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Molecular Interactions in Glycylglycine−$MnCl_2$ Aqueous Solutions at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K

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The viscosities, ultrasonic velocities, densities, and refractive indices of glycylglycine and $MnCl_2$ in water have been studied at different temperatures and concentrations. Excess thermodynamic parameters such as adiabatic compressibility (β_{ad}), apparent molar volume (Φ_V), apparent molar compressibility (Φ_K), intermolecular free length (L_f), specific acoustic impedance (Z), relative association (R_A), and solvation number (S_n) have been calculated. The variations in apparent molar volume were confirmed by Scaled particle theory, and the changes in apparent molar compressibilities were interpreted using the Kirkwood model. The variations in apparent molar volumes were fitted with Masson's equation. The viscosity data have been fitted using the Jones-Dole empirical equation. The molecular relaxation of $MnCl_2$ and glycylglycine in water gives an idea about solute−solute interactions. The interactions also suggest the formation of H-bonding in the system. The structure forming tendency of the solute has also been indicated by the solvation number.

Introduction

Interactions of amino acids with their surrounding environment play an important role in their conformational characteristics. These interactions are mainly those between the amino acid molecules and solvent ions. Most of these interactions such as hydrogen bonding and electrostatic interactions have a noncovalent nature. The study of these interactions provides an important insight into the conformational stability and unfolding behavior of amino acids and proteins.[1] The properties of amino acids and proteins such as their structure, solubility, denaturation, activity of enzymes, etc. are greatly influenced by electrolytes. The effect of electrolytes on structure and function of both proteins and amino acids has been widely studied in terms of structure making and structure breaking properties. Proteins are complex molecules, and their behavior in solutions is governed by a number of specific interactions.[2] Protein hydration plays a crucial role in this matter. Salt solutions are known to produce remarkable effects on the conformation and properties of proteins. Due to the complex structure of proteins, a variety of different interactions with salts may occur, and it is difficult to resolve straightaway the various interactions participating in protein hydration.[3]

Most of the previous studies[4−10] on amino acids have been carried out in different solvents and aqueous solutions at a given temperature, but interesting results have been obtained when they were studied under various temperatures and pressures in water, not only because it is used in chemistry and other related fields to control factors such as solubility, reactivity, and stability of the system but also for the fact that biological molecules are ultimately found in water.[11] Most of the studies on amino acids and biomolecules have been carried out in pure and mixed aqueous solvents. But such investigations in the presence of metal ions, which play a vital role in the functioning of living organisms, are still scanty. Transition metal ions play an important role in plant growth, lipid metabolism, and regulation of physiological systems. Hence, it is of interest to study the dynamics of dipeptide−transition metal salt solution systems which would fill the gap and may provide new insights and better understanding of this field of science. Through this paper, we make an attempt to present variations occurring under diverse conditions. Accordingly, this paper presents a systematic study of the viscosities, ultrasonic velocities, densities, and refractive indices of the aqueous solutions of glycylglycine and $MnCl_2$ as a function of concentration and temperature over wide ranges.

Table 1. Viscosities (η) of Aqueous Glycylglycine (1) + Densities (ρ) of Aqueous Sodium Chloride Solutions (2) at Various Temperatures and Concentrations[a]

M	T	obtained values η	lit. values η
$mol \cdot dm^{-3}$	K	$m \cdot Pa \cdot s$	$m \cdot Pa \cdot s$
0.025 (Gly-Gly)	293.15	1.0190 ± 0.0004	1.0194 ± 0.0010
	298.15	0.9026 ± 0.0002	0.9028 ± 0.0007
	303.15	0.8068 ± 0.0003	0.8065 ± 0.0019
		ρ	ρ
		$kg \cdot m^{-3}$	$kg \cdot m^{-3}$
0.20910 (NaCl)	298.15	1005.459	1005.571 (0.20918)
0.50660		1015.258	1017.344 (0.50653)
1.01276		1034.190	1036.690 (1.01279)
1.50258		1049.726	1054.672 (1.50262)
1.97404		1074.453	1071.353 (1.97403)
2.44956		1088.006	1087.608 (2.44952)

[a] The values given in brackets are the concentrations of aqueous sodium chloride solution.

Experimental Section

Glycylglycine of 99 % purity from the Sigma Aldrich Company and $MnCl_2 \cdot 4H_2O$ of 99 % purity analytical grade from the Central Drug House were used. $MnCl_2$ was used after drying for 72 h in a vacuum desiccator at room temperature. Deionized, doubly distilled, degassed water with a specific conductance less than $1.29 \cdot 10^{-6}\ \Omega^{-1} \cdot cm^{-1}$ was used for the preparation of all solutions. The solutions were prepared on a weight basis by using a Mettler balance having a precision of ± 0.01 mg. In the first case (Tables 2 and 4), the concentration

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Table 2. Viscosity (η), Ultrasonic Velocity (U), Density (ρ), Refractive Index (n_D), and Adiabatic Compressibility (β_{ad}) for (1) Glygylglycine + $MnCl_2$ (2) in Water (3) at T = (288.15 to 318.15) K Keeping Glycylglycine Constant at 0.020 M

