



Study of interactions of L-histidine/L-glutamic acid/L-tryptophan/glycylglycine with KCl/KNO₃ at different temperatures: 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 K

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ABSTRACT

Density (ρ) and ultrasonic velocity (u) values of amino acid/peptide: L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl and 2 M aqueous KNO₃ solutions have been measured as a function of amino acid/peptide concentration at different temperatures: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K. Using the ρ and u data, the partial molar volumes (ϕ_v^o) and partial molar isentropic compressibilities (ϕ_k^o) have been computed. The increase in partial molar volume with an increase in temperature has been attributed to the volume expansion of hydrated zwitterions. The ϕ_v^o and ϕ_k^o values of L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl and 2 M aqueous KNO₃ solutions have been found to be larger than the corresponding values in water. The larger partial molar volumes of L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl and 2 M aqueous KNO₃ solutions have been ascribed to the probable formation of 'zwitterion-K⁺/Cl⁻/NO₃⁻' and 'K⁺/Cl⁻/NO₃⁻-water dipole' aggregates in solutions. The zwitterions-ions interactions in solutions may cause the release of water associated with zwitterions to the bulk water. The larger partial molar isentropic compressibilities of L-histidine/L-glutamic acid/L-tryptophan/glycylglycine in 2 M aqueous KCl/2 M aqueous KNO₃ solutions than the corresponding values in water have been attributed to the zwitterions-ions and ions-waters dipoles interactions in solutions.

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1. Introduction

The study of amino acid/peptide-salt interactions [1–31] has been of interest with a view to improve the comprehension about the stability of proteins and the equilibrium process between "folded" versus "unfolded" forms of proteins. Khoshkbarchi et al. [20] have studied the partial molar volumes (ϕ_v^o) and partial molar isentropic compressibilities (ϕ_k^o) of glycine in aqueous KCl and KNO₃ solutions. The observed behaviours of these properties have been attributed to the formation of ion pairs between glycine and K⁺, Cl⁻, NO₃⁻ and to the effects of the size difference of ions. Yasuda et al. [21] investigated ϕ_v^o and ϕ_k^o for a number of amino acids in potassium chloride solutions. They explain the effect of potassium chloride on the ϕ_v^o and ϕ_k^o values of some amino acids in terms of hydration phenomena and electrostriction effects.

The present study is a continuation of our research project on the thermodynamic studies of amino acid/peptide-aqueous salt solution systems [27–33]. This study reports a systematic study

of partial molar volumes and partial molar isentropic compressibilities of amino acids and peptide such as: L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl and 2 M aqueous KNO₃ solutions as functions of solute concentration and temperature: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K with a view to investigating the zwitterion-salt interactions in the systems.

2. Experimental

2.1. Materials

The amino acids and peptide: L-histidine, L-glutamic acid, L-tryptophan and glycylglycine; and the salts: potassium chloride and potassium nitrate of high purity ($\geq 99\%$), used in this study, were purchased from SRL (India) and E. Merck (India), respectively. The amino acids were recrystallized twice in ethanol + water mixtures, dried at 383.15 K and kept in a vacuum desiccator over P₂O₅ for at least 72 h before use. The salts were recrystallized twice in triply distilled water, dried at 423.15 K for at least 3 h and then kept over P₂O₅ 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 KNO₃ were prepared in triply distilled

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water and were used as solvents for the preparation of amino acid and peptide solutions. The specific electrical conductivity of triply distilled water used was less than $18 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. All the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation.

2.2. Experimental procedure

An ultrasonic interferometer (Mittal Model M-77, India) based on the variable-path principle was used for the measurement of the ultrasonic velocity at a frequency of 4 MHz at different temper-

atures using a method described elsewhere [28–31,34]. An average of 10 readings was taken as a final value of the ultrasonic velocity. Water from a thermostat was circulated through 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 uncertainty of 0.01 K. The densities of solutions were measured with a pycnometer using a method described elsewhere [27,28,34]. All mass quantities were corrected for buoyancy. The densities of toluene at various required temperatures were taken from the literature for calibration purposes [35]. The thermostated water bath used for measurements of ultrasonic velocity

Table 1
Least-squares fit coefficients of equation, $\phi_v = \phi_v^0 + S_v m$ at different temperatures.

