

Research Article



Evaluation of Thermo-Acoustic and Non-Linearity Parameters (B/A) of Glycine, α -alanine, β -alanine and Phenyl Alanine in D-fructose Solutions at 298.15 K

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ABSTRACT

Ultrasonic measurements have been made on the solutions of glycine, α -alanine, β -alanine and phenyl alanine in aqueous D-fructose solutions at 298.15 K. The derived acoustic parameters like isentropic compressibility (K_s), acoustic impedance (Z), molar compressibility (W), molar sound velocity (R), relative association (R_A), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), ultrasonic attenuation (α/f^2), van der Waals constant (b) have been calculated from the experimental data. Also the non-linearity parameters (B/A), isothermal compressibility (β_T), co-efficient of thermal expansion (α) and heat capacity ratio (γ) have been calculated. These parameters are used to discuss the molecular interactions in the solutions.

Keywords: Acoustical parameters, Amino acid, Compressibility, D-fructose, Ultrasonic velocity.

INTRODUCTION

In living organisms, proteins interact with carbohydrates and this interaction plays a key role in a wide range of biochemical processes. The importance of these biomolecules is well recognized due to their applications mainly in the food, pharmaceutical, and cosmetic industries. The behavior of proteins is governed by their interactions with the surrounding environment. Due to the structural complexity of proteins, the low molecular weight model compounds such as amino acids have been studied. The complete knowledge of amino acid – carbohydrate interaction in aqueous medium is essential for a clear understanding of solution properties of these biomolecules. Measurement of ultrasonic velocity provides qualitative information about the nature and strength of the molecular interactions in solution.

In continuation of our earlier work¹ on the measurements of ultrasonic velocity and density of the solutions of amino acids in aqueous solution of D-glucose, the present investigation aims at evaluating the isentropic compressibility (K_s), acoustic impedance (Z), molar compressibility (W), molar sound velocity (R), relative association (R_A), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), ultrasonic attenuation (α/f^2), van der Waals constant (b), isothermal compressibility (β_T), co-efficient of thermal expansion (α), heat capacity ratio (γ) and non-linearity parameter B/A of glycine, α -alanine, β -alanine and phenyl alanine in aqueous D-fructose solutions (5 and 10 wt%) at 298.15 K. The results are discussed in the light of molecular interactions.

MATERIALS AND METHODS

All chemicals used were of AnalaR grades and used as such. Conductivity water (Sp.cond. $\sim 10^{-6}$ S cm^{-1}) was used to prepare solutions of D-fructose (5 and 10 wt %) and the solutions were used on the same day. The solutions of

glycine, α -alanine, β -alanine and phenyl alanine were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression² using the density values of the solutions determined at 298.15 K. Solutions were kept for 2 hours in a water thermostat maintained at the required temperature accurate to within ± 0.1 K before use for density measurements. Density measurements were done by using a specific gravity bottle (25ml capacity) as described elsewhere³. At least five observations were taken and differences in any two readings did not exceed $\pm 0.02\%$. An ultrasonic interferometer (Model No.F-81, Mittal Enterprises, New Delhi) operating at a frequency of 2MHz and overall accuracy of ± 0.5 m/s was used for the velocity measurement at 298.15K only. Viscosity measurements were made by using an Ostwald's viscometer (25 ml capacity) in a water thermostat whose temperature was controlled to ± 0.05 K. The flow time of water and flow time of solution were measured with a digital stop clock with an accuracy of 0.01s. The values of viscosity so obtained were accurate to within $\pm 0.3 \times 10^{-3}$ c P. The amino acid content in the solutions varied over a range of 0.01 to 0.08 M in all the solvents.

Theoretical Aspects

From the ultrasonic velocity (U), density (d) and viscosity co-efficient (η) data, the following parameters have been calculated.

(1) The isentropic compressibility K_s : The isentropic compressibility K_s is related to the density, d of the solution and ultrasonic velocity, U by the relation

$$K_s = 1/U^2 d \dots \dots \dots (1)$$

(2) The specific acoustic impedance, Z was calculated by using the relation

$$Z = U d \dots \dots \dots (2)$$



(3) Molar Compressibility (W) : According to Wada,

$$W = \bar{M} d^{-1} K_s^{-1/7} \dots\dots\dots (3)$$

Where, W is a constant called Wada's constant or molecular compressibility which is independent of temperature and pressure.

(4) Molar sound velocity (R):

$$R = \bar{M} d^{-1} U^{1/3} \dots\dots\dots (4)$$

Where, \bar{M} is the effective molecular weight ($\bar{M} = \sum m_i x_i$), in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents, respectively.

