Volumetric Properties of Cyclic Alanylalanine in Aqueous Solutions of $MnCl_2$, $NiCl_2$ and $ZnCl_2$ at Temperatures T = (293.15 to 313.15) K

V.R. Karanth and D. Krishna Bhat*

Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India

Abstract: The partial molar volumes, isentropic compressibilities, partial molar isentropic compressions and transfer molar quantities of cyclic alanylalanine in water and in aqueous solutions of $MnCl_2$, $NiCl_2$ and $ZnCl_2$ were determined using the experimental density and speed of sound values. Refractive indices of all the solutions were recorded to calculate the molar refractions. The molecular interactions existing in the systems have been discussed based on the derived parameters. It has been found that M^{2+}-O_2H bond distances of hydrated cations influence on the volumetric properties of cyclic alanylalanine. Further, the greater effect of hydrophobic hydration has been substantiated by the S_v values of least square fits of apparent molar volume against solute molality.

Keywords: Partial molar volume, Partial molar isentropic compression, cyclic alanylalanine, hydrophobic hydration.

1. INTRODUCTION

The behavior of protein molecules in various environments is of vital importance to the scientific world. The stability of protein structures can be best described by hydrophobic interactions [1]. Since the protein core is more accurately described as a solid, the interactions of solid-like core of globular proteins with the surrounding molecules are beneficiary than protein as a whole [2]. Accordingly, cyclic dipeptides are found to be the most suited model compounds for the thermodynamic studies of protein molecules. In particular they have the properties like close packed amino-acid groups, hydrogen bonding, Van der Waals contact and absence of end groups [3].

Cyclic dipeptides or 2, 5- diketopiperazines are the most common peptides found in nature imparting a metallic bitter taste in a various foods and beverages [4, 5]. Several authors have studied the thermodynamics of dissolution of cyclic dipeptides in water and aqueous urea solutions and also reported the heat capacities, enthalpies, and entropies of fusion [6, 7]. The apparent molar volumes and heat capacities of different cyclic dipeptides in aqueous media have also been reported in the literature [8, 9]. But the study concerning the effect of metal ions on the solution properties of cyclic alanylalanine are limited [10]. Owing to the biological importance of transition metal ions [11-15], the volumetric, acoustic and refractometric study of cyclic alanylalanine in aqueous metal salt solutions can reveal some of the structural interactions taking place in such systems. Since hydration also plays a major role in determining the structural properties, the role of metal ions on the variation of these properties needs systematic explorations. In the present paper, we report the densities, ultrasonic velocities and refractive indices of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions over a wide range of composition and temperature T = (293.15 to 313.15) K. The derived parameters calculated from these experimental values have been discussed in the light of various interactions taking place in the above said system.

2. EXPERIMENTAL

2.1. Materials

Detailed description of the chemicals utilized in the present work has been provided in Table **1**. The samples were used without further purification except drying over anhydrous P_2O_5 in a vacuum desiccator for 72 h at room temperature. The samples were prepared on weight basis using Mettler balance with precision of ±0.1 mg. Deionized, doubly distilled water (specific conductance $<1.6\times10^{-6}$ Ω^{-1} cm^{-1}) was used in the solution preparation. The concentrations of metal salt in each of the cases were: for $MnCl_2$ (0.0899 mol kg^{-1}), for $NiCl_2$ (0.0981 mol kg^{-1}) and for $ZnCl_2$ (0.0933 mol kg^{-1}). The concentration of cyclic alanylalanine was varied from 0 to 0.15 mol kg^{-1} (with respect to 1 kg of electrolyte solution).

2.2. Methods

The densities of the solutions were determined using a single stem pycnometer made of Pyrex glass

*Address correspondence to this author at the Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India; Tel: +91-9481271262; Fax: 0824-2474033;
E-mail: denthajekb@gmail.com

E-ISSN: 1929-5030/15

Table 1: Sample Information

Chemical Name	CAS No.	Source	Mass Fraction Purity
Cyclic Alanylalanine (mixture of DL and meso)	5625-46-7	Aldrich	0.99
Manganese Chloride Tetrahydrate	13446-34-9	Sigma-Aldrich	0.99
Nickel Chloride	7718-54-9	Aldrich	0.98
Zinc Chloride	7646-85-7	Alfa- Aesar	0.99

(bulb capacity 10×10^{-3} dm^3). It was fitted with a Teflon cap and the stem had graduated marks on it. The calibration was done using double distilled water and the formation of air bubble was avoided by heating the samples in an Eppendrof tube to 5 K above the measuring temperature taking sufficient care. The reproducibility of density measurements was found to be $\pm3\times10^{-2}$ kg m^{-3}. The speed of sound values were determined using ultrasonic interferometer (Mittal Enterprises make, model F-05), with a fixed frequency of 2 MHz. The uncertainty of ultrasonic interferometer was found to be 0.2 m s^{-1}. Atago 7000α digital refractometer was used to record the refractive indices of the samples. The uncertainty of which was estimated to be 0.00011; and was equipped with an internal peltier control for temperature adjustment. The temperature of the sample cells in case of density and speed of sound measurements was maintained using a well stirred temperature bath with an accuracy of ±0.01 K. Each of the experiments was repeated three times and the average of the triplicate measurements has been reported as the final value.

3. RESULTS AND DISCUSSION

Experimentally determined values of density (ρ) and speed of sound (u) and refractive index (n_D) of cyclic

Table 2: Density, ρ, speed of sound, u, and refractive index , n_D, of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, T = (293.15 to 313.15) K, as a function of molality of cyclic alanylalanine

m^a/(mol kg^{-1})	T/K				
	293.15	298.15	303.15	308.15	313.15
Cyclic alanylalanine in water					
$\rho\cdot10^{-3}$/(kg m^{-3})					
0.0000	0.99821	0.99705	0.99568	0.99406	0.99222
0.0110	0.99855	0.99738	0.99600	0.99438	0.99253
0.0261	0.99902	0.99783	0.99645	0.99482	0.99296
0.0352	0.99931	0.99810	0.99672	0.99509	0.99322
0.0750	1.00058	0.99929	0.99791	0.99627	0.99436
0.0965	1.00129	0.99993	0.99856	0.99692	0.99499
0.1264	1.00227	1.00083	0.99945	0.99783	0.99585
0.1502	1.00306	1.00154	1.00017	0.99856	0.99655
u/(m s^{-1})					
0.0000	1482.38	1496.67	1509.46	1519.44	1528.88
0.0110	1483.51	1497.82	1510.60	1520.59	1530.04
0.0261	1485.05	1499.39	1512.14	1522.15	1531.62
0.0352	1485.96	1500.33	1513.07	1523.07	1532.55
0.0750	1489.90	1504.37	1517.02	1527.07	1536.57
0.0965	1491.93	1506.52	1519.12	1529.17	1538.66
0.1264	1494.70	1509.45	1522.01	1532.01	1541.53
0.1502	1496.82	1511.74	1524.23	1534.22	1543.77

(Table 2). Continued.

