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Molecular Interactions between Glycylglycine and $Mn(COOCH_3)_2$ in Aqueous and Aqueous Ethanol Mixtures

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ABSTRACT: This paper reports the variations of different physical and thermodynamic properties of a mixture of dipeptide−metal salt in aqueous solutions as well as in aqueous ethanol mixtures. Specifically, the apparent molar volumes and apparent molar compressibilities of glycylglycine and $Mn(COOCH_3)_2$ have been determined at T = (288.15 to 318.15) K, and the resulting data have been used to estimate the limiting volume ($\Phi^0{}_V$) and compressibility ($\Phi^0{}_K$). Their concentration variations are examined to study the effect due to solute−solute and solvent−solvent interactions. The resulting data have been used to interpret the volume and compressibility contributions of the components in terms of H-bonding and dipole−dipole interactions. It was found that these interactions in aqueous solutions were measurably distinct in some cases from those in alcohols. An unusual behavior in the refractive index values indicates a measure of the relative extent of the polar domains.

■ INTRODUCTION

The hydration of biomolecules is an important factor in determining biological structure and function. Understanding the interactions among the solute, solvent, and substrate at the molecular scale may provide important information regarding the role of solvent in the folding mechanisms and structural biology of proteins. The presence of charged groups at the surface of proteins is believed to have an immobilizing or electrostrictive effect on the surrounding solvent environment. The electrostatic field of the proteins or peptide orients and orders the dipole moments of the surrounding water molecules.[1] The properties and behavior of amino acids in solution have always been a matter of interest mainly because amino acids are the basic structural building units of biomolecules. Elucidating and predicting the effect of solvent on the structure and reactivity of solutes have been challenging tasks for some time. These interactions are mainly those between the amino acid molecules and the solvent molecules. The effect of electrolytes on the structure and function of both proteins and nucleic acids has been widely studied in terms of their structure-making and structure-breaking properties.[2] Because of 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. Salt-induced electrostatic forces are known to play a vital role in modifying the amino acid structure by affecting the properties like solubility, denaturation, and activity of enzymes.[3] Thermodynamic and transport properties of amino acids in aqueous metal salt solutions provide information about solute−solvent and solute−solute interactions. The study of the viscous behavior of macromolecules in solution is important in understanding the mechanism of transport processes.[4] A microscopic description of the hydration of biological molecules, as well as the bulk water structure present around biomolecules at the atomic length scale, will necessarily increase the understanding of the role of water and other solvents have in the fundamental process of molecular stability and structural integrity.[5]

Previous studies on amino acids[6−11] have been restricted to water at a given temperature, but interesting results have been obtained when the studies have been extended to changes in temperature, pressure, and use of mixed solvent systems not only because they are 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 fluids are ultimately not pure water. Earlier studies on amino acids and biomolecules have been carried out in pure and mixed aqueous solvents.[12] However, such investigations in the presence of metal ions which play an important role in vital functions of living organisms are still scant. Transition metal ions play an important role in plant growth, lipid metabolism, and regulation of physiological systems. There have been various investigations on the partial molar volumes of amino acids in aqueous solutions since the volumetric studies by Zymantin and Chalikian.[13] However, to the best of our knowledge, studies on the interactions of glycylglycine with manganese acetate in aqueous and aqueous ethanol solutions at different temperatures and concentrations are still scant.[14] Accordingly, this paper presents a systematic study of the viscosities, ultrasonic velocities, densities, and refractive indices of glycylglycine and $Mn(COOCH_3)_2$ in aqueous solution and in aqueous ethanol mixtures as a function of concentration, solvent ratio, and temperature over wide ranges. We also report the acoustic properties based on the values obtained from the above-mentioned physical parameters.

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Table 1. Viscosity (η), Ultrasonic Velocity (u), Density (ρ), Refractive Index (n_D), and Adiabatic Compressibility (β_{ad}) for Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping $Mn(COOCH_3)_2$ Constant at 0.25 $mol \cdot kg^{-1}$

m	η	u	$\rho \cdot 10^{-3}$		$\beta_{ad} \cdot 10^{10}$
$mol \cdot kg^{-1}$	$m \cdot Pa \cdot s$	$m \cdot s^{-1}$	$kg \cdot m^{-3}$	n_D	$m^2 \cdot N^{-1}$
		T/K = 288.15			
0.000	0.99	1545.221	0.9999	1.3352	4.3849
0.005	1.09	1549.464	1.0046	1.3358	4.2290
0.007	1.18	1554.186	1.0094	1.3365	4.0731
0.010	1.30	1560.778	1.0140	1.3370	3.9172
0.020	1.42	1567.432	1.0188	1.3376	3.7617
0.030	1.53	1575.483	1.0225	1.3383	3.6054
0.050	1.66	1582.050	1.0273	1.3390	3.4495
0.100	1.80	1594.617	1.0313	1.3398	3.2936
		T/K = 293.15			
0.000	0.92	1640.258	0.9945	1.3342	3.7374
0.005	1.01	1645.764	0.9958	1.3347	3.7073
0.007	1.10	1651.283	0.9972	1.3353	3.6772
0.010	1.19	1656.835	0.9985	1.3358	3.6471
0.020	1.29	1661.200	0.9999	1.3364	3.6168
0.030	1.40	1667.947	1.0013	1.3369	3.5869
0.050	1.51	1673.149	1.0026	1.3375	3.5568
0.100	1.64	1679.561	1.0040	1.3383	3.5267
		T/K = 298.15			
0.000	0.86	1700.184	0.9910	1.3328	3.4908
0.005	0.93	1707.377	0.9918	1.3333	3.4577
0.007	1.00	1715.429	0.9927	1.3338	3.4246
0.010	1.08	1722.833	0.9936	1.3343	3.3915
0.020	1.17	1729.825	0.9945	1.3348	3.3584
0.030	1.26	1737.354	0.9954	1.3354	3.3253
0.050	1.37	1743.786	0.9965	1.3360	3.2922
0.100	1.49	1752.062	0.9976	1.3367	3.2591
		T/K = 303.15			
0.000	0.77	1762.857	0.9889	1.331	3.2539
0.005	0.85	1768.436	0.9895	1.3316	3.2297
0.007	0.93	1774.523	0.9901	1.3322	3.2055
0.010	1.01	1780.314	0.9907	1.3328	3.1813
0.020	1.09	1786.351	0.9913	1.3334	3.1570
0.030	1.16	1794.167	0.9920	1.3340	3.1329
0.050	1.25	1802.279	0.9927	1.3348	3.1087
0.100	1.34	1810.680	0.9936	1.3356	3.0845
		T/K = 308.15			
0.000	0.70	1815.267	0.9853	1.3296	3.0808
0.005	0.76	1820.386	0.9859	1.3301	3.0604
0.007	0.83	1825.174	0.9865	1.3306	3.0408
0.010	0.89	1830.643	0.9871	1.3311	3.0212
0.020	0.97	1835.748	0.9877	1.3316	3.0016
0.030	1.04	1840.826	0.9881	1.3322	2.9820
0.050	1.12	1846.091	0.9889	1.3328	2.9624
0.100	1.21	1853.104	0.9896	1.3335	2.9428
		T/K = 313.15			
0.000	0.62	1910.259	0.9836	1.3279	2.7861
0.005	0.68	1916.764	0.9841	1.3285	2.7338
0.007	0.74	1922.536	0.9846	1.3291	2.6815
0.010	0.80	1928.273	0.9851	1.3296	2.6292
0.020	0.87	1935.837	0.9856	1.3303	2.5769
0.030	0.94	1942.142	0.9862	1.3309	2.5246
0.050	1.01	1950.371	0.9868	1.3316	2.4723
0.100	1.08	1959.885	0.9874	1.3324	2.4207
		T/K = 318.15			
0.000	0.57	2005.314	0.9809	1.3258	2.4853
0.005	0.62	2011.483	0.9817	1.3264	2.4676
0.007	0.68	2017.789	0.9825	1.3270	2.4499
0.010	0.74	2023.568	0.9833	1.3276	2.4322
0.020	0.80	2030.646	0.9841	1.3282	2.4142
0.030	0.86	2036.057	0.9849	1.3289	2.3968
0.050	0.94	2044.175	0.9857	1.3295	2.3791
0.100	1.00	2052.704	0.9866	1.3304	2.3614

EXPERIMENTAL SECTION

Materials. Glycylglycine of 99 % purity and manganese acetate dihydrate of 99 + % purity used in our studies were purchased from Sigma-Aldrich, Germany. Commercially available glycylglycine was used without further purification. Manganese acetate dihydrate 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. Ethanol of 99.9 % analytical grade purity used after redistillation to ensure maximum purity was purchased from Changshu Yanguan Chemicals, China. The solutions were prepared on a weight basis by using a Mettler balance having a precision of ± 0.01 mg. The temperature of water was controlled within ± 0.01 K using a thermostat. In the first case, the concentration of metal salt was kept constant at (0.25, 0.50, and 1) $mol \cdot kg^{-1}$ with the concentration of glycylglycine being varied. In the second case, the concentration of glycylglycine was kept constant at 0.020 $mol \cdot kg^{-1}$, and the concentration of metal salt was varied. In the third case, the concentrations of metal salt and glycylglycine were kept constant at (0.25 and 0.020) $mol \cdot kg^{-1}$, respectively, and the water−ethanol composition was varied. To prevent formation of air bubbles, all solutions were preheated in sealed Eppendorf tubes to 5 °C above the measurement temperature before filling the ultrasonic and densimetric cells.

