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Interactions in L-alanine–/L-proline–/L-valine–/L-leucine–aqueous KCl/KNO_3 systems at different temperatures: An isentropic compressibility study

Riyazuddeen*, Imran Khan

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, U.P., India

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ABSTRACT

Ultrasonic velocity and density values of amino acids: L-alanine/L-proline/L-valine/L-leucine in 2.0 M aqueous KCl and 2.0 M aqueous KNO_3 solutions have been measured for several concentrations of amino acids at different temperatures: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K. Using ultrasonic velocity and density data, the thermodynamic parameters such as isentropic compressibility (κ_s), change in isentropic compressibility ($\Delta\kappa_s$) and relative change ($\Delta\kappa_s/\kappa_0$) in isentropic compressibility have been computed. The trends in the behaviour of κ_s, $\Delta\kappa_s$ and $\Delta\kappa_s/\kappa_0$ with changes in the concentration of amino acids/zwitterions as well as in temperature have been discussed in terms of zwitterions–ions, zwitterions–water dipoles, ions–ions, ions–water dipoles intermolecular/interionic interactions operative in the said systems.

1. Introduction

Metal ions play essential roles in about one-third of enzymes [1]. These ions can modify electron flow in a substrate or enzyme, thus effectively controlling an enzyme-catalyzed reaction. They can serve to bind and orient substrate with respect to functional groups in the active site, and they can provide a site for redox activity if the metal has several valence states. Enzymes activated by monovalent cations, viz. Na^+ and K^+ are abundantly represented in plants and animals [2]. It is well known that the conformational and configurational factors that affect the structures of proteins/enzymes in different solvents are very complicated. Therefore, the direct study of the interactions mechanism of protein is not easy. However, the investigations of the behaviour of model compounds of proteins, such as amino acids and peptides can make the problem much simpler. The ultrasonic velocity and its derived parameter isentropic compressibility are sensitive to structural changes that occur in solutions and to any interactions between solvent and solute [3–7]. The isentropic compressibility studies of amino acids in salts solutions are few [8–18].

This work is a continuation of our research program on the thermodynamic studies of amino acids-aqueous salts solution systems [19–22]. In this study, the ultrasonic velocity (u) and density (ρ) values for the amino acids: L-alanine, L-proline, L-valine and L-leucine in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions as functions of amino acids concentration and temperature: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K have been reported. Using these u and ρ data, the isentropic compressibility (κ_s), change in isentropic compressibility ($\Delta\kappa_s$) and relative change in isentropic compressibility ($\Delta\kappa_s/\kappa_o$) have been evaluated with a view to investigate the zwitterions–ions, zwitterions–water dipoles, ions–water dipoles and ions–ions interactions operative in the systems under investigation.

2. Materials and methods

The amino acids: L-alanine, L-proline, L-valine and L-leucine; and the salts: potassium chloride and potassium nitrate of high purity (≥99%), used in this study, were purchased from SRL (India) and E. Merck (India), respectively. The amino acids were recrystalysed twice in (ethanol + water) mixtures, dried at 383.15 K and kept in vacuum desiccator over P_2O_5 for at least 72 h before use. The salts were recrystalysed twice in triply distilled water, dried at 423.15 K for at least 3 h and then kept over P_2O_5 in a vacuum desiccator at room temperature for a minimum of 48 h prior to their use. Stock solutions of 2 M aqueous KCl and 2 M aqueous KNO_3 were prepared in triply distilled water and were used as solvents for the preparation of amino acid solutions. The specific conductivity of triply distilled water used was less than $18 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. All the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation. An ultrasonic interferometer (Mittal's model: M-77, India) based on variable-path principle was used

* Corresponding author. Tel.: +91 989 7898152/91 571 2703515.
E-mail address: rz1@rediffmail.com (Riyazuddeen).