M	η	U	$\rho \cdot 10^{-3}$		$\beta_{ad} \cdot 10^{10}$
$mol \cdot dm^{-3}$	$m \cdot Pa \cdot s$	$m \cdot s^{-1}$	$kg \cdot m^{-3}$	n_D	$m^2 \cdot N^{-1}$
		T/K = 288.15			
0.005	1.10	1035.20	0.9990	1.3331	9.340
0.010	1.20	1040.36	0.9993	1.3332	9.245
0.030	1.32	1045.15	0.9999	1.3336	9.155
0.050	1.43	1050.28	1.0030	1.3342	9.038
0.100	1.56	1057.01	1.0076	1.3351	8.882
0.250	1.69	1065.33	1.0102	1.3363	8.722
0.500	1.83	1071.00	1.0121	1.3378	8.613
		T/K = 293.15			
0.005	0.99	1105.10	0.9982	1.3328	8.2031
0.010	1.05	1110.22	0.9987	1.3332	8.1235
0.030	1.12	1115.18	0.9993	1.3338	8.0466
0.050	1.20	1120.31	0.9999	1.3345	7.9683
0.100	1.27	1125.15	1.0007	1.3351	7.8936
0.250	1.36	1132.27	1.0016	1.3359	7.7876
0.500	1.47	1137.38	1.0025	1.3368	7.7108
		T/K = 298.15			
0.005	0.90	1180.15	0.9970	1.3324	7.2016
0.010	0.95	1184.23	0.9975	1.3327	7.1485
0.030	0.99	1189.10	0.9981	1.3331	7.0821
0.050	1.04	1197.36	0.9988	1.3336	6.9834
0.100	1.12	1203.29	0.9996	1.3343	6.9092
0.250	1.17	1208.41	1.0004	1.3348	6.8453
0.500	1.23	1213.32	1.0008	1.3354	6.7866
		T/K = 303.15			
0.005	0.81	1250.10	0.9957	1.3317	6.4266
0.010	0.84	1256.21	0.9963	1.3324	6.3604
0.030	0.88	1263.29	0.9968	1.3332	6.2861
0.050	0.93	1271.34	0.9974	1.3340	6.2030
0.100	0.99	1278.16	0.9979	1.3349	6.1339
0.250	1.04	1284.20	0.9985	1.3357	6.0727
0.500	1.09	1290.06	0.9991	1.3364	6.0141
		T/K = 308.15			
0.005	0.71	1316.00	0.9940	1.3310	5.8090
0.010	0.73	1320.15	0.9946	1.3313	5.7690
0.030	0.77	1325.07	0.9952	1.3318	5.7228
0.050	0.82	1329.23	0.9958	1.3322	5.6836
0.100	0.88	1335.18	0.9964	1.3328	5.6297
0.250	0.93	1340.27	0.9969	1.3333	5.5842
0.500	0.97	1347.36	0.9975	1.3339	5.5222
		T/K = 313.15			
0.005	0.66	1400.05	0.9922	1.3302	5.1417
0.010	0.69	1407.17	0.9925	1.3304	5.0883
0.030	0.73	1413.23	0.9931	1.3308	5.0422
0.050	0.76	1420.28	0.9934	1.3312	4.9903
0.100	0.79	1428.16	0.9940	1.3317	4.9324
0.250	0.83	1435.81	0.9945	1.3321	4.8775
0.500	0.88	1442.08	0.9951	1.3327	4.8318
		T/K = 318.15			
0.005	0.47	1483.31	0.9904	1.3295	4.5890
0.010	0.50	1487.14	0.9908	1.3299	4.5636
0.030	0.53	1492.10	0.9913	1.3304	4.5310
0.050	0.57	1496.22	0.9917	1.3309	4.5043
0.100	0.62	1506.29	0.9924	1.3317	4.4411
0.250	0.64	1512.18	0.9928	1.3321	4.4048
0.500	0.69	1519.37	0.9933	1.3327	4.3610

Table 3. Viscosity (η), Ultrasonic Velocity (U), Density (ρ), Refractive Index (n_D), and Adiabatic Compressibility (β_{ad}) for (1) Glygylglycine + $MnCl_2$ (2) in Water (3) at T = (288.15 to 318.15) K Keeping $MnCl_2$ Constant at 0.25 M