Methods. Viscosities were measured using a Brookfield DV-III ultra programmable rheometer (Brookfield Engineering Laboratories, Inc., USA) which was calibrated using double-distilled water and ethanol, and their uncertainty was found to be ±0.5 % for both solutions. The ultrasonic velocities of pure components and their mixtures were measured by a variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (model 83). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocity

Table 2. Viscosity (η), Ultrasonic Velocity (u), Density (ρ), Refractive Index (n_D), and Adiabatic Compressibility (β_{ad}) for Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping $Mn(COOCH_3)_2$ Constant at 0.50 $mol \cdot kg^{-1}$

m / $mol \cdot kg^{-1}$	η / $m \cdot Pa \cdot s$	u / $m \cdot s^{-1}$	$\rho \cdot 10^{-3}$ / $kg \cdot m^{-3}$	n_D	$\beta_{ad} \cdot 10^{10}$ / $m^2 \cdot N^{-1}$
		T/K = 288.15			
0.000	1.20	1720.14	1.0053	1.3361	3.3618
0.005	1.28	1726.26	1.0058	1.3370	3.3191
0.007	1.36	1732.05	1.0064	1.3379	3.2764
0.010	1.45	1739.43	1.0071	1.3388	3.2337
0.020	1.55	1746.57	1.0078	1.3400	3.1910
0.030	1.66	1755.76	1.0087	1.3413	3.1483
0.050	1.78	1765.19	1.0094	1.3427	3.1056
0.100	1.92	1777.82	1.0105	1.3442	3.0628
		T/K = 293.15			
0.000	1.11	1810.35	1.0042	1.3348	3.0384
0.005	1.22	1817.41	1.0048	1.3356	3.0077
0.007	1.29	1824.56	1.0055	1.3364	2.9770
0.010	1.38	1832.38	1.0063	1.3372	2.9473
0.020	1.47	1840.16	1.0071	1.3381	2.9164
0.030	1.58	1849.27	1.0080	1.3390	2.8856
0.050	1.70	1860.13	1.0089	1.3399	2.8549
0.100	1.83	1872.68	1.0101	1.3414	2.8229
		T/K = 298.15			
0.000	1.02	1920.33	1.0034	1.3335	2.7025
0.005	1.16	1926.14	1.0041	1.3342	2.6846
0.007	1.21	1933.05	1.0049	1.3349	2.6605
0.010	1.29	1940.58	1.0057	1.3357	2.6364
0.020	1.37	1947.26	1.0066	1.3366	2.6123
0.030	1.46	1955.88	1.0074	1.3375	2.5882
0.050	1.57	1963.96	1.0082	1.3384	2.5642
0.100	1.70	1975.72	1.0093	1.3395	2.5397
		T/K = 303.15			
0.000	0.90	2005.18	1.0024	1.3321	2.4816
0.005	0.99	2013.26	1.0030	1.3328	2.4583
0.007	1.08	2022.07	1.0037	1.3333	2.4350
0.010	1.17	2031.64	1.0043	1.3338	2.4117
0.020	1.24	2040.53	1.0050	1.3344	2.3884
0.030	1.31	2049.85	1.0058	1.3351	2.3651
0.050	1.39	2058.67	1.0067	1.3358	2.3479
0.100	1.50	2070.14	1.0077	1.3369	2.3228
		T/K = 308.15			
0.000	0.81	2110.04	1.0010	1.3308	2.2480
0.005	0.90	2117.36	1.0019	1.3316	2.2281
0.007	0.98	2124.58	1.0027	1.3320	2.2082
0.010	1.06	2132.75	1.0035	1.3324	2.1883
0.020	1.14	2140.96	1.0044	1.3328	2.1684
0.030	1.21	2149.69	1.0053	1.3333	2.1485
0.050	1.29	2158.44	1.0061	1.3339	2.1286
0.100	1.40	2171.68	1.0069	1.3348	2.1085
		T/K = 313.15			
0.000	0.72	2235.08	0.9998	1.3295	2.0021
0.005	0.80	2242.16	1.0004	1.3301	1.9893
0.007	0.88	2247.27	1.0010	1.3305	1.9765
0.010	0.96	2253.63	1.0017	1.3309	1.9637
0.020	1.04	2259.57	1.0025	1.3314	1.9509
0.030	1.12	2266.18	1.0033	1.3320	1.9381
0.050	1.19	2273.85	1.0044	1.3326	1.9253
0.100	1.26	2282.94	1.0055	1.3333	1.9125
		T/K = 318.15			
0.000	0.66	2330.15	0.9986	1.3280	1.8443
0.005	0.74	2336.27	0.9995	1.3289	1.8331
0.007	0.82	2342.81	1.0003	1.3293	1.8219
0.010	0.90	2348.76	1.0011	1.3298	1.8107
0.020	0.98	2354.39	1.0019	1.3304	1.7995
0.030	1.04	2361.67	1.0027	1.3310	1.7883
0.050	1.12	2368.42	1.0035	1.3316	1.7771
0.100	1.18	2376.58	1.0043	1.3324	1.7657

were taken at a fixed frequency of 2 MHz. The capacity of the measurement cell was 7 mL. The calibration of the ultrasonic interferometer was done by measuring the velocity in AR grade benzene and carbon tetrachloride. The maximum estimated error in the ultrasonic velocity measurements was found to be ± 0.08 %. The temperature was controlled by circulating water around the liquid cell from a thermostatically controlled adequately stirred water bath (precision ± 0.1 °C). Densities were measured 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 measured using a (Mettler Toledo) Refracto 30PX and 30Gs digital refractometer, and its uncertainty was found to be ± 0.0005 %. The densitometer and refractometer were calibrated using double-distilled water. The sample and reference resonator cells with minimum volumes of 0.5 cm^3 were thermostatted with a precision of ± 0.01 K, and a previously described differential technique was employed for all measurements.[15] Theoretical analyses[16] have shown that, for the type of ultrasonic cells used in our studies, the accuracy of the sound velocity measurements is about $\pm 10^{-4}$ % at a frequency of 2 MHz. The physical parameters for solutions of glycylglycine−$Mn(COOCH_3)_2$ were measured at temperatures of (288.15 to 318.15) K in all three cases. The measured viscosity and density values, and their uncertainties, of (0.5002, 1.0006, and 3.0009) M and (0.5007, 0.9999, and 2.0001) M aqueous solutions of glycylglycine in KCl agree well with literature values.[17] On the basis of the above-mentioned physical parameters, the acoustic 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 an average of all of the three trials.