T (K)	ϕ_v^0 ($\times 10^6 \text{ m}^3 \text{ mol}^{-1}$)	S_v ($\times 10^7 \text{ m}^3 \text{ mol}^{-2} \text{ kg}$)	σ ($\times 10^6 \text{ m}^3 \text{ mol}^{-1}$)
(i) L-Histidine in 2 M aqueous KCl solution			
298.15	119.59	−9.021	4.6
303.15	115.73	−6.580	3.2
308.15	114.74	−5.718	3.4
313.15	114.91	−5.571	3.4
318.15	116.21	−6.338	4.5
323.15	115.95	−6.340	4.6
(ii) L-Histidine in 2 M aqueous KNO ₃ solution			
298.15	108.62	−2.470	2.8
303.15	109.72	−2.862	2.2
308.15	110.24	−2.980	2.2
313.15	113.76	−4.695	2.1
318.15	114.27	−4.786	2.0
323.15	115.60	−5.071	1.5
(iii) L-Glutamic acid in 2 M aqueous KCl solution			
298.15	123.82	−41.404	3.3
303.15	124.05	−47.118	2.6
308.15	130.68	−63.283	2.2
313.15	124.01	−50.673	2.5
318.15	122.61	−48.977	2.5
323.15	107.20	−15.640	5.2
(iv) L-Glutamic acid in 2 M aqueous KNO ₃ solution			
298.15	91.85	−7.828	2.7
303.15	87.99	−8.563	3.0
308.15	82.09	5.684	4.3
313.15	82.18	5.690	4.3
318.15	78.19	20.169	6.9
323.15	75.01	21.222	6.3
(v) L-Tryptophan in 2 M aqueous KCl solution			
298.15	178.02	−97.109	3.6
303.15	164.07	−50.092	2.1
308.15	170.26	−62.873	3.5
313.15	158.35	−23.068	3.4
318.15	159.55	−28.540	3.2
323.15	159.96	−37.007	3.9
(vi) L-Tryptophan in 2 M aqueous KNO ₃ solution			
298.15	157.11	−43.483	3.5
303.15	161.67	−56.068	5.7
308.15	161.67	−55.072	5.7
313.15	160.57	−45.795	6.1
318.15	160.95	−46.048	6.2
323.15	160.85	−38.464	6.1
(vii) Glycylglycine in 2 M aqueous KCl solution			
298.15	95.65	−11.378	6.1
303.15	93.42	−8.333	3.9
308.15	94.08	−7.455	3.5
313.15	90.97	−4.726	2.5
318.15	87.42	−1.624	1.8
323.15	83.48	0.393	2.2
(viii) Glycylglycine in 2 M aqueous KNO ₃ solution			
298.15	93.72	−10.039	2.3
303.15	94.62	−11.588	2.9
308.15	91.04	−9.093	2.7
313.15	90.97	−9.154	3.2
318.15	91.12	−9.686	3.8
323.15	92.53	−11.008	3.6

and the thermostated paraffin bath used for measurements of density were maintained at a desired temperature (± 0.01 K) 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 uncertainties in measurements of the ultrasonic velocity and density values were ascertained by comparing the experimental values with corresponding literature values at different temperatures for water. The measured values of the ultrasonic velocity of water were found to be 1496.8, 1519.9 and 1536.4 m s^{-1} at 298.15, 308.15, and 318.15 K, respectively whereas the corresponding literature values [36] are 1496.687, 1519.808 and 1536.409 m s^{-1} . The experimental values of the density of water were 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 whereas the corresponding literature values [37] are 0.997045, 0.994032, 0.990213, and 0.988036 g cm^{-3} . The uncertainties in the ultrasonic velocity, density and molal concentration values have been found to be within 0.2 m s^{-1} , 1.0×10^{-4} g cm^{-3} and 1.0×10^{-4} mol kg^{-1} , respectively.

