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Intermolecular/interionic interactions in L-leucine-, L-asparagine-, and glycylglycine-aqueous electrolyte systems

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Abstract

Ultrasonic velocity and density values have been measured for ternary systems (amino acid/di-peptide + salt + water): L-leucine/L-asparagine/glycylglycine each in 1.5 M aqueous solutions of NaCl or $NaNO_3$ or KNO_3 used as solvents for several concentrations of amino acids/di-peptide at different temperatures in the range of 298.15–323.15 K. The ultrasonic velocity values have been found to increase with increase in amino acids/di-peptide concentration and temperature in all the systems. The increase in ultrasonic velocity with increase in concentration has been discussed in terms of electrostatic interactions occurring between terminal groups of zwitterions (NH_4^+ and COO^-) and Na^+, K^+, Cl^-, NO_3^- ions. The interactions of water dipoles with cations/anions and with zwitterions have also been taken into consideration. It has been observed that the ion-zwitterion and ion-dipole attractive forces are stronger than those of ion-hydrophobic repulsive forces. These interactions comprehensively introduce the cohesion into solutions under investigation. The cohesive forces are further enhanced on successive increases in solute concentration. Using ultrasonic velocity and density data, the parameters such as isentropic compressibility (κ_s), change ($\Delta\kappa_s$) and relative change ($\Delta\kappa_s/\kappa_0$) in isentropic compressibility, specific acoustic impedance (Z) and relative association (RA) have been computed. The isentropic compressibility values decrease with increase in the concentration of solutes as well as with temperature. The decrease in κ_s values with increase in concentration of L-leucine, L-asparagine and glycylglycine in 1.5 M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 have been explained in terms of an increase in the number of incompressible molecules/zwitterions in solutions and the formation of compact zwitterions–water dipole and zwitterions-ions structures in solutions. The decrease in κ_s values with increase in temperature has been attributed to the corresponding decrease of $\kappa_{relax.}$ (relaxational part of compressibility), which is dominant over the corresponding increase in κ_∞ (instantaneous part of compressibility). The trends of variations of $\Delta\kappa_s$, $\Delta\kappa_s/\kappa_0$, Z and RA with change of concentration and temperature have also been interpreted in terms of various intermolecular/interionic interactions existing in the systems.

Keywords: Ultrasonic velocity; Intermolecular/interionic interactions; L-Leucine; L-Asparagine; Glycylglycine; NaCl; $NaNO_3$; KNO_3

1. Introduction

The properties of proteins such as their structure, solubility, denaturation, activity of enzymes, etc. are greatly influenced by electrolytes [1–4]. The effect of electrolytes on structure and function of both proteins and nucleic acids has been widely studied in terms of their structure-making and structure-breaking properties [1–11]. Proteins are complex molecules and their behaviour in solutions is governed by a number of specific interactions. One approach that reduces the degree of complexity in the study of these interactions and requires less complex measurement techniques is to study the interactions in systems containing smaller bio-molecules, such as amino acids and peptides. As amino acids and peptides are the building blocks of the proteins, their study provides important information, which can be related to the behaviour of larger biomolecules such as proteins.

All pure liquids except water and heavy water are found to have negative temperature coefficient of ultrasound velocity. Randall [12] found that water has a large positive coefficient of ultrasound velocity at room temperature. The temperature coefficient of ultrasound velocity of water decreases to zero at 74 °C and then becomes negative as for ordinary liquids. However, the temperature coefficient of isentropic compressibility of water becomes zero at 64 °C [13]. The peculiar structure of water [14] seems to be responsible for this anomalous behaviour.

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Ultrasonic velocity studies of amino acids [15–21], peptides [17,18,22–24] and proteins [25–28] in aqueous medium, aqueous urea solutions, mixed aqueous solutions and organic solvents have been carried out by a number of researchers for investigating the solute–solute, solute–solvent and solvent–solvent intermolecular/interionic interactions. However, few authors [15,18,19,23,24] have studied the behaviour of amino acids and peptides in aqueous electrolyte solutions. For this purpose, the ultrasonic velocity (u) and density (ρ) values for ternary systems (amino acid/di-peptide + salt + water): L-leucine/L-asparagine/glycylglycine + (1.5 M) NaCl/$NaNO_3$/KNO_3 + water as functions of concentration of amino acid/di-peptide and temperature have been measured. Using the u and ρ data, the κ_s, $\Delta\kappa_s$, $\Delta\kappa_s/\kappa_0$, Z and RA values have been computed, which in turn provide interesting information about the various interactions operative in solutions.