Table 3. Viscosity (η), Ultrasonic Velocity (u), Density (ρ), Refractive Index (n_D), and Adiabatic Compressibility (β_{ad}) for Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping $Mn(COOCH_3)_2$ Constant at 1.0 mol·kg^{-1}

m / mol·kg^{-1}	η / m·Pa·s	u / m·s^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	n_D	$\beta_{ad}\cdot10^{10}$ / m^2·N^{-1}
		T/K = 288.15			
0.000	1.32	1826.23	1.0087	1.3412	2.9725
0.005	1.41	1831.48	1.0092	1.3417	2.9505
0.007	1.50	1836.67	1.0097	1.3424	2.9285
0.010	1.59	1842.84	1.0103	1.3432	2.9065
0.020	1.68	1848.15	1.0109	1.3438	2.8845
0.030	1.77	1855.08	1.0115	1.3445	2.8625
0.050	1.87	1862.93	1.0121	1.3452	2.8405
0.100	2.00	1871.59	1.0129	1.3460	2.8184
		T/K = 293.15			
0.000	1.25	1905.48	1.0075	1.3402	2.7336
0.005	1.34	1911.25	1.0081	1.3407	2.7145
0.007	1.40	1916.32	1.0087	1.3413	2.6954
0.010	1.46	1922.49	1.0093	1.3419	2.6763
0.020	1.53	1928.56	1.0099	1.3423	2.6572
0.030	1.60	1934.16	1.0105	1.3430	2.6381
0.050	1.67	1941.04	1.0112	1.3436	2.6190
0.100	1.76	1949.73	1.0120	1.3445	2.5993
		T/K = 298.15			
0.000	1.16	2010.26	1.0062	1.3387	2.4592
0.005	1.20	2015.37	1.0067	1.3391	2.4435
0.007	1.25	2020.13	1.0070	1.3395	2.4278
0.010	1.30	2026.81	1.0073	1.3399	2.4121
0.020	1.36	2032.79	1.0076	1.3404	2.3964
0.030	1.41	2038.44	1.0079	1.3409	2.3807
0.050	1.47	2045.57	1.0084	1.3413	2.3650
0.100	1.53	2053.95	1.0090	1.3420	2.3492
		T/K = 303.15			
0.000	1.10	2115.38	1.0050	1.3362	2.1418
0.005	1.14	2119.46	1.0053	1.3365	2.1404
0.007	1.18	2123.32	1.0056	1.3369	2.1390
0.010	1.23	2127.54	1.0060	1.3374	2.1376
0.020	1.28	2132.07	1.0064	1.3379	2.1362
0.030	1.34	2136.88	1.0068	1.3385	2.1348
0.050	1.40	2141.51	1.0073	1.3391	2.1334
0.100	1.46	2147.26	1.0078	1.3397	2.1320
		T/K = 308.15			
0.000	1.01	2200.57	1.0034	1.3347	2.0580
0.005	1.04	2205.18	1.0036	1.3351	2.0471
0.007	1.07	2210.36	1.0038	1.3354	2.0359
0.010	1.10	2216.81	1.0041	1.3358	2.0247
0.020	1.15	2222.45	1.0045	1.3363	2.0135
0.030	1.20	2228.04	1.0049	1.3368	2.0023
0.050	1.25	2234.69	1.0054	1.3374	1.9911
0.100	1.31	2241.86	1.0059	1.3381	1.9780

Table 3. Continued

m / mol·kg^{-1}	η / m·Pa·s	u / m·s^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	n_D	$\beta_{ad}\cdot10^{10}$ / m^2·N^{-1}
		T/K = 313.15			
0.000	0.93	2310.32	1.0020	1.3331	1.8697
0.005	0.97	2313.65	1.0023	1.3335	1.8622
0.007	1.01	2316.57	1.0026	1.3339	1.8547
0.010	1.05	2319.04	1.0029	1.3344	1.8472
0.020	1.09	2324.18	1.0034	1.3349	1.8397
0.030	1.14	2329.85	1.0038	1.3354	1.8322
0.050	1.19	2334.58	1.0043	1.3360	1.8247
0.100	1.24	2340.23	1.0050	1.3366	1.8168
		T/K = 318.15			
0.000	0.82	2398.31	1.0008	1.3317	1.7371
0.005	0.85	2405.27	1.0011	1.3321	1.7264
0.007	0.89	2412.64	1.0014	1.3325	1.7157
0.010	0.93	2419.08	1.0018	1.3329	1.705
0.020	0.98	2426.57	1.0022	1.3334	1.6943
0.030	1.03	2433.83	1.0026	1.3339	1.6836
0.050	1.09	2439.16	1.003	1.3344	1.6721
0.100	1.16	2448.75	1.0036	1.335	1.6616

Results. The experimental data of viscosity (η), ultrasonic velocity (u), density (ρ), refractive index (n_D), and adiabatic compressibility (β_{ad}) of a mixture of glycylglycine and manganese acetate in an aqueous solution at temperatures of (288.15 to 318.15) K for the first (metal salt constant) and second (glycylglycine constant) cases are given in Tables 1, 2, 3, and 4, respectively. The variations of the above-mentioned physical parameters for glycylglycine and manganese acetate in aqueous ethanol mixtures are shown in Figures 1, 2, 3, 4, and 5, respectively. The adiabatic compressibility (β_{ad}) was obtained using the Laplace equation $\beta_{ad} = 1/(u^2\rho)$. The uncertainties in β_{ad} values were obtained using

$$\Delta\beta_{ad} = \beta_{ad}[(2\Delta u/u) + (\Delta\rho/\rho)] \quad (1)$$

and were found to be of the order of $\pm$ 0.05·10^{-11} Pa^{-1} for all cases. Various acoustical parameters such as 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) for the first (metal salt constant) and second (glycylglycine constant) cases are given in Tables 5, 6, 7, and 8, respectively, and were calculated using the following equations:

$$\Phi_V = (M_2/\rho) + [n_1M_1(\rho_0 - \rho)/m\rho\rho_0] \quad (2)$$

$$\Phi_K = (M_2\beta_{ad}/\rho) + [n_1M_1(\beta_{ad}\rho_0 - \beta^0_{ad}\rho)/m\rho\rho_0] \quad (3)$$

where n_1 is the number of moles of solute in 1 kg, M_1 is molar mass of the solute, M_2 is the molar mass of water, and m is the molality, while β^0_{ad}, ρ_0, β_{ad}, and ρ are the adiabatic compressibility and density of solute and solvent, respectively. The errors in Φ_V and Φ_K values were obtained using

$$\Delta\Phi_V = -(n_1M_1/m^2)(1/\rho - 1/\rho_0)\delta m + [-(n_1M_1/c)(1/\rho)\delta\rho] \quad (4)$$

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Table 4. Viscosity (η), Ultrasonic Velocity (u), Density (ρ), Refractive Index (n_D), and Adiabatic Compressibility (β_{ad}) for Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping Glycylglycine Constant at 0.020 $mol \cdot kg^{-1}$

