Research Article

Volumetric Properties of the Peptide ($C_4H_8N_2O_3$) in Water and in Various Aqueous Solutions of Sodium Nitrate, Potassium Nitrate and Magnesium Nitrate Hexahydrate at different Temperatures (288.15-318.15) K

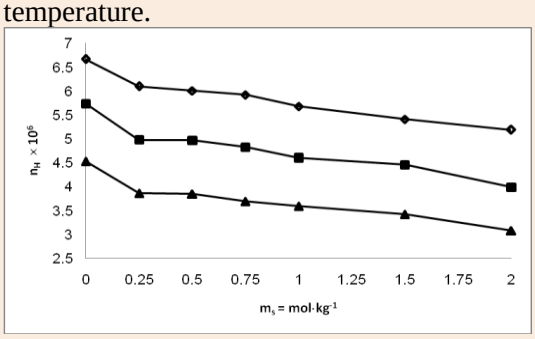
Vaneet Dhir[1,a] , Jasbinder Kaur[1] , R. P. Singh Grewal [2*]

[1]Post Graduate Department of Chemistry, G.H.G Khalsa College,
Gurusar Sadhar(Affiliated to Panjab University, Chandigarh) Punjab, India
[a]Punjab Technical University, Jalandhar
[2]Department of Applied Chemistry, Guru Nanak Dev Engineering College (GNDEC), Ludhiana, Punjab, 141006, India

Abstract

Densities, ρ, of peptide ($C_4H_8N_2O_3$, diglycine) in water and in (0.25, 0.5, 0.75, 1.0, 1.5, 2.0) mol·kg^{-1} aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions have been determined at various temperatures (288.15, 298.15, 308.15 and 318.15) K. The apparent molar volumes, $V_{2,\Phi}$ of diglycine have been derived. The standard partial molar volumes, $V_2^{0}{}_{,\Phi}$, obtained from $V_{2,\Phi}$ obtained from these data have been used to calculate the corresponding transfer parameter, $\Delta_t V^0$ for the studied diglycine from water to aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate. The hydration number, n_H, side chain contributions of amino acids, and concentration effect of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate as well as temperature effects have been discussed in terms of various interactions. The structure making / breaking capacities of diglycine in water and also in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate investigated have been discussed.

The interaction coefficients and hydration number, n_H, of diglycine, partial molar expansibilities in aqueous solutions have also been calculated to see the effect of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate on the hydration of amino acids. It has been found that diglycine in aqueous KNO_3 solution is behaving like common salt because its partial molar expansibilities decrease with the rise in temperature.



Keywords: Amino acids; Sodium nitrate; Potassium nitrate; Magnesium nitrate hexahydrate; Partial molar volume; Transfer volumes; Hydration numbers; Interaction coefficients; Partial molar expansibilities.

***Correspondence**
R. P. Singh Grewal,
Email: rpsinghgrewal@gmail.com

Introduction

Proteins are large giant molecules. Therefore, direct study of electrolyte-protein interactions is an cumbersome task for biochemist [1]. These interactions are affected by the surrounding solutes and solvent of macromolecules; for this reason, the physicochemical behaviors of proteins are strongly affected by the interactions of solutes [2]. Because of direct solute solvent interactions or alteration of the water structure, these solutes can change many properties of globular proteins such as their hydration, solubility, stability and the activity of enzymes [3-7]. The side chain groups of the amino acids residues provide a very important range of properties, from hydrophilic to hydrophobic groups.

The side chain groups are involved in a wide range of interactions. For example; the phenomenon of electrostriction that is caused by the polar end groups; the structure enforcing influences of the hydrophobic alkyl

groups; the interactions in between the hydrophilic and hydrophobic groups, hydrogen bonds that provides the peptide bonds in the polypeptide backbone.

All these wide ranges of interactions are being are being affected with the change in the concentration of aqueous electrolyte that is being studied. Attempts are being made for the systematic study of the volumetric in aqueous solutions of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate at various temperatures (288.15, 298.15, 308.15 and 318.15) K. Salt induced electrostatic forces are known to play an very significant role in modifying the protein structure by affecting the properties like solubility, denaturation of enzymes [8-9].

Remarkable experimental work has been reported on thermodynamics of amino acids in aqueous alkali metal salts [10-23]. Despite the ample use and importance of amino acids in many industries, their interactions with electrolytes and physicochemical properties in electrolyte solutions have been the subject of few investigations [23-27]. The role of Mg^{2+} ions as components of all body fluids are indispensable, among others (Ca^{2+}, Na^{+} and K^{+}), for a correct functioning of the nervous system. In addition Mg^{2+} ion is one amongst the enzyme activators [28]. Consequently, in the present paper, the apparent molar volumes, $V_{2,\Phi}$, of peptide (diglycine) in water and in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate (0.25, 0.5, 0.75, 1.0, 1.5, 2.0) mol·kg^{-1} have been determined by measuring the densities using a vibrating-tube digital densimeter at various temperatures (288.15, 298.15, 308.15 and 318.15) K.

The standard partial molar volumes, $V_2^{0}{}_{,\Phi}$, obtained from $V_{2,\Phi}$ obtained from these data have been used to calculate the corresponding transfer parameters , $\Delta_t V^0$, for the studied peptide from water to aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate. From these data, the partial molar volumes, $V_{2,\Phi}$ and the hydration number, n_H, side chain contributions of peptide (diglycine) and concentration effect of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate have been discussed in terms of various interactions.

The structure making / breaking capacities of these amino acids in water and also in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate investigated have been discussed. The interaction coefficients and hydration number, n_H, of diglycine in aqueous solutions have also been calculated to see the effect of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate on the hydration of diglycine.

Experimental section

The diglycine (G-1002) selected for the present study was obtained from sigma chemicals co. These along with sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate (AR, S.d. fine chemicals Ltd., India), were used without further purification and dried over anhydrous $CaCl_2$ in a vacuum desiccator before use. Deionized, doubly distilled degassed water with a specific conductance of less than 1.3×10^{-9} Ωm^{-1} was used for all of the measurements. All solutions were prepared by mass using a mettler balance with an accuracy of ± 0.01 mg.

The solution densities were measured using a vibrating tube digital densimeter (model DMA 60/602, Anton paar), accuracy of 3 x10^{-9} kg·m^{-3}. Densities function was checked by measuring the densities of aqueous sodium chloride solutions [29], which agreed well with the literature values [literature values of density are: (1005.571, 1017.344, 1036.690, 1054.672, 1071.353 and 1087.608) kg·m^{-3} at 0.20918, 0.50653, 1.01279, 1.50262, 1.97403, and 2.44952) mol·kg^{-1}of sodium chloride, respectively] at 298.15 K. The temperature of water around the densimeter cell was controlled to within 0.01K.

Results and discussion

The densities, ρ, and apparent molar volumes, $V_{2,\Phi}$ of diglycine in water and in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions of various molalities (m_s, molality of sodium nitrate and potassium nitrate solutions, mol·kg^{-1}) at (288.15, 298.15, 308.15 and 318.15) K are given in **Table 1.**

Table 1. Solutions densities, ρ, and apparent molar volumes, $V_{2,\phi}$, for the diglycine in aqueous solutions of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate at different concentrations and at various temperatures (288.15-218.15)K.

m_s (mol·kg^1)	$\rho \times 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \times 10^6$ (m^3·mol^{-1})	m_s (mol·kg^{-1})	$\rho \times 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \times 10^6$ (m^3·mol^{-1})	m_s (mol·kg^{-1})	$\rho \times 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \times 10^6$ (m^3·mol^{-1})
				T=288.15K				
				Diglycine				
				m_s=0.00000				
0.00000	0.999098		0.01508	0.999944	75.94	0.10178	1.004688	76.77
0.01145	0.999747	75.38	0.03030	1.000788	76.21	0.11492	1.005378	76.99
0.01390	0.999883	75.60	0.03329	1.000944	76.52	0.18268	1.008988	77.22
				m_s=0.25 mol·kg^{-1}				
0.00000	1.012001		0.09318	1.017008	77.68	0.27111	1.026144	78.50
0.04948	1.014689	77.28	0.11220	1.017994	77.92	0.29133	1.027098	78.76
0.06373	1.015447	77.47	0.15280	1.020088	78.23	0.29953	1.027446	78.98
				m_s=0.5 mol·kg^{-1}				
0.00000	1.025494		0.08746	1.030115	78.22	0.15793	1.033665	78.99
0.03024	1.027113	77.79	0.13669	1.032648	78.50	0.18754	1.035117	79.28
0.06596	1.028994	78.09	0.14247	1.032907	78.77	0.20613	1.036008	79.50
				m_s=0.75 mol·kg^{-1}				
0.00000	1.038264		0.12927	1.044944	78.79	0.19381	1.048092	79.44
0.02240	1.039445	78.24	0.14150	1.045538	78.99	0.23566	1.050088	79.78
0.05223	1.040996	78.50	0.17487	1.047188	79.21	0.25882	1.051148	80.06
				m_s=1.0 mol·kg^{-1}				
0.00000	1.053246		0.07234	1.056948	79.01	0.15278	1.060885	79.77
0.03163	1.054885	78.59	0.09586	1.058115	79.27	0.17632	1.062008	79.96
0.03630	1.055117	78.82	0.13297	1.059948	79.48	0.23136	1.064617	80.25
				m_s=1.5 mol·kg^{-1}				
0.00000	1.080338		0.11732	1.086044	80.18	0.20155	1.089968	80.62
0.07318	1.083962	79.58	0.13551	1.086889	80.37	0.21308	1.090445	80.88
0.08846	1.084688	79.82	0.15542	1.087817	80.49	0.24759	1.092088	81.01
				m_s=2.0 mol·kg^{-1}				
0.00000	1.104299		0.22636	1.114779	80.89	0.29961	1.117866	81.49
0.09661	1.108888	80.34	0.25630	1.116088	81.04	0.30641	1.118044	81.82
0.16601	1.112088	80.58	0.29503	1.117749	81.25	0.32735	1.118862	82.06
				T=298.15K				
				Diglycine				
				m_s=0.00000				
0.00000	0.997047		0.09026	1.002008	76.82	0.10688	1.002862	77.31
0.03860	0.999188	76.53	0.10053	1.002549	77.01	0.11366	1.003204	77.52
0.05138	0.999886	76.69	0.10376	1.002708	77.17	0.16670	1.005998	77.78
				m_s=0.25 mol·kg^{-1}				
0.00000	1.011740		0.07532	1.015708	78.79	0.12100	1.018008	79.47
0.02381	1.013008	78.44	0.07899	1.015884	78.99	0.14308	1.019115	79.63
0.07006	1.15446	78.60	0.09020	1.016447	79.22	0.16333	1.020094	79.94
				m_s=0.5 mol·kg^{-1}				
0.00000	1.025077		0.05405	1.027888	79.16	0.09360	1.029886	79.60
0.02693	1.026489	78.86	0.06828	1.028614	79.30	0.10208	1.030288	79.88