2. Materials and methods

The amino acids: L-leucine, and L-asparagine hydrate; and di-peptide: glycylglycine used in this work were obtained from SRL (India). The salts: sodium chloride, sodium nitrate and potassium nitrate were purchased from E. Merck (India). All the chemicals were of ≥99% purity. The amino acids and di-peptide were dried at ∼110 °C and kept in vacuum desiccator over P_2O_5 for several hours before use. The salts were recrystallized twice in triply distilled water, dried in a vacuum oven and then kept over P_2O_5 in a vacuum desiccator at room temperature for a minimum of 24 h before use. Stock solutions of 1.5 M concentration of NaCl, $NaNO_3$ and KNO_3 were prepared by weight in triply distilled water and were used as solvents for the preparation of amino acids and di-peptide solutions of different molal concentration. The specific conductivity of the water used was less than $18 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. An ultrasonic interferometer based on variable-path principle was used for the measurement of ultrasound velocity at a frequency of 4 MHz in the temperature range: 298.15–323.15 K by a method described elsewhere [29]. The instrument was calibrated with the triple distilled water. The densities of solutions were measured by pyknometer [29]. Thermostated water/paraffin bath was maintained at a desired temperature (±0.01 °C) for about 30 min prior to recording of readings at each temperature of study. Several very close readings recorded at each temperature were averaged. The accuracies in measurements of the ultrasonic velocity and density were ascertained by comparing the measured values of these parameters for water with the corresponding literature values at different temperatures (Table 1) [30,31]. The uncertainties in ultrasonic velocity and density measurements were found to be within ±0.2 m s^{-1} and ±0.0002 g cm^{-3}, respectively.

3. Results and discussion

The experimentally measured density values for L-leucine, L-asparagine and glycylglycine in 1.5 M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 as functions of molal concentration and temperature have been listed in Table 2. The measured ultrasonic velocity values for the L-leucine, L-asparagine and glycylglycine in the said aqueous electrolyte solutions have been least-squares fitted to the following second order polynomial equation,

$$u = u_0 + u_1\, m + u_2\, m^2 \quad (1)$$

where u_0, u_1, and u_2 are the fitted coefficients, and m is the molality of the amino acids/di-peptide. The fitted coefficients alongwith standard deviations are listed in Table 3. Fig. 1 is given as representative of plots of u versus m. The ultrasonic velocity values increase with increase in concentration of amino acids/di-peptide as well as with temperature in all the systems under investigation. This increase in ultrasonic velocity values in aqueous amino acids/di-peptide-electrolyte solutions may be attributed to the overall increase of cohesion brought about by the solute-solute, solute–solvent and solvent–solvent interactions in solutions. Amino acids and di-peptide in aqueous solutions essentially behave as zwitterions having NH_4^+ and COO^- groups at two ends of the molecule. The Na^+, K^+, Cl^- and NO_3^- ions furnished by electrolytes interact electrostatically with NH_4^+ and COO^- groups of amino acids and di-peptide zwitterions. In addition, the water dipoles are strongly aligned to the cations/anions as well as to the amino acids/di-peptide zwit-

Table 1
Observed and literature ultrasonic velocity (u, m s^{-1}) and density (ρ, g cm^{-3}) values of water as function of temperature (T, K)

T (K)	Observed values	Literature values[a,b]
u (m s^{-1})		
298.15	1496.8	1496.687
308.15	1519.9	1519.808
318.15	1536.4	1536.409
ρ (g cm^{-3})		
298.15	0.9971	0.997045
308.15	0.9942	0.994032
318.15	0.9903	0.990213
323.15	0.9879	0.988036

[a] Ref. [30].
[b] Ref. [31].

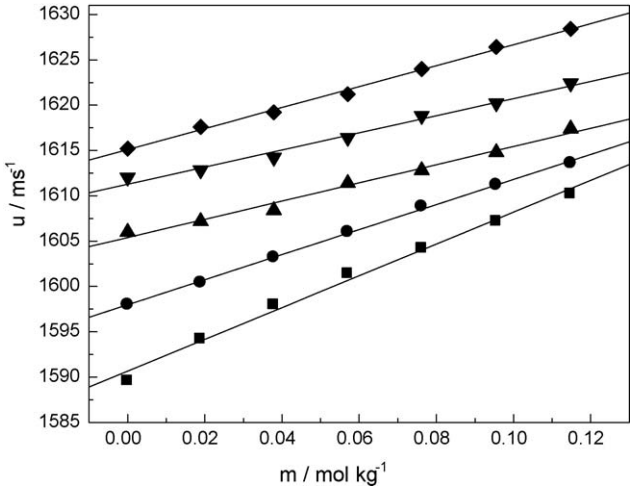

Fig. 1. Ultrasonic velocity vs. concentration of L-leucine in 1.5 M aqueous NaCl solution: (■) 303.15 K; (●) 308.15 K; (▲) 313.15 K; (▼) 318.15 K; (♦) 323.15 K.