m / $mol \cdot kg^{-1}$	η / $m \cdot Pa \cdot s$	u / $m \cdot s^{-1}$	$\rho \cdot 10^{-3}$ / $kg \cdot m^{-3}$	n_D	$\beta_{ad} \cdot 10^{10}$ / $m^2 \cdot N^{-1}$
		T/K = 288.15			
0.000	1.00	1560.28	0.9967	1.3348	4.1212
0.005	1.07	1565.72	0.9977	1.3351	4.0612
0.010	1.12	1571.54	0.9988	1.3355	4.0010
0.030	1.16	1577.06	0.9999	1.3359	3.9412
0.050	1.19	1583.18	1.0010	1.3364	3.8814
0.100	1.25	1590.25	1.0021	1.3370	3.8215
0.250	1.32	1597.43	1.0032	1.3376	3.7610
0.500	1.40	1606.51	1.0044	1.3382	3.7007
		T/K = 293.15			
0.000	0.89	1630.42	0.9935	1.3335	3.7864
0.005	0.95	1634.32	0.9944	1.3338	3.7584
0.010	1.01	1637.87	0.9954	1.3342	3.7306
0.030	1.05	1642.16	0.9963	1.3346	3.7021
0.050	1.10	1648.05	0.9974	1.3352	3.6738
0.100	1.16	1654.63	0.9986	1.3358	3.6450
0.250	1.23	1661.20	0.9999	1.3364	3.6168
0.500	1.31	1668.56	1.0013	1.3371	3.5871
		T/K = 298.15			
0.000	0.81	1689.44	0.9907	1.3321	3.5364
0.005	0.83	1695.26	0.9912	1.3324	3.5067
0.010	0.89	1702.58	0.9918	1.3327	3.4770
0.030	0.96	1708.13	0.9925	1.3331	3.4474
0.050	1.03	1714.07	0.9932	1.3336	3.4177
0.100	1.11	1722.66	0.9939	1.3342	3.3881
0.250	1.17	1729.82	0.9945	1.3348	3.3584
0.500	1.24	1737.38	0.9952	1.3354	3.3288
		T/K = 303.15			
0.000	0.72	1756.12	0.9882	1.3306	3.2813
0.005	0.74	1760.31	0.9884	1.3309	3.2605
0.010	0.79	1764.27	0.9888	1.3312	3.2398
0.030	0.86	1769.08	0.9893	1.3317	3.2191
0.050	0.93	1775.53	0.9898	1.3322	3.1984
0.100	1.02	1780.49	0.9906	1.3328	3.1777
0.250	1.09	1786.35	0.9913	1.3333	3.1570
0.500	1.17	1792.88	0.9919	1.3339	3.1363
		T/K = 308.15			
0.000	0.64	1810.91	0.9848	1.3290	3.0964
0.005	0.66	1813.47	0.9851	1.3293	3.0806
0.010	0.69	1817.35	0.9854	1.3296	3.0648
0.030	0.75	1820.56	0.9858	1.3300	3.0490
0.050	0.81	1824.06	0.9864	1.3304	3.0332
0.100	0.89	1829.13	0.9871	1.3310	3.0174
0.250	0.97	1835.74	0.9877	1.3316	3.0016
0.500	1.05	1840.86	0.9883	1.3323	2.9858
		T/K = 313.15			
0.000	0.59	1865.32	0.9826	1.3274	2.9249
0.005	0.62	1868.15	0.9829	1.3278	2.8668
0.010	0.65	1871.44	0.9833	1.3282	2.8089
0.030	0.69	1875.08	0.9838	1.3286	2.7506
0.050	0.74	1879.59	0.9843	1.3291	2.6924
0.100	0.81	1885.62	0.9850	1.3297	2.6347
0.250	0.87	1890.83	0.9856	1.3303	2.5769
0.500	0.94	1896.57	0.9862	1.3309	2.5184
		T/K = 318.15			
0.000	0.51	1920.43	0.9808	1.3250	2.4976
0.005	0.53	1924.15	0.9812	1.3253	2.4837
0.010	0.57	1928.37	0.9816	1.3258	2.4698
0.030	0.61	1933.88	0.9821	1.3263	2.4559
0.050	0.67	1939.56	0.9826	1.3269	2.4420
0.100	0.74	1944.27	0.9834	1.3276	2.4281
0.250	0.80	1950.64	0.9841	1.3282	2.4142
0.500	0.88	1956.76	0.9849	1.3288	2.4001

and

$$(\Delta\Phi_K)^2 = [-(\beta_{ad}/\rho^2)(n_1M_1/m + M_2)]^2(\delta\rho)^2 + [-(1/\rho)(n_1M_1/m + M_2)]^2(\Delta\beta_{ad})^2 \quad (5)$$

and found to be of the order of $\pm$ 0.5$\cdot 10^{-3}$ $cm^3 \cdot mol^{-1}$ for Φ_V and $\pm$ 5 $mm^3 \cdot MPa^{-1} \cdot mol^{-1}$ for Φ_K, and c is the electrolyte molality ($mol \cdot kg^{-1}$). The data of Φ_V and Φ_K for aqueous solutions in case one (metal salt constant) and two (glycylglycine constant) are given in the Tables 5 to 8. The variations of apparent molar volume and apparent molar compressibility in aqueous ethanol mixtures are shown in Figures 6 and 7, respectively. For dilute solutions, Φ_V can be represented in the form:

$$\Phi_V = \Phi_V^0 + S_v c \quad (6)$$

where $\Phi^0{}_V$ is the partial molar volume of the water at infinite dilution and S_v is a constant. The density of solution is given by

$$\rho = \rho_0 + Ac + Bc^2 \quad (7)$$

where $A = (M_2 - \rho_0\Phi^0{}_V)$ and $B = -\rho_0 S_V$. Values of A, B, $\Phi^0{}_V$, and S_V obtained from a least-squares analysis of each set of results are listed in Table 9. An analogous approach was adopted[18] for the apparent molar compressibility data to derive equations in the following way:

$$\Phi_K = (\beta - \beta_0)/c + \beta_0\Phi_V^0 + \beta_0 S_v c \quad (8)$$

and

$$\Phi_K = \Phi_K^0 + S_K c \quad (9)$$

Since the data of apparent molar compressibility of water (Φ_{Ks}) is obtained from adiabatic compressibility of solution (β_s), it can

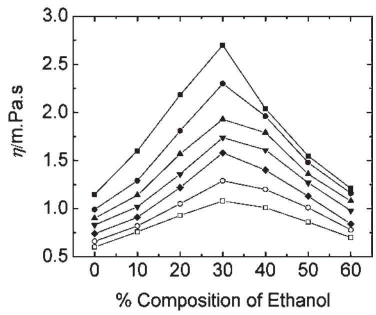

Figure 1. Variation of viscosity (η) as a function of composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

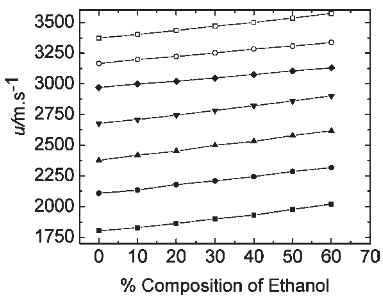

Figure 2. Ultrasonic velocity (u) variation with composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

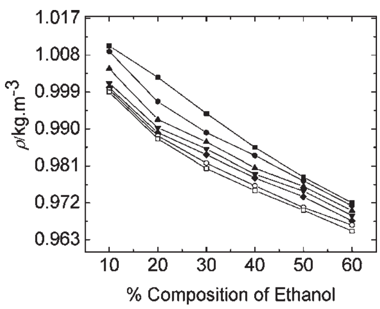

Figure 3. Variation of density (ρ) as a function of composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

be written as

$$\beta_s = \beta_0 + A'c + B'c^2 \tag{10}$$

where $A' = (\Phi_K^0 + \beta_0 \Phi_V^0)$ and $B' = (S_K - \beta_0 S_V)$

The least-squares fitting method was used to obtain the A' and B' values, although there is a variation of the data of Φ_K using eq 8. The data for concentration (S_K) based on eq 10 is summarized along with A' and B' values in Table 9.

The intermolecular free length (L_f), specific acoustic impedance (Z), relative association (R_A), and solvation number (S_n) are determined using the following equations:

$$L_f = K \cdot (\beta_{ad})^{1/2} \tag{11}$$

$$Z = u\rho \tag{12}$$

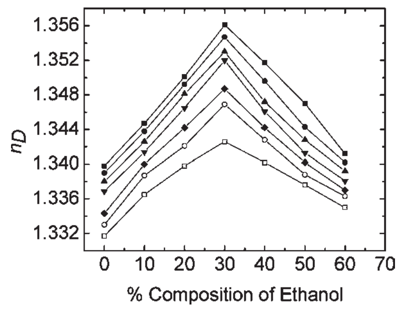

Figure 4. Refractive index (n_D) variation with composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

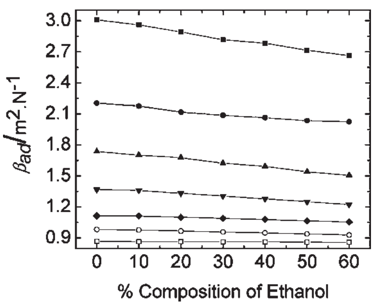

Figure 5. Variation of adiabatic compressibility (β_{ad}) with composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

$$R_A = (\rho/\rho_0)(u_0/u)^{1/3} \tag{13}$$

$$S_n = (n_1/n_2)(1 - \beta_{ad}/\beta_{ad}^0) \tag{14}$$

where K is the Jacobson constant,[18] ρ and ρ_0 and u and u_0 are the densities and ultrasonic velocities of solute (dipeptide and metal salt) and solvent, respectively, n_1 and n_2 and β_{ad} and $\beta^0{}_{ad}$ are the number of moles of solvent and solute in solution and compressibility of the solution and that of pure water, respectively. The variations of L_f, Z, R_A, and S_n of glycylglycine and manganese acetate in aqueous ethanol mixtures are shown in Figures 8, 9, 10, and 11.