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for the measurement of ultrasonic velocity at a frequency of 4 MHz at different temperatures using a method described elsewhere [11,23]. Water from ultra-thermostat (Type U-10) was circulated through the brass jacket surrounding the cell and the quartz crystal. The jacket was well insulated and the temperature of the solution under study was maintained to an accuracy of ±0.01°. An average of 10 readings was taken as a final value of ultrasonic velocity. The instrument was calibrated with the triple distilled water. The ultrasonic velocity values of water at different temperatures were taken from the literature for calibration purpose [24]. The densities of solutions were measured by pyknometer using a method described elsewhere [11]. The densities of pure water at various required temperatures were taken from the literature for the calibration purpose [25,26]. Thermostated water bath used for measurements of ultrasonic velocity and thermostated paraffin bath used for measurements of density values were maintained at a desired temperature (±0.01°) for about 30 min prior to recording of readings at each temperature of study. Several very close readings of density calculated at each temperature were averaged.

The accuracies in the measurements of ultrasonic velocity and density have been ascertained by comparing the measured values for the water with the corresponding literature values at different temperatures. For instance, the measured values of the ultrasonic velocity of water have been found to be 1496.8, 1519.9 and 1536.4 m s^{-1} at 298.15, 308.15 and 318.15 K, respectively (corresponding literature values [24] are: 1496.687, 1519.808, 1536.409 m s^{-1}); the experimental values of density of water have been found to be 0.9971, 0.9942, 0.9903 and 0.9879 g cm^{-3} at 298.15, 308.15, 318.15 and 323.15 K respectively (corresponding literature values [25] are: 0.997045, 0.994032, 0.990213 and 0.988036 g cm^{-3}). The uncertainties in ultrasonic velocity and density measurements have been found to be within ±0.2 m s^{-1} and ±0.0001 g cm^{-3}, respectively. The computed uncertainty in isentropic compressibility has been found to be within $\pm 0.02 \times 10^{-11}$ m^2 N^{-1}.

3. Results and discussion

The experimentally measured ultrasonic velocity and density values of amino acids: L-alanine, L-proline, L-valine and L-leucine in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions as functions of molal concentration of amino acids and temperature have been listed in Tables A1 and A2 of Appendix, respectively. The ultrasonic velocity values increase with increase in concentration of amino acids as well as with temperature in all the systems under investigation. The density values of the said systems increase with increase in concentration of amino acids and have been found to be higher than those of water at all temperatures. All the systems seem to exhibit almost linear behaviour in variation of ultrasonic velocity and density values with amino acid concentration as well as with temperature. The increase in ultrasonic velocity values of L-alanine–/L-proline–/L-valine–/L-leucine–2 M aqueous KCl/KNO_3 solutions may be attributed to the overall increase of cohesion brought about by the solute–solute, solute–solvent and solvent–solvent interactions in solutions. K^+ ions furnished by KCl and KNO_3 will have affinity for $-COO^-$ end group of zwitterions of L-alanine, L-proline, L-valine and L-leucine whereas the Cl^- and NO_3^- ions of salts may interact with $-NH_3^+$ group of zwitterions of the said amino acids. In addition, the water dipoles are strongly aligned to the ions, i.e. K^+, Cl^-, NO_3^- as well as to the zwitterions as the result of electrostatic forces. These interactions comprehensively introduce the cohesion into solutions. The added amount of amino acids/zwitterions to 2 M aqueous KCl and 2 M aqueous KNO_3 solutions may have occupied the cavities of water clusters which may lead to the formation of denser structure of the aqueous electrolyte solution [27]. This process may have continued until a concentration of amino acids is reached at which all cavities are filled. Raman studies substantiate the view that the zwitterions–water entities formed in solutions increase on the addition of amino acids in solution. Hirata and Arakawa [28], Magazu et al. [29], Rohman and Mahiuddin [30], and Ragouramane and Rao [31] 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. Kumar and Badarayani [32] reported that the ultrasonic velocity and density values of glycine–aqueous NaBr/KCl/KBr/$MgCl_2$ increases with increases in concentration of solute and temperature. 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 further seems that the cohesion factors dominate over the thermal expansion factor in solutions with increase in temperature.