(5) Relative Association: From the density and sound velocity values, the magnitude of relative association, R_A was calculated from the relation

$$R_A = (d/d_0)(U_0/U)^{1/3} \dots\dots\dots (5)$$

(6) Intermolecular free length (L_f): It is the distance between the surfaces of the molecules. It can be calculated using isentropic compressibility by Jacobson's empirical relation;

$$L_f = K^1 K_s^{1/2} \dots\dots\dots (6)$$

Where, K^1 is the Jacobson's constant which is temperature dependent and is obtained from the literature.^{4,5}

(7) Free Volume (V_f): Suryanarayan et al obtained a formula for free volume in terms of the ultrasonic velocity (U) and the viscosity co-efficient of the liquid (η) as

$$V_f = (\bar{M}U/K\eta)^{3/2} \dots\dots\dots (7)$$

Where, \bar{M} is the effective molecular weight ($\bar{M} = \sum m_i x_i$), in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents, respectively. K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

(8) Internal pressure (π_i): According to Suryanarayan⁷, internal pressure is given by

$$\pi_i = b^1 RT (K \eta / U)^{1/2} (d^{2/3} / \bar{M}^{7/6}) \dots\dots\dots (8)$$

Where, b^1 is the packing factor of liquid which is equal to 1.78 for close packed hexagonal structure and 2 for cubic packing. For many liquids b^1 is equal to 2. K^1 is a dimensionless constant having a value of 4.28×10^9 , independent of temperature and nature of liquid.

(9) Ultrasonic attenuation

$$(\alpha/f^2): \alpha/f^2 = 4\pi^2 \tau / 2U \dots\dots\dots (9)$$

Where, τ is the relaxation time.

(10) van der Waals constant⁸: van der Waals constant (b) also called co-volume in the van der Waals equation is given by the formula

$$b = \bar{M}/d [1 - (RT/\bar{M}U^2) \{1 + (\bar{M}U^2/3RT)\}^{1/2} - 1] \dots\dots\dots (10)$$

Where, R is the gas constant, \bar{M} is the effective molecular weight.

(11) The apparent isentropic molar compressibility $K_{s,\phi}$ has been computed from equation(11)

$$K_{s,\phi} = 1000K_s c^{-1} - K_s^0 d_0^{-1} (1000c^{-1} d - M_2) \dots\dots\dots (11)$$

The $K_{s,\phi}$ data were fitted to equation (12)

$$K_{s,\phi} = K_{s,\phi}^0 + F' c^{1/2} + G' c \dots\dots\dots (12)$$

to obtain $K_{s,\phi}^0$ (the limiting apparent isentropic molar compressibility).

The solvation number, S_n of a solute can be related to the isentropic compressibility by equation (13)

$$S_n = n_1 n_2^{-1} [1 - V K_s (n_1 v_1^0 K_s^0)^{-1}] \dots\dots\dots (13)$$

Where, V is the volume of the solution containing n_2 moles of solute.

v_1^0 is the molar volume of solvent and n_1 is the number of moles of solvent.

The variation of solvation number with molar concentration of the solute leads to the limiting solvation number, S_n^0 which was obtained from the relation (14)

$$\lim_{c \rightarrow 0} K_{s,\phi} = - S_n^0 V_1^0 K_s^0 \dots\dots\dots (14)$$

The expression for the non-linearity parameter due to Hartmann and Balizer⁹ is given as

$$B/A = 2 + (0.98 \times 10^4)/U \dots\dots\dots (15)$$

and from the empirical relation of Ballou employed by Hartmann¹⁰, B/A is given below.

$$B/A = - 0.5 + (1.2 \times 10^4)/U \dots\dots\dots (16)$$

From the thermodynamic relation¹¹ Isothermal compressibility

$$\beta_T = 17.1 \times 10^{-4} / (T^{4/9} d^{4/3} U^2) \dots\dots\dots (17)$$

Co-efficient of thermal expansion

$$\alpha = 75.6 \times 10^{-3} / (T^{1/9} d^{1/3} U^{1/2}) \dots\dots\dots (18) \text{ and}$$

$$\text{Heat capacity ratio } (\gamma) = \beta_T / K_s \dots\dots\dots (19)$$

RESULTS AND DISCUSSION

The measured values of ultrasonic velocity (U) for different concentrations of glycine, α -alanine, β -alanine and phenyl alanine in aqueous fructose solutions (5 and 10 wt %) at 298.15 K are shown in Figures 1 and 2.