■ DISCUSSION

It is observed from the Tables 1 to 4 that the viscosity values increase with an increase in concentration and decrease with an increase in temperature. The relative viscosity, $\eta_r = \eta/\eta_0$ (where η_0 is the viscosity of pure water) of the investigated systems was analyzed by the Kaminsky relation[19]

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2 \tag{15}$$

which is valid for electrolyte solutions. In eq 15, c is the electrolyte molality ($mol \cdot kg^{-1}$) calculated from the relation $c = md/(1 + mM_2 \cdot 10^{-3})$ where d is the density of solution[20] and M_2 the molecular weight of the solute in $g \cdot mol^{-1}$. The A-coefficient depends on the interionic forces, and the B-coefficient takes into account the ion−solvent interaction; the D-coefficient includes all solute−solvent and solute−solute structural interactions that are not accounted for by the $Ac^{1/2}$ and Bc terms at different concentrations. The A-coefficient is a measure of the long-range ion−ion interaction (Coulombic forces) and can be

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 Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping $Mn(COOCH_3)_2$ Constant at 0.25 mol·kg^{-1}

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
mol·kg^{-1}	m^3·mol^{-1}	mm^{-3}·MPa^{-1}·mol^{-1}	A^0	kg·m^{-2}·s^{-1}	R_A	S_n
		T/K = 288.15				
0.005	19.32	19.04 ± 3	1.2561	1547.076	0.9884	0.1045
0.007	18.10	18.89 ± 4	1.2329	1584.364	0.9993	0.1067
0.010	17.88	18.74 ± 2	1.2097	1621.465	1.0082	0.1089
0.020	15.65	18.58 ± 6	1.1863	1659.238	1.0184	0.1112
0.030	14.44	18.44 ± 2	1.1633	1695.158	1.0280	0.1136
0.050	13.22	18.29 ± 4	1.4012	1732.413	1.0379	0.1160
0.100	11.14	18.14 ± 3	1.1169	1769.733	1.0477	0.1185
		T/K = 293.15				
0.005	19.41	18.94 ± 1	1.1895	1639.067	0.9778	0.1065
0.007	18.67	18.76 ± 5	1.1843	1646.906	0.9793	0.1088
0.010	16.77	18.62 ± 3	1.1791	1654.745	0.9808	0.1111
0.020	15.24	18.46 ± 6	1.1739	1662.584	0.9823	0.1135
0.030	13.86	18.34 ± 7	1.1687	1670.423	0.9839	0.1158
0.050	12.25	18.26 ± 2	1.1635	1678.262	0.9855	0.1184
0.100	11.32	18.06 ± 4	1.1583	1686.101	0.9870	0.1208
		T/K = 298.15				
0.005	19.83	18.78 ± 5	1.1621	1693.784	0.9754	0.1098
0.007	17.58	18.64 ± 2	1.1565	1702.69	0.9765	0.1122
0.010	16.33	18.50 ± 6	1.1509	1711.596	0.9776	0.1146
0.020	14.05	18.34 ± 4	1.1451	1720.502	0.9788	0.1170
0.030	13.83	18.21 ± 2	1.1397	1729.408	0.9799	0.1195
0.050	12.58	18.08 ± 3	1.1341	1738.314	0.9809	0.1219
0.100	10.33	17.94 ± 4	1.1285	1747.22	0.9821	0.1244
		T/K = 303.15				
0.005	18.26	18.62 ± 2	1.1340	1750.414	0.9753	0.1124
0.007	17.71	18.48 ± 6	1.1298	1757.546	0.9764	0.1148
0.010	16.15	18.34 ± 3	1.1256	1764.678	0.9768	0.1163
0.020	14.58	18.26 ± 4	1.1212	1771.812	0.9776	0.1188
0.030	13.02	18.06 ± 7	1.1172	1778.642	0.9784	0.1214
0.050	11.43	17.92 ± 2	1.1130	1786.074	0.9792	0.1239
0.100	10.86	17.78 ± 1	1.1088	1793.206	0.9826	0.1265
		T/K = 308.15				
0.005	18.23	18.46 ± 4	1.1118	1794.721	0.9739	0.1147
0.007	17.45	18.32 ± 2	1.1057	1800.867	0.9746	0.1173
0.010	15.36	18.18 ± 6	1.0996	1807.013	0.9754	0.1199
0.020	14.85	18.04 ± 1	1.0932	1813.160	0.9761	0.1225
0.030	12.16	17.90 ± 3	1.0873	1819.305	0.9769	0.1250
0.050	11.83	17.76 ± 7	1.0814	1825.451	0.9777	0.1276
0.100	10.07	17.62 ± 5	1.0752	1831.597	0.9786	0.1302
		T/K = 313.15				
0.005	18.25	18.36 ± 7	1.0594	1896.247	0.9746	0.1165
0.007	16.36	18.17 ± 2	1.0472	1914.513	0.9748	0.1188
0.010	15.22	17.98 ± 6	1.0350	1932.463	0.9751	0.1214
0.020	14.65	17.80 ± 4	1.0225	1951.487	0.9754	0.1238
0.030	12.74	17.60 ± 3	1.0106	1968.292	0.9757	0.1265
0.050	11.38	17.41 ± 5	0.9984	1986.754	0.976	0.1291
0.100	98.16	17.22 ± 2	0.9862	2004.016	0.9764	0.1316

Table 5. Continued

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
mol·kg^{-1}	m^3·mol^{-1}	mm^{-3}·MPa^{-1}·mol^{-1}	A^0	kg·m^{-2}·s^{-1}	R_A	S_n
			T/K = 318.15			
0.005	17.50	18.16 ± 2	1.0144	1994.551	0.9424	0.1188
0.007	16.92	17.97 ± 4	1.0132	2002.476	0.9728	0.1213
0.010	15.42	17.75 ± 6	1.0063	2010.407	0.9732	0.1237
0.020	13.82	17.54 ± 5	1.0021	2018.328	0.9736	0.1262
0.030	12.34	17.34 ± 7	0.9981	2026.256	0.9741	0.1286
0.050	10.75	17.16 ± 3	0.9942	2034.175	0.9746	0.1311
0.100	96.24	16.93 ± 6	0.9901	2042.103	0.9752	0.1335

Table 6. 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 Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping $Mn(COOCH_3)_2$ Constant at 0.50 mol·kg^{-1}

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
mol·kg^{-1}	m^3·mol^{-1}	mm^{-3}·MPa^{-1}·mol^{-1}	A^0	kg·m^{-2}·s^{-1}	R_A	S_n
			T/K = 288.15			
0.005	21.15	24.85 ± 2	1.1130	1744.568	0.9877	0.1256
0.007	21.21	24.44 ± 3	1.1058	1759.874	0.9920	0.1325
0.010	20.27	24.00 ± 4	1.0986	1775.182	0.9963	0.1380
0.020	19.33	23.59 ± 6	1.0914	1790.495	1.0006	0.1455
0.030	18.39	23.17 ± 2	1.0842	1805.807	1.0049	0.1520
0.050	18.45	22.75 ± 4	1.0770	1821.116	1.0092	0.1594
0.100	17.50	22.38 ± 1	1.0693	1836.480	1.0136	0.1669
			T/K = 293.15			
0.005	21.23	24.12 ± 4	1.0717	1826.133	0.9883	0.1299
0.007	20.11	23.81 ± 5	1.0662	1836.966	0.9892	0.1375
0.010	20.99	23.50 ± 3	1.0607	1847.799	0.9901	0.1448
0.020	19.87	23.19 ± 4	1.0552	1858.632	0.9910	0.1523
0.030	18.75	22.88 ± 1	1.0497	1869.465	0.9919	0.1601
0.050	18.63	22.57 ± 7	1.0442	1880.298	0.9928	0.1676
0.100	17.51	22.22 ± 2	1.0383	1891.594	0.9941	0.1749
			T/K = 298.15			
0.005	21.06	23.93 ± 6	1.0240	1933.841	0.9901	0.1344
0.007	20.41	23.62 ± 3	1.0194	1943.674	0.9908	0.1421
0.010	19.64	23.31 ± 4	1.0148	1954.507	0.9916	0.1498
0.020	19.53	23.00 ± 3	1.0102	1965.340	0.9925	0.1572
0.030	18.32	22.69 ± 2	1.0056	1976.173	0.9932	0.1647
0.050	17.82	22.38 ± 5	1.0010	1987.006	0.9941	0.1720
0.100	17.38	22.02 ± 6	0.9960	1999.908	0.9950	0.1795
			T/K = 303.15			
0.005	21.45	23.35 ± 2	0.9893	2019.299	0.9908	0.1398
0.007	20.93	23.09 ± 5	0.9846	2030.785	0.9915	0.1470
0.010	19.41	22.83 ± 4	0.9799	2041.345	0.9923	0.1542
0.020	18.89	22.56 ± 6	0.9752	2052.832	0.9931	0.1616
0.030	18.37	22.30 ± 3	0.9705	2063.516	0.9938	0.1700
0.050	17.85	22.05 ± 4	0.9658	2073.128	0.9945	0.1773
0.100	16.32	21.78 ± 1	0.9606	2084.009	0.9953	0.1851
			T/K = 308.15			
0.005	20.56	22.88 ± 7	0.9493	2121.382	0.9923	0.1443
0.007	19.88	22.51 ± 5	0.9450	2131.791	0.9930	0.1522