0.03901	1.027115	78.99	0.07124	1.028753	79.48	0.12529	1.031444	80.01
				m_s=0.75 mol·kg^{-1}				
0.00000	1.037864		0.06454	1.041162	79.59	0.20280	1.048004	80.08
0.02092	1.038944	79.28	0.16269	1.046088	79.72	0.21200	1.048483	80.22
0.04154	1.039998	79.43	0.18015	1.046917	79.93	0.21861	1.048708	80.39
				m_s=1.0 mol·kg^{-1}				
0.00000	1.050713		0.12134	1.056775	80.01	0.20886	1.060889	80.81
0.03811	1.052644	79.68	0.14723	1.058009	80.28	0.24954	1.062775	81.01
0.06750	1.054117	79.79	0.17079	1.059115	80.52	0.25704	1.063116	81.06
				m_s=1.5 mol·kg^{-1}				
0.00000	1.075983		0.08398	1.080044	80.70	0.17411	1.084233	81.22
0.02085	1.077004	80.40	0.12834	1.082133	80.92	0.19348	1.085098	81.39
0.05935	1.078868	80.57	0.16877	1.084009	81.09	0.22322	1.086444	81.50
				m_s=2.0 mol·kg^{-1}				
0.00000	1.099888		0.10043	1.104489	81.89	0.20765	1.109214	82.28
0.04314	1.101894	81.52	0.17355	1.107746	82.09	0.21365	1.109448	82.40
0.04761	1.102088	81.74	0.19334	1.108608	82.17	0.21983	1.109669	82.59
				T=308.15K				
				Diglycine				
				m_s=0.00000				
0.00000	0.994033		0.09261	0.999046	77.72	0.12643	1.000788	78.29
0.01862	0.995054	77.32	0.11923	1.000448	77.94	0.13172	1.001048	78.44
0.07290	0.997998	77.54	0.12426	1.000689	78.16	0.13548	1.001225	78.60
				m_s=0.25 mol·kg^{-1}				
0.00000	1.011264		0.06603	1.014664	80.01	0.19334	1.021004	80.59
0.02162	1.012389	79.67	0.11406	1.017089	8.23	0.23721	1.023117	80.82
0.02919	1.012775	79.89	0.15503	1.019117	80.47	0.24473	1.023448	80.97
				m_s=0.5 mol·kg^{-1}				
0.00000	1.024287		0.07550	1.028115	80.34	0.14489	1.031483	81.06
0.03577	1.026118	80.04	0.08729	1.028683	80.62	0.17904	1.033115	81.27
0.07030	1.027864	80.19	0.11669	1.030114	80.91	0.21885	1.035004	81.44
				m_s=0.75 mol·kg^{-1}				
0.00000	1.037442		0.06493	1.040689	80.62	0.15655	1.045117	81.18
0.03078	1.038998	80.24	0.10035	1.042417	80.88	0.19365	1.046884	81.29
0.04722	1.039818	80.40	0.13291	1.043998	80.99	0.19882	1.047115	81.52
				m_s=1.0 mol·kg^{-1}				
0.00000	1.049864		0.09802	1.054668	80.99	0.17132	1.058115	81.49
0.02447	1.051083	80.53	0.11378	1.055417	81.12	0.21358	1.060088	81.60
0.06647	1.083146	80.78	0.12648	1.056009	81.27	0.24360	1.061448	81.78
				m_s=1.5 mol·kg^{-1}				
0.00000	1.071848		0.13355	1.078115	81.92	0.23112	1.082445	82.52
0.04749	1.074115	81.52	0.16322	1.079443	82.16	0.23799	1.082683	82.78
0.08789	1.076008	81.73	0.20152	1.081162	82.30	0.24516	1.082944	82.99
				m_s=2.0 mol·kg^{-1}				
0.00000	1.095014		0.10894	1.099885	82.98	0.15823	1.101888	83.88
0.04149	1.096885	82.89	0.11210	1.099994	83.21	0.16384	1.102089	84.08
0.06628	1.098004	82.79	0.15106	1.101649	83.50	0.24724	1.105546	84.30
				T=318.15K				
				Diglycine				
				m_s=0.00000				
0.00000	0.990244		0.12484	0.996877	78.69	0.18287	0.999808	79.30

0.07031	0.994018	78.36	0.12807	0.997022	78.89	0.23025	1.002188	79.54
0.10109	0.995644	78.50	0.17040	0.999188	79.16	0.23947	1.002604	79.77
				m_s=0.25 mol·kg^{-1}				
0.00000	1.004062		0.03824	1.005998	81.19	0.12854	1.010445	81.79
0.1248	1.004699	80.88	0.05920	1.007046	81.33	0.13822	1.010894	81.98
0.01878	1.005017	81.04	0.11108	1.009618	81.50	0.15484	1.011677	82.16
				m_s=0.5 mol·kg^{-1}				
0.00000	1.016923		0.07990	1.020886	81.62	0.14545	1.024009	82.22
0.01917	1.017885	81.29	0.10117	1.021904	81.89	0.15771	1.024558	82.47
0.03962	1.018904	81.40	0.12166	1.022888	82.01	0.18898	1.026007	82.68
				m_s=0.75 mol·kg^{-1}				
0.00000	1.029652		0.09105	1.034088	81.99	0.19661	1.039004	82.68
0.02498	1.030884	81.68	0.11286	1.035114	82.21	0.24479	1.041218	82.80
0.05022	1.032117	81.80	0.15073	1.036889	82.43	0.25424	1.041604	82.99
				m_s=1.0 mol·kg^{-1}				
0.00000	1.041006		0.122396	1.046782	82.89	0.16302	1.048553	83.57
0.08094	1.044883	82.39	0.12543	1.046898	83.08	0.20020	1.050204	83.76
0.10480	1.045994	82.58	0.13795	1.047448	83.29	0.24406	1.052117	83.99
				m_s=1.5 mol·kg^{-1}				
0.00000	1.063447		0.12298	1.069117	83.01	0.23737	1.074115	83.64
0.03575	1.065118	82.76	0.14507	1.070088	83.20	0.25158	1.074689	83.82
0.06546	1.066489	82.89	0.22962	1.073812	83.49	0.25736	1.074887	84.01
				m_s=2.0 mol·kg^{-1}				
0.00000	1.084235		0.08885	1.088115	84.39	0.18517	1.092117	85.01
0.02586	1.085382	84.02	0.13295	1.089988	84.58	0.21913	1.093488	85.19
0.06036	1.086889	84.23	0.13884	1.090204	84.80	0.22409	1.093644	82.38
				KNO_3				
				T=288.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.014284		0.12726	1.021148	77.29	0.15707	1.022638	77.90
0.02983	1.015917	76.90	0.13791	1.021689	77.48	0.18434	1.024009	78.21
0.04997	1.017004	77.12	0.14323	1.021944	77.67	0.24059	1.026884	78.36
				m_s=0.5 mol·kg^{-1}				
0.00000	1.028587		0.06640	1.032115	77.94	0.14458	1.036118	78.62
0.01539	1.029415	77.51	0.11974	1.034887	78.22	0.18243	1.038009	78.89
0.04508	1.030994	77.78	0.12273	1.035009	78.48	0.20469	1.039114	79.01
				m_s=0.75 mol·kg^{-1}				
0.00000	1.042648		0.10252	1.048006	78.22	0.18495	1.052118	78.88
0.02391	1.043915	77.86	0.10848	1.048283	78.49	0.20390	1.053044	79.01
0.04245	1.044887	78.01	0.16279	1.051044	78.62	0.22757	1.054177	79.22
				m_s=1.0 mol·kg^{-1}				
0.00000	1.053514		0.08978	1.058133	78.69	0.1304	1.061744	79.29
0.03294	1.055233	78.24	0.13578	1.060445	78.88	0.18687	1.062885	79.50
0.06613	1.056944	78.40	0.14918	1.061089	79.07	0.23134	1.065004	79.77
				m_s=1.5 mol·kg^{-1}				
0.00000	1.079506		0.08989	1.083998	79.16	0.15826	1.087288	79.60
0.03411	1.081233	78.80	0.11286	1.085115	79.31	0.17125	1.087862	79.88
0.06248	1.082648	78.99	0.13319	1.086088	79.48	0.19589	1.089004	80.06
				m_s=2.0 mol·kg^{-1}				