M	η	U	$\rho \cdot 10^{-3}$		$\beta_{ad} \cdot 10^{10}$
$mol \cdot dm^{-3}$	$m \cdot Pa \cdot s$	$m \cdot s^{-1}$	$kg \cdot m^{-3}$	n_D	$m^2 \cdot N^{-1}$
		T/K = 288.15			
0.005	1.16	1042.01	0.9998	1.3340	9.2117
0.007	1.33	1050.12	1.0033	1.3349	9.0410
0.010	1.50	1057.16	1.0068	1.3356	8.8970
0.020	1.68	1065.33	1.0104	1.3364	8.7220
0.030	1.85	1072.99	1.0140	1.3373	8.5658
0.050	2.00	1080.28	1.0173	1.3380	8.4232
0.100	2.19	1087.57	1.0201	1.3386	8.2878
		T/K = 293.15			
0.005	1.05	1103.15	0.9989	1.3327	8.2263
0.007	1.14	1111.85	0.9998	1.3336	8.0801
0.010	1.25	1121.56	1.0007	1.3348	7.9339
0.020	1.37	1132.27	1.0016	1.3359	7.7876
0.030	1.44	1140.23	1.0026	1.3367	7.6415
0.050	1.55	1148.73	1.0035	1.3378	7.4953
0.100	1.66	1159.66	1.0045	1.3389	7.3491
		T/K = 298.15			
0.005	0.94	1184.32	0.9976	1.3320	7.1466
0.007	1.02	1193.35	0.9984	1.3329	7.0462
0.010	1.10	1200.65	0.9995	1.3339	6.9458
0.020	1.17	1208.41	1.0004	1.3348	6.8453
0.030	1.26	1215.10	1.0013	1.3356	6.7449
0.050	1.35	1223.53	1.0023	1.3364	6.6445
0.100	1.47	1234.66	1.0035	1.3378	6.5441
		T/K = 303.15			
0.005	0.83	1257.16	0.9961	1.3313	6.3520
0.007	0.91	1266.40	0.9970	1.3328	6.2589
0.010	0.99	1274.32	0.9977	1.3343	6.1486
0.020	1.04	1284.20	0.9985	1.3356	6.0727
0.030	1.11	1293.81	0.9994	1.3370	5.9796
0.050	1.19	1302.56	0.9999	1.3384	5.8865
0.100	1.28	1315.27	1.0009	1.3399	5.7934
		T/K = 308.15			
0.005	0.74	1321.07	0.9946	1.3303	5.7610
0.007	0.80	1329.16	0.9954	1.3312	5.7021
0.010	0.87	1335.43	0.9961	1.3324	5.6432
0.020	0.93	1340.27	0.9969	1.3334	5.5842
0.030	1.00	1346.15	0.9977	1.3342	5.5266
0.050	1.08	1354.83	0.9984	1.3354	5.4646
0.100	1.20	1363.06	0.9992	1.3366	5.4075
		T/K = 313.15			
0.005	0.62	1406.31	0.9924	1.3296	5.0950
0.007	0.65	1414.56	0.9931	1.3304	5.0225
0.010	0.69	1425.92	0.9938	1.3313	4.9505
0.020	0.73	1435.81	0.9945	1.3321	4.8775
0.030	0.77	1444.43	0.9951	1.3330	4.8050
0.050	0.82	1455.18	0.9958	1.3338	4.7325
0.100	0.86	1468.39	0.9969	1.3350	4.6605
		T/K = 318.15			
0.005	0.50	1490.56	0.9907	1.3290	4.5431
0.007	0.56	1498.31	0.9915	1.3301	4.4970
0.010	0.60	1505.63	0.9920	1.3311	4.4509
0.020	0.65	1512.18	0.9928	1.3321	4.4048
0.030	0.71	1520.27	0.9935	1.3330	4.3587
0.050	0.77	1527.84	0.9943	1.3339	4.3132
0.100	0.86	1538.11	0.9953	1.3352	4.2660

of glycylglycine was kept constant at 0.020 M, and that of $MnCl_2$ was varied as 0.005 M, 0.010 M, 0.030 M, 0.050 M, 0.10 M, 0.25 M, and 0.50 M. In the second case (Tables 3 and 5), the concentration of glycylglycine was varied as 0.005 M, 0.007 M, 0.010 M, 0.020 M, 0.030 M, 0.050 M, and 0.10 M, and that of $MnCl_2$ was kept constant at 0.25 M. The temperature of water was controlled within ± 0.01 K using a thermostat.

Viscosities were measured using a Brookfield DV-III Ultra Programmable Rheometer (Brookfield Engineering Laboratories, Inc., USA) which was calibrated using double distilled water, ethanol, DMSO, and THF, and the uncertainty was found to be ± 0.0001 % for all solutions. Ultrasonic velocities were measured using a variable path ultrasonic interferometer, M-83 (Mittal Enterprises, India), at 3 MHz. Densities of the solutions were calculated using a (Mettler Toledo) Density 30PX digital densitometer having a precision of $\pm 1 \cdot 10^{-3}$ $kg \cdot m^{-3}$ and an accuracy of $\pm 3 \cdot 10^{-3}$ $kg \cdot m^{-3}$. Refractive indices were calculated using a (Mettler Toledo) Refracto 30PX and 30Gs digital

Table 4. Apparent Molar Volume (Φ_V), Apparent Molar Compressibility (Φ_K), Intermolecular Free Length (L_f), Specific Acoustic Impedance (Z), Relative Association (R_A), and Solvation Number (S_n) of (1) Glycylglycine + $MnCl_2$ (2) in Water (3) at T = (288.15 to 318.15) K Keeping Glycylglycine Constant at 0.020 M