Table 6. Continued

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
$mol \cdot kg^{-1}$	$m^3 \cdot mol^{-1}$	$mm^{-3} \cdot MPa^{-1} \cdot mol^{-1}$	A^0	$kg \cdot m^{-2} \cdot s^{-1}$	R_A	S_n
0.010	19.20	22.14 ± 1	0.9407	2142.207	0.9936	0.1598
0.020	18.52	21.77 ± 6	0.9367	2152.609	0.9943	0.1671
0.030	17.84	21.40 ± 4	0.9321	2163.018	0.9949	0.1743
0.050	16.16	21.03 ± 2	0.9278	2173.427	0.9956	0.1825
0.100	16.48	20.65 ± 3	0.9235	2183.841	0.9964	0.1901
			T/K = 313.15			
0.005	20.36	21.57 ± 4	0.9054	2243.056	0.9936	0.1495
0.007	19.64	21.20 ± 6	0.9025	2250.382	0.9940	0.1575
0.010	19.26	20.83 ± 3	0.8996	2258.016	0.9944	0.1643
0.020	18.15	20.46 ± 8	0.8967	2265.489	0.9949	0.1721
0.030	17.82	20.09 ± 4	0.8938	2272.618	0.9954	0.1796
0.050	16.57	19.72 ± 2	0.8909	2280.725	0.9959	0.1867
0.100	15.40	19.35 ± 6	0.8878	2290.245	0.9964	0.1943
			T/K = 318.15			
0.005	20.42	20.66 ± 1	0.8773	2335.101	0.9953	0.1540
0.007	19.16	20.35 ± 7	0.8746	2343.246	0.9958	0.1615
0.010	18.57	20.04 ± 2	0.8719	2351.817	0.9964	0.1699
0.020	17.48	19.73 ± 4	0.8692	2359.654	0.9968	0.1776
0.030	16.35	19.42 ± 5	0.8665	2367.362	0.9973	0.1848
0.050	16.73	19.11 ± 6	0.8638	2374.478	0.9979	0.1921
0.100	15.38	18.78 ± 4	0.8610	2382.996	0.9984	0.1998

Table 7. 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 Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping $Mn(COOCH_3)_2$ Constant at 1.0 $mol \cdot kg^{-1}$

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
$mol \cdot kg^{-1}$	$m^3 \cdot mol^{-1}$	$mm^{-3} \cdot MPa^{-1} \cdot mol^{-1}$	A^0	$kg \cdot m^{-2} \cdot s^{-1}$	R_A	S_n
			T/K = 288.15			
0.005	22.49	31.42 ± 1	1.0495	1848.320	0.9911	0.1812
0.007	22.36	31.21 ± 7	1.0456	1856.222	0.9918	0.1907
0.010	21.94	31.00 ± 3	1.0417	1864.124	0.9925	0.1997
0.020	20.81	30.79 ± 4	1.0378	1872.026	0.9932	0.2087
0.030	19.45	30.58 ± 6	1.0339	1879.928	0.9939	0.2174
0.050	19.03	30.37 ± 5	1.0300	1887.830	0.9946	0.2262
0.100	18.24	30.16 ± 2	1.0257	1895.733	0.9954	0.2353
			T/K = 293.15			
0.005	22.38	30.80 ± 4	1.0182	1926.731	0.9927	0.1857
0.007	21.61	30.58 ± 1	1.0146	1933.991	0.9933	0.1944
0.010	20.84	30.36 ± 2	1.0110	1941.255	0.9939	0.2030
0.020	20.07	30.14 ± 6	1.0074	1948.519	0.9945	0.2115
0.030	19.30	29.92 ± 6	1.0038	1955.785	0.9951	0.2200
0.050	18.53	29.70 ± 4	1.0002	1963.051	0.9958	0.2287
0.100	18.76	29.45 ± 3	0.9963	1973.126	0.9966	0.2375
			T/K = 298.15			
0.005	21.54	30.15 ± 2	0.9769	2028.872	0.9935	0.1902
0.007	20.80	29.94 ± 8	0.9738	2036.122	0.9939	0.1985
0.010	20.06	29.73 ± 2	0.9707	2043.374	0.9943	0.2070
0.020	19.32	29.52 ± 7	0.9676	2050.623	0.9947	0.2158
0.030	18.58	29.31 ± 6	0.9645	2057.845	0.9951	0.2244

Table 7. Continued

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
$mol \cdot kg^{-1}$	$m^3 \cdot mol^{-1}$	$mm^{-3} \cdot MPa^{-1} \cdot mol^{-1}$	A^0	$kg \cdot m^{-2} \cdot s^{-1}$	R_A	S_n
0.050	18.84	29.10 ± 4	0.9614	2065.098	0.9955	0.2326
0.100	17.08	28.90 ± 5	0.9579	2072.430	0.9961	0.2418
		T/K = 303.15				
0.005	21.32	29.43 ± 2	0.9231	2130.693	0.994	0.1947
0.007	20.34	29.21 ± 8	0.9228	2136.245	0.9944	0.2032
0.010	19.36	28.99 ± 4	0.9225	2141.797	0.9948	0.2115
0.020	19.38	28.77 ± 3	0.9222	2147.349	0.9952	0.2201
0.030	18.40	28.55 ± 5	0.9219	2152.901	0.9957	0.2288
0.050	17.42	28.33 ± 1	0.9216	2158.453	0.9962	0.2373
0.100	17.43	28.06 ± 6	0.9213	2164.008	0.9968	0.2452
		T/K = 308.15				
0.005	20.45	29.04 ± 4	0.9113	2213.118	0.9946	0.2003
0.007	20.44	28.82 ± 6	0.9088	2220.112	0.9950	0.2086
0.010	19.53	28.60 ± 3	0.9063	2227.106	0.9954	0.2172
0.020	18.36	28.38 ± 2	0.9038	2234.1	0.9958	0.2255
0.030	18.74	28.16 ± 7	0.9013	2241.094	0.9962	0.2340
0.050	17.40	27.94 ± 1	0.8988	2248.088	0.9966	0.2426
0.100	16.38	27.72 ± 5	0.8958	2255.086	0.9970	0.2512
		T/K = 313.15				
0.005	20.21	28.28 ± 6	0.876	2318.97	0.9959	0.2048
0.007	19.07	28.04 ± 2	0.8537	2324.463	0.9964	0.2132
0.010	19.93	27.80 ± 4	0.8314	2329.956	0.9968	0.2215
0.020	18.79	27.56 ± 3	0.8291	2335.449	0.9972	0.2302
0.030	17.65	27.32 ± 5	0.8068	2340.942	0.9976	0.2389
0.050	17.51	27.08 ± 1	0.7845	2346.435	0.9983	0.2463
0.100	16.37	26.82 ± 5	0.7422	2351.931	0.9990	0.2547
		T/K = 318.15				
0.005	20.14	27.56 ± 2	0.8514	2407.915	0.9972	0.2103
0.007	19.05	27.33 ± 3	0.8487	2399.64	0.9976	0.2190
0.010	18.96	27.10 ± 4	0.846	2391.365	0.9980	0.2274
0.020	18.87	26.87 ± 6	0.8433	2383.093	0.9985	0.2358
0.030	17.47	26.64 ± 1	0.8406	2374.815	0.9990	0.2440
0.050	16.69	26.41 ± 7	0.8379	2366.54	0.9995	0.2522
0.100	16.56	26.14 ± 5	0.8352	2457.565	1.0000	0.2605