0.00000	1.097447		0.05261	1.099988	80.08	0.23089	1.108288	80.59
0.02540	1.098688	79.72	0.08854	1.101688	80.29	0.26512	1.109814	80.73
0.04181	1.099477	79.91	0.11747	1.103044	80.40	0.26845	1.109886	80.98
				T=298.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.011764		0.11986	1.018086	78.55	0.17141	1.020688	79.01
0.02479	1.013088	78.28	0.13162	1.018674	78.74	0.19870	1.022044	79.22
0.06067	1.014989	78.39	0.13846	1.019008	78.89	0.22192	1.023188	79.38
				m_s=0.5 mol·kg^{-1}				
0.00000	1.026123		0.09876	1.031233	79.20	0.15528	1.034009	79.89
0.02080	1.027214	78.84	0.13494	1.033048	79.46	0.16944	1.034688	80.06
0.06728	1.029628	78.99	0.15216	1.033886	79.68	0.18791	1.035572	80.24
				m_s=0.75 mol·kg^{-1}				
0.00000	1.039984		0.09603	1.044888	79.43	0.14157	1.047088	80.08
0.05399	1.042775	79.01	0.11326	1.045728	79.69	0.16618	1.048288	80.18
0.06745	1.043449	79.26	0.12151	1.046115	79.90	0.20946	1.050389	80.29
				m_s=1.0 mol·kg^{-1}				
0.00000	1.050724		0.10378	1.055889	80.24	0.16996	1.058998	80.99
0.06271	1.053889	79.77	0.11572	1.056443	80.52	0.22296	1.061474	81.22
0.08514	1.054995	79.96	0.15094	1.058117	80.79	0.27531	1.063862	81.48
				m_s=1.5 mol·kg^{-1}				
0.00000	1.075328		0.09796	1.080064	80.68	0.18066	1.083889	81.22
0.03493	1.077044	80.23	0.14200	1.082133	80.89	0.18426	1.084006	81.46
0.07182	1.078828	80.44	0.17028	1.083445	81.01	0.18983	1.084229	81.62
				m_s=2.0 mol·kg^{-1}				
0.00000	1.098608		0.14300	1.105289	81.04	0.19258	1.107417	81.69
0.02899	1.099988	80.70	0.15984	1.106017	81.29	0.20652	1.107996	81.88
0.13355	1.104877	80.89	0.17983	1.106888	81.48	0.21241	1.108213	82.06
				T=308.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.008586		0.03865	1.010588	79.90	0.08879	1.013115	80.47
0.01954	1.008611	79.40	0.06557	1.011964	80.06	0.10214	1.013779	80.58
0.02693	1.009988	79.68	0.07803	1.012588	80.24	0.12013	1.014668	80.72
				m_s=0.5 mol·kg^{-1}				
0.00000	1.022904		0.06977	1.026445	80.36	0.12431	1.029115	80.90
0.03866	1.024888	79.94	0.10129	1.028008	80.58	0.14742	1.030228	81.08
0.04109	1.025004	80.14	0.11721	1.028783	80.74	0.20732	1.033115	81.26
				m_s=0.75 mol·kg^{-1}				
0.00000	1.036012		0.12178	1.042117	80.33	0.18431	1.045096	80.88
0.04139	1.038115	80.01	0.13733	1.042864	80.49	0.20585	1.046111	81.01
0.08364	1.040228	80.22	0.14282	1.043115	80.62	0.22776	1.047115	81.22
				m_s=1.0 mol·kg^{-1}				
0.00000	1.046447		0.08145	1.050447	81.08	0.20150	1.056088	81.79
0.03312	1.048094	80.70	0.17404	1.054888	81.29	0.20999	1.056444	81.98
0.07160	1.049982	80.88	0.17956	1.055116	81.53	0.22593	1.057112	82.29
				m_s=1.5 mol·kg^{-1}				
0.00000	1.071208		0.14572	1.078096	81.60	0.23590	1.082088	82.29
0.04695	1.073469	81.18	0.15825	1.078628	81.89	0.25505	1.082888	82.51
0.08183	1.075117	81.39	0.19139	1.080115	82.08	0.26205	1.083115	82.80
				m_s=2.0 mol·kg^{-1}				
0.00000	1.088443		0.14611	1.095116	82.31	0.21688	1.098114	82.99
0.03313	1.089989	81.86	0.18938	1.096997	82.59	0.24821	1.099428	83.17

0.14044	1.094887	82.15	0.20024	1.097446	82.73	0.26194	1.099988	83.28
				T=318.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.004008		0.11889	1.009988	81.19	0.20195	1.013977	81.79
0.03951	1.006014	81.04	0.16177	1.012086	81.38	0.21173	1.014388	82.09
0.10080	1.009046	80.99	0.19508	1.013688	81.56	0.22337	1.014906	82.28
				m_s=0.5 mol·kg^{-1}				
0.00000	1.016886		0.09363	1.021557	81.29	0.24460	1.028884	81.89
0.04059	1.018936	80.90	0.14610	1.024116	81.47	0.27348	1.030115	82.06
0.06133	1.019964	81.13	0.20171	1.026775	81.70	0.29350	1.031009	82.23
				m_s=0.75 mol·kg^{-1}				
0.00000	1.028764		0.14870	1.036044	81.57	0.21354	1.039008	82.26
0.03373	1.030445	81.18	0.18157	1.037589	81.78	0.23830	1.040115	82.49
0.06764	1.032116	81.32	0.20845	1.038823	82.01	0.28229	1.042099	82.70
				m_s=1.0 mol·kg^{-1}				
0.00000	1.039446		0.13895	1.046094	82.28	0.24477	1.050885	82.92
0.06659	1.042688	81.77	0.16206	1.047148	82.49	0.27178	1.052046	83.17
0.09681	1.044117	82.06	0.20062	1.048904	82.70	0.27991	1.052333	83.44
				m_s=1.5 mol·kg^{-1}				
0.00000	1.059117		0.12733	1.065022	82.92	0.24269	1.070115	83.46
0.06324	1.062099	82.46	0.15209	1.066128	83.08	0.28804	1.072046	83.69
0.10833	1.064177	82.69	0.23842	1.069984	83.24	0.29936	1.072445	83.98
				m_s=2.0 mol·kg^{-1}				
0.00000	1.078623		0.11732	1.083888	83.49	0.21431	1.087983	84.20
0.03991	1.080445	83.09	0.14390	1.085044	83.62	0.22019	1.088164	84.48
0.11217	1.083689	83.26	0.17790	1.086488	83.86	0.25523	1.089557	84.79
				$MgNO_3$				
				T=288.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.018204		0.16488	1.046898	78.21	0.25720	1.031462	78.99
0.05191	1.020983	77.89	0.18795	1.028046	78.47	0.26819	1.032008	79.02
0.09885	1.023464	78.01	0.22919	1.030115	78.69	0.27331	1.032446	79.38
				m_s=0.5 mol·kg^{-1}				
0.00000	1.035008		0.17171	1.043888	78.68	0.19697	1.045004	79.49
0.04623	1.037447	78.20	0.17896	1.044208	78.94	0.24047	1.047115	79.70
0.09774	1.040115	78.47	0.19347	1.044883	79.23	0.25258	1.047648	79.94
				m_s=0.75 mol·kg^{-1}				
0.00000	1.049868		0.14194	1.057113	78.97	0.17552	1.058649	79.77
0.04314	1.052117	78.49	0.15439	1.057689	79.28	0.21057	1.060333	79.94
0.09985	1.055009	78.73	0.16372	1.058115	79.50	0.24974	1.062144	80.29
				m_s=1.0 mol·kg^{-1}				
0.00000	1.061934		0.13408	1.068648	79.49	0.20578	1.072009	80.22
0.03000	1.063468	78.94	0.14418	1.069117	79.68	0.22473	1.072854	80.48
0.06282	1.065117	79.23	0.17209	1.070445	79.90	0.23128	1.073117	80.67
				m_s=1.5 mol·kg^{-1}				
0.00000	1.085948		0.10763	1.091175	80.08	0.19262	1.095099	80.68
0.03035	1.087446	79.68	0.12619	1.092044	80.23	0.21623	1.096144	80.90
0.08253	1.089983	79.89	0.15706	1.093473	80.46	0.24959	1.097628	81.09
				m_s=2.0 mol·kg^{-1}				