As observed, the ultrasonic velocity increases with increase in concentrations of amino acids as well as with increase in fructose content in water. The sound velocity of phenyl alanine is more as compared to other amino acids and are in the order: phenyl alanine > α -alanine > β -alanine > glycine.

The values of the isentropic compressibility (K_s), molar compressibility (W), acoustic impedance (Z), molar sound velocity (R), relative association (R_A), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), ultrasonic attenuation (α/f^2), van der Waals constant (b), S_n and $K_{s,\phi}$ are given in Table 1 and 2.

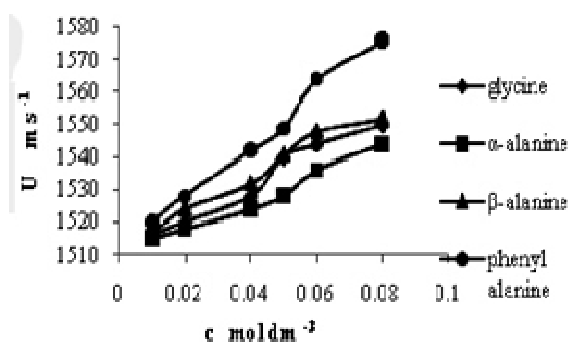


Figure 1: Plot of ultrasonic velocity vs conc. in 5 wt % D-fructose

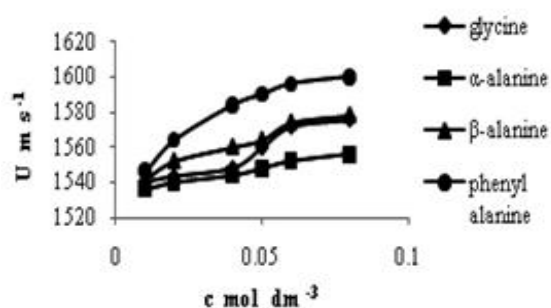


Figure 2: Plot of ultrasonic velocity Vs conc. in 10wt% D-fructose

From Table 1 it is observed that the isentropic compressibility (K_s) decreases as the concentrations of amino acids increases and also with increase in fructose content in water. The decrease in K_s with concentration may be due to the fact that the interstitial spaces of water are occupied by the solute molecules making the medium less compressible, i.e., providing greater electrostriction. Further, the decrease in compressibility with increase in fructose content in water may be due to the filling of the interstitial spaces of water molecules by organic co-solvent, fructose molecules thereby making a tight structure. The values of W increase with concentration as well as with increase in fructose content in water.

Further it is observed that the acoustic impedance, Z increases with increase in fructose content in water as well as with increase in solute concentration.¹²

This is in agreement with the theoretical requirements as both ultrasonic velocity and density increase with increase in the concentration of solute. The increase in Z values with solute concentration can be attributed to the effective solute-solvent interactions. Similar type of behaviour has been obtained for some amino acids studied in various solvent systems¹ (5, 10, 15 and 20 wt% D-glucose). Since the acoustic impedance is a measure of the resistance offered by the liquid medium to the sound wave and is a function of the elastic property of the medium, which depend on the structural changes of the

solution. The increasingly higher values with increase in the solute concentration and also with increase in fructose content in water point to the fact that the solution medium in each case starts gaining its elastic property. As observed, the molar sound velocity, R increases with increase in concentration of the solutions for all the amino acids in all the solvents studied. This type of behaviour is similar to that observed earlier.¹³

Another property¹⁴ which also can be studied to understand the ion-ion or ion-solvent interactions is the relative association, R_A . It is influenced by two factors: (i) breaking up of the associated solvent molecules on addition of the solute to it, and (ii) the solvation of solute molecules. The former leads to the decrease and the latter to the increase of relative association. In the present study, R_A decreases with increase in the solute concentration for all the amino acids in all solvents. Typical plot of R_A vs c in 5wt% fructose for all the amino acids is shown in Figure 3.

