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PARTIAL MOLAL VOLUMES AND PARTIAL MOLAL ISENTROPIC COMPRESSIBILI-TIES OF L-LEUCINE, L-ASPARAGINE AND GLYCYLGLYCINE IN AQUEOUS ELECTROLYTE SOLUTIONS

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ABSTRACT

Partial molal volume is a thermodynamic quantity, which provides important information about solute-solvent interactions in a solution. Moreover, its temperature-dependence may be quite useful in characterizing the structural hydration effects, as the intrinsic volume of the solute is almost independent of temperature. Partial molal isentropic compressibility is another thermodynamic parameter for investigating the behaviour of solutes in solution. It is independent of solute-solute interactions and thus determined only by the respective intrinsic value and the solute-solvent interactions.

The volumetric properties that is apparent / partial molal volume values of a solute in solution have proven to be reflective of and sensitive of solute-solvent and solute-solute interactions. These properties represent useful observables for studying the hydration properties of bio-molecules. Several authors have investigated the apparent / partial molal volume properties of amino acids, peptides and proteins in aqueous and mixed aqueous solutions. Apparent / partial molal volumes data for amino acids / peptides in aqueous electrolyte systems reflect the combined effect of various hydrophilic and hydrophobic interactions operative in these systems.

***Keywords*:** Apparent / partial molal volume; Apparent / partial molal isentropic compressibility; L-Leucine; L-Asparagine; Glycylglycine; NaCl; $NaNO_3$; KNO_3

INTRODUCTION

The investigation on volumetric properties of proteins' model compounds such as amino acids and small peptides provide valuable information that ultimately leads to a better

understanding of the behaviour of biological macromolecules or proteins. Amino acids and peptides are essentially zwitterions in aqueous solutions and therefore their volume and compressibility properties should reflect structural interactions with solvent systems.

A number of researchers have investigated the apparent / partial molal volumes; and apparent / partial molal isentropic compressibilities for amino acids and peptides in aqueous alkali metal halides (LiCl, NaCl, KCl, CsCl, KBr, KI), alkaline earth metal chlorides ($MgCl_2$, $CaCl_2$, $BaCl_2$), sodium sulphate, vanadyl sulphate, ammonium chloride, sodium acetate, sodium butyrate, sodium caprylate, potassium thiocyanate, and guanidine hydrochloride solutions.

In this paper, the studies of the apparent molal volumes (φ_v) and apparent molal isentropic compressibilities (φ_k), and their corresponding partial molal volumes (φ_v^o) and partial molal isentropic compressibilities (φ_k^o) for L-leucine, L-asparagine and glycylglycine in aqueous solutions of 1.5M NaCl, $NaNO_3$ and KNO_3 (used as solvents) have been focussed.

RESULTS AND DISCUSSION

The apparent molal volumes of amino acids and di-peptide in aqueous electrolyte solutions have been determined from the density values of solvent and solution employing the following equation,

$$\varphi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{mp\rho_0}$$

where M and m are the molar mass and the molality of the amino acids / di-peptide, respectively; and ρ and ρ_0 are the density of solution and solvent (aqueous electrolyte solution), respectively. The calculated apparent molal volumes as functions of concentration and temperature for the L-leucine, L-asparagine and glycylglycine in aqueous electrolyte solutions have been listed in Table 1. The apparent molal volume values have been found to vary linearly with molality of solution at a constant temperature and the values have been least-squares fitted to the following equation,

$$\varphi_v = \varphi_v^0 + S_v m$$

where φ_v^o stands for the apparent molal volume at infinite dilution and is also known as the partial molal volume of solute. φ_v^0 is a measure of the solute-solvent interactions whereas S_v, the corresponding experimental slope, is a measure of the solute-solute interactions in solutions. The φ_v^o values have been obtained by linear fitting of φ_v values with m using the least-squares method at each temperature. The φ_v^o and S_v values alongwith their standard deviations at temperatures: 298.15 - 323.15 K have been presented in Table 2.