M	$\Phi_V \cdot 10^{-6}$	Φ_K	$L_f \cdot 10^5$	$Z \cdot 10^{-3}$		
$mol \cdot dm^{-3}$	$m^3 \cdot mol^{-1}$	$mol^{-1} \cdot Pa^{-1}$	A^0	$kg \cdot m^{-2} \cdot s^{-1}$	R_A	S_n
T/K = 288.15						
0.005	112.214	0.0651	1.8673	1034.164	0.9883	0.0250
0.010	112.179	0.0251	1.8577	1039.631	0.9885	0.0942
0.030	105.439	0.0150	1.8487	1045.045	0.9886	0.4875
0.050	100.357	0.0087	1.8368	1053.430	0.9888	1.1314
0.100	91.689	0.0056	1.8209	1065.043	0.9890	2.8560
0.250	83.785	0.0023	1.8044	1076.196	0.9891	7.9961
0.500	77.828	0.0002	1.7931	1083.959	0.9892	18.227
T/K = 293.15						
0.005	130.340	0.0212	1.7700	1103.110	0.9842	0.0101
0.010	127.135	0.0175	1.7614	1108.776	0.9843	0.0310
0.030	122.430	0.0129	1.7530	1114.399	0.9845	0.1794
0.050	118.038	0.0089	1.7445	1120.197	0.9847	0.4583
0.100	112.993	0.0043	1.7363	1125.937	0.9848	1.1740
0.250	108.431	0.0018	1.7246	1134.081	0.9850	3.4402
0.500	103.694	0.0007	1.7160	1140.223	0.9851	8.3333
T/K = 298.15						
0.005	130.498	0.0162	1.6772	1176.609	0.9679	0.0277
0.010	127.174	0.0132	1.6710	1181.269	0.9689	0.0322
0.030	122.524	0.0103	1.6632	1186.840	0.9697	0.1515
0.050	119.126	0.0081	1.6516	1195.923	1.0004	0.3706
0.100	116.084	0.0056	1.6428	1202.808	1.0011	1.0786
0.250	112.148	0.0035	1.6352	1208.893	1.0018	2.9938
0.500	107.632	0.0004	1.6281	1214.411	1.0028	6.9962
T/K = 303.15						
0.005	112.514	0.0238	1.5996	1244.724	0.9811	0.0609
0.010	105.040	0.0161	1.5913	1251.562	0.9816	0.0842
0.030	98.235	0.0084	1.5820	1259.247	0.9820	0.1363
0.050	91.068	0.0057	1.5715	1268.034	0.9825	0.3592
0.100	85.346	0.0012	1.5627	1275.475	0.9831	1.0075
0.250	78.179	0.00096	1.5549	1282.273	0.9843	2.8869
0.500	70.456	0.00058	1.5474	1288.898	0.9853	6.7338
T/K = 308.15						
0.005	130.885	0.0212	1.5352	1308.104	0.9658	0.0352
0.010	126.141	0.0160	1.5299	1313.021	0.9663	0.0902
0.030	122.038	0.0115	1.5238	1318.709	0.9672	0.1363
0.050	117.961	0.0089	1.5186	1323.647	0.9676	0.3760
0.100	112.534	0.0048	1.5114	1330.373	0.9687	1.0738
0.250	108.385	0.0013	1.5052	1336.115	0.9692	3.0938
0.500	104.874	0.00081	1.4969	1343.991	0.9699	7.0450
T/K = 313.15						
0.005	127.055	0.0246	1.4557	1389.129	0.9781	0.0189
0.010	119.654	0.0212	1.4481	1396.616	0.9788	0.0591
0.030	110.864	0.0178	1.4416	1403.478	0.9796	0.2465
0.050	102.365	0.0144	1.4341	1410.906	0.9806	0.5072
0.100	94.686	0.0110	1.4258	1419.591	0.9816	1.1962
0.250	86.289	0.0076	1.4178	1427.913	0.9820	3.3159
0.500	78.532	0.0042	1.4112	1435.158	0.9829	7.7655
T/K = 318.15						
0.005	131.361	0.0253	1.3838	1469.070	0.9727	0.0531
0.010	128.584	0.0213	1.3790	1473.458	0.9734	0.0708
0.030	124.723	0.0178	1.3750	1479.118	0.9743	0.1981
0.050	119.432	0.0135	1.3710	1483.801	0.9750	0.4959
0.100	115.218	0.0094	1.3613	1494.842	0.9756	1.3548
0.250	109.834	0.0052	1.3557	1501.292	0.9764	3.5184
0.500	104.726	0.0008	1.3490	1509.190	0.9771	8.4366

refractometer, and its uncertainty was found to be ± 0.0001 %. The densitometer and refractometer were calibrated using double distilled water. The physical parameters for solutions of glycylglycine−$MnCl_2$ were measured at temperatures 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K. The measured viscosity values and their uncertainties of 0.025 M aqueous solutions of glycylglycine agree well with literature values.[12] The densitometer was checked for its accuracy by measuring the densities of aqueous sodium chloride solutions which were found to agree well with literature values[13] at 298.15 K (Table 1). On the basis of the above-mentioned physical parameters, the excess thermodynamic properties such as adiabatic compressibility (β_{ad}), apparent molar volume (Φ_V), apparent molar compressibility (Φ_K), intermolecular free length (L_f), specific acoustic impedance (Z), relative association (R_A), and solvation number (S_n) were calculated for the substrates at different concentrations and temperatures. Each measurement was repeated thrice, and the reported values are the average values of all three trials.

Results and Discussion

The experimental data of viscosity, ultrasonic velocity, density, refractive index, and the acoustical parameter adiabatic compressibility of glycylglycine and $MnCl_2$ in water at temperatures of 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K for the first and second cases are given in Table 2 and Table 3, respectively.