Table 2
Density values (ρ, 10^3 kg m^{-3}) as functions of concentration and temperature

m (mol kg^{-1})	T (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
(i) L-Leucine in 1.5 M aqueous NaCl solution						
0.0000	1.0588	1.0561	1.0538	1.0514	1.0488	1.0462
0.0189	1.0591	1.0563	1.0540	1.0516	1.0490	1.0463
0.0379	1.0594	1.0566	1.0543	1.0518	1.0492	1.0465
0.0570	1.0598	1.0570	1.0547	1.0522	1.0496	1.0470
0.0762	1.0601	1.0575	1.0551	1.0526	1.0501	1.0475
0.0955	1.0604	1.0579	1.0555	1.0530	1.0505	1.0479
0.1148	1.0607	1.0584	1.0559	1.0535	1.0509	1.0484
(ii) L-Leucine in 1.5 M aqueous $NaNO_3$ solution						
0.0000	1.0791	1.0765	1.0735	1.0703	1.0670	1.0637
0.0186	1.0792	1.0767	1.0737	1.0706	1.0675	1.0642
0.0372	1.0797	1.0769	1.0739	1.0709	1.0678	1.0647
0.0560	1.0801	1.0774	1.0745	1.0716	1.0686	1.0655
0.0748	1.0806	1.0779	1.0750	1.0723	1.0693	1.0663
0.0936	1.0811	1.0783	1.0756	1.0730	1.0700	1.0671
0.1126	1.0815	1.0788	1.0762	1.0737	1.0708	1.0679
(iii) L-Leucine in 1.5 M aqueous KNO_3 solution						
0.0000	1.0869	1.0850	1.0830	1.0806	1.0779	1.0750
0.0184	1.0872	1.0852	1.0831	1.0807	1.0780	1.0751
0.0370	1.0875	1.0854	1.0832	1.0808	1.0781	1.0752
0.0556	1.0876	1.0856	1.0833	1.0810	1.0782	1.0753
0.0742	1.0881	1.0859	1.0836	1.0812	1.0785	1.0755
0.0930	1.0885	1.0863	1.0840	1.0816	1.0789	1.0759
0.1118	1.0891	1.0871	1.0849	1.0824	1.0798	1.0768
(iv) L-Asparagine in 1.5 M aqueous NaCl solution						
0.0000	1.0588	1.0561	1.0538	1.0514	1.0488	1.0462
0.0189	1.0596	1.0571	1.0549	1.0525	1.0500	1.0476
0.0379	1.0606	1.0581	1.0558	1.0534	1.0509	1.0484
0.0570	1.0617	1.0591	1.0568	1.0544	1.0518	1.0493
0.0761	1.0627	1.0601	1.0577	1.0553	1.0527	1.0501
0.0953	1.0638	1.0611	1.0587	1.0562	1.0536	1.0510
0.1146	1.0648	1.0621	1.0596	1.0571	1.0545	1.0518
0.1340	1.0658	1.0631	1.0606	1.0580	1.0554	1.0527
0.1534	1.0669	1.0641	1.0615	1.0590	1.0563	1.0536
(v) L-Asparagine in 1.5 M aqueous $NaNO_3$ solution						
0.0000	1.0791	1.0765	1.0735	1.0703	1.0670	1.0637
0.0186	1.0799	1.0772	1.0742	1.0710	1.0678	1.0647
0.0372	1.0809	1.0781	1.0751	1.0719	1.0688	1.0656
0.0559	1.0819	1.0790	1.0760	1.0728	1.0698	1.0666
0.0747	1.0829	1.0799	1.0769	1.0737	1.0708	1.0676
0.0936	1.0839	1.0809	1.0778	1.0746	1.0717	1.0685
0.1125	1.0849	1.0818	1.0787	1.0755	1.0727	1.0695
0.1315	1.0859	1.0827	1.0796	1.0764	1.0737	1.0704
0.1505	1.0869	1.0836	1.0805	1.0773	1.0746	1.0714
(vi) L-Asparagine in 1.5 M aqueous KNO_3 solution						
0.0000	1.0869	1.0850	1.0830	1.0806	1.0779	1.0750
0.0184	1.0872	1.0853	1.0832	1.0810	1.0784	1.0757
0.0369	1.0887	1.0866	1.0845	1.0821	1.0795	1.0769
0.0555	1.0902	1.0879	1.0857	1.0833	1.0806	1.0781
0.0741	1.0916	1.0893	1.0870	1.0844	1.0816	1.0793
0.0928	1.0931	1.0907	1.0883	1.0856	1.0827	1.0805
0.1115	1.0946	1.0920	1.0896	1.0867	1.0838	1.0817
0.1302	1.0961	1.0934	1.0908	1.0878	1.0847	1.0829
0.1490	1.0975	1.0947	1.0921	1.0890	1.0860	1.0841
(vii) Glycylglycine in 1.5 M aqueous NaCl solution						
0.0000	1.0588	1.0561	1.0538	1.0514	1.0488	1.0462
0.0189	1.0597	1.0572	1.0549	1.0524	1.0498	1.0468
0.0379	1.0605	1.0581	1.0558	1.0533	1.0505	1.0475
0.0570	1.0612	1.0589	1.0566	1.0541	1.0513	1.0482