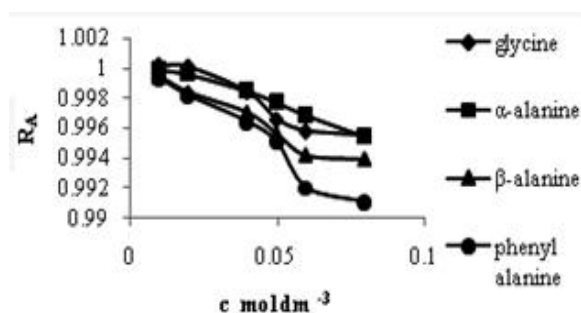


Figure 3: Plot of R_A vs c in 5wt% fructose

This implies that the breaking up of the associated solvent molecules on addition of the solute takes place in all solvents. It is known that when a solute dissolves in a solvent, some of the solvent molecules are attached to the ions (generated from the solute) because of ion-solvent interactions. Since the solvent molecules are oriented in the ionic field (i.e., electrostatic fields of ions) the solvent molecules are more compactly packed in the primary solvation shell as compared to the packing in the absence of the ions. This is the reason, why the solvent is compressed by the introduction of ions. Thus the electrostatic field of the ions causes compression of the medium giving rise to a phenomenon called electrostriction. Since the solvent molecules are compressed they do not respond to any further application of pressure. So the solution becomes harder to compress, i.e., the compressibility decreases and internal pressure increases. Hence isentropic compressibility as well as internal pressure describes the molecular arrangement in the liquid medium. The increase in internal pressure, π_i due to electrostatic field of ions is given by eqn (8).

Table 1: Values of parameters K_s ($m^2 N^{-1}$), W ($N^{-1}m^{-1}$), Z ($Kgm^{-2}s^{-1}$), R ($m^{-8/3} s^{-1/3}$), R_A and L_f (m) for glycine, α -alanine, β -alanine and phenyl alanine in D-fructose at 298.15 K.

Conc. mol dm ⁻³	Isentropic compressibility $K_s \times 10^{10} m^2 N^{-1}$	Molar compressibility $W N^{-1}m^{-1}$	Acoustic impedance $Z Kgm^{-2}s^{-1} \times 10^{-4}$	Molar sound velocity $R m^{-8/3} s^{-1/3}$	Relative association R_A	Free length $L_f \times 10^{10} m$
Glycine + 5 wt% fructose						
0.01	4.28	0.4042	154.1469	0.2131	1.0001	4.25
0.02	4.25	0.4045	154.6752	0.2132	1.0000	4.24
0.04	4.21	0.4055	155.5046	0.2138	0.9984	4.22
0.05	4.14	0.4064	156.8490	0.2143	0.9966	4.18
0.06	4.12	0.4069	157.2718	0.2146	0.9958	4.17
0.08	4.08	0.4074	158.0380	0.2149	0.9955	4.15
Glycine + 10wt% fructose						
0.01	4.06	0.4187	159.8058	0.2202	0.9998	4.14
0.02	4.04	0.4190	160.2459	0.2204	0.9997	4.13
0.04	4.02	0.4198	160.7598	0.2208	0.9988	4.12
0.05	3.96	0.4209	162.0216	0.2215	0.9963	4.09
0.06	3.89	0.4219	163.3465	0.2220	0.9943	4.06
0.08	3.87	0.4225	163.8567	0.2224	0.9940	4.05
α-alanine + 5wt% fructose						
0.01	4.29	0.4044	154.0049	0.2131	0.9999	4.26
0.02	4.27	0.4048	154.3351	0.2133	0.9996	4.25
0.04	4.23	0.4057	154.9756	0.2139	0.9985	4.23
0.05	4.21	0.4063	155.3976	0.2142	0.9977	4.22
0.06	4.16	0.4069	156.3494	0.2145	0.9968	4.2
0.08	4.12	0.4079	157.2101	0.2151	0.9954	4.17
α-alanine + 10wt% fructose						
0.01	4.09	0.4188	159.2525	0.2203	0.9998	4.16
0.02	4.07	0.4194	159.6826	0.2206	0.9990	4.15
0.04	4.04	0.4201	160.1591	0.2210	0.9985	4.14
0.05	4.02	0.4207	160.5895	0.2213	0.9977	4.12
0.06	4.00	0.4213	161.0200	0.2217	0.9970	4.11
0.08	3.98	0.4219	161.5595	0.2219	0.9969	4.1
β-alanine+5wt% fructose						
0.01	4.28	0.4045	154.1524	0.2132	0.9995	4.25
0.02	4.23	0.4052	154.9603	0.2136	0.9984	4.23
0.04	4.19	0.4062	155.8350	0.2142	0.9970	4.21
0.05	4.14	0.4070	156.8072	0.2147	0.9956	4.18
0.06	4.10	0.4078	157.5554	0.2151	0.9942	4.16
0.08	4.08	0.4085	158.0557	0.2155	0.9939	4.15
β-alanine + 10wt% fructose						
0.01	4.06	0.4193	159.8023	0.2206	0.9984	4.14
0.02	4.00	0.4204	160.9114	0.2212	0.9963	4.11
0.04	3.96	0.4215	161.7720	0.2218	0.9948	4.09
0.05	3.94	0.4221	162.2024	0.2221	0.9940	4.08
0.06	3.89	0.4229	163.3182	0.2227	0.9924	4.06
0.08	3.87	0.4236	163.8280	0.2230	0.9921	4.04
Phenyl alanine + 5wt% fructose						
0.01	4.26	0.4049	154.5688	0.2134	0.9994	4.24
0.02	4.21	0.4059	155.4740	0.2140	0.9982	4.22
0.04	4.13	0.4077	157.0990	0.2149	0.9964	4.18
0.05	4.09	0.4087	157.8072	0.2156	0.9951	4.16
0.06	4.01	0.4104	159.3872	0.2166	0.9920	4.12
0.08	3.94	0.4119	160.8623	0.2174	0.9911	4.08
Phenyl alanine + 10wt% fructose						
0.01	4.04	0.4199	160.3047	0.2209	0.9977	4.13
0.02	3.94	0.4216	162.2806	0.2219	0.9945	4.08
0.04	3.84	0.4239	164.5776	0.2232	0.9916	4.03
0.05	3.81	0.4249	165.2487	0.2237	0.9907	4.01
0.06	3.78	0.4259	165.8882	0.2243	0.9895	4.00
0.08	3.76	0.4272	166.4000	0.2250	0.9893	3.99