Various acoustical parameters such as apparent molar volume, apparent molar compressibility, intermolecular free length, acoustic impedance, relative association, and solvation number for the first and second cases are given in Table 4 and Table 5, respectively, and were calculated using the following equations

$$\beta_{ad} = 1/U^2 d \tag{1}$$

$$\Phi_v = (M_1/d) + \{1000(d_0 - d)/Mdd_0\} \tag{2}$$

$$\Phi_K = \{(d_0\beta_{ad} - d\beta_{ad}^0) \cdot 1000\}/Md_0 + (\beta_{ad}^0 M_1)/d_0 \tag{3}$$

$$L_f = k\sqrt{\beta_{ad}} \tag{4}$$

$$Z = U \cdot d \tag{5}$$

$$R_A = (d/d_0) \cdot (U_0/U)^{1/3} \tag{6}$$

$$S_n = (1 - \eta_0/\eta) \cdot (1 - N_2/N_2) \tag{7}$$

where d and d_0 are the densities of the solute and solvent; η and η_0 are the viscosities of the solute and solvent; M is the molarity of the solute; k is the Jacobson constant[14] which is different for different temperatures; N_2 is the mole fraction of the dissolved material; M_1 is the molecular weight of the solute; and β_{ad} and β_{ad}^0 are the adiabatic compressibilities of solvent and solute. The variations in apparent molar volumes were least-squares fitted using Masson's equation given below (eq 12).[15]

The present investigation is concerned with the study of the substrate glycylglycine and transition metal salt of $MnCl_2$ in water. The variation of viscosity with concentration in case one and in case two has been observed to increase (Table 2 and Table 3). A regular change in the viscosity data for different concentrations in water confirms the interactions of solvent−solute. This phenomenon may appear due to H-bond formation, and it may be attributed to the formation of strong intermolecular forces in the solute. The viscosity data have been fitted using the Jones-Dole empirical equation[16] which describes the relative viscosities of electrolyte solutions as a function of concentration (eq 8).

$$\eta/\eta_o = 1 + AC^{1/2} + BC \tag{8}$$

where C is the molarity; A is the constant arising from the interactions between the ions; and B is the viscosity B-coefficient. The above equation upon rearrangement becomes

$$(\eta/\eta_o - 1)/C^{1/2} = A + BC^{1/2} \tag{9}$$

The values have been found to be in accordance with the Jones-Dole equation. The values of the A- and B-coefficients obtained

Table 5. Apparent Molar Volume (Φ_V), Apparent Molar Compressibility (Φ_K), Intermolecular Free Length (L_f), Specific Acoustic Impedance (Z), Relative Association (R_A), and Solvation Number (S_n) of (1) Glycylglycine + $MnCl_2$ (2) in Water (3) at T = (288.15 to 318.15) K Keeping $MnCl_2$ Constant at 0.25 M

M $mol\cdot dm^{-3}$	$\Phi_V\cdot 10^{-6}$ $m^3\cdot mol^{-1}$	Φ_K $mol^{-1}\cdot Pa^{-1}$	$L_f\cdot 10^5$ A^0	$Z\cdot 10^{-3}$ $kg\cdot m^{-2}\cdot s^{-1}$	R_A	S_n
			T/K = 288.15			
0.005	157.785	0.0221	1.8544	1041.801	0.9562	0.0293
0.007	135.753	0.0155	1.8377	1053.266	0.9668	0.0736
0.010	114.721	0.0091	1.8218	1064.731	0.9763	0.1361
0.020	83.785	0.0023	1.8044	1076.196	0.9885	0.3281
0.030	69.657	0.00016	1.7884	1088.652	0.9986	0.5580
0.050	46.625	0.00009	1.7717	1100.108	1.0084	1.0102
0.100	25.593	0.00002	1.7552	1112.564	1.0183	2.1925
			T/K = 293.15			
0.005	183.711	0.0228	1.7725	1101.936	0.9692	0.0133
0.007	158.618	0.0186	1.7566	1112.650	0.9744	0.0404
0.010	132.525	0.0144	1.7407	1123.364	0.9792	0.0864
0.020	108.431	0.0104	1.7246	1134.081	0.9843	0.2277
0.030	85.338	0.0062	1.7089	1144.795	0.9908	0.3833
0.050	59.422	0.0025	1.6930	1155.509	0.9945	0.7354
0.100	32.156	0.00018	1.6771	1167.223	0.9983	1.6389
			T/K = 298.15			
0.005	177.726	0.0250	1.6708	1181.477	0.9642	0.0127
0.007	155.866	0.0185	1.6590	1190.615	0.9767	0.0395
0.010	134.013	0.0120	1.6472	1198.753	0.9892	0.0800
0.020	112.148	0.0056	1.6352	1208.893	1.0018	0.1982
0.030	92.065	0.0049	1.6234	1217.136	1.0146	0.3619
0.050	68.289	0.0043	1.6116	1228.619	1.0269	0.6962
0.100	47.989	0.0035	1.5926	1236.307	1.0392	1.6058
			T/K = 303.15			
0.005	187.839	0.0283	1.5903	1252.257	0.9755	0.0072
0.007	161.286	0.0251	1.5785	1263.262	0.9784	0.0348
0.010	134.733	0.0219	1.5678	1272.267	0.9817	0.0767
0.020	98.179	0.0190	1.5549	1282.273	0.9843	0.1846
0.030	73.276	0.0153	1.5413	1293.278	0.9873	0.3351
0.050	45.074	0.0120	1.5343	1301.832	0.9901	0.6554
0.100	8.5210	0.0089	1.5195	1312.288	0.9929	1.5003
			T/K = 308.15			
0.005	186.595	0.0239	1.5289	1313.936	0.9650	0.0010
0.007	160.525	0.0208	1.5210	1321.329	0.9666	0.0036
0.010	134.455	0.0177	1.5133	1328.722	0.9679	0.0078
0.020	108.385	0.0150	1.5052	1336.115	0.9692	0.0197
0.030	82.315	0.0119	1.4972	1343.508	0.9709	0.0360
0.050	56.245	0.0088	1.4896	1351.901	0.9724	0.7037
0.100	30.175	0.0059	1.4815	1357.294	0.9739	1.6670
			T/K = 313.15			
0.005	184.792	0.0204	1.4491	1395.622	0.9790	0.0032
0.007	163.168	0.0176	1.4386	1406.385	0.9800	0.0177
0.010	131.544	0.0150	1.4282	1417.148	0.9809	0.0463
0.020	86.289	0.0118	1.4178	1427.913	0.9820	0.1315
0.030	64.665	0.0091	1.4075	1438.674	0.9831	0.2493
0.050	33.041	0.0064	1.3980	1449.437	0.9841	0.5121
0.100	1.417	0.0036	1.3866	1460.200	0.9850	1.1630
			T/K = 318.15			
0.005	183.607	0.0188	1.3769	1476.697	0.9745	0.0016
0.007	159.076	0.0163	1.3699	1484.895	0.9751	0.0051
0.010	134.545	0.0140	1.3629	1493.093	0.9758	0.0093
0.020	109.834	0.0112	1.3557	1501.292	0.9764	0.0233
0.030	85.483	0.0088	1.3489	1509.489	0.9771	0.0422
0.050	60.952	0.0064	1.3419	1518.687	0.9778	0.0805
0.100	36.421	0.0038	1.3349	1524.885	0.9784	0.1860