Table 2 (*Continued*)

m (mol kg^{-1})	T (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
0.0761	1.0620	1.0598	1.0576	1.0549	1.0521	1.0489
0.0953	1.0627	1.0606	1.0583	1.0557	1.0528	1.0496
0.1145	1.0635	1.0615	1.0592	1.0566	1.0536	1.0503
0.1339	1.0642	1.0624	1.0600	1.0574	1.0544	1.0510
0.1533	1.0650	1.0632	1.0609	1.0582	1.0552	1.0517
(viii) Glycylglycine in 1.5 M aqueous $NaNO_3$ solution						
0.0000	1.0791	1.0765	1.0735	1.0703	1.0670	1.0637
0.0186	1.0804	1.0778	1.0749	1.0718	1.0680	1.0651
0.0372	1.0810	1.0784	1.0755	1.0724	1.0692	1.0657
0.0559	1.0817	1.0790	1.0760	1.0730	1.0698	1.0664
0.0746	1.0823	1.0796	1.0766	1.0735	1.0704	1.0670
0.0935	1.0830	1.0802	1.0772	1.0741	1.0710	1.0677
0.1124	1.0836	1.0808	1.0777	1.0747	1.0716	1.0683
0.1314	1.0843	1.0814	1.0783	1.0753	1.0722	1.0689
0.1504	1.0849	1.0820	1.0789	1.0759	1.0729	1.0696
(ix) Glycylglycine in 1.5 M aqueous KNO_3 solution						
0.0000	1.0869	1.0850	1.0830	1.0806	1.0779	1.0750
0.0184	1.0883	1.0859	1.0837	1.0811	1.0782	1.0751
0.0369	1.0888	1.0863	1.0840	1.0815	1.0785	1.0754
0.0555	1.0893	1.0867	1.0844	1.0818	1.0788	1.0757
0.0741	1.0899	1.0871	1.0848	1.0822	1.0792	1.0760
0.0928	1.0904	1.0872	1.0851	1.0825	1.0795	1.0764
0.1116	1.0909	1.0878	1.0855	1.0828	1.0798	1.0767
0.1305	1.0914	1.0882	1.0858	1.0832	1.0802	1.0770
0.1494	1.0920	1.0886	1.0862	1.0835	1.0805	1.0773

terions by electrostatic forces. These interactions comprehensively introduce the cohesion into solutions under investigation. The cohesive forces are further enhanced on successive increases in solute concentration. The added amount of amino acids/dipeptide zwitterions may also occupy the cavities of water clusters which may lead to the formation of denser structure of the aqueous electrolyte solution [32]. This process may have continued until a concentration of solute is reached at which all cavities are filled. Raman studies substantiate the view that more number of compact zwitterions–water structures is formed in solutions with the addition of solute. Hirata and Arakawa [33], Magazu et al. [34], Rohman and Mahiuddin [35], and Ragouvamane and Rao [36] have reported similar increasing trend of variation of ultrasonic velocity with increase in solute concentration in tetraalkylammonium salts–water; α,α-trehalose–water; sodium nitrate/sodium thiosulphate–water, amino acids–ethanol–water systems, respectively. It appears that the rise in temperature causes the thermal rupture of the ice-like structure of water, which in turn, enhances the cohesion in solutions. It seems that the cohesion factor dominates over the thermal expansion factor in solutions with increase in temperature.

The isentropic compressibility of the amino acids and dipeptide in aqueous electrolyte solutions have been calculated from the ultrasonic velocity and density data using the Newton–Laplace expression [37],

$$\kappa_s = \frac{1}{\rho u^2} \quad (2)$$

The κ_s values as functions of concentration and temperature have been listed in Table 4. The isentropic compressibility values decrease with increase in the concentration of solutes as well as with temperature. This trend of variation of κ_s is in consonance with the variation of u with concentration and temperature. The decrease in κ_s values with increase in concentration of L-leucine, L-asparagine and glycylglycine in 1.5 M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 may be due to (i) an increase in the number of incompressible molecules/zwitterions in solutions and (ii) the formation of compact structure of zwitterions–water dipole and zwitterions-ions structures in solutions. The decrease in isentropic compressibility values with increase in temperature in all systems under study may be explained in terms of the changes occurred in water structure around zwitterions and ions. Water is regarded as an equilibrium mixture of two structures such as an ice-like structure and a close packed structure [14,38]. Compressibility of liquid water is given by, $\kappa_s = \kappa_\infty + \kappa_{relax.}/(1 + \omega^2\tau^2)$, where κ_∞ is an instantaneous part of compressibility and $\kappa_{relax.}$ a relaxational part of compressibility [14]. The relaxational time τ, corresponding to $\kappa_{relax.}$ is of the order of 10^{-11} s. The relation $\omega\tau < 1$ holds in the present experiment, where ω is the angular frequency. Thus, the isentropic compressibility obtained is equal to $(\kappa_\infty + \kappa_{relax.})$. With the rise in temperature, κ_∞ increases due to thermal expansion while $\kappa_{relax.}$ decreases due to thermal rupture of the ice-like structure. Thus, the decrease in isentropic compressibility values with increase in temperature may be attributed to the corresponding decrease in $\kappa_{relax.}$, which is dominant over the corresponding increase in κ_∞. The isentropic