Table 2: Values of parameters V_f ($\text{m}^3 \text{mol}^{-1}$), π_i (N m^{-2}), α/f^2 , b ($\text{m}^3 \text{mol}^{-1}$), S_n and $K_{s,\phi}$ for glycine, α -alanine, β -alanine and phenyl alanine in D-fructose at 298.15 K.

Conc. mol dm^{-3}	$V_f \times 10^3 \text{ m}^3 \text{mol}^{-1}$	$\pi_i \times 10^{-2}$ N m^{-2}	α/f^2 $\times 10^{15}$	$b \times 10^2$ $\text{m}^3 \text{mol}^{-1}$	S_n	$K_{s,\phi} \times 10^7$
Glycine + 5wt% Fructose						
0.01	0.516	8816.803	7.71	1.8467	13.7913	-1.3263
0.02	0.514	8828.080	7.68	1.8463	22.8675	-2.1238
0.04	0.505	8878.464	7.71	1.8483	25.2906	-2.1931
0.05	0.501	8901.511	7.62	1.8479	37.1906	-3.1937
0.06	0.502	8890.206	7.57	1.8488	35.4895	-3.0322
0.08	0.504	8879.081	7.5	1.8491	32.1537	-2.7747
Glycine + 10wt% fructose						
0.01	0.487	8821.579	7.98	1.8993	44.6323	-4.0543
0.02	0.480	8865.774	8.02	1.8991	34.3768	-3.1435
0.04	0.468	8935.310	8.12	1.9010	25.0263	-2.2171
0.05	0.472	8907.756	7.95	1.9020	35.3022	-3.0208
0.06	0.475	8886.820	7.8	1.9021	42.1699	-3.5844
0.08	0.476	8881.642	7.76	1.9032	35.0151	-2.9926
α-alanine + 5wt%fructose						
0.01	0.517	8808.492	7.71	1.8477	6.1194	-0.5368
0.02	0.517	8803.921	7.68	1.8485	13.6016	-1.1842
0.04	0.514	8815.168	7.66	1.8507	17.4251	-1.4724
0.05	0.513	8815.265	7.63	1.8519	19.5163	-1.6373
0.06	0.511	8829.609	7.57	1.8516	26.0382	-2.2184
0.08	0.513	8813.015	7.49	1.8536	26.3671	-2.2327
α-alanine + 10wt% fructose						
0.01	0.483	8844.046	8.08	1.9012	14.1307	-1.2247
0.02	0.467	8936.954	8.22	1.9024	20.3834	-1.7120
0.04	0.467	8929.00	8.18	1.9043	17.1593	-1.4604
0.05	0.469	8918.262	8.13	1.9054	18.9703	-1.6014
0.06	0.465	8937.605	8.14	1.9066	20.1436	-1.6926
0.08	0.463	8945.123	8.12	1.9078	18.7475	-1.6040
β-alanine + 5wt% Fructose						
0.01	0.522	8777.042	7.64	1.8479	16.7703	-1.3561
0.02	0.521	8785.015	7.58	1.8483	34.5929	-2.9033
0.04	0.522	8769.662	7.5	1.8502	31.4380	-2.6376
0.05	0.521	8778.024	7.43	1.8507	37.4494	-3.1471
0.06	0.522	8766.612	7.35	1.8518	39.2054	-3.2764
0.08	0.523	8759.680	7.32	1.8533	33.0372	-2.7828
β-alanine + 10wt% fructose						
0.01	0.476	8880.238	8.09	1.9016	49.7215	-4.0320
0.02	0.478	8866.350	7.97	1.9026	58.7652	-4.8050
0.04	0.479	8854.594	7.89	1.9049	42.2460	-3.4653
0.05	0.468	8920.177	7.97	1.9061	38.8826	-3.1925
0.06	0.47	8907.941	7.86	1.9065	43.0484	-3.5567
0.08	0.459	8970.017	7.94	1.9080	35.6669	-2.9713
Phenyl alanine + 5wt% Fructose						
0.01	0.526	8758.328	7.58	1.8482	42.1154	-3.6593
0.02	0.518	8798.273	7.58	1.8499	50.0699	-4.3027
0.04	0.511	8827.379	7.52	1.8530	50.1810	-4.3222
0.05	0.510	8821.573	7.47	1.8555	49.1868	-4.1975
0.06	0.516	8780.656	7.28	1.8579	57.4575	-4.8440
0.08	0.518	8765.657	7.17	1.8604	53.4544	-4.5554
Phenyl alanine + 10wt%fructose						
0.01	0.46	8981.640	8.24	1.9025	79.6115	-6.5744
0.02	0.466	8937.843	7.99	1.9041	98.3776	-8.1754
0.04	0.469	8908.469	7.76	1.9071	81.2614	-6.8268
0.05	0.438	9107.257	8.07	1.9094	72.4062	-6.0850
0.06	0.427	9176.342	8.16	1.9120	66.2831	-5.5594
0.08	0.429	9146.896	8.11	1.9164	52.9537	-4.4619