Table 6. Viscosity A-Coefficient and B-Coefficient of Aqueous Glycylglycine and $MnCl_2$ Solutions at T = (288.15 to 318.15) K

T K	$A\cdot 10^{3/2}$ $m^{3/2}\cdot mol^{-1/2}$	$B\cdot 10^3$ $m^3\cdot mol^{-1}$	^{a}SD	$^bR^2$
		Glycylglycine		
288.15	−0.093	0.2156	0.0045	0.8743
293.15	−0.0132	0.1925	0.0036	0.8752
298.15	−0.0185	0.1746	0.0028	0.8759
303.15	−0.0020	0.1571	0.0022	0.8765
308.15	−0.0008	0.1384	0.0014	0.8772
313.15	0.0114	0.1093	0.0009	0.8753
318.15	0.0138	0.0868	0.0003	0.8758
		$MnCl_2$		
288.15	0.0051	0.8543	0.0047	0.8723
293.15	−0.0072	0.8321	0.0046	0.8726
298.15	−0.0086	0.8112	0.0044	0.8730
303.15	−0.0037	0.7943	0.0041	0.8734
308.15	−0.0045	0.7702	0.0038	0.8732
313.15	0.0138	0.7543	0.0037	0.8729
318.15	0.0152	0.7298	0.0034	0.8727

[a] SD = standard deviation for the fitting of eq 9. [b] R^2 = coefficients of determination.

along with their standard deviations are summarized in Table 6. The value of the viscosity A-coefficient of the Jones-Dole equation is a measure of long-range ion−ion interactions, while the B-coefficient is a manifestation of ion−solvent interactions. It is observed that the ultrasonic velocity values in aqueous dipeptide−electrolyte solutions increase with an increase in concentration in both cases, and this may be attributed to the overall increase of cohesion brought about by the solute−solute and solute−solvent interactions in the solutions.[17−19] The decrease in intermolecular free length causes an increase in ultrasonic velocity and vice versa.[20] The Mn^{2+} and Cl^- ions furnished by electrolytes interact electrostatically with $NH^+{}_3$ and COO^- groups of dipeptide zwitterions.[1,2] In addition, the water dipoles are strongly aligned to the cations/anions as well as to the dipeptide zwitterions by electrostatic forces. The added amount of dipeptide zwitterions may also occupy the cavities of water clusters which may lead to the formation of denser structure of the aqueous electrolyte solution. The rise in temperature and concentration causes the thermal rupture of the ice-like structure of water, which in turn enhances cohesion in the solutions. The density values reported show that there is an increase in the density with an increase in the concentration of $MnCl_2$ and glycylglycine in both the cases. This may be due to the molecular relaxation of $MnCl_2$ and glycylglycine in water. The refractive index also shows an increase in its values with an increase in concentration. It may be noted that such changes are due to the electronic perturbation of the individual molecules during mixing and therefore depends very much on the nature of the mixing molecules. The adiabatic compressibility values decrease with an increase in concentration. This trend of variation of β_{ad} is in consonance with the variation of ultrasonic velocity with concentration. This is somewhat similar to those observed for other inorganic salt solutions.[20,21] The smaller values of β_{ad} for aqueous electrolyte solutions may be attributed to cation−water dipole and anion−water dipole interactions in water, which ultimately may lead to an overall increase in cohesive forces in water.