3. Results and discussion

3.1. Partial molar volumes

The apparent molar volumes of amino acid/peptide: L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions have been computed from the solution density values using the relation:

$$\phi_v = \left(\frac{M}{\rho} \right) - \left\{ \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \right\} \quad (1)$$

where M is the solute molecular weight, m is molality of the solution, and ρ_0 and ρ are the density values of solvent and solution, respectively. The experimentally measured density values of L-histidine/L-glutamic acid/L-tryptophan and glycylglycine + 2 M aqueous KCl/2 M aqueous KNO_3 systems as functions of solute concentration and temperature: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K have been given in Table S1 of the supplementary material. The apparent molar volume values have been fitted by least-squares method to the linear

Table 2

The comparison of observed partial molar volumes ϕ_v^0 with the literature values at different temperatures.

T (K)	This work		Literature values			
	Solvent	ϕ_v^0 ($\times 10^6$ m^3 mol^{-1})	Solvent	ϕ_v^0 ($\times 10^6$ m^3 mol^{-1})	Ref.	
L-Histidine 298.15	2 M aqueous KCl 2 M aqueous KNO_3	119.59	Aqueous medium	98.81 \pm 0.04	[22]	
		108.62	Aqueous medium	98.96 \pm 0.05	[23]	
			2 m aqueous NaCl	101.84 \pm 0.04	[22]	
			2 m aqueous NaCl	101.80 \pm 0.05	[23]	
			0.15 m aqueous DMSO	98.68 \pm 0.06	[22]	
			2 m aqueous NaCl + 0.15 m DMSO	101.84 \pm 0.08	[22]	
			0.20 m aqueous tetramethyl-ammonium bromide	107.112	[40]	
308.15	2 M aqueous KCl 2 M aqueous KNO_3	114.74	Aqueous medium	100.35 \pm 0.99	[41]	
		110.24				
L-Glutamic acid 298.15	2 M aqueous KCl 2 M aqueous KNO_3	123.82	Aqueous medium	89.64	[42]	
		91.85	Aqueous medium	89.65 \pm 0.02	[43]	
			1.0 m aqueous sodium acetate	94.15 \pm 0.02	[43]	
			1.0 m aqueous sodium propionate	95.24 \pm 0.01	[43]	
			0.5 m aqueous sodium butyrate	95.46 \pm 0.01	[43]	
			1.0 m aqueous lithium acetate dihydrate	93.76 \pm 0.01	[44]	
			1.0 m aqueous magnesium acetate tetrahydrate	95.08 \pm 0.01	[44]	
			1.0 m aqueous calcium acetate	94.57 \pm 0.01	[44]	
L-Tryptophan 298.15	2 M aqueous KCl 2 M aqueous KNO_3	178.02	Aqueous medium	144.24	[45]	
		157.11	Aqueous medium	143.38	[46]	
			D-Tryptophan in aqueous medium	143.91	[47]	
			DL-Tryptophan in aqueous medium	143.8	[48]	
	303.15	2 M aqueous KCl 2 M aqueous KNO_3	164.07 161.67	0.005 m aqueous ZnCl_2	161.59	[49]
Glycylglycine 298.15	2 M aqueous KCl 2 M aqueous KNO_3	95.65	Aqueous medium	76.28 \pm 0.02	[22]	
		93.72	Aqueous medium	76.36 \pm 0.02	[23]	
			2.0117 m aqueous KCl	80.54 \pm 0.025	[24]	
			2 m aqueous NaCl	80.61 \pm 0.05	[22]	
			2 m aqueous NaCl	80.16 \pm 0.04	[23]	
			0.4797 m aqueous NaF	78.22 \pm 0.03	[25]	
			2.08221 m aqueous NaCl	80.66 \pm 0.03	[25]	
			1.9809 m aqueous NaBr	79.94 \pm 0.02	[25]	
			0.15 m aqueous DMSO	76.26 \pm 0.02	[22]	
			2 m aqueous NaCl + 0.15 m DMSO	80.60 \pm 0.03	[22]	
			1.5 m aqueous sodium sulphate	84.38	[26]	
	308.15	2 M aqueous KCl 2 M aqueous KNO_3	94.08	Aqueous medium	77.10	[22]
			91.04	2 m aqueous KCl	81.34 \pm 0.043	[24]
				0.4797 m aqueous NaF	78.87 \pm 0.04	[25]
			2.08221 m aqueous NaCl	81.17 \pm 0.03	[25]	
			1.9809 m aqueous NaBr	80.62 \pm 0.01	[25]	