Suryanarayan et al.⁷ showed that the free energy of activation, ΔG is almost equal to the cohesive energy, $\pi_i V_m$. The result indicates that ΔG increases with concentration and fructose content in the mixed solvent. Positive values of π_i indicate the presence of some specific interactions between unlike molecules in the components.

Free volume, V_f is the effective volume accessible to the centre of a molecule in a liquid. The structure of a liquid is determined by strong repulsive forces in the liquid with the relatively weak attractive forces providing the internal pressure which held the liquid molecules together. The free volume seems to be conditional by repulsive forces whereas the internal pressure is more sensitive to attractive forces. These two factors together uniquely determine the entropy of the system. Thus, the internal pressure, free volume and temperature seem to be the thermodynamic variables that describe the liquid system of fixed composition.¹⁵

It is seen that the free volume varies irregularly with solute concentration but decreases with increase in fructose content in water. As observed, internal pressure changes in a manner opposite to that of free volume. The decrease of V_f (or increase of π_i) indicates the formation of hard and/or tight solvation layer around the ion.^{16, 17} The fractional free volume (V_f / V) is a measure of disorderliness due to increased mobility of the molecules in a liquid. It is observed that mobility/ disorderliness decreases with concentration and also fructose content in water. This implies that the frictional force exerted by different layers of liquid increases with concentration as well as with fructose content. As the frictional force increases, ultrasonic absorption increases.¹⁸ In the present case, ultrasonic absorption or attenuation varies irregularly with concentration and fructose content.

The values of $K_{s,\phi}$ are negative and so also the values of $K_{s,\phi}^0$.¹⁹ The negative values may be explained by means of two different phenomena, viz., electrostriction and hydrophobic solvation. The loss of compressibility of the surrounding solvent molecules due to strong electrostrictive forces at the carboxyl group causes electrostrictive solvation. In other words, a tight solvation layer is formed around the ion for which the medium is little compressed by the application of pressure.

As observed, the values of $K_{s,\phi}^0$ of the amino acids follow the order : $K_{s,\phi}^0(\alpha\text{-alanine}) > K_{s,\phi}^0(\text{glycine}) > K_{s,\phi}^0(\beta\text{-alanine}) > K_{s,\phi}^0(\text{phenyl alanine})$. The values of $K_{s,\phi}^0$ are given in Table 3.

This trend in $K_{s,\phi}^0$ values implies that α -alanine shows stronger electrostriction as compared to other amino acids in all the solvents. In other words, the solvation layer formed around α -alanine is thick and / or hard in the solvent concerned.