Table 3
Least-squares fit coefficients of the ultrasonic velocity equation, $u = u_0 + u_1 m + u_2 m^2$ as a function of temperature

T (K)	u_0 (ms^{-1})	u_1 ($m\,s^{-1}$) ($mol\,kg^{-1}$)$^{-1}$	u_2 ($m\,s^{-1}$) ($mol\,kg^{-1}$)$^{-2}$	$\sigma_{[u]} \times 10$
(i) L-Leucine in 1.5 M aqueous NaCl solution				
303.15	1589.84	226.90	−449.19	3.0
308.15	1597.84	147.53	−82.37	1.8
313.15	1605.91	71.99	241.24	4.3
318.15	1611.70	68.30	227.83	4.2
323.15	1615.29	103.90	102.93	3.1
(ii) L-Leucine in 1.5 M aqueous $NaNO_3$ solution				
303.15	1568.23	83.15	392.24	2.2
308.15	1571.37	104.07	209.67	2.9
313.15	1576.50	123.76	7.66	2.1
318.15	1583.30	86.44	98.84	2.1
323.15	1588.70	75.28	66.07	3.3
(iii) L-Leucine in 1.5 M aqueous KNO_3 solution				
303.15	1555.59	134.13	99.77	4.5
308.15	1560.27	138.09	−42.14	3.4
313.15	1565.11	130.90	101.16	2.5
318.15	1570.78	134.28	−1.15	2.5
323.15	1575.55	175.91	−377.45	1.4
(iv) L-Asparagine in 1.5 M aqueous NaCl solution				
303.15	1589.40	88.79	284.08	5.9
308.15	1597.62	85.42	214.11	4.4
313.15	1605.81	81.74	179.09	5.4
318.15	1611.51	63.30	293.87	7.6
323.15	1614.91	106.41	63.40	6.3
(v) L-Asparagine in 1.5 M aqueous $NaNO_3$ solution				
303.15	1568.11	90.94	59.69	2.3
308.15	1571.46	108.65	−22.75	1.6
313.15	1576.61	104.01	4.54	2.3
318.15	1583.03	87.60	72.53	4.0
323.15	1588.54	79.65	66.46	3.4
(vi) L-Asparagine in 1.5 M aqueous KNO_3 solution				
303.15	1555.70	82.22	−37.95	3.1
308.15	1560.75	87.40	−152.15	3.6
313.15	1565.33	102.69	−173.18	3.7
318.15	1570.87	82.51	−44.75	3.0
323.15	1575.65	60.80	55.47	3.0
(vii) Glycylglycine in 1.5 M aqueous NaCl solution				
298.15	1582.82	159.66	−387.50	9.3
303.15	1590.81	164.44	−475.60	9.4
308.15	1598.82	163.88	−428.72	7.3
313.15	1606.71	132.66	−372.46	6.5
318.15	1612.24	114.00	−299.43	3.0
323.15	1616.34	103.33	−188.76	8.7
(viii) Glycylglycine in 1.5 M aqueous $NaNO_3$ solution				
298.15	1560.38	80.16	2.25	3.7
303.15	1568.47	79.42	9.52	3.7
308.15	1571.99	100.99	−1.84	4.2
313.15	1576.43	108.22	−80.74	2.5
318.15	1582.99	86.62	−23.04	3.8
323.15	1587.72	85.98	−53.09	5.9
(ix) Glycylglycine in 1.5 M aqueous KNO_3 solution				
298.15	1546.86	105.2	−153.35	6.4
303.15	1556.18	35.31	146.22	3.6
308.15	1560.45	69.19	−2.01	1.9
313.15	1565.33	79.11	−46.97	2.6
318.15	1570.81	67.18	−48.40	1.9
323.15	1575.71	52.16	44.01	2.5

Table 4
Isentropic compressibility values (κ_s, 10^{-11} m^2 N^{-1}) as functions of concentration and temperature