Table 3
Least-squares fit coefficients of equation, $\phi_k = \phi_k^0 + S_k m$ at different temperatures.

T (K)	ϕ_k^0 ($\times 10^{11}$ bar $^{-1}$ m 3 mol $^{-1}$)	S_k ($\times 10^{11}$ bar $^{-1}$ m 3 mol $^{-2}$ kg)	σ ($\times 10^{11}$ bar $^{-1}$ m 3 mol $^{-1}$)
(i) L-Histidine in 2 M aqueous KCl solution			
298.15	−0.486	0.875	0.4
303.15	−1.501	3.536	0.3
308.15	−0.642	−0.423	0.3
313.15	−0.780	2.100	0.1
318.15	−2.429	9.639	0.4
323.15	−0.912	2.118	0.2
(ii) L-Histidine in 2 M aqueous KNO $_3$ solution			
298.15	−2.257	6.679	0.3
303.15	−1.625	4.535	0.2
308.15	−2.389	8.816	0.5
313.15	−2.314	8.467	0.4
318.15	−2.064	8.455	0.6
323.15	−1.252	5.063	0.3
(iii) L-Glutamic acid in 2 M aqueous KCl solution			
298.15	−0.888	18.740	0.9
303.15	−2.343	−38.219	0.3
308.15	2.695	−44.896	0.1
313.15	2.299	−40.233	0.2
318.15	1.158	−29.036	0.1
323.15	0.581	−20.432	0.8
(iv) L-Glutamic acid in 2 M aqueous KNO $_3$ solution			
298.15	−0.893	−35.272	0.7
303.15	−2.449	−6.916	0.4
308.15	−1.353	−37.660	0.7
313.15	−4.032	8.762	0.6
318.15	−6.707	67.655	0.8
323.15	−3.038	17.829	0.5
(v) L-Tryptophan in 2 M aqueous KCl solution			
298.15	3.402	−144.016	0.4
303.15	0.313	−96.777	0.5
308.15	1.424	−59.543	0.6
313.15	1.459	−45.790	0.4
318.15	−7.588	142.148	0.9
323.15	−1.811	−3.840	0.4
(vi) L-Tryptophan in 2 M aqueous KNO $_3$ solution			
298.15	−4.265	38.155	0.5
303.15	2.382	−119.994	0.3
308.15	4.637	−207.745	1.2
313.15	3.640	−133.415	1.0
318.15	1.962	−103.972	0.5
323.15	4.153	−147.871	0.5
(vii) Glycylglycine in 2 M aqueous KCl solution			
298.15	−1.191	−6.577	0.9
303.15	−0.557	−10.256	1.0
308.15	−0.560	−4.460	0.5
313.15	−0.087	−8.715	0.3
318.15	−6.121	37.544	1.2
323.15	−4.442	26.736	0.8
(viii) Glycylglycine in 2 M aqueous KNO $_3$ solution			
298.15	−2.766	8.964	0.6
303.15	−1.125	−6.027	0.3
308.15	−2.993	10.644	0.7
313.15	−3.050	13.249	0.5
318.15	−3.743	14.268	0.8
323.15	−3.830	16.508	0.8

equation:

$$\phi_v = \phi_v^0 + S_v m \quad (2)$$

where ϕ_v^0 is the apparent molar volume at infinite dilution which is also referred as the partial molar volume of the solute. The S_v is the experimental slope which refers to the volumetric pair wise interaction coefficients [38,39]. The ϕ_v^0 and S_v values have been listed in Table 1.