m^a/(mol kg^{-1})	*T*/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
n_D					
0.0000	1.33300	1.33252	1.33194	1.33131	1.33059
0.0110	1.33348	1.33295	1.33232	1.33172	1.33097
0.0261	1.33409	1.33352	1.33284	1.33222	1.33155
0.0352	1.33497	1.33433	1.33368	1.33309	1.33235
0.0750	1.33618	1.33545	1.33471	1.33397	1.33323
0.0965	1.33703	1.33626	1.33551	1.33473	1.33394
0.1264	1.33832	1.33746	1.33665	1.33582	1.33500
0.1502	1.33934	1.33843	1.33756	1.33667	1.33579
Cyclic alanylalanine in 0.0899 mol kg^{-1} aqueous $MnCl_2$ solution					
$\rho \cdot 10^{-3}$/(kg m^{-3})					
0.0000	1.00795	1.00650	1.00544	1.00412	1.00287
0.0097	1.00823	1.00676	1.00568	1.00434	1.00306
0.0254	1.00869	1.00719	1.00608	1.00470	1.00338
0.0349	1.00898	1.00746	1.00633	1.00493	1.00358
0.0758	1.01022	1.00862	1.00742	1.00592	1.00446
0.0991	1.01094	1.00931	1.00807	1.00653	1.00499
0.1254	1.01178	1.01011	1.00883	1.00722	1.00560
0.1516	1.01263	1.01092	1.00961	1.00794	1.00624
u/(m s^{-1})					
0.0000	1500.92	1505.19	1511.64	1515.88	1521.54
0.0097	1501.95	1506.22	1512.66	1516.91	1522.60
0.0254	1503.56	1507.85	1514.28	1518.55	1524.29
0.0349	1504.51	1508.81	1515.23	1519.51	1525.28
0.0758	1508.46	1512.80	1519.25	1523.62	1529.53
0.0991	1510.60	1514.94	1521.44	1525.83	1531.84
0.1254	1512.85	1517.24	1523.76	1528.30	1534.42
0.1516	1515.02	1519.40	1526.10	1530.66	1536.90
n_D					
0.0000	1.33416	1.33399	1.33381	1.33364	1.33345
0.0097	1.33456	1.33445	1.33434	1.33414	1.33392
0.0254	1.33500	1.33486	1.33473	1.33455	1.33435
0.0349	1.33554	1.33535	1.33520	1.33495	1.33476
0.0758	1.33666	1.33642	1.33627	1.33600	1.33588
0.0991	1.33735	1.33699	1.33685	1.33655	1.33638
0.1254	1.33830	1.33798	1.33778	1.33748	1.33734
0.1516	1.33952	1.33912	1.33893	1.33865	1.33852

(Table 2). Continued.

m^a/(mol kg^{-1})	*T*/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
Cyclic alanylalanine in 0.0981 mol kg^{-1} aqueous $NiCl_2$ solution					
$\rho \cdot 10^{-3}$/(kg m^{-3})					
0.0000	1.01048	1.00886	1.00723	1.00561	1.00398
0.0112	1.01067	1.00901	1.00738	1.00575	1.00410
0.0246	1.01091	1.00920	1.00757	1.00593	1.00426
0.0353	1.01110	1.00937	1.00772	1.00608	1.00439
0.0735	1.01183	1.01000	1.00831	1.00664	1.00488
0.0987	1.01232	1.01044	1.00872	1.00705	1.00525
0.1261	1.01289	1.01094	1.00920	1.00751	1.00567
0.1511	1.01344	1.01141	1.00965	1.00797	1.00606
***u*/(m s^{-1})**					
0.0000	1491.58	1505.50	1517.96	1528.65	1537.70
0.0112	1492.83	1506.78	1519.20	1529.89	1538.95
0.0246	1494.28	1508.28	1520.65	1531.34	1540.40
0.0353	1495.44	1509.44	1521.79	1532.47	1541.55
0.0735	1499.44	1513.53	1525.77	1536.42	1545.52
0.0987	1502.02	1516.10	1528.30	1538.88	1548.00
0.1261	1504.72	1518.80	1530.92	1541.48	1550.62
0.1511	1507.10	1521.16	1533.20	1543.78	1552.90
n_D					
0.0000	1.33604	1.33549	1.33506	1.33457	1.33419
0.0112	1.33635	1.33580	1.33534	1.33484	1.33440
0.0246	1.33668	1.33618	1.33574	1.33521	1.33472
0.0353	1.33716	1.33663	1.33604	1.33552	1.33494
0.0735	1.33776	1.33719	1.33657	1.33593	1.33539
0.0987	1.33830	1.33776	1.33719	1.33653	1.33600
0.1261	1.33891	1.33836	1.33777	1.33715	1.33658
0.1511	1.33949	1.33893	1.33831	1.33771	1.33711
Cyclic alanylalanine in 0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution					
$\rho \cdot 10^{-3}$/(kg m^{-3})					
0.0000	1.00992	1.00848	1.00735	1.00609	1.00484
0.0115	1.01026	1.00879	1.00764	1.00637	1.00510
0.0253	1.01068	1.00917	1.00800	1.00671	1.00542
0.0353	1.01099	1.00945	1.00826	1.00697	1.00566
0.0762	1.01229	1.01064	1.00938	1.00806	1.00666
0.1022	1.01314	1.01144	1.01011	1.00877	1.00733
0.1260	1.01394	1.01217	1.01079	1.00946	1.00795
0.1502	1.01477	1.01293	1.01152	1.01018	1.00863

(Table 2). Continued.

m^a/(mol kg^{-1})	*T*/K				
	293.15	**298.15**	**303.15**	**308.15**	**313.15**
***u*/(m s^{-1})**					
0.0000	1495.53	1503.67	1516.61	1526.78	1534.08
0.0115	1496.71	1504.88	1517.81	1527.98	1535.28
0.0253	1498.08	1506.30	1519.20	1529.39	1536.69
0.0353	1499.04	1507.30	1520.20	1530.38	1537.68
0.0762	1502.66	1511.10	1524.06	1534.30	1541.68
0.1022	1504.74	1513.30	1526.38	1536.70	1544.10
0.1260	1506.53	1515.20	1528.40	1538.72	1546.24
0.1502	1508.19	1516.94	1530.36	1540.66	1548.30
n_D					
0.0000	1.33568	1.33521	1.33462	1.33390	1.33311
0.0115	1.33602	1.33560	1.33500	1.33428	1.33349
0.0253	1.33635	1.33585	1.33522	1.33453	1.33371
0.0353	1.33660	1.33604	1.33545	1.33473	1.33393
0.0762	1.33763	1.33706	1.33643	1.33564	1.33488
0.1022	1.33829	1.33765	1.33709	1.33631	1.33552
0.1260	1.33890	1.33824	1.33762	1.33679	1.33600
0.1502	1.33946	1.33878	1.33812	1.33725	1.33651

[a]Standard uncertainty for temperature u(*T*) = 0.01 K; for pressure u(*p*) = 0.05; for molality u(*m*) = 0.0001; for density u(*ρ*) = 0.05 kg m^{-3}; for speed of sound u(*u*) = 0.2 m s^{-1} and for refractive index u(n_D) = 0.00011. The combined expanded uncertainties, U_c are $U_c(\rho)$ = 0.1 kg m^{-3}; $U_c(c)$ = 0.4 m s^{-1} and $U_c(n_D)$ = 0.00022 with 0.95 level of confidence. The experiment was carried out under atmosphere pressure.
[b]*m* is the molality of cyclic alanylalanine in aqueous solutions.

alanylalanine in water and in aqueous solutions of $MnCl_2$, $NiCl_2$ and $ZnCl_2$ at temperatures *T* = (293.15, 298.15, 303.15, 308.15 and 313.15) K are presented in Table **2**.

3.1. Isentropic Compressibility

The isentropic compressibility (κ_s) of cyclic alanylalanine in aqueous metal salt solutions was calculated by the Newton-Laplace equation [16],

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

where *ρ* and *u* are the density and speed of sound in the solution respectively. The κ_S values of cyclic alanylalanine in each of the aqueous metal salt solutions decrease with an increase in concentration and increasing temperature. The variation in the isentropic compressibility values of cyclic alanylalanine in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions have been presented in Figures **1-3** respectively. As depicted by the figures, the decrease in isentropic compressibility values with the solute concentration indicates that the water molecules which are in association with ionic groups of cyclic alanylalanine are less compressible compared to those in the bulk of the solution.