m (mol kg^{-1})	T (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
(i) L-Leucine in 1.5 M aqueous NaCl solution						
0.0000		37.47	37.16	36.88	36.69	36.64
0.0189		37.25	37.04	36.81	36.65	36.53
0.0379		37.06	36.90	36.75	36.58	36.45
0.0570		36.89	36.76	36.60	36.47	36.34
0.0762		36.75	36.62	36.52	36.34	36.20
0.0955		36.59	36.50	36.42	36.26	36.08
0.1148		36.44	36.37	36.29	36.15	35.97
(ii) L-Leucine in 1.5 M aqueous $NaNO_3$ solution						
0.0000		37.76	37.71	37.60	37.39	37.26
0.0186		37.69	37.63	37.46	37.29	37.14
0.0372		37.60	37.53	37.35	37.19	37.08
0.0560		37.45	37.37	37.23	37.08	36.97
0.0748		37.31	37.23	37.08	36.99	36.89
0.0936		37.17	37.10	36.96	36.87	36.78
0.1126		37.02	36.96	36.81	36.74	36.66
(iii) L-Leucine in 1.5 M aqueous KNO_3 solution						
0.0000		38.07	37.92	37.77	37.60	37.47
0.0184		37.98	37.80	37.66	37.50	37.33
0.0370		37.84	37.69	37.55	37.36	37.18
0.0556		37.69	37.56	37.41	37.25	37.06
0.0742		37.52	37.40	37.26	37.10	36.94
0.0930		37.39	37.29	37.11	36.98	36.82
0.1118		37.24	37.16	36.97	36.85	36.72
(iv) L-Asparagine in 1.5 M aqueous NaCl solution						
0.0000		37.47	37.16	36.88	36.69	36.64
0.0189		37.37	37.08	36.76	36.61	36.51
0.0379		37.22	36.95	36.70	36.54	36.40
0.0570		37.11	36.84	36.54	36.43	36.30
0.0761		36.98	36.69	36.41	36.30	36.16
0.0953		36.80	36.52	36.26	36.11	35.97
0.1146		36.58	36.38	36.14	35.97	35.84
0.1340		36.44	36.24	36.05	35.89	35.75
0.1534		36.29	36.10	35.86	35.73	35.62
(v) L-Asparagine in 1.5 M aqueous $NaNO_3$ solution						
0.0000		37.76	37.71	37.60	37.39	37.26
0.0186		37.69	37.60	37.47	37.31	37.14
0.0372		37.55	37.48	37.33	37.19	37.06
0.0559		37.44	37.36	37.22	37.04	36.92
0.0747		37.32	37.22	37.11	36.95	36.83
0.0936		37.19	37.09	36.98	36.81	36.70
0.1125		37.07	36.98	36.86	36.70	36.62
0.1315		36.94	36.85	36.74	36.60	36.50
0.1505		36.83	36.74	36.59	36.43	36.35
(vi) L-Asparagine in 1.5 M aqueous KNO_3 solution						
0.0000		38.07	37.92	37.77	37.60	37.47
0.0184		38.02	37.82	37.67	37.51	37.39
0.0369		37.88	37.69	37.53	37.39	37.30
0.0555		37.77	37.59	37.42	37.27	37.18
0.0741		37.63	37.50	37.30	37.20	37.08
0.0928		37.52	37.40	37.23	37.10	36.99
0.1115		37.43	37.31	37.12	36.98	36.91
0.1302		37.31	37.23	37.04	36.90	36.79
0.1490		37.19	37.11	36.92	36.77	36.66
(vii) Glycylglycine in 1.5 M aqueous NaCl solution						
0.0000	37.76	37.47	37.16	36.88	36.69	36.64
0.0189	37.48	37.20	36.93	36.69	36.55	36.44
0.0379	37.33	37.04	36.75	36.54	36.42	36.33
0.0570	37.24	36.93	36.64	36.44	36.35	36.27

Table 4 (*Continued*)

m (mol kg^{-1})	T (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
0.0761	37.15	36.86	36.57	36.37	36.25	36.21
0.0953	37.04	36.76	36.44	36.31	36.19	36.13
0.1145	36.92	36.67	36.35	36.21	36.09	36.05
0.1339	36.82	36.59	36.27	36.14	36.05	35.93
0.1533	36.75	36.48	36.17	36.06	35.99	35.88
(viii) Glycylglycine in 1.5 M aqueous $NaNO_3$ solution						
0.0000	38.04	37.76	37.71	37.60	37.39	37.27
0.0186	37.96	37.64	37.55	37.45	37.30	37.19
0.0372	37.86	37.56	37.42	37.32	37.17	37.12
0.0559	37.76	37.45	37.34	37.24	37.09	36.98
0.0746	37.64	37.35	37.24	37.13	36.99	36.87
0.0935	37.56	37.27	37.13	37.03	36.91	36.81
0.1124	37.46	37.21	37.04	36.90	36.74	36.69
0.1314	37.38	37.08	36.89	36.82	36.71	36.64
0.1504	37.28	36.98	36.79	36.73	36.63	36.56
(ix) Glycylglycine in 1.5 M aqueous KNO_3 solution						
0.0000	38.49	38.07	37.92	37.77	37.60	37.47
0.0184	38.27	38.00	37.84	37.68	37.53	37.41
0.0369	38.18	37.92	37.75	37.59	37.46	37.34
0.0555	38.09	37.87	37.68	37.52	37.40	37.31
0.0741	38.01	37.82	37.61	37.45	37.23	37.25
0.0928	37.92	37.75	37.54	37.36	37.26	37.16
0.1116	37.86	37.70	37.48	37.30	37.21	37.11
0.1305	37.75	37.63	37.38	37.24	37.16	37.03
0.1494	37.67	37.50	37.31	37.14	37.06	36.98