The observed partial molal volume values of L-leucine, L-asparagine and glycylglycine in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 have been compared to the available literature values of φ_v^o in aqueous medium at 298.15 K. The reported values of φ_v^o for L-leucine in aqueous medium at 298.15 K are 107.75, 107.73, 107.77, 107.72, 107.59, 107.96, 107.74 and 107.83 cm^3/mol whereas our observed values in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 are 109.17, 109.71 and 108.84 cm^3/mol, respectively. The reported value of φ_v^o for L-asparagine in aqueous medium at 298.15 K is 95.63 cm^3/mol whereas the observed values in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 are 99.12, 97.66 and 98.11 cm^3/mol, respectively. The literature values of φ_v^o for the glycylglycine in water at 298.15 K are 76.27, 76.63, 76.76, 76.34, 76.23 and 77.2 cm^3/mol. The observed values of φ_v^o for the glycylglycine in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 at 298.15 K are 84.78, 77.31 and 77.56 cm^3/mol, respectively. It is noteworthy that the values of φ_v^o for the amino acids / di-peptide in aqueous electrolyte solutions are larger than that in aqueous medium at 298.15 K.

The partial molal volume of transfer ($\Delta_{tr}\varphi_v^o$) of a solute from water to an aqueous electrolyte solution has been calculated using the following equation,

$\Delta_{tr}\varphi_v^o = \varphi_v^o$ (in aqueous electrolyte solution) - φ_v^o (in water)

The $\Delta_{tr}\varphi_v^o$ for the solutes under investigation has been calculated at 298.15K by taking the corresponding average of reported φ_v^o values in water. The calculated $\Delta_{tr}\varphi_v^o$ values have been listed in Table 3. The $\Delta_{tr}\varphi_v^o$ values for all the three solutes in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 have been found to be positive.

Franks et al. have shown that the partial molal volume of a non-electrolyte is a combination of two factors, viz., the intrinsic volume of solute and the volume changes due to its interactions with solvent. The intrinsic volume has been considered to be made up of two types of contributions,

$$V_{intrinsic} = V_{vw} + V_{void}$$

where V_{vw} is Van der Waals volume, and V_{void} is the volume associated with the voids or empty spaces present therein.

Shahidi et al. have modified the above equation in order to evaluate the contribution of a solute molecule towards its partial molal volume as,

$$\varphi_v^o = V_w + V_{void} - n\,\sigma_s$$

where σ_s is the shrinkage in volume produced by the interactions of hydrogen bonding groups present in the solute with water molecules and n is the potential number of hydrogen bonding sites in the molecule. For electrolytes and zwitterionic solutes, the shrinkage is caused by electrostriction and therefore the φ_v^o of an amino acid / di-peptide can be evaluated by employing the relation,

$$\varphi_v^o = V_{vw} + V_{void} - V_{shrinkage}\,.$$

It may be assumed that V_{vw} and V_{void} have the same magnitude in water and in mixed solvent for the same class of compounds**.** Hence, the observed positive $\Delta_{tr}\varphi_v^o$ values of amino acids and di-peptide under investigation may be attributed to a decrease in the shrinkage volume in

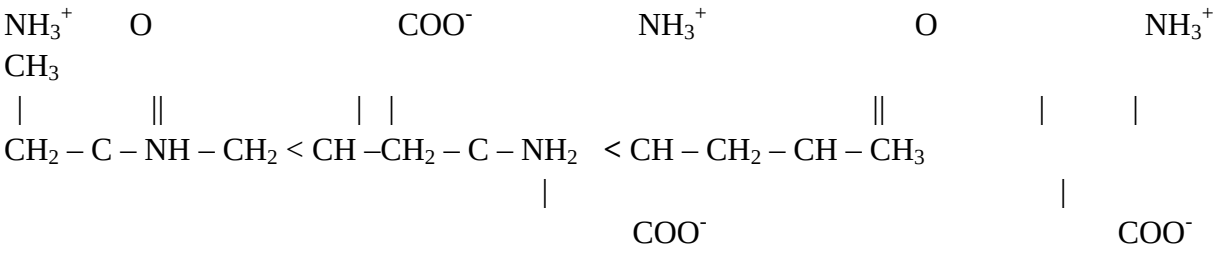
the presence of Na^+, K^+, Cl^- and NO_3^- ions of NaCl, $NaNO_3$ and KNO_3 in aqueous solution. Because of the interactions of these ions and the zwitterionic centres of the amino acids and di-peptide, the electrostriction of the water molecules lying in the vicinity of the NH_3^+ and COO^- centres of the amino acid and di-peptide would get reduced and would consequently lead to a positive volume contribution.