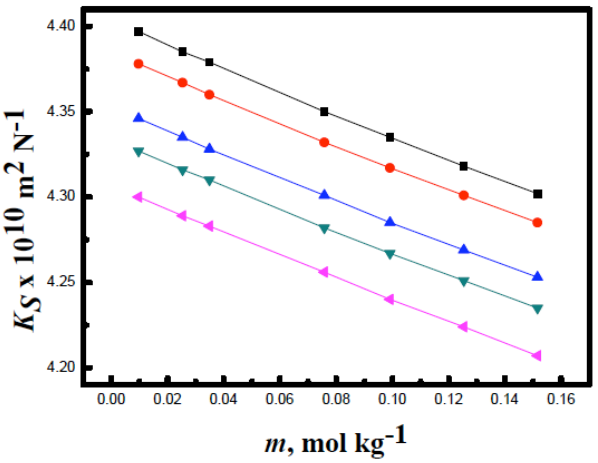

Figure 1: Plot of κ_S versus molal concentration (*m*) of cyclic alanylalanine in aqueous $MnCl_2$ solution.■, *T* = 293.15 K; ●, *T* = 298.15 K; ▲, *T* = 303.15 K; ▼, *T* = 308.15 K; ◀, *T* = 313.15 K, keeping the concentration of $MnCl_2$ constant at 0.0899 mol kg^{-1}.

For a system forming the typical three-dimensional cage-like structure of water, the predominant

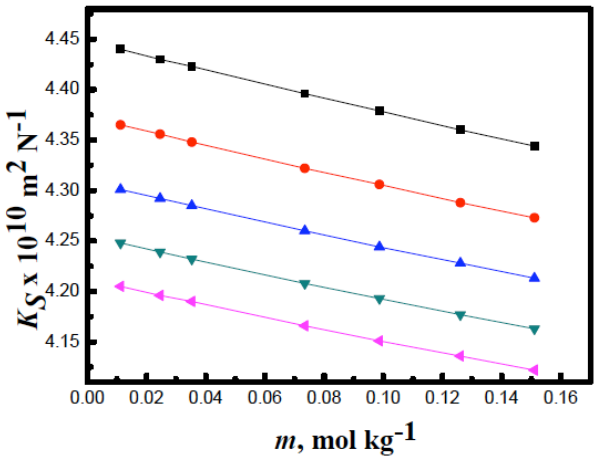

Figure 2: Plot of κ_S versus molal concentration (*m*) of cyclic alanylalanine in aqueous $NiCl_2$ solution.■, *T* = 293.15 K; ●, *T* = 298.15 K; ▲, *T* = 303.15 K; ▼, *T* = 308.15 K; ◄, *T* = 313.15 K, keeping the concentration of $NiCl_2$ constant at 0.0981 mol kg^{-1}.

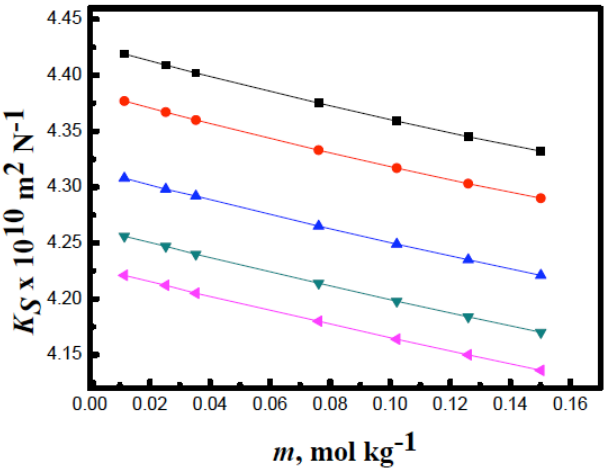

Figure 3: Plot of κ_S versus molal concentration (*m*) of cyclic alanylalanine in aqueous $ZnCl_2$ solution.■, *T* = 293.15 K; ●, *T* = 298.15 K; ▲, *T* = 303.15 K; ▼, *T* = 308.15 K; ◄, *T* = 313.15 K, keeping the concentration of $ZnCl_2$ constant at 0.0933 mol kg^{-1}.

interaction is water–water interaction. The isentropic compressibility is considered to be the sum of two contributions: $\kappa_{S\,(Solvent\ intrinsic)}$ and $\kappa_{S\,(Solute\ intrinsic)}$. For low concentrations, the $\kappa_{S\,(Solvent\ \ intrinsic)}$ is the dominant contributor to the total value of κ_S over $\kappa_{S\,(Solute\ \ intrinsic)}$. Thus it may be concluded that the compressibility of a dilute electrolyte solution is mainly due to the effect of pressure on non-hydrated (bulk) water molecules. Since, the size of the cyclic dipeptide and electrolyte ions is not pressure dependent and the electrostricted water is already compressed to its maximum extent due to the charge on the ions and cyclic dipeptide [17], the compressibility of a solution is mainly due to the effect of pressure on the non-hydrated (bulk) water molecules. Hence with the increase in solute concentration, a large portion of the water molecules becomes electrostricted and the amount of bulk water decreases which causes decrease in the compressibility [18].

The compressibility values follow the order of $NiCl_2$< $ZnCl_2$ < $MnCl_2$ attributed to the fact that these ions hydrate differently in water. The Ni^{2+}-OH_2, Zn^{2+}-OH_2 and Mn^{2+}-OH_2 bond distances due to cation hydration from the X-ray diffraction studies are 206.2 pm, 209.6 pm and 220.0 pm, respectively [19, 20]. The Mn^{2+}-OH_2 bond distance is longer in comparison to Ni^{2+}-OH_2 or Zn^{2+}-OH_2, the same trend can be observed in the isentropic compressibility of cyclic alanylalanine in these solvents.

3.2. Apparent and Partial Molar Volume

The apparent molar volumes, ϕ_v of cyclic alanylalanine in water and in aqueous metal salt solutions were calculated from the experimental density values of the solutions using the relation [21],

$$\phi_v = \frac{(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M_2}{\rho}, \qquad (2)$$

where, *m* is the molality of cyclic alanylalanine in water or in aqueous metal salt solutions, M_2 is the molar mass of cyclic alanylalanine, ρ_0 and ρ are the densities of solvents (water, aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$) and that of solutions respectively. The calculated ϕ_v values with their uncertainties are presented in Table **3**. The uncertainties were estimated using propagation of errors method [22]. The ϕ_v values have been fitted by the method of least-squares described by the expression,

$$\phi_v = \phi_v^{\,0} + S_v m, \qquad (3)$$

where $\phi_v^{\,0}$ is the partial molar volume of the solute, S_v is the volumetric pairwise interaction coefficient and *m* is the molality of the solute.

The $\phi_v^{\,0}$ values of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions have been computed using equation (3) and are compared with available literature in Table **4**. A fair agreement can be observed between the values reported here and those available in literature.

The $\phi_v^{\,0}$ values give an insight into the solute-solvent interactions, whereas S_v values represent the

Table 3: Apparent molar volume, ϕ_v, of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, T = (293.15 to 313.15) K