Again, from Table 3 it is found that the limiting solvation number, S_n^0 for glycine and α -alanine is larger in water than in water+ D-fructose mixtures and the reverse is the

case for β -alanine and phenyl alanine.¹ The decrease in S_n^0 value in the mixed solvent medium indicates a structure breaking process. Higher S_n^0 value indicates strong electrostriction in water as compared to water + fructose mixtures. It is considered that the solvation layer formed around the ion is thick and/or hard in water than in water + fructose mixtures. However, the variation of S_n^0 as well as of S_n values predicts the degree of hard electrostrictive solvation. It represents the structural effect of the solute on the solvent in a solution.

Table 3: Values of $K_{s,\phi}^0$ ($\text{m}^3 \text{mol}^{-1} \text{pa}^{-1}$) and S_n^0 of glycine, α -alanine, β -alanine and phenyl alanine in D-fructose

Amino acid	D-fructose	$S_n^0 \times 10^2$	$K_{s,\phi}^0 \times 10^{-7}$
Glycine	5wt%	6.18	-0.683
	10wt%	6.17	-3.920
α -alanine	5wt%	3.71	-0.291
	10wt%	3.70	-1.244
β -alanine	5wt%	6.18	-1.243
	10wt%	7.40	-5.208
Phenyl alanine	5wt%	9.89	-3.381
	10wt%	12.3	-9.133

Table 4 gives the B/A values as calculated from Hartmann and Ballou relation.

The B/A values shows decreased trend with increase in concentration.²⁰ The B/A values represent the magnitude of the hardness of liquids. As the B/A values decrease with increase in concentration, it shows the interaction between the components of the binary mixtures is weaker at lower concentration of amino acids.²¹

Isothermal compressibility decreases with increase in concentration as well as with increase in fructose content. The decrease in isothermal compressibility is attributed to the influence of the electrostatic field of ions of the amino acids on the surrounding solvent molecules, called electrostriction. The magnitude of β values (Isothermal compressibility) is larger in 5 wt% fructose + water than in 10wt% fructose solutions. The decrease in both isothermal and isentropic compressibility suggests that there is association of fructose and water which leads to compression in volume.

A perusal of Table 5 shows that the co-efficient of thermal expansion (α) decreases with increase in the concentration of amino acids.

It can be explained on the basis of the fact that the increase in concentration causes more ion-solvent interactions resulting in compactness. Further, the heat capacity ratio (γ) of the solutions decreases with increase in concentration of amino acids and also with increase in the fructose content in water.

Table 4: Values of non- linearity parameter (B/A) of glycine, α -alanine, β -alanine and phenyl alanine in D-fructose at 298.15 K using Hartmann and Balizer equation and Ballou relation.

Amino acid	Conc.	5wt%fructose		10wt%fructose	
	mol dm ⁻³	B/A Hartmann	B/A Ballou	B/A Hartmann	B/A Ballou
Glycine	0.01	8.4643	7.4155	8.3636	7.2922
	0.02	8.4473	7.3947	8.3504	7.2760
	0.04	8.4136	7.3534	8.3307	7.2519
	0.05	8.3636	7.2922	8.2820	7.1923
	0.06	8.3471	7.2720	8.2340	7.1335
	0.08	8.3226	7.2419	8.2182	7.1142
α -alanine	0.01	8.4677	7.4197	8.3802	7.3125
	0.02	8.4558	7.4051	8.3636	7.2922
	0.04	8.4304	7.3740	8.3471	7.2720
	0.05	8.4136	7.3534	8.3307	7.2519
	0.06	8.3802	7.3125	8.3144	7.2319
	0.08	8.3471	7.2720	8.2982	7.2120
β -alanine	0.01	8.4609	7.4113	8.3570	7.2841
	0.02	8.4304	7.3740	8.3144	7.2319
	0.04	8.3968	7.3328	8.2820	7.1923
	0.05	8.3603	7.2881	8.2659	7.1726
	0.06	8.3307	7.2519	8.2261	7.1238
	0.08	8.3144	7.2319	8.2103	7.1045
Phenyl alanine	0.01	8.4473	7.3947	8.3389	7.2619
	0.02	8.4136	7.3534	8.2659	7.1726
	0.04	8.3553	7.2821	8.1868	7.0757
	0.05	8.3274	7.2479	8.1635	7.0471
	0.06	8.2659	7.1726	8.1403	7.0187
	0.08	8.2182	7.1142	8.125	7.0000

Table 5: Values of Isothermal compressibility β_T (m² N⁻¹), Co-efficient of thermal expansion α (N⁻¹) and Heat capacity ratio γ of glycine, α -alanine, β -alanine and phenyl alanine in D-fructose at 298.15 K

