group	$\Delta\mu_2^{0*}$ (kJ·mol^{-1})				
	$m_S = 0$ mol·kg^{-1}	$m_S = 0.05$ mol·kg^{-1}	$m_S = 0.10$ mol·kg^{-1}	$m_S = 0.15$ mol·kg^{-1}	$m_S = 0.20$ mol·kg^{-1}
NH_3^+, COO^-	21.87 20.54 [j]	22.36	23.92	24.88	26.22
CH_2-	13.75 13.69 [j]	14.04	14.01	14.14	14.13
CH_3CH-	27.50	28.08	28.02	28.28	28.26
$(CH_3)_2CHCH-$	55.00	56.16	56.04	56.56	56.52
$(CH_3)_2CH\ CH_2\ CH -$	68.75	70.20	70.05	70.70	70.65

[j] Ref 28

solvent water due to increased amino acid–fructose interactions, thereby contributing to the more positive values of the partial molar volume Table 9 shows that the $\Delta V\varphi 0$ (NH_3^+, COO^-) is less than ΔV_φ^0(CH_2) and increases with increasing concentration of fructose and the contribution to ΔV_φ^0 increases with increase in the size of alkyl side of the amino acids. This also indicates that the interactions between fructose and charged end groups (NH_3^+, COO^-) of amino acids are stronger. A similar linear correlation has also been reported for some amino acids in aqueous guanidine hydrochloride [60] and potassium thiocynate [61] solutions.

A linear regression analysis of the K_φ^0 values as a function of n_c at various fructose concentrations gives the contributions of (NH_3^+, COO^-) and (CH_2). It is seen from table 10 that the contributions of (NH_3^+, COO^-) to K_φ^0 is smaller than that of (CH_2) and increases with increasing concentration of fructose. This indicates that the interactions between co solute and charged end groups (NH_3^+, COO^-) of amino acids are much stronger than those between the co solute and (CH_2). Similar conclusion is obtained by Pal et al [17] for some amino acids in aqueous magnesium chloride. Table 10 shows that the contributions of (NH_3^+, COO^-) to ΔK_φ^0 is smaller than (CH_2) and increases with increasing concentration of fructose except at 0.02M of fructose. This also supports the conclusion drawn from volumetric studies.

Tables 11 – 12, show the group contribution values of viscosity B-coefficient, ΔB and $\Delta\mu_2^{0*}$. It is observed that viscosity B-coefficient increases with increase in number of carbon atoms (n_c), in the alkyl chain of the amino acids. From table 11, it is seen that the contributions of (NH_3^+, COO^-) and (CH_2) groups to viscosity B-coefficient in water, at $T = 298.15$ K, agree well with the literature values [28, 29]. Moreover, the magnitudes of B(NH_3^+, COO^-) systematically increase, in negligible manner, with the increase in the concentration of fructose. The variation of B (CH_2) with concentration of fructose is almost insensitive. Similar results on group contribution to B-coefficient are available in literature [34, 62, 63]. This indicates the predominance of the interactions between zwitterionic centers with fructose in the structure making ability of the solute. From table 11, we could infer that the magnitudes of ΔB (NH_3^+, COO^-) are relatively larger than that of ΔB (CH_2) in the presence of fructose. It is seen from table 12, that the contribution of $\Delta\mu_2^{0*}$ (NH_3^+, COO^-) group is greater than the contribution of (CH_2) group and increases with the increase in concentration of fructose. This indicates that the interactions between co-solute and charged end groups (NH_3^+, COO^-) of amino acids are much stronger than those between the co-solute and (CH_2) groups. Thus fairly complement the results obtained from volumetric studies.

Conclusions

In the present work, the volumetric, compressibility and viscometric properties of some amino acids in aqueous fructose are reported at T=298.15 K. The reported values of partial molar volumes and partial molar compressibility indicate the presence of strong solute-solvent interactions in the solution. Our study further concludes the existence of hydrophobic –ionic interactions over hydrophilic – ionic interactions in the studied systems. Furthermore, from the viscometric data , it may be concluded that all the four amino acids reported in this work behave as structure maker in aqueous fructose solutions. The thermodynamics of viscous flow has also been discussed.

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