The co-sphere overlap model, developed by Gurney, and Frank and Evans can also be utilized to rationalize the $\Delta_{tr}\varphi_v^o$ values in terms of solute and co-solute interactions. According to this model, properties of water molecules in the hydration co-sphere depend on the nature of solute molecules. When two solute particles come close enough such that their co-spheres overlap, some of the co-sphere material is displaced and this is accompanied by changes in thermodynamic parameters. The following types of interactions are possible: (i) ion-zwitterion interactions occurring between ion and zwitterionic centres of amino acid / di-peptide. (ii) ion-hydrophobic interactions occurring between ion and non-polar part of amino acid/ di-peptide.

According to the co-sphere overlap model, overlapping between ion and zwitterion hydration spheres results in the positive volume of transfer whereas the ion-hydrophobic interactions lead to a negative volume of transfer. Therefore, the observed positive $\Delta_{tr}\varphi_v^o$ obtained for the amino acids and di-peptide under investigations in aqueous electrolyte solutions suggest that the ion-zwitterion interactions are dominating over the ion-hydrophobic interactions. The overlapping between hydration spheres of ion and zwitterion having opposite charges would squeeze out water resulting in positive $\Delta_{tr}\varphi_v^o$ values.

The trend of variation of φ_v^o values of amino acids and di-peptide, in an aqueous electrolyte solution that is in 1.5M aqueous solution of NaCl, $NaNO_3$ or KNO_3 is found to be as follows:

Glycylglycine < L-asparagine < L-leucine



This trend of variation of φ_v^o may be explained as follows:

(a) L-leucine contains a structure making hydrophobic alkyl group. This hydrophobic group should exhibit a repulsive tendency towards water dipoles. L-asparagine and glycylglycine both contain hydrophilic amide and peptide groups, respectively. These hydrophilic groups are structure-breaking groups. The presence of hydrophobic group in L-leucine may cause the largest φ_v^0 values.

(b) Peptide group (-C–NH-) of glycylglycine seems more hydrophilic in nature than amide group (-C–NH_2) of L-asparagine due to the steric effect between $–COO^-$, NH_3^+ and amide groups of L-asparagine. Although the $–CONH_2$ group of L-asparagine appears more hydrophilic in nature than that of –CONH-group of glycylglycine but the close proximity of COO^-, NH_3^+ and amide groups in L-asparagine may have made the glycylglycine more structure breaker than that of L-asparagine. This would cause the smaller value of φ_v^0 for glycylglycine than L-asparagine.

An examination of Table 2 shows that the S_V values for L-leucine are negative in all three aqueous electrolyte systems at all temperatures. The values for L-asparagine are negative in 1.5M aqueous solutions of $NaNO_3$ and KNO_3 systems whereas in 1.5M aqueous NaCl solutions the S_v values are negative between 298.15 K and 303.15 K and are positive from 308.15 K to 323.15 K. The S_v values for glycylglycine are positive in all solvent systems over

complete range of temperature except in 1.5M aqueous KNO_3 solvents at 318.15 K and 323.15 K. The negative S_v values represent weak solute-solute interactions whereas the positive results indicate strong solute-solute interactions in ternary systems under investigation. The negative values of S_v for L-leucine may be attributed to the hydrophobic-hydrophobic interactions due to alkyl group of L-leucine. In glycylglycine the positive S_v values may be due to electrostatic interactions of zwitterions and –CONH group. The negative S_v values in L-asparagine may be due to the presence of hydrophobic methylene group.