The observed and the literature values of ϕ_v^0 of the studied amino acids and peptide have been listed in Table 2 for the comparison purpose. The partial molar volume values of the amino

acid/peptide: L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous solutions of KCl and KNO $_3$ are higher than the corresponding values in aqueous medium at all temperatures of study. The ϕ_v^0 values are positive for L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl and 2 M aqueous KNO $_3$ solutions at all temperatures of study thereby showing the strong solute–solvent interactions. The ϕ_v^0 values of L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous solutions of KCl and KNO $_3$ show irregular trends of variation with an increase in temperature. In neutral solutions, the amino acid and peptide molecules exist as zwitterions [9,22–24,26]. The elec-

Table 4
The comparison of observed partial molar compressibility ϕ_k^o with the literature values at different temperatures.

T (K)	This work		Literature values		
	Solvent	ϕ_k^o ($\times 10^{11}$ bar $^{-1}$ m 3 mol $^{-1}$)	Solvent	ϕ_k^o ($\times 10^{11}$ bar $^{-1}$ m 3 mol $^{-1}$)	Ref.
L-Histidine	298.15	2 M aqueous KCl	Aqueous medium	-3.484	[45]
		2 M aqueous KNO ₃	Aqueous medium	-3.25	[50]
	308.15	2 M aqueous KCl	Aqueous medium	-2.96	[51]
			2 M aqueous KNO ₃	Aqueous medium	-2.59
		2 M aqueous KCl	Aqueous medium	-2.68	[51]
			2 M aqueous KNO ₃	Aqueous medium	-2.68
L-Glutamic acid	298.15	2 M aqueous KCl	Aqueous medium	-3.917	[45]
		2 M aqueous KNO ₃	Aqueous medium	-2.950	[50]
	318.15	2 M aqueous KCl	L-Glutamic acid monosodium in aqueous medium	-7.00	[51]
		2 M aqueous KNO ₃			
L-Tryptophan	298.15	2 M aqueous KCl	Aqueous medium	-3.064	[46]
		2 M aqueous KNO ₃	Aqueous medium	-3.324	[45]
	298.15	2 M aqueous KCl	D-Tryptophan in aqueous medium	-3.050	[50]
			D-L-Tryptophan in aqueous medium	-3.449	[47]
		2 M aqueous KNO ₃			
Glycylglycine	298.15	2 M aqueous KCl	Aqueous medium	-3.69	[52]
		2 M aqueous KNO ₃	Aqueous medium	-3.878	[26]
			Aqueous medium	-3.591	[53]
			1.5 m aqueous sodium sulphate	-1.279	[26]
	308.15	2 M aqueous KCl	1.5 m aqueous sodium sulphate	84.38	[26]
		2 M aqueous KNO ₃	Aqueous medium	77.10	[22]
			2 m aqueous KCl	81.34 \pm 0.043	[24]
			0.4797 m aqueous NaF	78.87 \pm 0.04	[25]
			2.08221 m aqueous NaCl	81.17 \pm 0.03	[25]
			1.9809 m aqueous NaBr	80.62 \pm 0.01	[25]

trostriction of water molecules occurs near the terminal groups of zwitterions, NH_3^+ and COO^- . The presence of KCl and KNO_3 seems to affect the hydration spheres of charged terminal groups of zwitterions. As a result of $\text{K}^+ - \text{COO}^-$, $\text{Cl}^- - \text{NH}_3^+$ and $\text{NO}_3^- - \text{NH}_3^+$ interactions, the hydrated zwitterions may relax water molecules to the bulk water which in turn, may cause an increase in the volume. The increase in ϕ_k^o value with an increase in temperature may be attributed to the volume expansion of hydrated zwitterions of amino acids/peptide or reduction in electrostriction. The increase in temperature may cause relax of water molecules to the bulk water. The observed higher ϕ_k^o values for amino acid/peptide in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions as compared with their values in water suggest the domination of zwitterions–ions interactions and the zwitterions–water dipoles interactions. Banipal et al. [43] also have observed the higher ϕ_k^o values for acidic/basic amino acids, as compared to amino acids with non-polar side chain in the presence of cosolutes such as: sodium acetate, sodium propionate and sodium butyrate. This behaviour can be attributed to the combined effect of interactions of the ($-\text{NH}_3^+$, $-\text{COO}^-$) end groups of amino acids and the polar side chains present in acidic/basic amino acids.