0.00000	1.105833		0.08334	1.109775	80.49	0.17689	1.113988	81.16
0.02366	1.106988	80.01	0.08955	1.110046	80.68	0.24561	1.117046	81.30
0.04985	1.108214	80.23	0.14642	1.112644	80.92	0.29121	1.119008	81.49
				T=298.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.015826		0.18063	1.025117	79.47	0.23896	1.027862	80.28
0.03071	1.017443	78.89	0.22062	1.027088	79.69	0.24531	1.028115	80.52
0.06524	1.019228	79.24	0.22969	1.027486	79.93	0.25434	1.028488	80.79
				m_s=0.5 mol·kg^{-1}				
0.00000	1.032428		0.13515	1.039288	79.80	0.20226	1.042489	80.50
0.05100	1.035066	79.22	0.14575	1.039786	80.02	0.22541	1.043555	80.77
0.09199	1.037144	79.49	0.15323	1.040115	80.29	0.24053	1.044218	81.04
				m_s=0.75 mol·kg^{-1}				
0.00000	1.047017		0.15340	1.054644	80.23	0.20273	1.056888	80.99
0.05020	1.049562	79.73	0.16869	1.055333	80.56	0.22045	1.057665	81.28
0.08003	1.051044	79.76	0.18641	1.056144	80.80	0.23109	1.058114	81.50
				m_s=1.0 mol·kg^{-1}				
0.00000	1.058884		0.13542	1.065483	80.79	0.23575	1.070092	81.49
0.04345	1.061046	80.21	0.14888	1.066099	80.98	0.27820	1.071998	81.70
0.10600	1.064094	80.52	0.19985	1.068463	81.27	0.29231	1.072553	81.99
				m_s=1.5 mol·kg^{-1}				
0.00000	1.082898		0.08894	1.087144	80.96	0.19414	1.091888	81.82
0.02620	1.084155	80.98	0.14834	1.089888	81.28	0.21043	1.092533	82.21
0.08317	1.086888	80.78	0.16120	1.090444	81.50	0.21766	1.092777	82.53
				m_s=2.0 mol·kg^{-1}				
0.00000	1.102673		0.07384	1.106014	82.34	0.16592	1.109988	82.99
0.02669	1.103899	81.93	0.10068	1.107188	82.58	0.17781	1.110446	83.26
0.05083	1.104988	82.17	0.11881	1.107962	82.79	0.27922	1.114688	83.50
				T=308.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.012447		0.15796	1.020462	80.34	0.23271	1.024009	81.08
0.02353	1.013665	79.88	0.20764	1.022888	80.59	0.24333	1.024462	81.34
0.04976	1.015008	80.06	0.21353	1.023116	80.88	0.25139	1.024788	81.59
				m_s=0.5 mol·kg^{-1}				
0.00000	1.027118		0.13909	1.034099	80.49	0.21044	1.037445	81.28
0.03702	1.029004	80.18	0.16064	1.035116	80.79	0.22280	1.037989	81.50
0.08595	1.031468	80.30	0.19775	1.036888	81.01	0.22687	1.038115	81.79
				m_s=0.75 mol·kg^{-1}				
0.00000	1.040223		0.14112	1.047133	81.20	0.19720	1.049688	81.89
0.03941	1.042178	80.88	0.16180	1.048099	81.39	0.23603	1.051444	82.17
0.11910	1.046099	80.94	0.16537	1.048233	81.60	0.25102	1.052099	82.33
				m_s=1.0 mol·kg^{-1}				
0.00000	1.051628		0.11458	1.057116	81.88	0.13757	1.058113	82.48
0.08477	1.055717	81.68	0.12157	1.057449	82.09	0.16694	1.059447	82.64
0.10942	1.056894	81.69	0.12788	1.057688	82.29	0.20539	1.061162	82.89
				m_s=1.5 mol·kg^{-1}				
0.00000	1.071982		0.11104	1.077144	82.38	0.18638	1.080445	83.06
0.04500	1.074115	81.82	0.13516	1.078218	82.60	0.22523	1.082118	83.28
0.08776	1.076099	82.09	0.17477	1.079960	82.89	0.23457	1.082447	83.59
				m_s=2.0 mol·kg^{-1}				
0.00000	1.088004		0.12250	1.093446	83.47	0.21053	1.097113	84.16
0.03937	1.089776	83.26	0.13874	1.094119	83.71	0.21359	1.097208	84.30

0.09192	1.092118	83.29	0.16205	1.095088	83.94	0.21886	1.097333	84.68
				T=318.15K				
				m_s=0.25 mol·kg^{-1}				
0.00000	1.007288		0.07550	1.011046	81.78	0.20074	1.017009	82.62
0.02234	1.008417	81.24	0.14619	1.014489	82.01	0.22573	1.018115	82.98
0.04782	1.009688	81.49	0.15984	1.015117	82.23	0.27784	1.020446	83.38
				m_s=0.5 mol·kg^{-1}				
0.00000	1.022446		0.08889	1.026777	82.23	0.17339	1.030688	83.06
0.03155	1.024009	81.68	0.12454	1.028463	82.50	0.19164	1.031707	83.23
0.06606	1.025689	81.98	0.13939	1.029117	82.88	0.22308	1.032886	83.58
				m_s=0.75 mol·kg^{-1}				
0.00000	1.035082		0.14732	1.042117	82.49	0.21273	1.045009	83.27
0.04175	1.037115	82.01	0.16927	1.043098	82.78	0.22041	1.045288	83.58
0.08120	1.039004	82.23	0.19206	1.044117	82.99	0.23841	1.046044	83.82
				m_s=1.0 mol·kg^{-1}				
0.00000	1.045886		0.13212	1.052088	82.90	0.20932	1.055443	83.80
0.04626	1.048099	82.40	0.16296	1.053448	83.28	0.22585	1.056117	84.07
0.10527	1.050864	82.68	0.17866	1.054117	83.53	0.24941	1.057094	84.32
				m_s=1.5 mol·kg^{-1}				
0.00000	1.065838		0.11506	1.071086	83.38	0.23130	1.076117	84.01
0.02749	1.067117	82.89	0.16103	1.073115	83.59	0.26380	1.077448	84.28
0.09030	1.069988	83.16	0.20940	1.075204	83.83	0.27104	1.077665	84.59
				m_s=2.0 mol·kg^{-1}				
0.00000	1.082044		0.13688	1.087964	84.68	0.24011	1.092144	85.36
0.04740	1.084133	84.28	0.15008	1.088489	84.90	0.28550	1.093899	85.68
0.09274	1.086094	84.47	0.18875	1.090062	85.17	0.29576	1.094208	85.99

Apparent molar volumes of amino acids have been calculated as follows:

$$V_{2,\phi} = M / \rho - [(\rho - \rho_o)\ 1000/m\rho\rho_o] \quad (1)$$

Where M is the molar mass of diglycine, m (mol.kg^{-1}) is the molality, and ρ is the densities of solution and solvent, respectively. At infinite dilution, the apparent molar volumes, and partial molar volumes, are identical ($V_{2,\Phi} = V_2^{0},_{\Phi}$). In the case of negligible concentration dependence of $V_{2,\Phi}$, $V_{2,}^{0}{}_{\Phi}$ was determined by taking the average of all the data points. However, where finite concentration dependence was observed, $V_2^{0},_{\Phi}$ was determined by least-squares fitting of the data using the following equation.

$$V_{2,\phi} = V_{2,}^{0}{}_{\Phi} + S_v m \quad (2)$$

Where $V_{2,}^{0}{}_{\Phi}$ is the infinite dilution apparent molar volume and has the same meaning as the standard partial molar volume, and S_v is the experimental slope. The $V_{2,}^{0}{}_{\Phi}$ values along with their standard deviations are summarized in **Table 2** at T = (288.15, 298.15, 308.15 and 318.15) K. The experimental values of for the diglycine in water agreed well with those reported in the literature[30-31]. The $V_2^{0},_{\Phi}$ values for the diglycine increases with the increase in the concentration of sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate.

Table 2. Standard Partial molar volumes, $V_2^{0}{}_{,\phi} \times 10^6$ at infinite dilution for the peptide in water and in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions at (288.15-318.15) K

$V_2^{0}{}_{,\phi} \times 10^6$ /m^3·mol^{-1} at various m_s /mol·kg^{-1}[a]							
Peptide	Water	[a]m_s = 0.25	m_s = 0.5	m_s = 0.75	m_s = 1.0	m_s = 1.5	m_s = 2.0
			$NaNO_3$				
			T = 288.15 K				
Diglycine	75.74 ± 0.33 (9.32) 75.25[a] 75.22[b]	77.15 ± 0.16 (5.72)	77.59 ± 0.36 (1.85)	78.01 ± 0.11 (7.41)	78.44 ± 0.08 (8.18)	79.18 ± 0.12 (7.73)	79.49 ± 0.24 (6.88)
			T = 298.15 K				
Diglycine	76.12± 0.15 (10.21) 76.23[a] 76.28[b]	78.05± 0.14 (11.35)	78.52± 0.007 (12.22)	79.21± 0.14 (4.52)	79.34± 0.08 (6.69)	80.25± 0.05 (5.53)	81.41± 0.12 (4.50)
			T=308.15K				
Diglycine	76.95± 0.20 (10.23) 77.11[a] 77.10[b]	79.65± 0.07 (5.11)	79.78± 0.13 (8.18)	80.11± 0.08 (6.73)	80.44± 0.07 (5.69)	81.11± 0.14 (6.67)	82.36± 0.24 (8.34)
			T=318.15K				
Diglycine	77.74± 0.08 (8.22)	80.84± 0.11 (7.84)	81.05± 0.08 (8.40)	81.54± 0.06 (5.56)	81.69± 0.17 (10.17)	82.51± 0.13 (5.0)	83.83± 0.07 (6.50)
			KNO_3				
			T=288.15K				
Diglycine	75.74 ± 0.33 (9.32)	76.65 ± 0.18 (7.21)	77.40 ± 0.08 (8.04)	77.69 ± 0.09 (6.40)	77.92 ± 0.08 (6.40)	78.49 ± 0.07 (7.68)	79.80 ± 0.14 (3.94)
			T=298.15K				
Diglycine	76.12 ± 0.51 (10.21)	78.04 ± 0.09 (5.74)	78.48 ± 0.15 (8.62)	78.68 ± 0.15 (8.64)	79.41 ± 0.15 (8.13)	79.89 ± 0.16 (7.86)	80.23 ± 0.24 (7.31)
			T=308.15K				
Diglycine	76.95 ± 0.20 (10.23)	79.60 ± 0.28 (6.67)	79.79 ± 0.12 (7.85)	79.66 ± 0.07 (6.58)	80.40 ± 0.20 (7.10)	81.14 ± 0.23 (5.33)	81.45 ± 0.15 (6.61)
			T=318.15K				
Diglycine	77.74 ± 0.08 (8.22)	80.51 ± 0.24 (6.60)	80.78 ± 0.06 (4.71)	80.84 ± 0.16 (6.23)	81.33 ± 0.09 (6.23)	82.13 ± 0.09 (5.59)	82.53 ± 0.17 (8.21)
			$MgNO_3$				
			T=288.15K				
Diglycine	75.74 ± 0.33 (9.32)	77.40 ± 0.17 (6.15)	77.65 ± 0.22 (8.33)	77.91 ± 0.17 (9.45)	78.62 ± 0.14 (8.02)	79.39 ± 0.05 (6.75)	80.04 ± 0.13 (5.38)
			T=298.15K				
Diglycine	76.21 ± 0.51 (10.21)	78.64 ± 0.33 (6.62)	78.66 ± 0.11 (9.49)	79.14 ± 0.11 (9.25)	79.87 ± 0.07 (6.93)	80.35 ± 0.30 (8.22)	81.89 ± 0.14 (6.44)
			T=308.15K				
Diglycine	76.95±0.20 (10.23)	79.63 ± 0.26 (6.30)	79.66 ± 0.23 (7.84)	80.30 ± 0.19 (3.35)	80.71 ± 0.17 (3.76)	81.37 ± 0.08 (8.95)	82.74 ± 0.19 (7.41)
			T=318.15K				
Diglycine	77.74 ± 0.08 (8.22)	81.05 ± 0.13 (8.08)	81.35 ± 0.07 (9.98)	81.47 ± 0.21 (8.76)	81.74 ± 0.13 (9.96)	82.62 ± 0.13 (6.39)	83.89 ±0.10 (4.98)