The apparent molal isentropic compressibility values of amino acids and di-peptide in aqueous electrolyte solutions under investigation have been calculated from the density and the isentropic compressibility values of the solvents and solutions using the following equation,

$$\varphi_k = \frac{M\kappa_s}{\rho} - \frac{1000(\kappa_0\rho - \kappa_s\rho_0)}{m\rho\rho_0}$$

where M and m are the molar mass and the molality of the amino acid / di-peptide, respectively. ρ, κ_s and ρ_0, κ_0 are the density and the isentropic compressibility of solution and solvent, respectively. The φ_k values of L-leucine, L-asparagine and glycylglycine as functions of concentration and temperature are listed in Table 4. The φ_k values show a linear dependence with molality and the data have been least-squares fitted to the following equation,

$$\varphi_k = \varphi^0_k + S_k m$$

where φ^0_k is the apparent molal compressibility at infinite dilution and it is also referred to as partial molal isentropic compressibility. S_k is an experimental slope. The φ^0_k and S_k values along with their standard deviations have been presented in Table.5. It has been observed that the apparent isentropic compressibility values for the said amino acids and di-peptide are negative in all aqueous electrolyte solutions. The values show irregular trend of variations with temperature as well as with concentration. The negative φ_k values exhibit strong interactions between the solute and solvent. The ion-zwitterion interactions seem stronger than ion-hydrophobic interactions in systems under investigation.

CONCLUSION

The isentropic compressibility values (φ_k^0) values are negative, which indicate strong solute-solvent interactions. These values do not exhibit a regular trend of variation with temperature. The strong solute-solvent interactions may be attributed to the strong electrostatic interactions between ions (K^+, Na^+, Cl^-, NO_3^-) and the zwitterionic centres of amino acids and di-peptide. In addition, the amide group ($-CONH_2$) and peptide group (-CONH-) of amino acids and di-peptide should also interact electrostatically with ions of electrolytes. The interactions between the ion and hydrophobic group [alkyl group(s) of amino acids / di-peptide] seem weaker in nature than the interactions between ion and zwitterionic centre.

Table 1: Apparent molal volume (φ_v/ 10^{-6} m^3 mol^{-1}) as functions of concentration and temperature

Concentration/ mol kg^{-1}	Temperature/ K					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
L-Leucine in aqueous NaCl solution						
0.0189	109.70	114.70	114.93	115.17	115.43	120.54
0.0379	109.71	112.33	112.55	115.17	115.44	118.12
0.0570	108.14	109.96	110.17	111.99	112.23	112.48
0.0762	108.54	107.60	108.99	110.39	109.43	109.66
0.0955	108.79	107.13	108.28	109.44	108.72	108.95
0.1148	108.94	106.02	107.80	108.00	108.23	107.65
L-Leucine in aqueous $NaNO_3$ solution						
0.0186	112.26	112.56	112.85	108.45	104.02	99.52
0.0372	107.65	112.54	112.83	108.42	103.98	99.47
0.0560	106.13	107.90	106.60	102.18	97.70	94.75
0.0748	104.20	105.57	104.65	99.04	95.73	92.38
0.0936	103.02	105.09	102.53	97.14	94.52	90.93
0.1126	103.03	104.01	101.14	95.90	92.97	90.00
L-Leucine in aqueous KNO_3 solution						