evaluated theoretically. It is based on the drag that the ion atmosphere causes that retards the movement of the ion and indirectly diminishes the viscosity of the solution.[21] The values of the viscosity A-coefficients are given in Table 10. The values of viscosity B- and D-coefficients were determined by a least-squares analysis of eq 15 in the form

$$(\eta_r - 1 - Ac^{1/2})/c = B + Dc \qquad (16)$$

and are given in Table 10. It may be seen that the values of the viscosity A-coefficient are small and that the $Ac^{1/2}$ term in eq 15 appreciably affects the measured viscosity only for the data at the lowest concentration. The values of the viscosity A-coefficient at a definite temperature decrease with increasing concentration of manganese acetate. Furthermore, the viscosity A-coefficient slightly increases with increasing temperature in accordance with the theory. The values of the viscosity B-coefficients, given in Table 10, are positive and relatively large, which is typical of salts with large hydrophilic ions such as manganese acetate. The sign of the viscosity B-coefficient and its temperature coefficient depends on the degree of solvent structuring induced by the ions. Recently, a comprehensive model for calculating the viscosity B- and D-coefficients of electrolyte solutions has been developed.[22] The model includes a long-range electrostatic interaction term, contributions of individual ions, and a contribution from specific interactions between ions or neutral species. The viscosity D-coefficients given in Table 10 are positive and relatively large and at a definite temperature almost linearly depend on the concentration of the metal salt. With increasing temperature the viscosity D-coefficient initially decreases to a minimum value that depends on the concentration of the metal salt and then slightly increases. Figure 1 represents an initial increase in the viscosity values with an increase in ethanol composition up to 30 %, and at this point the ion-dipolar pair formation between the dipeptide molecule and metal ion takes place. Further, the viscosity values decrease gradually at higher

Table 8. 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 Glycylglycine + $Mn(COOCH_3)_2$ in Water at T = (288.15 to 318.15) K Keeping Glycylglycine Constant at 0.020 mol·kg^{-1}

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
mol·kg^{-1}	m^3·mol^{-1}	mm^{-3}·MPa^{-1}·mol^{-1}	A^0	kg·m^{-2}·s^{-1}	R_A	S_n
			T/K = 288.15			
0.005	21.96	20.19 ± 2	1.2403	1562.118	0.9779	0.1154
0.010	20.88	19.87 ± 4	1.2295	1569.654	0.9862	0.1176
0.030	19.74	19.54 ± 6	1.2186	1592.057	0.9941	0.1199
0.050	18.43	19.21 ± 3	1.2079	1614.452	1.0024	0.1222
0.100	17.58	18.91 ± 5	1.1971	1636.836	1.0105	0.1246
0.250	15.65	18.58 ± 7	1.1863	1659.238	1.0184	0.1270
0.500	14.47	18.26 ± 2	1.1753	1682.015	1.0266	0.1295
			T/K = 293.15			
0.005	21.48	19.92 ± 7	1.1961	1625.167	0.9767	0.1175
0.010	20.96	19.70 ± 6	1.1916	1632.518	0.9778	0.1198
0.030	19.45	19.48 ± 4	1.1872	1640.236	0.9789	0.1221
0.050	17.89	19.11 ± 6	1.1828	1647.524	0.9801	0.1245
0.100	16.66	18.83 ± 3	1.1783	1655.817	0.9813	0.1268
0.250	15.24	18.46 ± 2	1.1739	1662.584	0.9823	0.1294
0.500	14.48	18.17 ± 4	1.1695	1670.729	0.9835	0.1318
			T/K = 298.15			
0.005	21.16	19.75 ± 1	1.1703	1680.341	0.9748	0.1208
0.010	20.34	19.46 ± 6	1.1654	1688.136	0.9756	0.1232
0.030	18.53	19.18 ± 3	1.1602	1697.284	0.9765	0.1256
0.050	17.76	18.90 ± 4	1.1553	1704.381	0.9773	0.1280
0.100	16.88	18.62 ± 6	1.1505	1713.465	0.9780	0.1305
0.250	14.05	18.34 ± 2	1.1451	1720.502	0.9788	0.1329
0.500	13.24	18.05 ± 5	1.1403	1729.044	0.9796	0.1354
			T/K = 303.15			
0.005	21.54	19.56 ± 7	1.1393	1739.891	0.9745	0.1234
0.010	19.36	19.28 ± 4	1.1356	1745.236	0.9751	0.1258
0.030	18.87	19.01 ± 1	1.1320	1751.431	0.9758	0.1273
0.050	17.22	18.74 ± 6	1.1284	1758.525	0.9764	0.1298
0.100	15.18	18.47 ± 4	1.1248	1765.177	0.9770	0.1324
0.250	14.58	18.20 ± 3	1.1212	1771.812	0.9776	0.1349
0.500	13.72	17.92 ± 2	1.1174	1778.357	0.9782	0.1375
			T/K = 308.15			
0.005	20.43	19.40 ± 6	1.1075	1786.442	0.973	0.1257
0.010	19.32	19.12 ± 4	1.1047	1790.816	0.9736	0.1283
0.030	18.54	18.85 ± 3	1.1019	1794.708	0.9742	0.1309
0.050	16.79	18.58 ± 1	1.0991	1799.250	0.9748	0.1335
0.100	15.04	18.31 ± 5	1.0962	1805.534	0.9755	0.1360
0.250	14.85	18.04 ± 2	1.0932	1813.160	0.9761	0.1386
0.500	12.81	17.75 ± 7	1.0903	1819.323	0.9767	0.1412
			T/K = 313.15			
0.005	20.61	19.25 ± 5	1.0785	1836.209	0.9721	0.1275
0.010	19.43	18.96 ± 3	1.0673	1859.418	0.9728	0.1298
0.030	17.92	18.67 ± 1	1.0561	1882.615	0.9734	0.1324
0.050	16.45	18.38 ± 2	1.0449	1905.246	0.9741	0.1348
0.100	15.18	18.09 ± 4	1.0337	1928.836	0.9748	0.1375
0.250	14.65	17.80 ± 6	1.0225	1951.487	0.9754	0.1401
0.500	12.36	17.50 ± 2	1.0108	1978.879	0.9763	0.1426

Table 8. Continued

m	$\Phi_V \cdot 10^{-6}$	Φ_K	L_f	$Z \cdot 10^{-3}$		
$mol \cdot kg^{-1}$	$m^3 \cdot mol^{-1}$	$mm^{-3} \cdot MPa^{-1} \cdot mol^{-1}$	A^0	$kg \cdot m^{-2} \cdot s^{-1}$	R_A	S_n
			T/K = 318.15			
0.005	20.34	19.06 ± 3	1.0165	1986.095	0.9701	0.1298
0.010	18.07	18.76 ± 6	1.0136	1992.516	0.9708	0.1323
0.030	17.51	18.48 ± 4	1.0107	1999.074	0.9715	0.1347
0.050	16.43	18.15 ± 5	1.0078	2005.485	0.9722	0.1372
0.100	14.68	17.87 ± 2	1.0049	2013.984	0.9729	0.1396
0.250	13.82	17.54 ± 3	1.0021	2018.328	0.9736	0.1421
0.500	12.47	17.24 ± 1	0.9992	2025.702	0.9745	0.1445

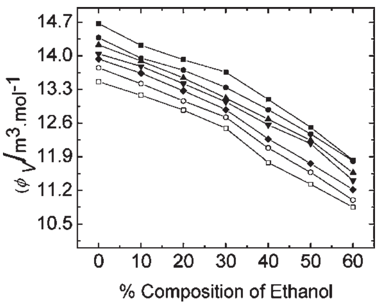

Figure 6. Dependence of apparent molar volume (Φ_V) on the composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

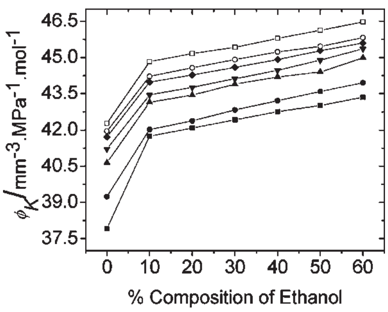

Figure 7. Dependence of apparent molar compressibility (Φ_K) on the composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

ethanol composition. This may be attributed to the formation of hydrogen bonds, and there may be another source of contribution due to the different sizes and shapes of component molecules of the mixture. It may be assumed that the small water molecules occupy the void space in ethanol. A similar explanation is given by Pikkarainen.[23] The positive values also suggest the strong interaction between water and ethanol molecules.