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

From the $V_2^{0}{}_{,\Phi}$ data, m the standard partial molar volumes of transfer, $\Delta_t V^0$, at infinite dilution from water to aqueous sodium nitrate, potassium nitrate solutions and magnesium nitrate hexahydrate solutions have been evaluated as follows:

$\Delta_t V^0_2$ [water→ aqueous $NaNO_3$ /KNO_3/ Mg $(NO_3)_2$] = V^0_2 [in aqueous $NaNO_3$/KNO_3/ Mg $(NO_3)_2$ – V^0_2 (in water)] (3.3) The $\Delta_t V^0$ values for diglycine in $NaNO_3$ / KNO_3 / Mg $(NO_3)_2 \cdot 6H_2O$ are summarized in **Table 3** and illustrated in **Figures 1a-c**.

Table 3. Standard Partial molar volumes of transfer, $\Delta_t V^o \times 10^6$, at infinite dilution for the peptide in water and in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions at (288.15-318.15) K

$\Delta_t V^o \times 10^6$ /$m^3 mol^{-1}$ at various m_S / $mol \cdot kg^{-1a}$						
			T=288.15 K **$NaNO_3$**			
Peptide	0.25 m	0.5 m	0.75 m	1.0 m	1.5 m	2.0 m
Diglycine	1.41± 0.37	1.85± 0.37	2.27± 0.35	2.70± 0.34	3.44± 0.35	3.75± 0.41
			T=298.15 K			
Diglycine	1.93± 0.20	2.40± 0.16	3.09± 0.20	3.22± 0.17	4.13± 0.16	5.29± 0.19
			T=308.15 K			
Diglycine	2.70± 0.21	2.83± 0.24	3.16± 0.21	3.49± 0.21	4.16± 0.24	5.41± 0.31
			T=318.15 K			
Diglycine	3.2± 0.14	3.31± 0.11	3.80± 0.10	3.95± 0.19	4.77± 0.15	6.09± 0.11
			KNO_3 **T=288.15 K**			
Diglycine	0.91± 0.38	1.66± 0.34	1.95± 0.34	2.18± 0.34	2.75± 0.34	4.06± 0.36
			T=298.15 K			
Diglycine	1.92± 0.52	2.36± 0.53	2.56± 0.53	3.29± 0.53	3.77± 0.53	4.11± 0.56
			T=308.15 K			
Diglycine	2.65± 0.34	2.84± 0.23	2.71± 0.21	3.45± 0.28	4.19± 0.30	4.50± 0.25
			T=318.15 K			
Diglycine	2.77± 0.25	3.04± 0.10	3.10± 0.18	3.59± 0.12	4.39± 0.12	4.79± 0.19
			$Mg(NO_3)_2$ **T=288.15 K**			
Diglycine	1.66± 0.37	1.91± 0.40	2.17± 0.37	2.88± 0.36	3.65± 0.33	4.30± 0.35
			T=298.15 K			
Diglycine	2.52± 0.61	2.54± 0.52	3.02± 0.54	3.75± 0.51	4.23± 0.59	5.76± 0.53
			T=308.15 K			
Diglycine	2.68 ±0.33	2.71± 0.30	3.35± 0.28	3.76 ± 0.26	4.42 ± 0.21	5.79 ± 0.28
			T=318.15 K			
Diglycine	3.31 ±0.15	3.61 ±0.11	3.73 ± 0.22	4.0 ±0.15	4.88± 0.15	6.15 ± 0.13

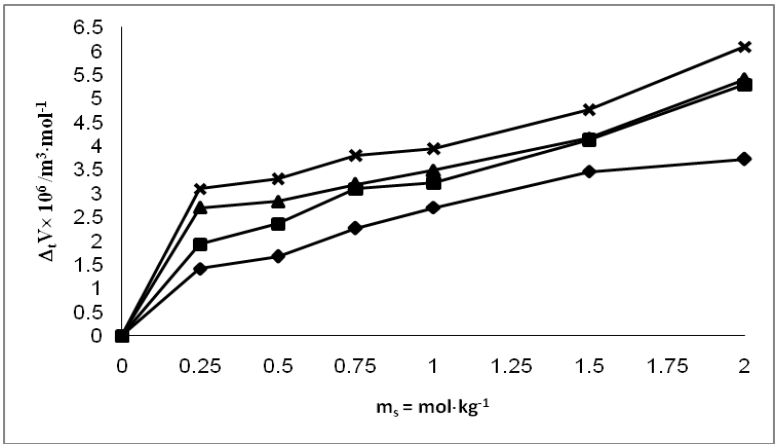


Figure 1a. Standard partial molar volumes of transfer, $\Delta_t V^0$, of diglycine vs. different molalities, m_s, of sodium nitrate solutions at (a)♦, 288.15 K; (b) ■, 298.15 K; (c) ▲, 308.15 K; (d) ×, 318.15 K.

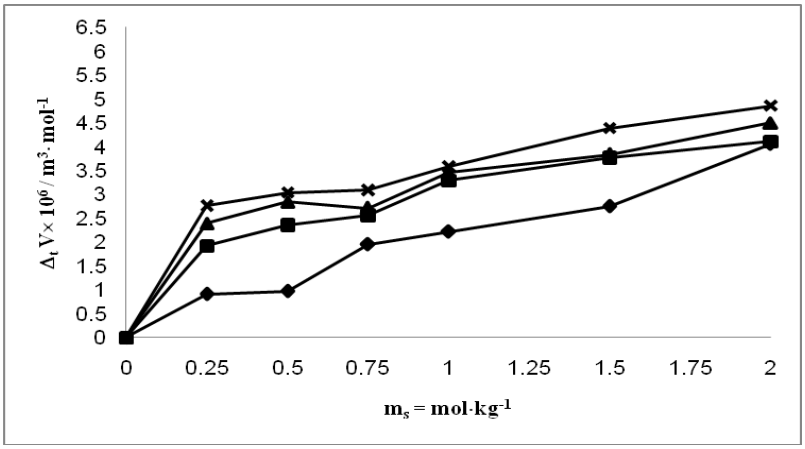


Figure 1b. Standard partial molar volumes of transfer, $\Delta_t V^0$, of diglycine vs. different molalities, m_s, of potassium nitrate solutions at (a)♦, 288.15 K; (b) ■, 298.15 K; (c) ▲, 308.15 K; (d) ×, 318.15 K.

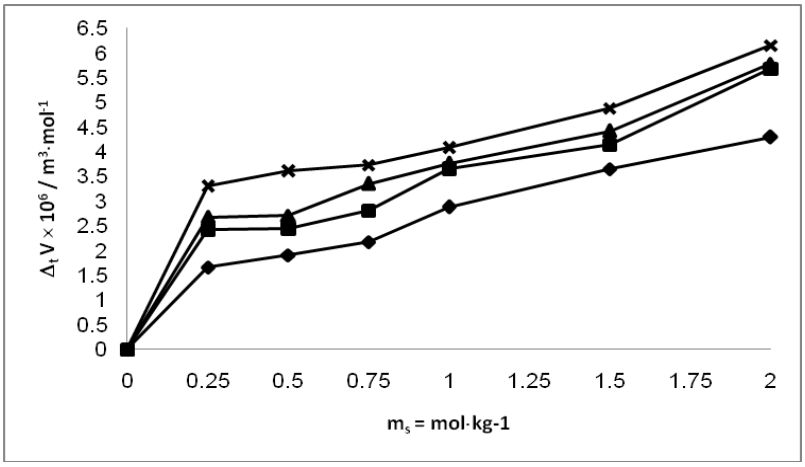


Figure 1c. Standard partial molar volumes of transfer, $\Delta_t V^0$, of diglycine vs. different molalities, m_s, of magnesium nitrate hexahydrate solutions at (a)♦, 288.15 K; (b) ■, 298.15 K; (c) ▲, 308.15 K; (d) ×, 318.15 K.