The apparent molar volume decreases with an increase in concentration and for a solution of $MnCl_2$ and glycylglycine indicates predominance of a structure breaking or hydrophilic type of interaction with water[15,22] (Table 4 and Table 5). The decrease in the values of apparent molar volume indicates weak dipeptide−electrolyte interactions since the concentration change is very significant.[23] This was further confirmed by the Scaled particle theory model.[1] The best description for a, b, and c is obtained using the equation

$$\Phi_v^0 = a + b(T - 298) + c(T - 298)^2 \qquad (10)$$

and it is evident from the above equation that the coefficients can be considered as the value of the limiting molar volume from (288.15 to 318.15) K. Further discussion on the influence of temperature on the limiting molar volumes is

Table 7. Parameters of Equation 10 and the Volume Expansibility of (1) $MnCl_2$ and Glycylglycine (2) in Water (3) at T = (288.15 to 318.15) K

salt/dipeptide	a / $cm^3 \cdot mol^{-1}$	b / $cm^3 \cdot mol^1 \cdot deg^{-1}$	c / $cm^3 \cdot mol^1 \cdot deg^{-2}$	σ / $cm^3 \cdot mol^{-1}$	$\alpha_V^o \cdot 10^3$ / deg^{-1}
T/K = 288.15					
$MnCl_2 \cdot 4H_2O$	22.60 ± 0.3	−0.383 ± 0.005	−0.0022	0.055	−14.30 ± 0.2
glycylglycine	24.51 ± 0.4	−0.678 ± 0.002	−0.0030	0.076	−22.15 ± 0.3
T/K = 293.15					
$MnCl_2 \cdot 4H_2O$	21.73 ± 0.2	−0.374 ± 0.005	−0.0021	0.052	−15.50 ± 0.3
glycylglycine	24.07 ± 0.4	−0.583 ± 0.003	−0.0029	0.064	−24.26 ± 0.4
T/K = 298.15					
$MnCl_2 \cdot 4H_2O$	21.42 ± 0.4	−0.368 ± 0.003	−0.0020	0.047	−16.16 ± 0.4
glycylglycine	23.67 ± 0.2	−0.492 ± 0.004	−0.0028	0.052	−25.49 ± 0.2
T/K = 303.15					
$MnCl_2 \cdot 4H_2O$	22.36 ± 0.3	−0.415 ± 0.002	−0.0022	0.052	−14.43 ± 0.3
glycylglycine	24.38 ± 0.2	−0.541 ± 0.005	−0.0030	0.070	−23.06 ± 0.4
T/K = 308.15					
$MnCl_2 \cdot 4H_2O$	23.16 ± 0.3	−0.547 ± 0.002	−0.0024	0.057	−13.08 ± 0.3
glycylglycine	25.24 ± 0.2	−0.596 ± 0.003	−0.0031	0.085	−20.38 ± 0.5
T/K = 313.15					
$MnCl_2 \cdot 4H_2O$	23.92 ± 0.2	−0.589 ± 0.004	−0.0025	0.058	−12.76 ± 0.4
glycylglycine	25.87 ± 0.4	−0.610 ± 0.003	0.0032	0.087	−19.52 ± 0.3
T/K = 318.15					
$MnCl_2 \cdot 4H_2O$	24.41 ± 0.4	−0.634 ± 0.005	−0.0026	0.059	−11.26 ± 0.4
glycylglycine	26.65 ± 0.5	−0.623 ± 0.004	−0.0034	0.089	−18.37 ± 0.2

possible using the volume expansibility defined for the limiting apparent molar volumes, by eq 11.

$$\alpha_v^0 = (d\Phi_v^o/dT)_p/\Phi_v^o \qquad (11)$$

It is evident that the values of the temperature coefficient depend on temperature. Moreover, their absolute values increase slightly with increasing temperature. The respective values derived for 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K are listed in Table 7. This relation is generally well described for solutions of electrolytes by the empirical relationship

$$\Phi_v = \Phi_v^o + S_v c^{1/2} \qquad (12)$$

known as the Masson equation,[24] where Φ_V^o is the apparent molar volume of the salt at infinite dilution which is equal to the respective limiting partial molar volume; c is the molar concentration; and S_V is the slope of the linear plot. Moreover, the data obtained from eq 12 are from a temperature range of (288.15 to 318.15) K.

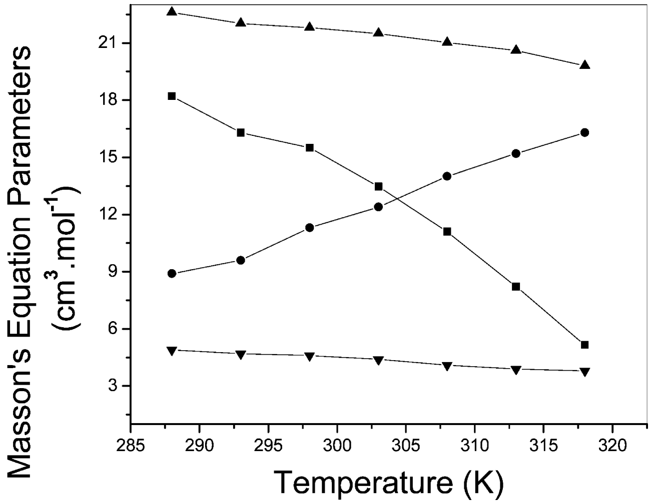

Figure 1. Variation of Masson's parameters with temperature for ■, Φ_V; ●, S_V; ▲, a_V; and ▼, b_V at a concentration of 0.25 M $MnCl_2$.