compressibility value of 1.5 M aqueous solution of NaCl or $NaNO_3$ or KNO_3 is lesser than that of water in the temperature range of 298.15–323.15 K. For instance, at 298.15 K the isentropic compressibility values of 1.5 M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 are 37.47×10^{-11}, 37.76×10^{-11} and 38.07×10^{-11} m^2 N^{-1}, respectively, whereas that of water is 44.773×10^{-11} m^2 N^{-1} [39]. The smaller values of κ_s for aqueous electrolyte solutions than that of water may be attributed to cations–water dipole and anions–water dipole interactions in solutions, which ultimately may lead to an overall increase in cohesive forces in solutions. The isentropic compressibility values of the said 1.5 M aqueous electrolyte solutions vary in the following order: NaCl < $NaNO_3$ < KNO_3. This trend of variation of κ_s values may be explained in terms of the structure-making behaviour of cations and anions. The Na^+ is more structure-making ion than K^+ due to its smaller size in comparison to K^+. Similarly, the smaller size of Cl^- than that of NO_3^- makes it more structure-making ion than that of NO_3^- ion. Owing to this, the aqueous NaCl solution becomes least compressible whereas the aqueous KNO_3 solution becomes most compressible. The order of variation of κ_s values for 0.0189 M solutions of L-leucine, L-asparagine and glycylglycine in aqueous NaCl solution at 303.15 K has been found to be as follows: glycylglycine (37.20×10^{-11} m^2 N^{-1}) < L-leucine (37.25×10^{-11} m^2 N^{-1}) < L-asparagine (37.37×10^{-11} m^2 N^{-1}). Similar trends in the variation of κ_s values for these amino acids/di-peptide have been observed for other concentrations and temperatures (Table 4). The smaller κ_s value for L-leucine than that for L-asparagine may be ascribed to the presence of hydrophobic nature of its side-chain. In addition, the ion-hydrophobic and dipole-hydrophobic repulsive forces due to the presence of hydrophobic side-chain in L-leucine appear stronger than that of ion-hydrophilic and dipole-hydrophilic attractive forces caused by the presence of hydrophilic side-chain in L-asparagine. On the other hand, the smallest κ_s value in the case of glycylglycine may be attributed to the largest ion-hydrophilic and dipole-hydrophilic attractive forces in the solution.

The change [40] and relative change [41] in isentropic compressibility values have been obtained by using the following equations,

$$\Delta\kappa_s = \kappa_0 - \kappa_s = A + Bm \tag{3}$$

$$\kappa_s = \kappa_0 - \alpha\kappa_0 \tag{4}$$

$$\alpha = \frac{\kappa_0 - \kappa_s}{\kappa_0} = \frac{\Delta\kappa_s}{\kappa_0} \tag{5}$$

$$\frac{\Delta\kappa_s}{\kappa_0} = A + B'm \tag{6}$$

where κ_0 and κ_s are the isentropic compressibilities of solvent and solution, respectively, while A and B are the intercept and slope values of $\Delta\kappa_s$ versus m plot, respectively. α represents the relative change in isentropic compressibility while A' and B' stand for the intercept and slope values of $(\Delta\kappa_s/\kappa_0)$ versus m plot, respectively. The calculated values of $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_0)$ show an increasing trends of variation with increase in concentration of amino acids/di-peptide. However, the trend of their variation

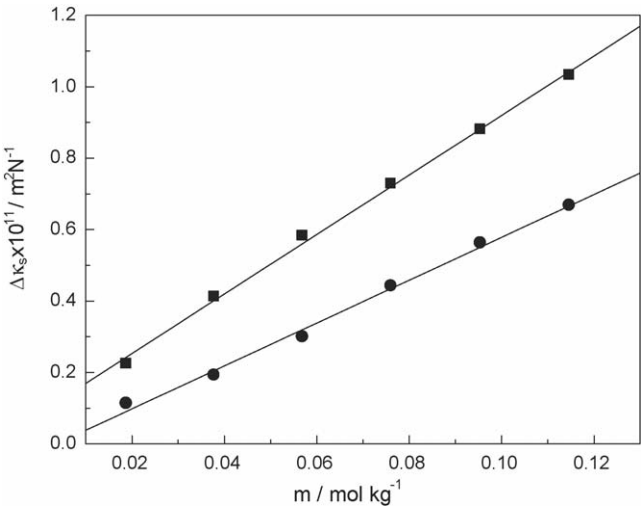

Fig. 2. $\Delta\kappa_s$ vs. concentration of L-leucine in 1.5 M aqueous NaCl solution: (■) 303.15 K; (●) 323.15 K.