0.0184	106.86	111.65	116.48	116.73	117.02	117.32
0.0370	106.91	111.68	116.50	116.74	117.03	117.33
0.0556	109.96	111.68	116.49	115.19	117.02	117.33
0.0742	106.88	110.51	114.17	114.41	114.68	116.14
0.0930	105.97	108.90	111.86	112.08	112.34	113.56
0.1118	103.82	104.74	106.45	107.43	106.88	107.92
L-Asparagine in aqueous NaCl solution						
0.0189	103.97	94.63	89.97	90.05	85.34	75.73
0.0379	99.27	94.67	94.78	94.88	92.6	90.29
0.0570	96.15	94.71	94.81	94.92	95.03	93.55
0.0761	95.74	95.68	95.97	96.08	96.21	96.33
0.0953	94.56	96.68	95.73	96.79	96.92	97.05
0.1146	94.56	94.68	96.37	97.28	97.41	98.34
0.1340	94.58	94.70	96.16	97.63	97.76	98.58
0.1534	93.98	94.69	96.57	97.28	98.01	98.74
L-Asparagine in aqueous $NaNO_3$ solution						
0.0186	102.12	106.93	107.13	107.36	102.86	93.54
0.0372	97.42	102.21	102.39	102.58	98.05	95.83
0.0559	95.87	100.65	100.82	101.00	96.46	95.04
0.0747	95.11	99.88	100.05	100.23	95.69	94.66
0.0936	94.67	98.50	99.60	99.77	96.18	95.39
0.1125	94.35	98.33	99.27	99.45	95.70	95.06
0.1315	94.13	98.22	99.04	99.22	95.36	95.52
0.1505	93.95	98.11	98.86	99.03	95.68	95.24
L-Asparagine in aqueous KNO_3 solution						
0.0184	124.30	124.50	129.34	120.28	115.85	106.68
0.0369	96.68	101.40	103.83	103.98	101.82	94.94
0.0555	87.54	93.74	96.91	97.04	97.18	91.07
0.0741	84.08	88.73	92.27	94.69	95.99	89.09
0.0928	81.12	85.75	89.50	92.37	94.35	87.93
0.1115	79.12	84.50	87.63	91.57	93.24	87.13
0.1302	77.67	82.93	86.93	90.98	93.75	86.52
0.1490	77.16	82.34	85.84	89.96	91.81	86.09
Glycylglycine in aqueous NaCl solution						
0.0189	82.23	72.84	72.89	77.72	77.80	97.23
0.0379	84.63	77.64	77.71	80.16	85.06	94.83
0.0570	87.03	80.85	80.92	82.60	85.89	94.05
0.0761	87.01	81.22	81.31	83.78	86.28	93.63
0.0953	87.95	82.41	82.50	84.50	87.48	93.39
0.1145	87.78	82.40	82.48	84.16	87.46	93.21
0.1339	88.36	82.43	83.19	84.64	87.48	93.11
0.1533	88.19	83.02	83.11	84.98	87.49	93.02
Glycylglycine in aqueous $NaNO_3$ solution						

0.0186	62.34	62.35	57.68	52.97	76.53	57.61
0.0372	78.44	78.52	76.28	74.02	71.73	76.54
0.0559	82.30	83.94	84.07	81.07	79.62	81.31
0.0746	85.35	86.62	86.77	85.74	83.53	84.85
0.0935	86.30	88.28	88.43	87.65	85.93	86.07
0.1124	87.69	89.36	90.30	88.90	87.50	87.66
0.1314	88.03	90.14	90.97	89.81	88.63	88.80
0.1504	88.84	90.71	91.46	90.47	88.88	89.04
Glycylglycine in aqueous KNO_3 solution						
0.0184	57.08	80.16	89.50	98.95	108.51	118.19
0.0369	77.84	91.73	98.80	101.29	108.52	113.48
0.0555	84.76	95.60	100.36	103.63	108.53	111.92
0.0741	87.05	97.51	101.11	103.62	107.34	111.12
0.0928	89.34	98.66	102.50	104.55	107.57	109.70
0.1116	90.88	100.20	102.66	105.17	107.73	109.55
0.1305	91.99	100.64	103.43	104.95	107.17	109.44
0.1494	95.66	100.97	103.43	105.36	107.33	109.35

Table 2: Least-squares fit parameters of equation, $\varphi_v = \varphi_v^0 + S_v m$ at different temperatures