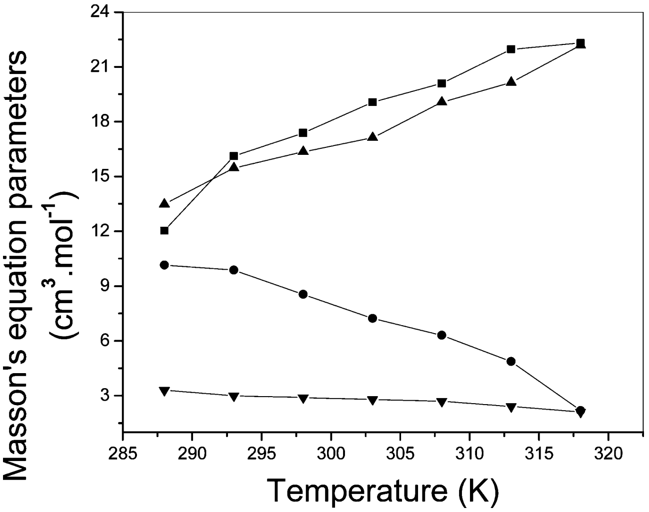

Figure 2. Variation of Masson's parameters with temperature for ■, Φ_V; ●, S_V; ▲, a_V; and ▼, b_V at a concentration of 0.020 M glycylglycine.

Figure 1 demonstrates the variation of apparent molar volume Φ_V, slope S_V, a_V, and b_V against temperature of an ionic solute $MnCl_2$ which depends strongly on the concentration. The plots for $MnCl_2$ are linear in the cases of a_V and b_V over the whole temperature range of (288.15 to 318.15) K and the linear relationship

$$\Phi_V^o = a_V + b_V c^{1/2} \qquad (13)$$

similar in its algebraic nature to the Masson equation (eq 12) is valid. Figure 2 explains the variations of Φ_V, S_V, a_V, and b_V of glycylglycine which may be due to the presence of amino groups in it. The coefficients of eq 13 are plotted in Figure 1 and Figure 2, respectively. The intercepts of the plots have no physical meaning; i.e., they cannot be considered as the limiting values of the apparent molar volumes of $MnCl_2$ and glycylglycine because they both consist of independent charge contributions.

The decrease in the apparent molar compressibility indicates strong interaction with the solvent to give a less compressible environment for the solute.[1,2] This may also be produced by electrostriction and structure breaking. The Kirkwood model[19] provides an interpretation for the apparent molar compressibility values. The electrostricted water has a less open structure as compared to bulk water and is therefore less compressible. The bulk water becomes like electrostricted water upon addition of $MnCl_2$, and this accounts for the apparent molar compressibilities of glycylglycine in water varying with the corresponding ones in mixed solvents. The decrease in intermolecular free length and adiabatic compressibility is due to the solvent−solute interaction, and there also exists a dipole−dipole interaction.[24−26] This indicates that the molecules are nearer in the system. Specific acoustic impedance is a quantity depending on the molecular packing of the system. The increase in the specific acoustic impedance suggests the presence of a strong interaction through hydrogen bonding.[25,26] This can also be attributed in the light of Eucken's theory[26] which states that there is a decrease in the number of aggregates of solvent molecules as the concentration and temperature increase. Consequently, water starts behaving like an unassociated liquid as the temperature rises. Further, the addition of a salt to a solvent enhances the process of breaking of aggregates of solvent molecules. Relative association is found to increase with an increase in concentration of $MnCl_2$ and glycylglycine in both cases while showing a regular trend in the breaking up of the solvent aggregates.[25] As the temperature of solution rises, the aggregates of solvent molecules break up themselves, resulting in increased solvent molecules. For all concentrations, the values of R_A increase with an increase in the temperature.[26−28] This indicates the decrease in degree of dissociation of aggregates of solvent molecules with an increase in temperature. The structure forming tendency of a solute can be determined by its solvation number. The solvation number increases with an increase in the concentration and temperature in cases one and two, and it is positive for all the concentrations. The positive solvation number indicates structure making tendency of the solute.

Conclusions

The study of the viscosities, ultrasonic velocities, densities, and refractive indices of glycylglycine and $MnCl_2$ in various concentrations and temperatures reveals the characteristics and structural properties prevalent in water. It also indicates the presence of interactions between solute, solvent, and substrate. These interactions also suggest the formation of hydrogen bonding in some cases and the extent to which the bonding accelerates the physical property. It is evident from the above study that the interactions of dipeptide and transition metal salt in water show tendencies of structure making of solute and solvent molecules together with solute−solute and solute−solvent interactions.

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