Using the measured ρ and u values, the isentropic compressibility, change in isentropic compressibility and relative change in isentropic compressibility (κ_r), values for the said systems have been calculated employing the following relations:

$$\kappa_s = \frac{1}{\rho u^2} \tag{1}$$

$$\Delta\kappa_s = \kappa_o - \kappa_s = A + Bm \tag{2}$$

$$\kappa_r = \frac{\Delta\kappa_s}{\kappa_o} = A' + B'm \tag{3}$$

where A and B are the intercept and slope values of $\Delta\kappa_s$ versus m plot while A' and B' are the intercept and slope values of $(\Delta\kappa_s/\kappa_o)$ versus m plot. The isentropic compressibility values for L-alanine, L-proline, L-valine and L-leucine in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions at different temperatures have been listed in Table 1. The κ_s values for 2 M aqueous KCl and 2 M aqueous KNO_3 solutions at 298.15 K have been found to be 36.08 and 36.50 ($\times 10^{-11}$, m^2 N^{-1}), respectively, whereas the corresponding literature value for water is 44.77×10^{-11} m^2 N^{-1} [33]. Thus, the κ_s values for 2 M aqueous KCl and 2 M aqueous KNO_3 solutions have been found to be smaller than that for the pure water at 298.15 K. The κ_s values for ~1.0 m (1.0104 m) proline in 2 M aqueous KCl and for ~1.0 m (0.9779 m) proline in 2 M aqueous KNO_3 at 303.15 K have been found to be 32.96 and 33.22 ($\times 10^{-11}$ m^2 N^{-1}), respectively, whereas in our earlier study [19] the κ_s values for ~1.0 m (0.9189 m) L-proline in 1.5 M aqueous KCl and ~1.0 m (0.9248 m) L-proline in 1.0 M aqueous KNO_3 at 303.15 K have been reported as 34.48 and 36.57 ($\times 10^{-11}$ m^2 N^{-1}), respectively. Thus, the κ_s values for ~1.0 m proline in 2 M aqueous KCl and KNO_3 solutions are smaller than those in 1.5 M aqueous KCl and 1.0 M aqueous KNO_3 solutions.

The decrease in κ_s value for water on addition of the KCl and KNO_3 in it may be ascribed to (i) the introduction of incompressible K^+, Cl^- and NO_3^-ions into water and (ii) the formation of 'K^+/Cl^-/NO_3^-–water dipole' incompressible entities in salt solutions. The presence of these entities in the salt solutions makes them less compressible than that of pure water. The smaller κ_s value for 2 M aqueous KCl (36.08×10^{-11}, m^2 N^{-1}) than that of 2 M aqueous KNO_3 (36.50×10^{-11}, m^2 N^{-1}) suggests that the decrease in isentropic compressibility value of water on addition of KCl and KNO_3 depends more on the number of ions introduced into water rather than on the kind of ions.

The decrease in isentropic compressibility values with increase in temperature in all the 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

Table 1
Isentropic compressibilities ($\kappa_s/10^{-11}$ m^2 N^{-1}) as functions of solute concentration and temperature.