Temperature/ K	**φ_v^0 / 10^{-6} m^3 mol^{-1}**	**S_v / 10^{-6} m^3 mol^{-2} kg**	**σ x 10^6 m^3 mol^{-1}**
L-Leucine in aqueous NaCl solution			
298.15	109.17	-4.592	0.7
303.15	114.73	-80.297	0.8
308.15	114.07	-59.186	0.7
313.15	117.69	-87.786	0.7
318.15	117.92	-93.165	1.2
323.15	121.07	-127.134	1.8
L-Leucine in aqueous $NaNO_3$ solution			
298.15	109.71	-65.513	0.7
303.15	114.91	-105.412	1.5
308.15	116.45	-145.639	1.7
313.15	112.48	-159.582	1.8
318.15	106.99	-133.699	1.8
323.15	102.54	-120.747	1.4
L-Leucine in aqueous KNO_3 solution			

298.15	108.84	-30.370	1.8
303.15	114.25	-67.510	1.5
308.15	120.27	-101.703	2.0
313.15	119.86	-93.824	1.5
318.15	120.84	-102.805	2.0
323.15	120.86	-91.176	2.2
L-Asparagine in aqueous NaCl solution			
298.15	99.12	-37.396	1.0
303.15	95.29	-1.826	0.9
308.15	94.27	15.701	0.3
313.15	93.96	25.615	0.4
318.15	92.23	42.411	0.8
323.15	89.51	69.325	1.4
L-Asparagine in aqueous $NaNO_3$ solution			
298.15	97.66	-27.668	0.5
303.15	102.73	-35.337	0.7
308.15	102.65	-28.197	0.5
313.15	102.86	-28.310	0.5
318.15	97.80	-17.551	0.6
323.15	95.32	-0.758	0.4
L-Asparagine in aqueous KNO_3 solution			
298.15	98.11	-159.065	2.9
303.15	103.21	-158.623	2.8
308.15	105.78	-150.108	2.6
313.15	104.53	-109.465	2.2
318.15	102.48	-75.740	1.4
323.15	95.64	-71.853	1.3
Glycylglycine in aqueous NaCl solution			
298.15	84.78	26.171	0.7
303.15	77.80	37.984	1.0
308.15	77.73	40.604	1.0
313.15	80.20	35.091	0.9
318.15	84.67	21.590	0.5
323.15	94.97	-14.340	0.3
Glycylglycine in aqueous $NaNO_3$ solution			
298.15	77.32	85.056	1.5
303.15	77.65	97.731	1.8
308.15	75.77	118.810	2.5
313.15	73.00	132.260	2.7
318.15	70.69	138.787	2.8
323.15	75.11	104.509	1.7
Glycylglycine in aqueous KNO_3 solution			

298.15	77.56	135.944	1.8
303.15	90.74	77.031	1.3
308.15	97.94	41.066	0.5
313.15	101.18	31.196	0.7
318.15	108.78	-11.223	0.4
323.15	113.99	-35.985	0.7

Table 3: Partial molal volume of transfer ($\Delta_{tr}\varphi_v^o$) of amino acids and di-peptide from water to aqueous electrolyte solutions

Amino acids/di peptide	$\Delta_{tr}\varphi_v^o$ /10^{-6} m^3 mol^{-1}		
	1.5M aq. NaCl	**1.5M aq. $NaNO_3$**	**1.5M aq. KNO_3**
L-leucine	1.39	1.93	1.06
L-asparagine	3.49	2.03	2.48
Glycylglycine	8.29	0.82	1.07

Table 4: Apparent molal isentropic compressibility (φ_k/10^{-10} $bar^{-1}m^3mol^{-1}$) as functions of concentration and temperature.

Concentration/ mol kg^{-1}	Temperature/ K				
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
L-Leucine in aqueous NaCl solution						
0.0189		-69.00	-16.88	-11.17	20.42	-12.68
0.0379		-60.92	-23.11	-11.22	13.57	-5.18
0.0570		-56.06	-26.21	-4.83	2.90	-9.18
0.0762		-50.89	-27.64	-3.62	-4.36	-15.62
0.0955		-47.91	-26.59	-5.58	-3.43	-16.89
0.1148		-46.49	-25.89	-9.73	-5.83	-16.83
L-Leucine in aqueous $NaNO_3$ solution						
0.0186		5.30	0.56	-26.79	-11.02	-23.93
0.0372		0.46	-4.28	-22.01	-11.05	-9.76
0.0560		-10.86	-16.73	-23.27	-15.55	-13.10
0.0748		-16.47	-20.85	-28.62	-14.57	-12.44
0.0936		-20.07	-23.05	-28.04	-17.74	-14.85
0.1126		-22.90	-25.17	-29.85	-20.31	-17.13
L-Leucine in aqueous KNO_3 solution						