The $\Delta_t V^0$ values for the studied diglycine are positive and increase almost linearly with the increase in concentration of aqueous $NaNO_3$ / KNO_3 / $Mg(NO_3)_2$ solutions. The more positive $\Delta_t V^0$ values in the case of diglycine indicate the dominance of the effect of charged end groups (NH_3^+ and COO^-).

The cosphere model [32] can be utilized to rationalize the $\Delta_t V^0$ values in terms of solute-cosolute interactions. According to this model, when two solute particles come close enough together so that their cosphere overlap some cosphere material is displaced, and this is accompanied by the change in thermodynamic parameters. The following types of interactions can occur between amino acids and $NaNO_3$ / KNO_3 / $Mg(NO_3)_2$ in solutions:

i. Ion-ion interactions occurring between Mg^{2+}/ Na^+/ K^+ ions and COO^- groups of amino acids and between NO_3^- ions of $NaNO_3$ / KNO_3 / $Mg(NO_3)_2$ and NH_3^+ groups of diglycine.
ii. Interactions between ions (Mg^{2+}/ Na^+/ K^+, NO_3^-) of $NaNO_3$ / KNO_3 / $Mg(NO_3)_2$ and nonpolar (hydrophobic) part of diglycine.

The ion-ion interactions dominate the ion- hydrophobic group interactions. Because of the first types of interactions, the electrostriction of water in the neighborhood of charged end groups (NH^+, COO^-) of diglycine gets reduced, and this will contribute positively to the volumes of transfers. Furthermore, the increase in $\Delta_t V^0$ values with increasing $NaNO_3$ / KNO_3 / $Mg(NO_3)_2$ concentration strengthens this view. This is a qualitative interpretation of the results.
Franks et al.[33] have shown that the partial molar volume of non-electrolyte is a combination of two types of contributions given by the following equation:

$$V^0_2 = V_{int} + V_s \quad (4)$$

where, V_{int} is the intrinsic volume of non-electrolyte and V_s volume due to it's interactions with the solvent.
It has been considered [36,37] that V_{int} is made up of two types of contributions.

$$V_{int} = V_{vw} + V_{void} \quad (5)$$

where, V_{vw}, is the van der Waals volume and V_{void} is the associated void or empty volume. Shahidi et al.[34] further modified **Eq. (5)** to include the contribution of interactions of a non-electrolyte solute with the solvent.

$$V^0_2 = V_{vw} + V_{void} - n\sigma_s \quad (6)$$

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 non-electrolytes and zwitterionic solutes the shrinkage is caused by electrostriction and finally V^0_2 can be evaluated as:

$$V^0_2 = V_{vw} + V_{void} - V_{shrinkage} \quad (7)$$

Where, $V_{shrinkage}$ is the volume due to shrinkage caused by the interaction of hydrogen bonding groups present in the solute with water molecules. It has been reported that V_{vw} and V_{void} have the same magnitude in water and in mixed solvents for the same class of compounds. Therefore positive $\Delta_t V^0$ values can be attributed to a decrease in the shrinkage volume in the presence of aqueous solutions of $Mg(NO_3)_2$ / $NaNO_3$ / KNO_3. Because of the stronger interactions of Mg^{2+}, Na^+ and NO_3^- with COO^- and NH_3^+ in the diglycine, the electrostriction of neighboring water molecules due to these charged centers / peptide backbone will be reduced which will result into a reduction in the shrinkage volume.

The increase of V^0_2 values with the increase in temperature may also be attributed to the reduction in electrostriction with temperature. This also gets support from the volumetric and compressibility studies of glycine and DL-α-alanine in aqueous sodium sulfate solutions by Wadi and Ramasami, who reported that the hydration number of amino acids decreases with increasing temperature and concentration of sodium sulfate[35]. The increase in positive V^0_2 values of

studied diglycine with the increase in the concentration of Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3 may further be attributed to the formation of non-covalent ion-pairs between the charged groups of the diglycine and the cation Mg^{2+} / Na^+/ K^+ and the anion (NO_3^-) of the electrolyte. This increases the apparent molar volume of diglycine and decreases electrostriction of water around diglycine in the presence of Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3. The decrease in the magnitude of $\Delta_t V^0$ values with the increase of temperature can be attributed to the enhanced thermal agitation and weakening of various interactions involving ions resulting in the relaxation to the bulk more of the electrostricted water molecules from the mutually interacting regions

Kozak et al. [36] have proposed formalism on the basis of McMillan-Mayer [37] theory of solutions which permits the formal separation of the effects due to interactions between pairs of solute molecules and those due to interactions involving three or more solute molecules. Friedman and Krishnan [38] and Franks et al. [39] have further discussed this approach to include the solute-cosolute interactions in the solvation sphere. Various workers [40,41] used this approach to study the interactions of amino acids and cosolutes in aqueous medium. The various transfer functions of the diglycine can be expressed by the following equation:

$$\Delta_t V^0 = 2V_{AB}.m_S + 3V_{ABB}.m^2_S + 4V_{ABBB}.m^3_S + \ldots\ldots\ldots\ldots \quad (8)$$

Where, $V_{AB,}$ $3V_{ABB}$ and V_{ABBB} are respectively, pair, triplet and quartet interaction coefficients (where A stands for the diglycine, B stands for [Mg $(NO_3)_2$ /$NaNO_3$ / KNO_3]. The data reveal that all pair volumetric interaction parameters V_{AB} are positive for the diglycine are larger than corresponding V_{ABB} values. This shows that the interactions between the diglycine and Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3 are mainly pair interactions. The pair, triplet and quartet interactions coefficients from volumes in case of diglycine are summarized in **Table 4** and illustrated in **Figure 2**.

Table 4. Hydration number, $n_H \times 10^6$ for the peptide in water and in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions at (288.15-318.15) K

Peptide	Water	m_s = 0.25	m_s = 0.5	m_s = 0.75	m_s = 1.0	m_s=1.5	m_s=2.0
			$NaNO_3$				
			T=288.15 K				
Diglycine	4.23±0.33	3.23±0.16	3.35±0.36	3.49±0.11	3.55±0.08	3.39±0.12	3.08±0.24
			T=298.15 K				
Diglycine	4.03±0.15	3.08±0.14	3.35±0.01	3.49±0.14	3.55±0.08	3.39±0.05	3.08±0.12
			T=308.15 K				
Diglycine	3.88±0.20	3.01±0.07	2.99±0.13	2.88±0.08	3.35±0.07	3.20±0.14	3.13±0.24
			KNO_3				
			T=288.15 K				
Diglycine	4.98±0.33	4.63±0.18	4.45±0.08	4.29±0.09	4.45±0.08	4.04±0.07	3.98±0.14
			T=298.15 K				
Diglycine	4.56±0.51	4.33±0.09	4.05±0.15	3.99±0.15	3.85±0.15	3.61±0.16	3.59±0.24
			T=308.15 K				
Diglycine	4.36±0.20	4.18±0.28	4.01±0.12	3.89±0.07	3.65±0.20	3.59±0.23	3.29±0.15
			$Mg(NO_3)_2$				
			T=288.15 K				
Diglycine	6.67±0.33	6.10±0.17	6.01±0.22	5.92±0.17	5.68±0.14	5.41±0.05	5.19±0.13
			T=298.15 K				
Diglycine	5.74±0.51	4.98±0.33	4.97±0.11	4.83±0.11	4.61±0.07	4.46±0.30	3.99±0.14
			T=308.15 K				
Diglycine	4.53±0.20	3.86±0.26	3.85±0.23	3.69±0.19	3.59±0.17	3.42±0.08	3.08±0.19

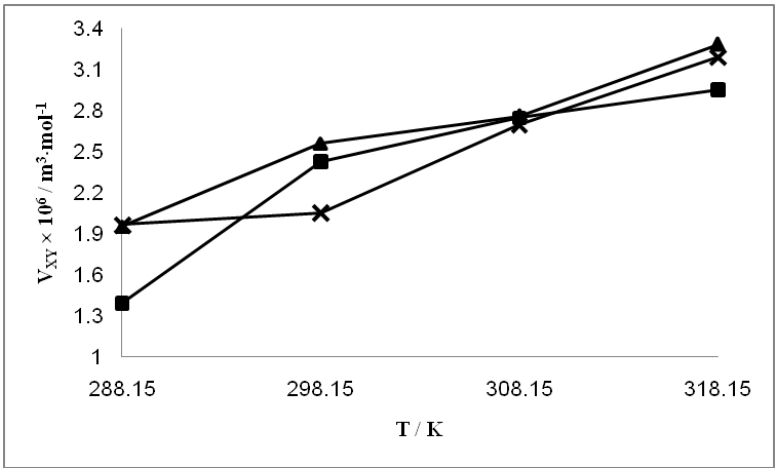


Figure 2. Pair interaction coefficient, V_{XY}, of diglycine at various temperatures in the aqueous solutions of different nitrates; ×, $NaNO_3$; ■, KNO_3; ▲, $Mg(NO_3)_2$.

The pair and quartet coefficients are all positive while triplet negative. This shows that the pair and quartet interactions in the case of two thermodynamic properties contribute positively, while triplet contribution is negative which is falling in magnitude with the rise in temperature.