The information concerning solute–solute interactions is given by S_v . The trends of variation of S_v with temperature in both the solvents, 2 M aqueous KCl and 2 M aqueous KNO_3 solutions are irregular. The positive values of S_v for the studied amino acids/peptide in 2 M aqueous KCl and 2 M aqueous KNO_3 solutions at all the temperatures of study indicate the presence of stronger ions–ions and zwitterions–zwitterions interactions than those of apolar–apolar interactions varying with the change of temperature, nature of amino acid/peptide and the nature of solvent. The negative values of S_v show that the solute–solute interactions are weak.

3.2. Partial molar isentropic compressibilities

The apparent molar isentropic compressibilities, ϕ_k have been calculated using the relation:

$$\phi_k = \left[\frac{1000(\kappa_s - \kappa_o)}{m\rho_o} \right] + \kappa_s \phi_v \quad (3)$$

In the above mentioned equation, m is the molality of the solution, ρ_o is the density of solvent (kg m^{-3}), and $\kappa_s = (1/\rho u^2)$ and $\kappa_o = (1/\rho_o u_o^2)$ are the isentropic compressibilities of solution and solvent, respectively. The experimentally measured ultrasonic velocity values of L-histidine/L-glutamic acid/L-tryptophan and glycylglycine + 2 M aqueous KCl/2 M aqueous KNO_3 systems as functions of solute concentration and temperature: 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K have been listed in Table S2 of the supplementary material. The ϕ_k values have been least squares fitted to the equation:

$$\phi_k = \phi_k^o + S_k m \quad (4)$$

where ϕ_k^o is the apparent molar isentropic compressibility at infinite dilution which is also referred as partial molar isentropic compressibility, and is a measure of solute–solvent interactions. The ϕ_k^o and S_k values have been listed in Table 3. The observed and the literature values of the studied amino acids and peptide have been listed in Table 4 for the comparison purpose. The ϕ_k^o values of L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KCl solution are higher than those of the corresponding values in aqueous medium whereas for L-histidine, L-glutamic acid, L-tryptophan and glycylglycine in 2 M aqueous KNO_3 solution, the ϕ_k^o values are quite close to the corresponding values in aqueous medium. The similar trends for ϕ_k^o have been reported by Yasuda et al. for some amino acids in 2 m aqueous lithium chloride,

2 m sodium chloride and 2 m potassium chloride solutions [21] and also reported by Banipal et al. for some amino acids in 1 M aqueous sodium chloride and 1 M aqueous glucose solutions [1]. The ϕ_k^o values apparently indicate a large ordering effect of solute molecules in 2 M aqueous KCl and 2 M aqueous KNO₃ solutions. A simple model can express the partial molar isentropic compressibilities of the amino acid/peptide as,

$$\phi_k^o = \phi_k^o(\text{int}) + \phi_k^o(\text{elect}) \quad (5)$$

where $\phi_k^o(\text{int})$ is the intrinsic partial molar isentropic compressibility of some amino acid/peptide molecule and $\phi_k^o(\text{elect})$ is the electrostriction partial molar isentropic compressibility due to hydration of the amino acid/peptide molecule. The $\phi_k^o(\text{int})$ for the said amino acid/peptide can be assumed to be zero as the value of $\phi_k^o(\text{int})$ is expected to be very small [45]. Thus, ϕ_k^o may be considered to represent $\phi_k^o(\text{elect})$. The reported ϕ_k^o values for the said amino acids/peptide in water are negative. The negative ϕ_k^o may be due to the hydration of the charged centers of the amino acid/peptide as the hydrated water appear to be less compressible than that the bulk water. The values of S_k for all systems under study are found to be negative, which suggest the presence of weak zwitterions–zwitterions interactions in the systems.

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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.2010.01.012.

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