m (mol kg^{-1})	T (K)					
	298.15	303.15	308.15	313.15	318.15	323.15
L-Alanine in 2.0 M aqueous KCl solution						
0.0000	36.08	35.65	35.53	35.41	35.19	35.05
0.1857	35.26	35.06	34.79	34.62	34.44	34.33
0.3762	34.66	34.50	34.29	34.15	33.99	33.84
0.5714	34.09	33.94	33.79	33.65	33.54	33.36
0.7706	33.51	33.39	33.22	33.04	32.94	32.85
0.9751	32.96	32.82	32.63	32.49	32.39	32.29
1.1864	32.44	32.34	32.17	32.03	31.93	31.63
1.4044	31.95	31.85	31.69	31.57	31.44	31.32
L-Alanine in 2.0 M aqueous KNO_3 solution						
0.0000	36.50	36.23	36.06	35.93	35.82	35.75
0.1802	35.91	35.71	35.47	35.35	35.24	35.16
0.3649	35.28	35.13	34.93	34.70	34.63	34.53
0.5543	34.55	34.39	34.30	34.09	34.01	33.94
0.7494	33.98	33.82	33.72	33.57	33.48	33.44
0.9499	33.54	33.40	33.28	33.13	33.04	32.91
1.1542	33.03	32.90	32.77	32.65	32.55	32.45
1.3650	32.55	32.42	32.29	32.17	32.06	31.96
L-Proline in 2.0 M aqueous KCl solution						
0.0000	36.08	35.65	35.53	35.41	35.19	35.05
0.1871	35.41	35.25	35.05	34.83	34.72	34.55
0.3813	34.77	34.59	34.46	34.24	34.14	34.02
0.5829	34.19	34.02	33.87	33.69	33.58	33.48
0.7925	33.60	33.43	33.33	33.11	33.04	32.90
1.0104	33.09	32.96	32.79	32.58	32.49	32.38
1.2376	32.56	32.37	32.23	32.02	31.98	31.86
1.4741	32.05	31.90	31.69	31.50	31.44	31.36
L-Proline in 2.0 M aqueous KNO_3 solution						
0.0000	36.50	36.23	36.06	35.93	35.82	35.75
0.1814	35.81	35.65	35.55	35.41	35.30	35.24
0.3694	35.21	35.02	34.91	34.82	34.73	34.71
0.5646	34.50	34.39	34.31	34.25	34.20	34.19
0.7673	33.86	33.78	33.72	33.67	33.64	33.63
0.9779	33.28	33.22	33.13	33.09	33.07	33.00
1.1969	32.66	32.61	32.53	32.49	32.45	32.45
1.4249	32.10	32.05	31.96	31.93	31.87	31.86
L-Valine in 2.0 M aqueous KCl solution						
0.0000	36.08	35.65	35.53	35.41	35.19	35.05
0.0184	36.07	35.64	35.52	35.32	35.18	35.04
0.0369	35.89	35.59	35.38	35.17	34.96	34.83
0.0554	35.58	35.31	35.09	34.88	34.67	34.55
0.0927	35.29	34.99	34.79	34.56	34.37	34.27
0.1303	35.02	34.71	34.51	34.28	34.08	33.98
0.1682	34.74	34.42	34.25	33.99	33.80	33.69
0.1873	34.48	34.17	33.99	33.74	33.56	33.44
L-Valine in 2.0 M aqueous KNO_3 solution						
0.0000	36.50	36.23	36.06	35.93	35.82	35.75
0.0178	36.35	36.07	35.91	35.78	35.68	35.59
0.0357	36.20	35.91	35.75	35.62	35.54	35.45
0.0537	36.04	35.77	35.61	35.47	35.38	35.30
0.0898	35.87	35.61	35.47	35.32	35.22	35.14
0.1264	35.75	35.46	35.29	35.14	35.03	34.98
0.1630	35.58	35.30	35.14	34.99	34.91	34.83
0.1814	35.42	35.15	35.01	34.86	34.77	34.68
L-Leucine in 2.0 M aqueous KCl solution						
0.0000	36.08	35.65	35.53	35.41	35.19	35.05
0.0184	35.95	35.64	35.42	35.21	35.02	34.90
0.0369	35.79	35.54	35.28	35.07	34.86	34.74
0.0555	35.61	35.36	35.12	34.88	34.71	34.58
0.0741	35.48	35.21	34.96	34.71	34.55	34.44
0.0928	35.30	35.01	34.80	34.56	34.39	34.26
0.1117	35.12	34.85	34.65	34.40	34.23	34.11
0.1306	34.94	34.69	34.49	34.25	34.08	33.96
L-Leucine in 2.0 M aqueous KNO_3 solution						
0.0000	36.50	36.23	36.06	35.93	35.82	35.75
0.0178	36.29	36.05	35.86	35.74	35.65	35.57
0.0358	36.12	35.86	35.67	35.55	35.45	35.40
0.0538	35.93	35.66	35.47	35.37	35.28	35.22
0.0719	35.72	35.50	35.30	35.17	35.10	35.06
0.0900	35.55	35.29	35.12	34.99	34.91	34.83
0.1083	35.34	35.12	34.94	34.80	34.74	34.65
0.1266	35.15	34.95	34.77	34.60	34.55	34.47