The positive values of pair interactions occur due to the overlap of hydration spheres of diglycine with $Mg(NO_3)_2$ / $NaNO_3$ / KNO_3 molecules, which supports the conclusion drawn earlier from the cosphere overlap model.

$$V_{2,\Phi}^{0} = V_{2,\Phi}^{0}(int) + n_H (V^0_E - V^0_B) \quad (9)$$

Where $V_{2,\Phi}^{0}(int)$ is the intrinsic volume of a solute molecule, V^0_E and V^0_B are the partial molar volumes of water in the bulk state and in the hydration shell of a solution. The standard partial molar volume of a non-electrolyte can be divided into two parts [42]:

$$V_{2,\Phi}^{0} = V_{int} + V_{elect} \quad (10)$$

where V_{int} is the intrinsic molar volume of the non-electrolyte solute and V_{elect} the electrostriction partial molar volume due to the hydration of the non-electrolyte. Millero et al. [27] reported that the intrinsic molar volume could be estimated from the molar volume of non-electrolyte crystal:

$$V_{int} = (0.7 / 0.634)\, V_{cryst} \quad (11)$$

where 0.7 is the packing density for molecules in organic crystals, 0.634 is the packing density for random packing spheres, and V_{cryst} is the molar volume of the non-electrolyte crystal.

The values of crystal densities for diglycine are 1.534 $g.cm^{-3}$ at 298.15 K [42] respectively, and crystal density values for these diglycine at 288.15 and 308.15 K were assumed to be same as at 298.15 K. Following the procedure described by Millero et al. [27] $(V^0_E - V^0_B)$ = -2.9, -3.3, -4.0 $cm^3.mol^{-1}$ at 288.15 K, 298.15 K and 308.15 K, respectively. Therefore, as an approximation, the hydration number n_H can be obtained by **Eq. (9)**, and the results are listed in **Table 5** and illustrated in figures **3a-c.**

Table 5. Pair and Triplet Interactions coefficients for the peptide in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions at (288.15-318.15) K

Peptide	$V_{XY} \times 10^6$ ($m^3 \cdot mol^{-2} \cdot kg$)	$V_{XYY} \times 10^6$ ($m^3 \cdot mol^{-2} \cdot kg^2$)
	$NaNO_3$	
	T = 288.15 K	
Diglycine	1.9638 ± 0.173	-0.3497 ± 0.070
	T = 298.15 K	
Diglycine	2.0538 ± 0.3905	-0.261 ± 0.1566
	T = 308.15 K	
Diglycine	2.6956 ± 0.5439	-0.4842 ± 0.2182
	T = 318.15 K	
Diglycine	3.1907±0.6501	-0.5993 ± 0.2608
	KNO_3	
	T = 288.15 K	
Diglycine	1.3903 ± 0.2149	-0.1455 ± 0.0862
	T = 298.15 K	
Diglycine	2.4288 ± 0.2915	-0.4824 ± 0.1169
	T = 308.15 K	
Diglycine	2.7469 ± 0.4978	-0.5613 ± 0.1169
	T = 318.15 K	
Diglycine	2.9522 ± 0.5135	-0.6101 ± 0.2060
	$Mg(NO_3)_2$	
	T = 288.15 K	
Diglycine	1.9512 ± 0.2558	-0.3029 ± 0.1026
	T = 298.15 K	
Diglycine	2.5579 ± 0.4847	-0.4067 ± 0.1944
	T = 308.15 K	
Diglycine	2.7592 ± 0.5086	-0.4723 ± 0.204
	T = 318.15 K	
Diglycine	3.2848 ± 0.6942	-0.6268 ± 0.2785

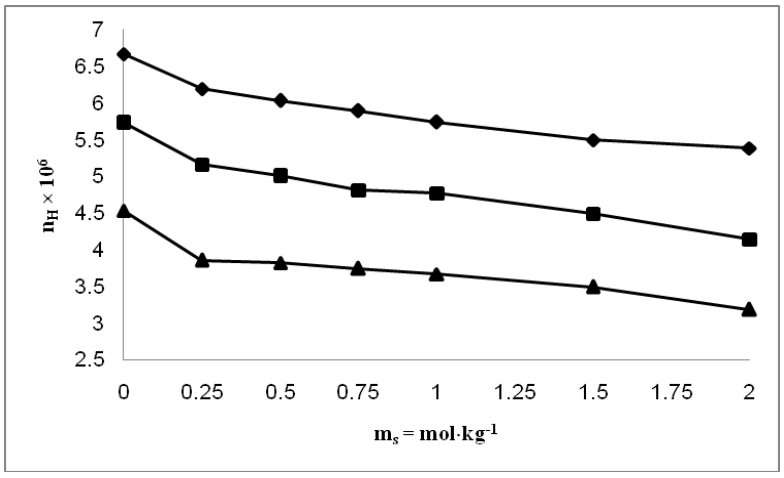


Figure 3a. Hydration number, $n_H \times 10^6$ for the diglycine in water and in aqueous sodium nitrate, solutions at different temperatures, ▲, 288.15; ■, 298.15; ♦, 308.15 K.

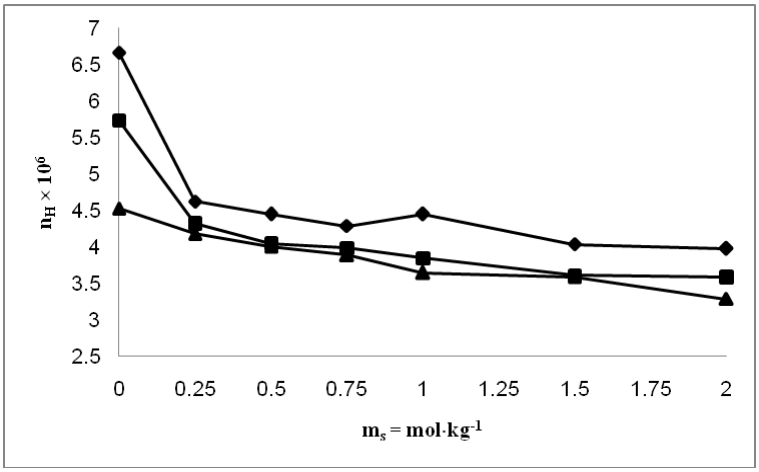


Figure 3b. Hydration number, $n_H \times 10^6$ for the diglycine in water and in aqueous potassium nitrate, solutions at different temperatures, ▲, 288.15; ■, 298.15; ♦, 308.15 K.

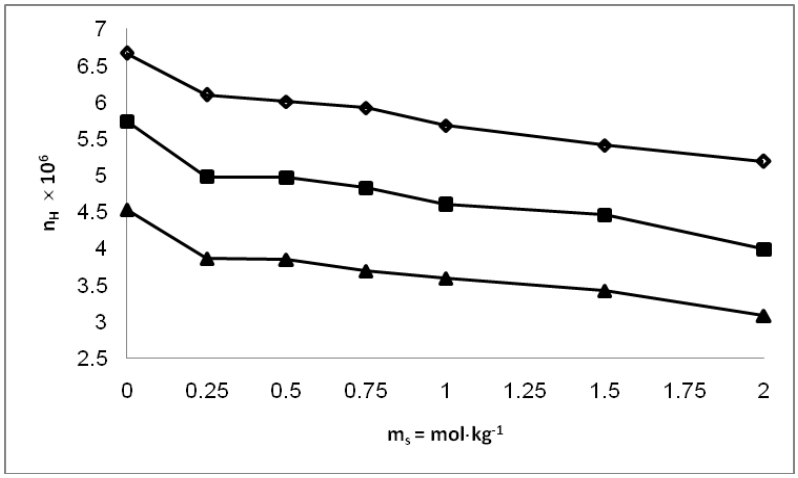


Figure 3c. Hydration number, $n_H \times 10^6$ for the diglycine in water and in aqueous magnesium nitrate hexahydrate, solutions at different temperatures, ▲, 288.15; ■, 298.15; ♦, 308.15 K.

As explained earlier, addition of Mg $(NO_3)_2$ / NaNO3 / KNO_3 decreases the electrostriction of water and this also means that n_H decreases as the electrostricted water becomes more like bulk water. The number of water molecules bound to the amino acids was calculated using the method reported by Millero et al [27].

$$n_H = V_2^0(elect) / V^0_E - V^0_B \quad (12)$$

Where V^0_E is the molar volume of electrostricted water and V^0_B is the molar volume of bulk water. The electrostriction partial molar volume, $V_2^0(elect)$ can be estimated from experimentally measured V_2^0 using following equation:

$$V_2^0(elect) = V_2^0(amino\ acid) - V_2(int) \quad (13)$$

The intrinsic volume, $V_2(int)$, consists of two terms: the vander Waals volume and the void volume. $V_2(int)$ can be obtained from crystal volume data [42]. The n_H values for the diglycine in the presence of Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3 are less than in water and decrease with increasing concentration of $Mg(NO_3)_2$ /$NaNO_3$ / KNO_3, which suggests that Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3 has a dehydration effect on the diglycine. As shown in **Table 2** the $V_{2,\Phi}^0$ increases with increasing temperature from 288.15 to 318.15K. An increase in temperature reduces the electrostriction and hence

increases $V_2^{0}{}_{,\Phi}$. The reduction in the electrostriction with increasing temperature is confirmed by the decreased n_H. Therefore, temperature effect on the electrostriction of water by the zwitterionic centers of the diglycine is a predominant factor in determining temperature dependence of $V_2^{0}{}_{,\Phi}$ of the diglycine.

The temperature dependence of V_2^{0} for various diglycine in water and in aqueous Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3 solutions, studied here can be expressed by the general equation as follows:

$$V_2^{0} = \alpha + \beta T + \gamma T^2 \qquad (14)$$

Values of various coefficients of the equation for diglycine in water and in aqueous Mg $(NO_3)_2$ / $NaNO_3$ / KNO_3 solutions are recorded in **Table 6**.