m^b/(mol kg^{-1})	*T*/K				
	293.15	298.15	303.15	308.15	313.15
ϕ_v /10^6 m^3 mol^{-1}					
Cyclic alanylalanine in water					
0.0110	111.08(±0.54)	112.37(±0.53)	113.40(±0.53)	113.86(±0.53)	114.61(±0.53)
0.0261	111.06(±0.23)	112.43(±0.22)	112.93(±0.22)	113.59(±0.22)	114.39(±0.22)
0.0352	110.84(±0.17)	112.46(±0.17)	112.86(±0.17)	113.38(±0.17)	114.30(±0.17)
0.0750	110.40(±0.08)	112.28(±0.08)	112.53(±0.08)	112.99(±0.08)	114.05(±0.08)
0.0965	110.01(±0.06)	112.23(±0.06)	112.35(±0.06)	112.73(±0.06)	113.80(±0.06)
0.1264	109.71(±0.05)	112.07(±0.05)	112.27(±0.05)	112.43(±0.05)	113.69(±0.05)
0.1502	109.46(±0.04)	112.01(±0.04)	112.12(±0.04)	112.21(±0.04)	113.50(±0.04)
Cyclic alanylalanine in 0.0899 mol kg^{-1} aqueous $MnCl_2$ solution					
0.0097	112.60(±0.59)	114.75(±0.58)	116.89(±0.57)	119.06(±0.56)	122.25(±0.55)
0.0254	112.28(±0.22)	114.35(±0.22)	116.39(±0.22)	118.86(±0.22)	121.73(±0.21)
0.0349	111.88(±0.16)	113.98(±0.16)	116.06(±0.16)	118.46(±0.16)	121.44(±0.15)
0.0758	111.31(±0.08)	113.39(±0.07)	115.32(±0.07)	117.81(±0.07)	120.71(±0.07)
0.0991	111.01(±0.06)	112.94(±0.06)	114.84(±0.06)	117.18(±0.05)	120.23(±0.05)
0.1254	110.56(±0.05)	112.42(±0.05)	114.26(±0.05)	116.70(±0.04)	119.78(±0.04)
0.1516	110.14(±0.04)	111.97(±0.04)	113.71(±0.04)	116.14(±0.04)	119.25(±0.04)
Cyclic alanylalanine in 0.0981 mol kg^{-1} aqueous $NiCl_2$ solution					
0.0112	111.62(±0.46)	115.29(±0.45)	115.45(±0.46)	116.50(±0.46)	118.44(±0.45)
0.0246	111.09(±0.21)	114.84(±0.21)	115.01(±0.21)	115.98(±0.21)	117.76(±0.21)
0.0353	110.99(±0.15)	114.21(±0.15)	114.93(±0.15)	115.66(±0.15)	117.51(±0.14)
0.0735	110.12(±0.07)	113.09(±0.07)	114.06(±0.07)	114.90(±0.07)	116.83(±0.07)
0.0987	109.80(±0.05)	112.56(±0.05)	113.62(±0.05)	114.29(±0.05)	116.17(±0.05)
0.1261	109.28(±0.04)	112.02(±0.04)	113.05(±0.04)	113.76(±0.04)	115.60(±0.04)
0.1511	108.75(±0.04)	111.60(±0.04)	112.61(±0.03)	113.17(±0.03)	115.19(±0.03)
Cyclic alanylalanine in 0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution					
0.0115	111.74(±0.50)	114.42(±0.49)	116.24(±0.48)	117.21(±0.48)	119.05(±0.47)
0.0253	111.23(±0.23)	114.07(±0.22)	115.73(±0.22)	117.02(±0.22)	118.70(±0.22)
0.0353	110.93(±0.16)	113.84(±0.16)	115.61(±0.16)	116.57(±0.16)	118.37(±0.16)
0.0762	110.01(±0.08)	112.85(±0.07)	114.64(±0.07)	115.53(±0.07)	117.61(±0.07)
0.1022	109.52(±0.06)	112.16(±0.06)	114.20(±0.06)	115.09(±0.05)	117.06(±0.05)
0.1260	109.05(±0.05)	111.76(±0.05)	113.83(±0.04)	114.49(±0.04)	116.67(±0.04)
0.1502	108.58(±0.04)	111.34(±0.04)	113.29(±0.04)	113.93(±0.04)	116.05(±0.04)

[a]The uncertainties in ϕ_v values are in parenthesis.

[b]*m* is the molality of cyclic alanylalanine in aqueous metal salt solutions. The experiment was carried out under atmosphere pressure.

Table 4: Least squares fit parameters of the equation $\phi_v = \phi_v^0 + S_v m$ for cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, T = (293.15 to 313.15) K

T/K	ϕ_v^0 /10^6 m^3mol^{-1}	S_v/ 10^6 m^3mol^{-2} kg	σ/10^6 m^3mol^{-1}
Cyclic alanylalanine in water			
293.15	111.28(±0.04)	-12.36(±0.53)	0.1
298.15	112.55(±0.02) 112.58(±0.06)[b] 112.43(±0.02)[c] 112.40(±0.03)[d]	-3.67(±0.26)	0.1
303.15	113.06(±0.05)	-6.55(±0.52)	0.1
308.15	113.88(±0.04)	-11.49(±0.55)	0.1
313.15	114.61(±0.04) 114.15(±0.06)[b]	-7.58(±0.45)	0.1
Cyclic alanylalanine in 0.0899 mol kg^{-1} aqueous $MnCl_2$ solution			
293.15	112.71(±0.04)	-17.25(±0.47)	0.1
298.15	114.81(±0.06)	-18.96(±0.72)	0.1
303.15	116.96(±0.06)	-21.56(±0.69)	0.1
308.15	119.28(±0.05)	-20.72(±0.61)	0.1
313.15	122.16(±0.03)	-19.21(±0.38)	0.1
Cyclic alanylalanine in 0.0981 mol kg^{-1} aqueous $NiCl_2$ solution			
293.15	111.68(±0.07)	-19.43(±0.82)	0.1
298.15	113.84(±0.08)	-69.41(±0.94)	0.1
303.15	115.59(±0.04)	-20.01(±0.51)	0.1
308.15	116.58(±0.06)	-22.80(±0.76)	0.1
313.15	118.26(±0.05)	-20.66(±0.57)	0.1
Cyclic alanylalanine in 0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution			
293.15	111.81(±0.07)	-22.08(±0.88)	0.1
298.15	114.62(±0.06)	-22.70(±0.70)	0.1
303.15	116.23(±0.06)	-19.58(±0.63)	0.1
308.15	117.48(±0.06)	-23.87(±0.73)	0.1
313.15	119.21(±0.04)	-20.85(±0.55)	0.1

[a]σ is the standard deviation of the fit.
[b]Ref [08].
[c]Ref [39].
[d]Ref [40].

solute-solute interactions. The ϕ_v^0 values in all the cases were found to be positive at all the composition and temperatures of the study where the concentration of the cyclic alanylalanine was varied.

The properties of water molecules in the vicinity of the solute differ from those in the bulk. Water molecules near polar groups of solutes take up less space than near non-polar groups or in bulk solution. This is called electrostriction [23] and the net volume of this coordinated water per solute molecule varies with concentration of the solute. Also, this volume decreases due to the lower probability of interactions among the neighboring coordinated water molecules. The observed trend in ϕ_v^0 values can be explained by taking into account of the structure of cyclic alanylalanine in aqueous solutions. Corey [24] proposed four resonating structures for cyclic alanylalanine molecule as shown in Figure **4**. Among these structures, the one with several partial charges was thought to be realistic [25] deduced from the calculations of thermodynamic parameters. Based on this model one can speculate the interactions occurring in the aqueous cyclic alanylalanine - transition metal salt systems as follows: the ionic interactions among the constituent ions of the electrolytes and the polar

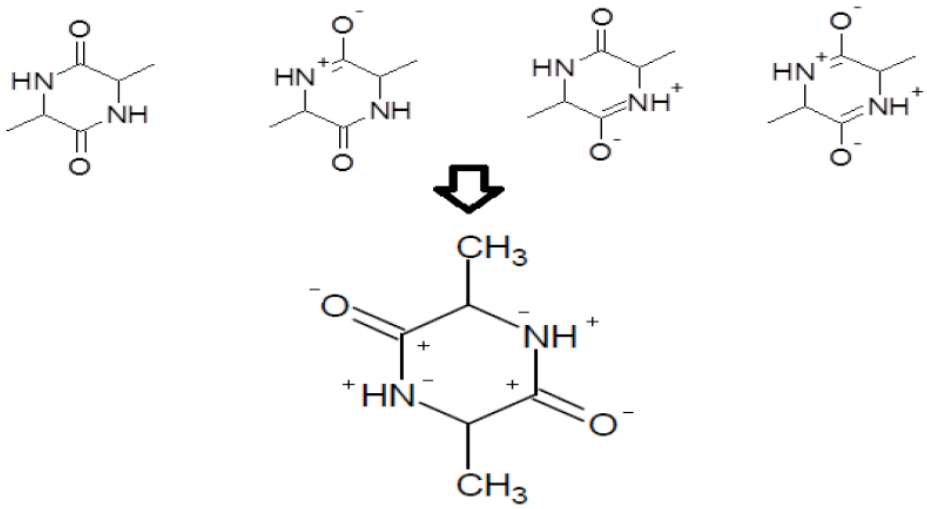

Figure 4: Resonance structures of cyclic alanylalanine molecule.

groups of cyclic alanylalanine and hydrophobic-hydrophilic interactions occurring among hydrophobic groups of cyclic alanylalanine and water. Thus, the coordination of hydration spheres of M^{2+} (M=Mn, Ni or Zn) with those of hydrophilic groups of cyclic alanylalanine and those of Cl^- ions with the hydration spheres of hydrophobic groups make the release of coordinated water molecules into the bulk. This results in positive ϕ_v^0 values of cyclic alanylalanine in metal salt solutions.