Conc. mol dm ⁻³	Isothermal compressibility β_T $\times 10^{15}$ m ² N ⁻¹	Co-efficient of thermal expansion $\alpha \times 10^3$ N ⁻¹	Heat capacity ratio (γ) $\times 10^5$
Glycine + 5wt% fructose			
0.01	5.7849	0.1039	1.3518
0.02	5.7485	0.1028	1.3515
0.04	5.6877	0.1026	1.3514
0.05	5.5935	0.1023	1.3511
0.06	5.5638	0.1021	1.3510
0.08	5.5136	0.1012	1.3506
Glycine + 10wt% fructose			
0.01	5.4559	0.1018	1.3427
0.02	5.4285	0.1017	1.3424
0.04	5.3942	0.1015	1.3423
0.05	5.3108	0.1012	1.3423
0.06	5.2267	0.1000	1.3421
0.08	5.1962	0.0998	1.3418
α-alanine + 5wt%fructose			
0.01	5.7940	0.1037	1.3520
0.02	5.7704	0.1025	1.3519
0.04	5.7236	0.1024	1.3518
0.05	5.6929	0.1022	1.3517
0.06	5.6271	0.1021	1.3513
0.08	5.5668	0.1020	1.3512
α-alanine + 10wt%fructose			
0.01	5.4908	0.1018	1.3431
0.02	5.4616	0.1016	1.3430
0.04	5.4305	0.1015	1.3429
0.05	5.4018	0.1012	1.3428
0.06	5.3733	0.1011	1.3428
0.08	5.3402	0.1009	1.3424

Table 5: Values of Isothermal compressibility β_T ($\text{m}^2 \text{N}^{-1}$), Co-efficient of thermal expansion α (N^{-1}) and Heat capacity ratio γ of glycine, α -alanine, β -alanine and phenyl alanine in D-fructose at 298.15 K (Continued.....)

Conc. mol dm^{-3}	Isothermal compressibility $\beta_T \times 10^{15} \text{ m}^2 \text{ N}^{-1}$	Co-efficient of thermal expansion $\alpha \times 10^3 \text{ N}^{-1}$	Heat capacity ratio (γ) $\times 10^5$
β-alanine + 5wt%fructose			
0.01	5.7826	0.1032	1.3520
0.02	5.7243	0.1024	1.3518
0.04	5.6617	0.1022	1.3516
0.05	5.5936	0.1021	1.3515
0.06	5.5409	0.1013	1.3514
0.08	5.5081	0.1011	1.3511
β-alanine + 10wt%fructose			
0.01	5.4523	0.1014	1.3432
0.02	5.3781	0.1012	1.3431
0.04	5.3217	0.1008	1.3430
0.05	5.2939	0.1003	1.3429
0.06	5.2235	0.0999	1.3427
0.08	5.1930	0.0998	1.3425
Phenyl alanine + 5wt%fructose			
0.01	5.7537	0.1023	1.3518
0.02	5.6892	0.1021	1.3515
0.04	5.5768	0.1020	1.3510
0.05	5.5272	0.1015	1.3509
0.06	5.4189	0.1011	1.3508
0.08	5.3255	0.1000	1.3501
Phenyl alanine + 10wt%fructose			
0.01	5.4193	0.1010	1.3430
0.02	5.2905	0.1000	1.3427
0.04	5.1484	0.0996	1.3421
0.05	5.1077	0.0994	1.3420
0.06	5.0687	0.0992	1.3419
0.08	5.0395	0.0991	1.3417

CONCLUSION

The results of the present investigation on the amino acids in aqueous fructose solutions reveal that the increase in sound velocity is due to the increase in their mass. The decrease in the value of isentropic compressibility (K_s) with increase in the solute concentration may be due to the occupation of the interstitial spaces of water by the solute molecules thereby making the medium less compressible. Lower K_s value of one amino acid in comparison to that of another implies that the former provides more electrostriction as compared to the latter. The decrease in the relative association (R_A) values with increase in the concentration of the solutions points to the fact that the breaking up of the associated solvent molecules on addition of the solute takes place in all solvents. The variation of S_n^0 values with the amino acids predicts the degree of hard electrostrictive solvation, i.e., it represents the structural effect of the amino acid on the solvent in the solution. Specific ion-ion, ion-solvent and solvent-solvent interactions play an important role for explaining the acoustic parameters. However, any deviation from the usual behaviour is probably due to characteristic structural changes in the system concerned.

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