with temperature is irregular. The representative trends of variation of $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_0)$ values with concentration of L-leucine in aqueous NaCl solution at 303.15 and 323.15 K are displayed in Figs. 2 and 3, respectively. Similar trends of variation of $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_0)$ values with amino acid/di-peptide concentration have been observed for other systems under investigation. The increase in $(\Delta\kappa_s/\kappa_0)$ values with increase in solute concentration may be attributed to an increase in the incompressible part in a solution. The variation of the change and relative change in isentropic compressibility values with temperature may be attributed to thermal rupture of water structure. A close observation of the plots of $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_0)$ versus amino acid/di-peptide concentration indicate that the intercept values for all the systems except those for L-leucine in aqueous NaCl at 303.15 K, L-leucine in aqueous KNO_3 at 323.15 K, glycylglycine in aqueous NaCl at 298.15 and 323.15 K, and glycylglycine in aqueous KNO_3 at 298.15 K are zero or close to zero. Such a behaviour

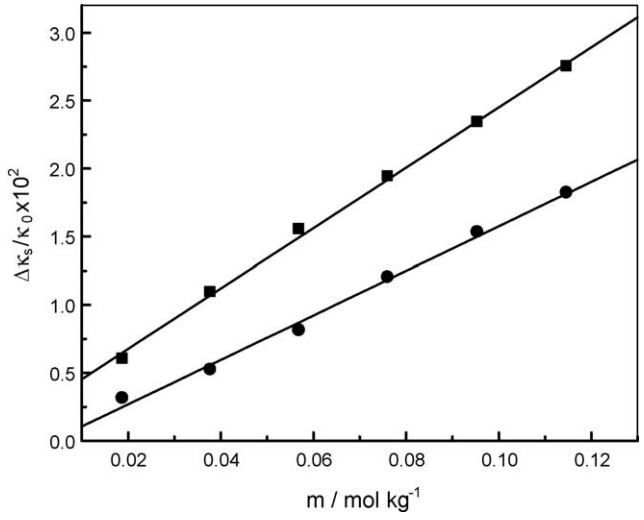

Fig. 3. $(\Delta\kappa_s/\kappa_0)$ vs. concentration of L-leucine in 1.5 M aqueous NaCl solution: (■) 303.15 K; (●) 323.15 K.

Table 5
Specific acoustic impedance values (Z, 10^{-3} kg m^{-2} s^{-1}) for L-leucine in 1.5 M aqueous NaCl solution as functions of concentration and temperature

m (mol kg^{-1})	T (K)				
	303.15	308.15	313.15	318.15	323.15
0.0000	1678.8	1684.0	1688.6	1690.7	1689.8
0.0189	1684.0	1686.8	1690.1	1691.8	1692.5
0.0379	1688.5	1690.3	1691.7	1693.6	1694.5
0.0570	1692.7	1693.9	1695.5	1696.6	1697.4
0.0762	1696.4	1697.5	1697.6	1699.9	1701.1
0.0955	1700.3	1700.6	1700.4	1702.0	1704.3
0.1148	1704.2	1703.8	1703.9	1705.0	1707.2

lend support to the strong solute–solute and solute–solvent intermolecular/interionic interactions in these systems.

The specific acoustic impedance is the product of density and ultrasonic velocity of solvent/solution and can be expressed as

$$Z_0 = \rho_0 u_0 \tag{7}$$

$$Z = \rho u \tag{8}$$

L-leucine + 1.5 M aqueous NaCl system has been chosen as a representative case for presenting the calculated values of specific acoustic impedance data in Table 5. These values increase with increase in the concentration of solutes as well as with temperature in all systems under investigation except in the case of aqueous NaCl solution used as solvent at 323.15 K. The trends of variation of Z with solute concentration and temperature are similar to those exhibited by the variation of ultrasonic velocity values.

Relative association parameter has been calculated using the following expression [42]:

$$\mathrm{RA} = \frac{\rho}{\rho_0}\left(\frac{u_0}{u}\right)^{1/3} \tag{9}$$

where ρ and ρ_0 are the densities of the solution and solvent, respectively, while u and u_0 are their ultrasonic velocities. The system, L-leucine in 1.5 M aqueous NaCl solution has been taken as a representative case for listing the relative association values (Table 6). The RA values show an increasing trend of variation with increase in concentration of amino acids/di-peptide in aqueous electrolyte solutions. A close examination of Table 6 reveals that the RA values are either one or close to one. This indicates that the systems under investigation are

Table 6
Relative association values (RA) for L-leucine in 1.5 M aqueous NaCl solution as functions of concentration and temperature

m (mol kg^{-1})	T (K)				
	303.15	308.15	313.15	318.15	323.15
0.0189	0.9992	0.9997	0.9999	1.0000	0.9996
0.0379	0.9987	0.9994	0.9999	0.9999	0.9995
0.0570	0.9984	0.9992	0.9996	0.9999	0.9995
0.0762	0.9983	0.9990	0.9997	0.9998	0.9994
0.0955	0.9980	0.9989	0.9997	0.9999	0.9993
0.1148	0.9979	0.9988	0.9996	0.9999	0.9994

essentially ideal in nature. However, the variation in RA values with temperature is insignificantly small over the temperature range of 298.15–323.15 K. Consequently, the variation in temperature over the said range does not seem to affect the nature of intermolecular/interionic interactions operative in solutions significantly.

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