The ϕ_v^0 values of cyclic alanylalanine-aqueous system were found to be higher than the corresponding values of cyclic alanylalanine-aqueous metal salt systems. This is due to increased electrostriction with the introduction of more number of ions into the system. The strong attractive interaction between ions and water molecules induce the dehydration of amino acid and therefore increase ϕ_v^0. In other words, addition of cyclic alanylalanine to aqueous electrolyte solution decreases the electrostriction in the solution, the effect being due to the electrolyte itself. Further, increasing temperature reduces electrostriction of cyclic alanylalanine and therefore at lower temperature reduction of electrostriction in presence of electrolyte is larger. The effect of temperature on ϕ_v^0 values can also be elucidated by considering the size of primary and secondary solvation sheaths around cyclic alanylalanine molecule. As the temperature increases, the water molecules from the solvation layer of cyclic alanylalanine are released into the bulk thereby increasing ϕ_v^0 values.

It can be predicted that the hydrophobic hydration plays a major role in the molar volume contribution. Since cyclic alanylalanine, a cyclic molecule, has distinguishable structure than other open chain dipeptides. With hydrophobic hydration, cyclic alanylalanine is solvated in such a way that the apparent molar volume gradually increases with the molar concentration of the solute. This can be attributed to the arrangement of water molecules in the hydration shells of hydrophobic groups of cyclic alanylalanine molecule. The hydrophobic interactions of –CH– and $–CH_3$ groups with water molecules overshadow the hydrophilic and electrostatic interactions among the constituents of the system. Whereas in the case of linear chain peptides or dipeptides, the hydration co-spheres of charged end groups overlap with those of the hydrophobic groups within the molecules and thus contribute to molar volume [26].

The prevalence hydrophobic hydration in the system studied is further evident by the trend of the slopes of the concentration dependence of the apparent molar volumes. The S_v values were found to be negative, which considerably indicates the hydrophobic hydration. Also the more negative slopes suggest an enhancement of the effect which leads to the compressibility reduction. Hence the water molecules in the vicinity of non-polar groups such as –CH– and $–CH_3$ groups are less compressible than the bulk, but not quite as incompressible as electrostricted water [27, 28].

As can be seen from the Table **4**, the ϕ_v^0 value of cyclic alanylalanine in $MnCl_2$ is much greater than those in $NiCl_2$ or $ZnCl_2$ solutions suggesting the influence of M^{2+}-OH_2 bond distance on the partial molar

volumes over ionic size. Being a larger molecule in volume, cyclic alanylalanine causes an increase in molar volume of water in its hydration sphere when dissolved in aqueous metal-salt solvent.

3.3. Partial Molar Isentropic Compression

The partial molar isentropic compression, ϕ_k of cyclic alanylalanine in water, in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions have been computed using the relation [27].

$$\phi_k = \left[\frac{\kappa_s - \kappa_0}{m\rho^0}\right] + \kappa_s \phi_{v,} \quad (4)$$

where m is the solution molality, ρ_0 and κ_0 (=1/ $\rho_0 u^2$) are the density and the isentropic compressibility of the solvent respectively and κ_s (=1/ρu^2) is the isentropic compressibility of the solution. The calculated ϕ_k values along with their uncertainties, calculated from the method of propagation of errors [29], are presented

Table 5: Apparent molar isentropic compression, ϕ_k, of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, *T* = (293.15 to 313.15) K

m^a/(mol kg^{-1})	*T*/K				
	293.15	298.15	303.15	308.15	313.15
ϕ_k /10^{15} Pa^{-1} m^3 mol^{-1}					
Cyclic alanylalanine in water					
0.0110	-26.92(±1.12)	-25.93(±1.09)	-23.74(±1.07)	-23.40(±1.05)	-22.87(±1.03)
0.0261	-26.64(±0.47)	-25.65(±0.46)	-23.57(±0.45)	-23.19(±0.44)	-22.77(±0.43)
0.0352	-26.46(±0.35)	-25.47(±0.34)	-23.55(±0.33)	-22.95(±0.33)	-22.43(±0.32)
0.0750	-25.91(±0.16)	-24.77(±0.16)	-22.74(±0.16)	-22.44(±0.15)	-21.62(±0.15)
0.0965	-25.42(±0.13)	-24.43(±0.12)	-22.47(±0.12)	-22.11(±0.12)	-21.13(±0.12)
0.1264	-24.73(±0.10)	-23.95(±0.09)	-22.03(±0.09)	-21.54(±0.09)	-20.48(±0.09)
0.1502	-24.11(±0.08)	-23.51(±0.08)	-21.57(±0.08)	-21.11(±0.08)	-20.08(±0.07)
Cyclic alanylalanine in 0.0899 mol kg^{-1} aqueous $MnCl_2$ solution					
0.0097	-24.75(±1.20)	-22.75(±1.19)	-20.01(±1.18)	-18.62(±1.17)	-17.43(±1.16)
0.0254	-23.69(±0.46)	-22.24(±0.45)	-19.73(±0.45)	-18.18(±0.45)	-17.30(±0.44)
0.0349	-23.41(±0.33)	-21.98(±0.33)	-19.39(±0.33)	-17.88(±0.33)	-16.93(±0.32)
0.0758	-21.88(±0.15)	-20.52(±0.15)	-18.59(±0.15)	-17.34(±0.15)	-16.55(±0.15)
0.0991	-21.08(±0.12)	-19.74(±0.12)	-18.13(±0.11)	-16.91(±0.11)	-16.12(±0.11)
0.1254	-19.97(±0.09)	-18.84(±0.09)	-17.33(±0.09)	-16.53(±0.09)	-15.81(±0.09)
0.1516	-19.08(±0.08)	-17.86(±0.08)	-17.07(±0.08)	-16.12(±0.08)	-15.47(±0.07)
Cyclic alanylalanine in 0.0981 mol kg^{-1} aqueous $NiCl_2$ solution					
0.0112	-23.61(±1.05)	-21.15(±1.03)	-18.35(±1.01)	-16.99(±0.99)	-15.50(±0.97)
0.0246	-22.98(±0.48)	-20.79(±0.47)	-17.95(±0.46)	-16.67(±0.45)	-15.06(±0.44)
0.0353	-22.82(±0.33)	-20.54(±0.33)	-17.54(±0.32)	-16.31(±0.31)	-14.89(±0.31)
0.0735	-22.13(±0.16)	-20.12(±0.16)	-17.01(±0.15)	-15.56(±0.15)	-14.01(±0.15)
0.0987	-21.70(±0.12)	-19.51(±0.12)	-16.54(±0.11)	-14.94(±0.11)	-13.45(±0.11)
0.1261	-21.21(±0.09)	-18.85(±0.09)	-15.91(±0.09)	-14.34(±0.09)	-12.91(±0.09)
0.1511	-20.78(±0.08)	-18.17(±0.08)	-15.21(±0.07)	-13.95(±0.07)	-12.24(±0.07)
Cyclic alanylalanine in 0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution					
0.0115	-23.52(±1.02)	-22.30(±1.00)	-19.52(±0.98)	-18.21(±0.96)	-16.38(±0.95)
0.0253	-22.88(±0.46)	-21.86(±0.46)	-18.83(±0.45)	-17.71(±0.44)	-16.02(±0.43)
0.0353	-22.34(±0.33)	-21.41(±0.33)	-18.54(±0.32)	-17.43(±0.31)	-15.65(±0.31)
0.0762	-19.68(±0.15)	-19.16(±0.15)	-17.14(±0.15)	-16.46(±0.14)	-15.05(±0.14)
0.1022	-18.07(±0.11)	-17.86(±0.11)	-16.28(±0.11)	-15.93(±0.11)	-14.58(±0.11)
0.1260	-16.83(±0.09)	-16.62(±0.09)	-15.44(±0.09)	-15.15(±0.09)	-14.06(±0.09)
0.1502	-15.47(±0.08)	-15.16(±0.08)	-14.75(±0.07)	-14.32(±0.07)	-13.57(±0.07)

[a]*m* is the molality of cyclic alanylalanine in aqueous metal salt solutions. The experiment was carried out under atmosphere pressure.