0.0184	-0.25	-16.13	-15.93	-6.05	-29.90
0.0370	-14.62	-13.38	-13.20	-12.97	-29.46
0.0556	-20.96	-15.69	-18.25	-15.26	-24.56
0.0742	-26.17	-22.16	-21.94	-19.32	-24.17
0.0930	-25.97	-20.85	-24.43	-20.40	-23.29
0.1118	-28.92	-23.63	-26.79	-23.21	-23.25
L-Asparagine in aqueous NaCl solution					
0.0189	-15.39	-9.41	-23.17	-8.25	-38.29
0.0379	-26.97	-19.69	-10.30	-5.15	-27.49
0.0570	-26.00	-18.00	-20.85	-8.62	-23.45
0.0761	-26.68	-23.20	-22.94	-13.76	-25.10
0.0953	-31.63	-28.74	-25.93	-23.08	-32.08
0.1146	-39.40	-29.48	-25.59	-24.69	-31.58
0.1340	-38.30	-30.43	-23.37	-21.96	-27.84
0.1534	-38.61	-30.71	-28.28	-24.92	-28.38
L-Asparagine in aqueous $NaNO_3$ solution					
0.0186	4.03	-15.19	-24.69	-4.25	-25.52
0.0372	-13.92	-21.12	-28.22	-14.94	-16.69
0.0559	-16.59	-21.38	-26.08	-23.11	-22.67
0.0747	-17.84	-24.98	-23.74	-20.02	-19.70
0.0936	-20.16	-25.20	-25.10	-23.04	-20.89
0.1125	-21.12	-24.50	-24.44	-22.51	-19.18
0.1315	-21.76	-24.64	-24.59	-21.42	-19.40
0.1505	-21.66	-24.17	-25.86	-24.80	-22.31
L-Asparagine in aqueous KNO_3 solution					
0.0184	22.47	-3.28	-5.32	0.94	-1.25
0.0369	-7.23	-19.98	-22.28	-14.28	-7.53
0.0555	-13.73	-19.40	-22.51	-19.21	-14.29
0.0741	-21.47	-17.59	-24.17	-14.85	-16.48
0.0928	-22.15	-18.37	-20.05	-14.79	-15.83
0.1115	-21.24	-18.09	-19.93	-17.12	-14.63
0.1302	-22.45	-16.73	-18.50	-15.11	-17.14
0.1490	-23.58	-18.48	-20.18	-17.64	-18.98
Glycylglycine in aqueous NaCl solution					
0.0189	-108.56	-109.86	-90.13	-67.37	-44.14	-66.58
0.0379	-75.47	-79.97	-74.49	-56.04	-36.33	-42.94
0.0570	-53.73	-60.92	-57.18	-43.34	-25.69	-27.42
0.0761	-42.63	-46.55	-43.73	-32.50	-23.81	-19.71
0.0953	-38.01	-40.85	-42.20	-25.95	-18.32	-16.86
0.1145	-36.29	-36.12	-37.22	-25.19	-18.26	-15.72
0.1339	-33.79	-32.64	-33.04	-21.49	-14.29	-16.74
0.1533	-29.49	-30.76	-31.52	-19.86	-12.45	-14.17
Glycylglycine in aqueous $NaNO_3$ solution					