The partial molar (limiting apparent molar) expansibilities, $\phi_E^{0} = (\partial V_\phi^{0}/\partial T)_p$, calculated from the general equation are given in **Table 7**. it is found that ϕ_E^{0} values for diglycine in aqueous solutions of $NaNO_3$ increases in magnitude with increase in temperature while in aqueous solutions of KNO_3, the values for ϕ_E^{0} of diglycine decrease with rise in temperature indicating thereby that the behavior of diglycine is just like that of common salts, because in the case of common salts the molar expansibility should decrease with rise in temperature. It is also evident from **Table 6** that the ϕ_E^{0} values increase in temperature for diglycine in water.

Table 6. Partial Apparent Molar Expansibility $\phi_E^{0}\times10^{-6}/m^3\cdot mol^{-1}K^{-1}$ and $(\partial^2 V_\phi{}^{0} / \partial T^2)_p \times 10^{-6}$ for the peptide in aqueous sodium nitrate, potassium nitrate and magnesium nitrate hexahydrate solutions at (288.15-318.15) K

	$\phi_E^{0}\times 10^{-6}$ ($m^3\cdot mol^{-1}K^{-1}$)				$(\partial^2 V_\phi{}^{0} / \partial T^2)_p \times 10^{-6}$ ($m^3\cdot mol^{-1}\cdot K^{-2}$)
Peptide	**288.15K**	**298.15K**	**308.15K**	**318.15K**	
			Diglycine		
Diglycine in water	0.0347	0.0551	0.0755	0.0959	0.002
$NaNO_3$					
0.25 m_s	0.105	0.1194	0.1349	0.1484	0.0014
0.5 m_s	0.0909	0.1079	0.1249	0.1419	0.0017
0.75 m_s	0.0976	0.1091	0.1206	0.1321	0.0015
1.0 m_s	0.0822	0.0997	0.1172	0.1347	0.0017
1.5 m_s	0.0837	0.1002	0.1167	0.1332	0.0016
KNO_3					
0.25 ms	0.1674	0.1434	0.1194	0.0954	-0.0012
0.5 ms	0.1212	0.1167	0.1122	0.1077	-0.0004
0.75 ms	0.0009	0.0900	0.0995	0.1090	0.1185
1.0 ms	0.1542	0.1262	0.0982	0.0702	-0.0014
1.5 ms	0.1496	0.1290	0.10837	0.0877	-0.0021
$Mg(NO_3)_2$					
0.25 ms	0.1059	0.1149	0.1239	0.1329	0.0009
0.5 m_s	0.07	0.104	0.138	0.172	0.0034
0.75 m_s	0.1229	0.1199	0.1169	0.1139	-0.0003
1.0 m_s	0.1187	0.1075	0.0965	0.0855	-0.0011
1.5 m_s	0.0853	0.0998	0.1143	0.1288	0.0014

During the past few years it has been emphasized by different workers that S_v^{*} is not the sole criterion for determining the structure making or structure breaking nature of any solute. Hepler [43] developed a technique of examining the

sign of $(\partial^2 V_\phi^0/\partial T^2)_p$ for various solutes in terms of long-range structure making and breaking capacity of the solutes in aqueous solutions using the general thermodynamic expression:

$$(\partial C^0_{P,2} / \partial P) = -T (\partial^2 V_2^0 / \partial T^2)_P \quad (15)$$

On the basis of this expression it has been deduced that structure making solutes should have positive values, whereas structure breaking solutes should have negative values.

Conclusion

Diglycine being doubly charged and showing more path length as compared to glycine shows greater interactions min terms of ion-ion as compared to ion-hydrophobic interactions. Therefore there transfer properties in terms of partial molar volumes before and after the addition of the various salts of nitrates are changing significantly clearly indicates the role of solution thermodynamics while positive value of expansibilities will indicate the structure breaking tendency of solute with the co solute in a solvent via various interactions.

Acknowledgement

V. Dhir is very thankful to UGC, New Delhi and Punjab Technical University, Jalandhar for providing research facilities.

References

[1] I. Haq, R.R.J. O'brien, J.E. Ladbury, "Drug-Receptor Thermodynamics: Introduction and Application", Ed. R.B. Raffa. Chapter 5 (2000)
[2] Chalikian, T.V., Sarvazyan, A.P., Breslauer, K.J. *Biophys. Chem.* 51, 89, (1994)
[3] Murphy, L.R., Matubayasi, N., Payne, V.A., Levy, R.M. *Folding Res*, 3, 105. (1998)
[4] Sorenson, J.M., Hura, G., Soper, A.K., Pertsemlidis, A., Head-Gaordon, T. *J. Phys. Chem. B* 103, 5413 (1999)
[5] Sabulal, B., Kishore, N. *J. Chem. Soc. Faraday Trans*., 91, 2101 (1995)
[6] Tait, M. J., Franks, F. *Nature* 91, 230 (1971)
[7] Daniel, J., Cohn, E.J. *J. Am. Chem. Soc*. 58, 415 (1936)
[8] Hedestrand, Z. *Anorg. Chem*. 124, 153 (1922)
[9] Jr Gucker, F.T., Allen, T.W., *J. Am. Chem. Soc*64, 191 (1947)
[10] Wadi, R.K , Goyal, R.K. *J. Chem. Eng. Data*. 37, 377-386 (1992)
[11] Kelley, B.P., Lilley, T.H. *J. Chem. Soc. Faraday Trans*. I 74, 2771-2778 (1978)
[12] Kelley, B.P., Lilley, T.H. *J. Chem. Soc. Faraday Trans*. I 74, 2779- 2785 (1978)
[13] Basumallick, I.N., Mohanty, R. *Ind. J. Chem. A* 25, 1089-1091 (1986)
[14] Owaga, T., K. Mizutani, M. Yasuda, *Bull. Chem. Soc. Jpn.* 57, 2064-2068 (1984)
[15] T.H. Lilley, E. Mosses, I.R. Tasker, *J. Chem. Soc. Faraday Trans. I* 76, 906-914 (1980)
[16] T.H.lilley, Tasker, I.R. *J. Chem. Soc. Faraday Trans. I* 78, 1-6 (1982)
[17] Natarajan, M., Wadi, R.K., Gaur, H.C. *J. Chem. Eng. Data.* 35, 87-93 (1990)
[18] Bhat, R., Ahluwalia, J. C. *Int. J. Peptide Protein Res.* 30, 145-152 (1987)
[19] Kankia, B.I. *Biophys. Chem.* 84, 227-237 (2000)
[20] Khoshhkbarchi, M.K. J.H. Vera, *Ind. Eng. Chem. Res.* 35, 87 (1990)
[21] Natarajan, M., Wadi, R.K., Gaur, H.C. *J. Chem. Eng. Data* 35, 87 (1990)
[22] Banipal, T.S., Singh, G., Lark, B.S. *J. Solution Chem.* 30, 657-670 (2001)
[23] Banipal, T.S., Sehgal, G. *Thermochem. Acta* 262, 175-183 (1995)
[24] Banipal, T.S., Kaur, D., Lal, P., Singh, G. *J. Chem. Eng. Data* (2002), 47, 1391-1395.
[25] Surdo, A.L., Alzola, E.M., Millero, F.J. *J.Chem.Thermodyn.(*1982), 14, 649-662.
[26] Bhat, R., Ahluwalia, J.C. *J. Phys. Chem. (*1985), 89, 1099-1105.
[27] Millero, F.J., Surdo, A. Lo, Shin. C. *J. Phys. Chem. (*1978), 82, 784-792.
[28] Dixit, S.B., Bhasin, R., Rajasekaran, E., Jayaram, B. *J. Chem. Soc. Faraday Trans.* (1997), 93, 1105.

[29] EXAM, W.H. Kirchoff, US Department of Energy, Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD, USA.
[30] Heding, G.R., Hastie, J.D., Hoiland, H. *J. Soln. Chem. (*1996), 25, 615.
[31] Shen, J.L., Li Z.F., Wang, B.H., Zhang, Y.M. *J. Soln. Chem.* (2000), 32, 805.
[32] Gurney, R. W. *Ionic Process in solution*; McGraw Hill: New York, 1953.
[33] Franks, F. , M.A.J. Quickenden, D.S. Reid, B. Watson, *Trans. Faraday Soc*. (1970), 66, 582.
[34] Shahidi, F.; Farrell, P. G. Partial molar volumes of some aminocarboxylic acid in water. *J. Chem. Soc.,Faraday Trans. (*1981), 77, 963–968.
[35] Wadi, R.K. , P. Ramasami, *J. Chem. Soc. Faraday Trans.* (1997), 93 (2), 243-247.
[36] Kozak, J.J., W. Knight, W. Kauzmann, *J. Chem. Phys.* (1968), 68, 675.
[37] McMillan, W. G., Jr.; Mayer, J. E. The statistical thermodynamic of multi components systems. *J. Chem. Phys. (*1945), 13, 276–305.
[38] Friedman, H.L.,C.V. Krishnan, in "Water-A Comprehensive Treatise", Plenum Press, New York, (1973), Vol. 3, Ch. 1.
[39] Franks, F., Pedley, M., D.S. Reid, *J. Chem. Soc. Faraday Trans.1*. (1976), 72, 359.
[40] Mishra, A. K., Ahluwalia, J.C. *J. Chem. Soc. Faraday Trans.1*. *(*1981), 77, 1469.
[41] Lark, B. S., Bala, K. *Nat. Acad. Sci. Letters* (1989), 12, 155.
[42] Hepler, L. *Can. J. Chem. (*1969), 47, 4613.

Publication History
Received 24th April 2014
Revised 20th May 2014
Accepted 12th June 2014
Online 29th June 2014