Table 6: Least Squares Fit Parameters of the Equation $\phi_k = \phi_k^0 + S_k m$ for Cyclic Alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at Temperatures *T* = (293.15 to 313.15) K

T/K	ϕ_k^0 /10^{15} $Pa^{-1}m^3mol^{-1}$	S_k /10^{15} $Pa^{-1}m^3mol^{-2}kg$	σ /10^{15} $Pa^{-1}m^3mol^{-1}$
Cyclic alanylalanine in water			
293.15	-27.19(±0.08)	19.58(±0.94)	0.1
298.15	-26.09(±0.01)	17.18(±0.19)	0.1
303.15	-23.98(±0.05)	15.85(±0.56)	0.1
308.15	-23.59(±0.04)	16.16(±0.47)	0.1
313.15	-23.18(±0.05)	21.00(±0.60)	0.1
Cyclic alanylalanine in 0.0899 mol kg^{-1} aqueous $MnCl_2$ solution			
293.15	-24.85(±0.11)	38.58(±1.22)	0.2
298.15	-23.12(±0.03)	34.44(±0.32)	0.1
303.15	-20.20(±0.07)	21.49(±0.83)	0.1
308.15	-18.62(±0.07)	16.82(±0.80)	0.1
313.15	-17.55(±0.06)	13.87(±0.64)	0.1
Cyclic alanylalanine in 0.0981 mol kg^{-1} aqueous $NiCl_2$ solution			
293.15	-23.58(±0.09)	18.91(±1.03)	0.1
298.15	-22.09(±0.06)	26.07(±0.72)	0.1
303.15	-18.48(±0.09)	20.90(±1.04)	0.1
308.15	-17.17(±0.05)	21.95(±0.59)	0.1
313.15	-15.68(±0.03)	22.57(±0.43)	0.1
Cyclic alanylalanine in 0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution			
293.15	-24.29(±0.09)	59.41(±0.95)	0.1
298.15	-23.11(±0.10)	52.04(±1.06)	0.1
303.15	-19.77(±0.06)	34.00(±0.67)	0.1
308.15	-18.45(±0.09)	26.58(±0.95)	0.1
313.15	-16.50(±0.06)	19.38(±0.71)	0.1

[a]σ is the standard deviation of the fit.

in Table **5** and the method least-squares fit has been employed to fit these values,

$$\phi_k = \phi_k^0 + S_k m, \quad (5)$$

where ϕ_k^0 is the apparent molar isentropic compression at infinite dilution or the partial molar isentropic compression of the system and S_k is the experimental slope. The calculated values of ϕ_k^0 and S_k along with their standard deviations have been presented in Table **6**. Large negative values of ϕ_k^0 may be attributed to the hydrogen bonding ability of cyclic alanylalanine molecule [30] resulting in negative contribution. By the values of ϕ_k^0 it is possible to predict the extent of solute-solvent interaction present in the system [31]. The dependence of ϕ_k^0 values of cyclic alanylalanine with temperature indicates the release of more number of water molecules from the secondary solvation layer of cyclic alanylalanine into the bulk, rendering the solutions more compressible at higher temperatures [27, 32-34].

3.4. Transfer Molar Properties

The transfer molar properties at infinite dilution of cyclic alanylalanine from water to aqueous metal salt solutions have been calculated from:

$\Delta_{tr}Y = Y_\phi^0$ (in aqueous metal salt solutions) - Y_ϕ^0 (in pure water) (6)

Table **7** represent the trends in transfer properties of cyclic alanylalanine from aqueous to aqueous metal salt solutions. It is evident from the table that the values of $\Delta_{tr}\phi_v^0$ are positive in aqueous metal salt solutions at

Table 7: Transfer partial molar volumes, $\Delta_{tr}\phi_v^0$, and transfer partial molar isentropic compressibilities, $\Delta_{tr}\phi_k^0$, of cyclic alanylalanine from water to aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions at temperatures, *T* = (293.15 to 313.15) K

T/K	$\Delta_{tr}\phi_v^0$ /10^6 m^3mol^{-1}	$\Delta_{tr}\phi_k^0$ /10^{15} $Pa^{-1}m^3mol^{-1}$
0.0899 mol kg^{-1} aqueous $MnCl_2$ solution		
293.15	1.43	2.34
298.15	2.26	2.97
303.15	3.90	3.78
308.15	5.40	4.97
313.15	8.01	5.63
0.0981 mol kg^{-1} aqueous $NiCl_2$ solution		
293.15	0.40	3.61
298.15	1.29	4.00
303.15	2.53	5.50
308.15	2.70	6.42
313.15	4.11	7.50
0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution		
293.15	0.53	2.90
298.15	2.07	2.98
303.15	3.17	4.21
308.15	3.60	5.14
313.15	5.06	6.68

all the temperatures and the overall values of $\Delta_{tr}\phi_v^0$ from water to aqueous $MnCl_2$ were found to be higher than those of aqueous $ZnCl_2$ or $NiCl_2$ systems.

Another important observation of the present communication is that the transfer molar volume increases by increasing the temperature. This cannot be explained based on either electrostriction or hydrophobic hydration of the cyclic dipeptide since hydrophobic hydration decreases at higher temperatures due to release of some water molecules at higher temperatures thus causing negative contribution to ϕ_v^0 values [35].Thermodynamically cyclic alanylalanine behaves as a hydrophobic gas than a hydrophobic liquid or solid and the behavior of hydrophobic gas can be attributed to its increasingly favorable enthalpic interaction with water largely due to its size, hydrophobicity, etc. [25]. Also, presence of strong cations such as Mn^{2+}, Ni^{2+} or Zn^{2+} cause shrinkage in hydrogen bonding groups present in cyclic alanylalanine with water. This effect along with enthalpic interaction of cyclic alanylalanine with water at higher temperatures may explain the positive trend in transfer molar quantities. The nature of transfer molar quantities with respect to temperature is depicted in Figures **5** and **6**. The transfer molar quantities of cyclic alanylalanine in all the studied aqueous metal salt solution generally vary linearly with temperature.

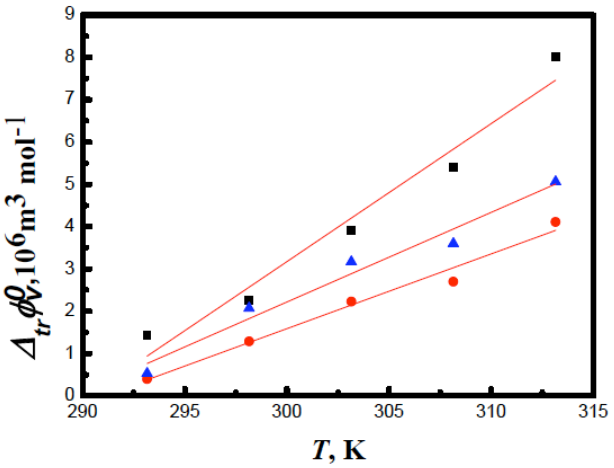

Figure 5: Plot of $\Delta_{tr}\phi_v^0$ of cyclic alanylalanine versus temperature (*T*). ■, In $MnCl_2$ solution; ●, In $NiCl_2$ solutions and ▲, In $ZnCl_2$ solutions.

3.5. Molar Refraction

The refractive indices, n_D, of the systems; cyclic alanylalanine – water and in aqueous metal salt

solutions were recorded as a function of the molar concentration of the solute. The values of n_D were found to increase with the solute concentration in all the cases.