0.0186	-18.53	-37.65	-60.42	-54.36	-17.60	-12.80
0.0372	-11.14	-20.64	-46.34	-40.88	-28.25	-8.17
0.0559	-16.21	-21.25	-30.81	-29.92	-21.49	-17.16
0.0746	-17.86	-19.18	-27.52	-27.15	-19.32	-18.41
0.0935	-15.59	-15.92	-25.40	-24.15	-16.95	-14.11
0.1124	-15.10	-12.20	-22.64	-25.30	-20.06	-15.35
0.1314	-13.85	-14.90	-25.14	-22.05	-16.24	-12.22
0.1504	-13.68	-14.57	-23.51	-20.81	-14.99	-11.48
Glycylglycine in aqueous KNO_3 solution						
0.0184	-92.13	-4.92	-7.64	-10.27	6.53	13.63
0.0369	-48.70	-0.96	-5.39	-8.39	6.59	10.16
0.0555	-34.16	3.66	-2.51	-3.33	6.66	15.42
0.0741	-26.59	5.94	-1.10	-1.70	5.79	13.25
0.0928	-23.25	5.38	0.47	-1.71	6.00	9.35
0.1116	-17.74	7.23	1.77	-0.42	7.75	10.54
0.1305	-17.94	6.69	0.47	1.52	8.51	9.37
0.1494	-14.73	2.66	0.84	-0.17	7.13	9.66

Table 5: Least-squares fit parameters of equation, $\varphi_k = \varphi_k^0 + S_k m$ at different temperatures

Temperature/ K	**φ_k^0 / 10^{-10} bar^{-1} m^3 mol^{-1}**	**S_k / 10^{-10} bar^{-1} m^3 mol^{-2} kg**	**σ x 10^{10} bar^{-1} m^3 mol^{-1}**
L-Leucine in aqueous NaCl solution			
303.15	-67.128	192.375	1.5
308.15	-23.540	-30.785	1.6
313.15	-14.391	-221.544	5.0
318.15	-18.452	-234.421	4.2
323.15	-0.449	-161.135	2.3
L-Leucine in aqueous $NaNO_3$ solution			
303.15	8.240	-296.740	3.1
308.15	1.081	-255.168	3.8
313.15	-18.237	-108.512	1.5
318.15	-7.616	-109.944	1.3
323.15	-6.904	-87.547	1.0
L-Leucine in aqueous KNO_3 solution			

303.15	-9.983	-179.561	2.2
308.15	-8.955	-137.042	2.0
313.15	-7.670	-178.312	1.1
318.15	-8.053	-136.965	0.7
323.15	-30.379	73.105	1.6
L-Asparagine in aqueous NaCl solution			
303.15	-19.716	-134.034	2.8
308.15	-14.387	-119.017	2.3
313.15	-11.570	-114.129	3.8
318.15	-0.309	-179.583	3.7
323.15	-24.821	-33.174	3.1
L-Asparagine in aqueous $NaNO_3$ solution			
303.15	-12.486	-69.597	1.0
308.15	-21.022	-28.654	1.4
313.15	-27.084	17.617	1.4
318.15	-16.330	-54.166	2.6
323.15	-18.387	-18.499	2.1
L-Asparagine in aqueous KNO_3 solution			
303.15	-7.085	-126.574	3.6
308.15	-20.033	178.278	0.9
313.15	-24.384	35.485	1.5
318.15	-15.405	-7.950	2.0
323.15	-8.199	-73.092	2.4
Glycylglycine in aqueous NaCl solution			
298.15	76.801	341.612	7.6
303.15	-84.825	398.148	7.3
308.15	-78.144	340.730	6.4
313.15	-60.300	296.000	5.3
318.15	-39.017	185.584	2.8
323.15	-41.693	207.024	6.1
Glycylglycine in aqueous $NaNO_3$ solution			
298.15	-14.765	-0.117	2.4
303.15	-23.660	71.649	2.0
308.15	-43.742	159.951	5.5
313.15	-40.947	147.033	3.4
318.15	-28.382	93.638	2.5
323.15	-14.398	5.930	3.9
Glycylglycine in aqueous KNO_3 solution			

298.15	-51.485	272.408	4.9
303.15	1.165	34.490	2.7
308.15	-5.642	52.314	1.4
313.15	-8.359	67.784	1.8
318.15	5.627	13.888	0.8
323.15	13.998	-31.091	2.1

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