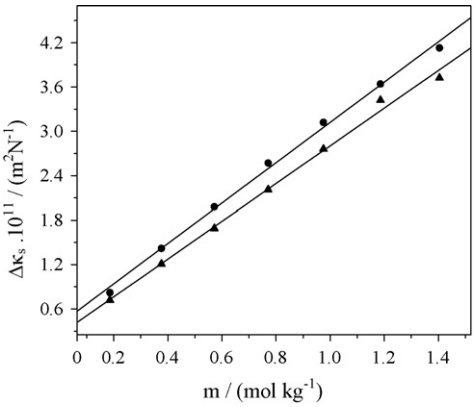

Fig. 1. Plots of change in isentropic compressibility versus concentration of L-alanine in 2.0 M aqueous KCl solution. At 298.15 K, ●; 323.15 K, ▲.

two structures such as an ice-like structure and a close packed structure [34,35]. Compressibility of liquid water is expressed by $\kappa_s = \kappa_\infty + \kappa_{relax}/(1+\omega^2\tau^2)$, where κ_∞ is an instantaneous part of compressibility and κ_{relax} a relaxational part of compressibility [34]. The relaxational time τ, corresponding to κ_{relax} is of the order of 10^{-11} s. The relation $\omega\tau < 1$ is assumed to be valid in the present study, 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 the thermal expansion and κ_{relax} decreases due to the 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 of κ_{relax}, which is dominant over the corresponding increase of κ_∞. The isentropic compressibility values of 2 M aqueous KCl and 2 M aqueous KNO_3 solutions are lesser than that of water in the temperature range of 298.15–323.15 K.

The $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_o)$ values exhibit increasing trends of variation with successive increases in amino acid concentration and decreasing trends with increase in temperature in both the solvents, i.e. 2 M aqueous KCl and 2 M aqueous KNO_3 solutions. Such an increase in $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_o)$ values with increase in amino acids/zwitterions concentration may be attributed to an overall increase in the cohesive forces in the solutions. These cohesive forces may be the result of zwitterions–ions and zwitterions–water dipoles interactions in solutions. In addition, the successive increase of amino acids concentration in the salt solution enhances the incompressible part of the solution. On the other hand, a decrease in $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_o)$ values with increase in temperature may be attributed to the thermal rupture of water structure with temperature. As representative cases, the variations of $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_o)$ values with amino acid concentration for L-alanine in 2 M aqueous KCl at the temperatures, 298.15 and 323.15 K have been plotted in Figs. 1 and 2, respectively. Similar trends of variations of $\Delta\kappa_s$ and $(\Delta\kappa_s/\kappa_o)$ values with amino acid concentration have been observed for other systems too. It is noteworthy that the intercept values for $\Delta\kappa_s$ versus m, and $(\Delta\kappa_s/\kappa_o)$ versus m plots are close to zero as envisaged in the light of the relevant equation. Such behaviour lends support to the weak solute–solute and solute–solvent intermolecular/interionic interactions in these systems.

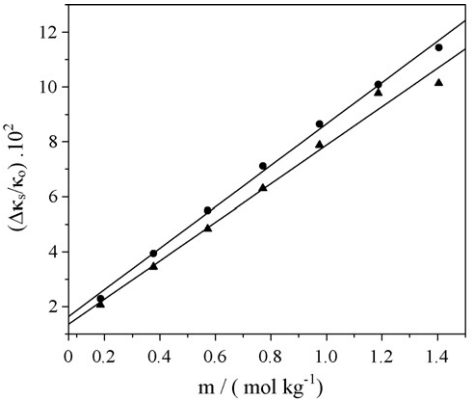

Fig. 2. Plots of relative change in isentropic compressibility versus concentration of L-alanine in 2.0 M aqueous KCl solution. At 298.15 K, ●; 323.15 K, ▲.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.10.023.

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