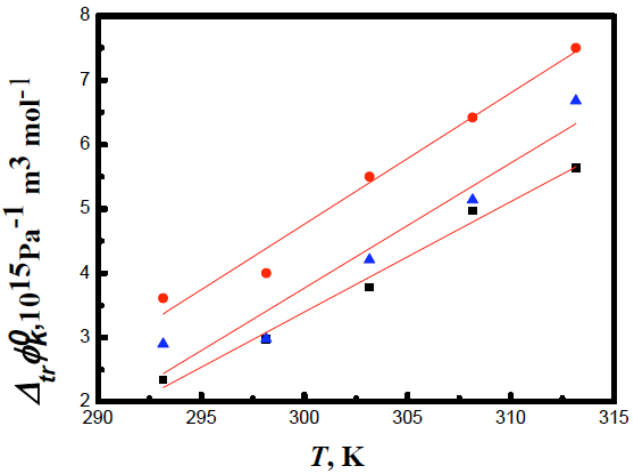

Figure 6: Plot of $\Delta_{tr}\phi_k^0$ of cyclic alanylalanine versus temperature (T). ■, In $MnCl_2$ solution; ●, In $NiCl_2$ solutions and ▲, In $ZnCl_2$ solutions.

The molar refraction, R_D, values have been computed using the Lorentz– Lorenz relation [36],

$$R_D = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\left(\frac{\sum_{i=1}^{3} x_i M_i}{\rho}\right), \quad (7)$$

The molar refraction values are fitted using the equation,

$$R_D = R_D^O + Bx_{i,} \quad (8)$$

where x_i is the mole fraction of the solute and B is the experimental slope. Table **8** presents the tabulated values of R_D°.

In order to examine the intermolecular forces existing in pure solvents and solutions, dependence of R_D on composition and temperature can be taken into account. This is mainly because molar refraction depends on the composition of the solution and

Table 8: Values of coefficients of the equation $R_D = R_D^0 + Bx_i$ at T = (293.15 to 313.15) K

T/K	R_D°/10^6 m^3 mol^{-1}	B/10^6 m^3 mol^{-1}	σ/10^6 m^3 mol^{-1}
Cyclic alanylalanine in water			
293.15	3.71347(±0.01)	42.06259(±0.69)	0.1
298.15	3.71258(±0.01)	41.03014(±0.62)	0.1
303.15	3.71160(±0.01)	40.09343(±0.65)	0.1
308.15	3.71178(±0.01)	38.99653(±0.75)	0.1
313.15	3.71153(±0.01)	38.66966(±0.74)	0.1
Cyclic alanylalanine in 0.0899 mol kg^{-1} aqueous $MnCl_2$ solution			
293.15	3.79264(±0.01)	38.94715(±0.56)	0.1
298.15	3.79300(±0.01)	37.32124(±0.60)	0.1
303.15	3.79339(±0.01)	36.90533(±0.59)	0.1
308.15	3.79461(±0.01)	36.46855(±0.63)	0.1
313.15	3.79547(±0.01)	36.94162(±0.63)	0.1
Cyclic alanylalanine in 0.0981 mol kg^{-1} aqueous $NiCl_2$ solution			
293.15	3.77550(±0.01)	31.28949(±0.70)	0.1
298.15	3.76525(±0.01)	32.57337(±0.39)	0.1
303.15	3.76456(±0.01)	1.16179(±0.04)	0.1
308.15	3.76456(±0.01)	33.49680(±0.66)	0.1
313.15	3.76386(±0.01)	32.97102(±0.48)	0.1
Cyclic alanylalanine in 0.0933 mol kg^{-1} aqueous $ZnCl_2$ Solution			
293.15	3.77748(±0.01)	33.60514(±0.15)	0.1
298.15	3.77657(±0.01)	33.92668(±0.26)	0.1
303.15	3.77447(±0.01)	33.69701(±0.25)	0.1
308.15	3.77212(±0.01)	33.18533(±0.28)	0.1
313.15	3.76704(±0.01)	33.91451(±0.26)	0.1

[a]σ is the standard deviation of the fit.

temperature [37]. Thus variation of R_D° suggests that the overall polarizability of cyclic alanylalanine in presence of metal salts increases with its concentration.

The molar refraction has the same units as the molar volume and could be understood, in fact, as a measure of the hard-core volume of a mole of liquid [38]. Thus, the dependence R_D values with the amount of cyclic alanylalanine in aqueous metal salt solutions in the above systems confirms the argument of solute-solvent interaction as indicated by the volumetric studies.

4. CONCLUSIONS

In summary, the molecular interactions of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions have been analyzed in this study. The experimental density, ultrasonic velocity and refractive index of cyclic alanylalanine in water and in aqueous $MnCl_2$, $NiCl_2$ and $ZnCl_2$ solutions have been reported at temperatures T = (293.15 to 313.15) K. The values of isentropic compressibility, apparent molar volume, apparent molar compression and transfer molar quantities were computed from the experimental values. The results have been discussed in terms of the interaction between cyclic alanylalanine and metal salts in aqueous solution. Electrostriction was found to increase with the solute concentration in all the systems studied. The larger values of partial molar volume of cyclic alanylalanine in aqueous $MnCl_2$ than that in aqueous $NiCl_2$ or $ZnCl_2$ solution attributes to larger Mn^{2+}-OH_2 bond distance in hydrated ions. It also indicated the ionic-electrophilic and hydrophilic-hydrophobic interactions present among various groups present in cyclic alanylalanine and constituents of metal salts. Furthermore the S_v values were found to be negative, considerably indicating the dominance of hydrophobic hydration in the systems considered. The results were substantiated by the transfer molar properties and refractive index studies. In general, the study and the results contribute towards the better understanding of bio-molecules in physiological systems.

REFERENCES

[1] Kauzmann W. Some factors in the interpretation of protein denaturation. Adv Protein Chem 1959; 14: 1-63. http://dx.doi.org/10.1016/S0065-3233(08)60608-7

[2] Chotia C. Principles that determine the structure of proteins. Ann Rev Biochem 1984; 53: 537-72. http://dx.doi.org/10.1146/annurev.bi.53.070184.002541

[3] Murphy KP, Gill SJ. Thermodynamics of dissolution of solid cyclic dipeptides containing hydrophobic side groups. J Chem Thermodyn 1989; 21: 903-13. http://dx.doi.org/10.1016/0021-9614(89)90149-3

[4] Prasad C. Bioactive Cyclic Dipeptides. Peptides 1995; 16: 151-64. http://dx.doi.org/10.1016/0196-9781(94)00017-Z

[5] Chen YH, Liou SU, Chen CC. Two-step mass spectrometric approach for the identification of diketopiperazines in chicken essence. Eur Food Res Technol 2004; 218: 589-97. http://dx.doi.org/10.1007/s00217-004-0901-x

[6] Sijpkes AH, Kleut GJVD, Gill SC. The solubilities of five cyclic dipeptides in water and in aqueous urea at 298. 15 K: a quantitative model for the denaturation of proteins in aqueous urea solutions. Biophys Chem 1994; 52: 75-82. http://dx.doi.org/10.1016/0301-4622(94)00067-0

[7] Abate L, Palecz B, Giancola C, Gatta GD. Heat capacities and enthalpies and entropies of fusion of some uncharged small peptides (N-acetylamino acid amides and 2,5-diketopiperazines). J Chem Thermodyn 1997; 29: 359-68. http://dx.doi.org/10.1006/jcht.1996.0161

[8] Hakin AW, Kowalchuck MG, Liu JL, Marriott RA. Thermodynamics of protein model compounds: Apparent and partial molar heat capacities and volumes of several cyclic dipeptides in water. J Solution Chem 2000; 29: 131-51. http://dx.doi.org/10.1023/A:1005169114258

[9] Hakin AW, Cavilla B, Liu JL, Zorzetti B. Thermodynamics of protein model compounds: An investigation of the apparent and partial molar heat capacities and volumes of aqueous solutions of alanyl and seryl side-chain containing cyclic dipeptides. Phys Chem Chem Phys 2001; 3: 3805-10. http://dx.doi.org/10.1039/b103629g

[10] Karanth VR, Bhat DK. Volumetric, acoustic, and refractometric study of cyclic alanylalanine in aqueous cobalt chloride solutions at temperatures T = (293.15 to 313.15) K. J Chem Eng Data 2013; 58: 271–8. http://dx.doi.org/10.1021/je3009123

[11] Crichton RR. Biological Inorganic Chemistry An Introduction, Amsterdam: Elsevier; 2008.

[12] Roat-Malone RM. Bioinorganic Chemistry A Short Course. 2nd ed. New Jersey: John Wiley & Sons Inc.: 2007. http://dx.doi.org/10.1002/9780470191712

[13] Main RK, Schmidt CLA. The combination of divalent manganese with certain proteins, amino acids, and related compounds. J Gen Physiol 1935; 19: 127-47. http://dx.doi.org/10.1085/jgp.19.1.127

[14] Jeanvoine Y, Spezia R. Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}Binding Chalcogen− Chalcogen Bridges: A Compared MP2 and B3LYP Study. J Phys Chem A 2009; 133: 7878-87. http://dx.doi.org/10.1021/jp811460f

[15] Chohan ZH, Sherazi SKA. Biological role of cobalt(II), copper(II) and nickel(II) metal ions on the antibacterial properties of some nicotinoyl-hydrazine derived compounds, Met-Based Drugs 1997; 4: 69-74. http://dx.doi.org/10.1155/MBD.1997.69

[16] Hedwig GR, Hoiland H. Thermodynamic properties of peptide solutions. Part 11. Partial molar isentropic pressure coefficients in aqueous solutions of some tripeptides that model protein side-chains. Biophys Chem 1994; 49: 175-81. http://dx.doi.org/10.1016/0301-4622(93)E0068-G

[17] Millero FJ, Ward GK, Lepple FK, Hoff EV. Isothermal compressibility of aqueous sodium chloride, magnesium chloride, sodium sulphate, and magnesium sulphate solutions from 0°C to 45°C at 1 Atm. J Phys Chem 1974; 78: 1636-43. http://dx.doi.org/10.1021/j100609a008

[18] Sadeghi R, Gholamireza A. Thermodynamics of the ternary systems: (water + glycine, l-alanine and l-serine + di-ammonium hydrogen citrate) from volumetric,

compressibility, and (vapour + liquid) equilibria measurements. J Chem Thermodyn 2011; 43: 200-15. http://dx.doi.org/10.1016/j.jct.2010.08.021

[19] Bol W, Gerrits GJA, Van Panthaleon Van Eck CL, The hydration of divalent cations in aqueous solution. An X-ray investigation with isomorphous replacement. J Appl Crst; 1970: 3; 486-92. http://dx.doi.org/10.1107/S0021889870006738

[20] Ohtaki H, Radnai T, Structure and dynamics of hydrated ions. Chem Rev 1993; 93: 1157-204. http://dx.doi.org/10.1021/cr00019a014

[21] Pal A, Chauhan N. Partial molar volumes, expansibilities and compressibilities of glyglyglycine in aqueous sucrose and fructose solutions between 288.15 and 308.15 K, Thermochim Acta 2011; 513: 68-74. http://dx.doi.org/10.1016/j.tca.2010.11.013

[22] Hedwig GR, Høiland H. Thermodynamic properties of peptide solutions: 7. Partial molar isentropic pressure coefficients of some dipeptides in aqueous solution. J Solution Chem 1991; 20: 1113-27. http://dx.doi.org/10.1007/BF00649100

[23] Gerstein M, Tsai J, Levitt M. The volume of atoms on the protein surface: calculated from simulation, using voronoi polyhedral. J Mol Biol 1995; 249: 955-66. http://dx.doi.org/10.1006/jmbi.1995.0351

[24] Corey RB, The crystal structure of diketopiperazine. J Am Chem Soc 1938; 60: 1598-1604. http://dx.doi.org/10.1021/ja01274a023

[25] Brady GP, Sharp KA. Energetics of cyclic dipeptide crystal packing and solvation. Biophys J 1997; 72: 913-27. http://dx.doi.org/10.1016/S0006-3495(97)78725-3

[26] Lilley TH, Barrett GT, Eds. The Chemistry and Biochemistry of the Amino Acids. London: Chapman and Hall 1988.

[27] Riyazuddeen, Usmani MA, Interactions in (glycylglycine + 1 M aqueous glucose/1 M aqueous sucrose) systems at 298.15–323.15 K. Thermochim Acta 2012 532 36-40. http://dx.doi.org/10.1016/j.tca.2011.03.024

[28] Afanas'ev VN. A study on hydration of urea and urotropin by density and speed of sound measurements in aqueous solutions. J Solution Chem 2012; 41: 1447-61. http://dx.doi.org/10.1007/s10953-012-9879-3

[29] Marriott RA, Hakin AW, Liu JL, Lutter E. The volumetric properties of aqueous solutions of glycylglycine and l -serine at elevated temperatures and pressures. J Chem Thermodyn 2001; 33: 959-82. http://dx.doi.org/10.1006/jcht.2001.0823

[30] Benedetti E, Corradini P, Pedone C. Crystal and molecular structure of trans-3,6-Dimethyl-2,5-piperazinedione (L-Alanyl-D-alanyl-2,5-diketopiperazine). J Phys Chem 1969; 73: 2891-95. http://dx.doi.org/10.1021/j100843a018

[31] Yan Z, Wang J, Kong W, Lu J. Effect of temperature on volumetric and viscosity properties of some α-amino acids in aqueous calcium chloride solutions. Fluid Phase Equil 2003; 215: 143-50. http://dx.doi.org/10.1016/j.fluid.2003.07.001

[32] Bhat R, Kishore N. Ahluwalia JC. Thermodynamic studies of transfer of some amino acids and peptides from water to aqueous glucose and sucrose solutions at 298.15 K. J Chem Soc Faraday Trans 1 1988; 84: 2651-65. http://dx.doi.org/10.1039/f19888402651

[33] Nain AK, Pal R, Sharma RK. Volumetric, ultrasonic, and viscometric behaviour of l-histidine in aqueous-glucose solutions at different temperatures. J Chem Thermodyn 2011; 43: 603-12. http://dx.doi.org/10.1016/j.jct.2010.11.017

[34] Mishra AK, Ahluwalia JC, Apparent molal volumes of amino acids, n-acetylamino acids, and peptides in aqueous solutions. J Phys Chem 1984; 88: 86-92. http://dx.doi.org/10.1021/j150645a021

[35] Chen A, Liu M, Zheng Y, Sun D, Wang B, Wang L. Volumetric, viscometric, and refractive index behavior of 7-Hydroxy-4-methylcoumarin in aqueous ethanol or 1-propanol solutions in the temperature range of (293.15 to 313.15) K. J Chem Eng Data 2013; 58: 2474−82. http://dx.doi.org/10.1021/je4003515

[36] Shekaari H, Kazempour A. Thermodynamic properties of d-glucose in aqueous 1-hexyl-3-methylimidazolium bromide solutions at 298.15 K. Fluid Phase Equil 2012; 336: 122-7. http://dx.doi.org/10.1016/j.fluid.2012.08.024

[37] Marchetti A, Tassi L, Ulrici A, Vaccari G, Sanna G. Refractive indices of binary mixtures of (1,2-dichloroethane + 2-chloroethanol) at various temperatures. J Chem Thermodyn 1999; 31: 647-60. http://dx.doi.org/10.1006/jcht.1998.0475

[38] Glasstone S. Textbook of physical chemistry. New York: Interscience; 1946.

[39] Cabani S, Gianni P, Mollica V, Lepori L. Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. J Solution Chem 1981; 10: 563-95. http://dx.doi.org/10.1007/BF00646936

[40] Cabani S, Conti G, Matteoli E, Tine MR. Volumetric properties of amphionic molecules in water. Part 2.-Thermal expansibility and compressibility related to the formation of zwitterionic structures. J Chem Soc Faraday Trans 1 1981; 77: 2385-94. http://dx.doi.org/10.1039/f19817702385

Received on 25-11-2014 Accepted on 06-02-2015 Published on 25-02-2015

DOI: http://dx.doi.org/10.6000/1929-5030.2015.04.01.4