The ultrasonic velocity (u) increases with an increase in concentration. This variation also depends on the concentration derivatives of density and compressibility according to equation given below:

$$du/dc = -u/2(1/\rho \cdot \partial\rho/\partial c + 1/\beta \cdot \partial\beta/\partial c) \qquad (17)$$

The gradual increase of sound velocity with concentration strongly supports the intermolecular association between solute and solvent molecules. Because of the strong interaction, the closed-packed water structures absorb the sound energy, and hence the sound velocity increases at all temperatures. The experimental results indicate that the density increases and the adiabatic compressibility decreases with increasing concentration. Thus, the quantity ($d\rho/dc$) is positive, and ($d\beta/dc$) is negative. Because the values of $[(1/\beta)(d\beta/dc)]$ are larger than those of $[(1/\rho)(d\rho/dc)]$ for dipeptide−metal acetate solutions, the concentration derivative of sound velocity (du/dc) is positive, which is in agreement with the results of other workers[24−26] reported for electrolyte solutions. It is observed from Figure 2 that the speed of sound increases with an increase in the ratio of ethanol added to the solution. The rise in speed is much larger with an increase in ethanol composition which signifies comparatively more structural interaction with water. From Figure 3 it is observed that the decrease in density with an increase in the ethanol composition may be due to the high molecular aggregation of solute components in the solution. An unusual behavior is observed in Figure 4 which shows an initial increase and later a gradual decrease in the refractive index values. As stated by Deetlefs et al.,[27] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. But in our case, this is true until a certain ethanol composition (30 %) and at that particular point of maxima; the formation of a close ion pair takes place which clearly indicates the interactions among cation, anion, and solvent molecules. Later, as the solution became more and more dense, there is a decrease in the refractive index values which shows that such changes can be regarded as a measure of the relative extent of the polar domains which is dominated by dispersive molecular interactions and intermolecular dipolar interactions of the molecules or geometrical fitting between components during mixing and therefore depend very much on the nature of the mixing molecules. The adiabatic compressibility values indicate a decrease with an increase in the concentration of ethanol (Figure 5). This is explained on the basis that the ions in solution are surrounded by a layer of solvent molecules, which results in increasing the internal pressure and lowering of the compressibility of solutions.

The apparent molar volume decreases as functions of salt concentration in case one and two (i.e., $d\Phi_V/dm$ parameter), while the $d\Phi_V/dm$ parameters are (analogous to the S_V parameter) positive in both cases. Thus, on the basis of $d\Phi_V/dm$, we can arrive at a conclusion that solute−solute interactions are more predominant than water−water interactions. The limiting apparent molar volume of water (Φ^0_V) in Figure 6 is found to be less than the

Table 9. Volumetric and Adiabatic Compressibility Properties of $Mn(COOCH_3)_2$ at T = 298.15 K for Various Concentrations Obtained from Equation 10

m	A	B	$\Phi^0_V \cdot 10^6$	S_V	$A' \cdot 10^{11}$	$B' \cdot 10^{11}$	S_K
$mol \cdot kg^{-1}$	$g \cdot mol^{-1}$	$g \cdot cm^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-2}$	$cm^3 \cdot Pa^{-1} \cdot mol^{-1}$	$cm^6 \cdot Pa^{-1} \cdot mol^{-2}$	$mm^6 \cdot MPa^{-1} \cdot mol^{-2}$
0.005	8.63	−264.38	12.2	512.34	−2213.41	532145.25	8.5
0.010	7.84	−310.54	13.4	534.61	−2304.85	541426.76	6.9
0.030	6.48	−356.71	14.3	568.47	−2389.76	556423.18	5.3
0.050	5.32	−415.46	15.2	604.82	−2456.32	564879.37	4.1
0.100	3.95	−592.18	17.1	629.65	−2522.17	578412.69	3.0
0.250	2.87	−674.42	18.3	660.14	−2596.48	589432.75	1.8
0.500	1.06	−804.25	20.4	697.07	−2667.50	601275.83	0.7

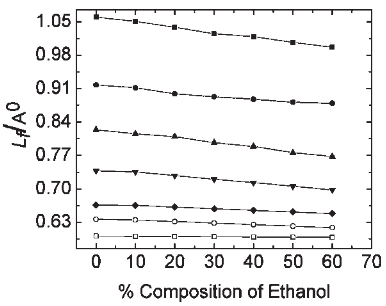

Figure 8. Variation of intermolecular free length (L_f) as a function of composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

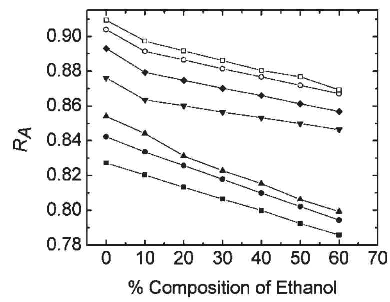

Figure 10. Variation of relative association (R_A) with composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

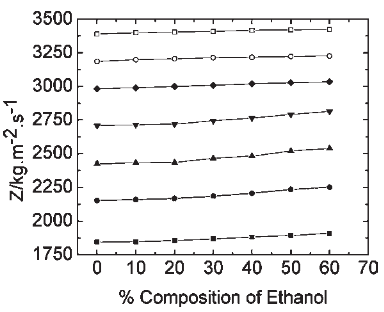

Figure 9. Variation of specific acoustic impedance (Z) with composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

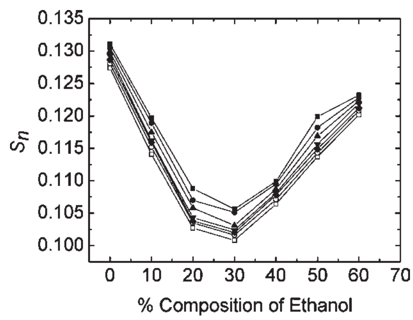

Figure 11. Variation of solvation number (S_n) as a function of composition of ethanol at different temperatures: ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K; ○, 313.15 K; □, 318.15 K.

molar volume of pure water ($18.068 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$ at T = 298.15 K) meaning a contraction in volume in transferring pure liquid water to organic solvents. The results are in good agreement with the data reported for water in alcohols by Sakurai and Nakagawa.[28] Thus, the solvation of water that takes place in ethanol may be due to dipole−dipole and H-bonding interaction, which are similar to those existing in water. Alcohols are known to form linear one-dimensional H-bonded structures. When it is brought under the influence of water, H-bonding with alcoholic −OH is linked to account for the variation of thermodynamic and viscosity properties. Seen in this light in the extreme alcohol-rich concentrations, H-bonding interaction affects the Φ^0_V and $d\Phi_V/dm$, showing individualistic differences.

The pressure derivative of apparent molar volume (Φ_V) is the apparent molar compressibility of solute (Φ_K), that is, $\Phi_K = d\Phi_V/dP$. In turn, knowledge of Φ_K behavior can be used to have some insight on the pressure effect on various equilibria and interactions. It is known that the Φ^0_K values of metal−acetates are negative, meaning a loss in the compressibility of water around the cations. Similar effects are exhibited by carbohydrates having unique conformational interacting sites such as axial and equatorial substitutions. Such values are attributed to strong dipole−dipole interactions.[29] Mathieson and Conway have differentiated hydrophobic and hydrophilic ions on the basis of their Φ^0_K magnitudes.[30] A clear distinction must be made between the soft structures promoted by H-bonding and the stiff structures promoted by hydrophobic interaction. Many types of solutes are differentiated in water as a structure maker or breaker on the basis of excess partial molar volumes. In this criterion, the standard state of solute is restricted to the solute as a

Table 10. Values of Viscosity *A*-, *B*-, and *D*-Coefficients of Aqueous Solutions of Glycylglycine and $Mn(COOCH_3)_2$ as a Function of Temperature[a]

m / $mol \cdot kg^{-1}$	$A \cdot 10^3$	B	D
	T/K = 288.15		
0.005	4.18	0.842 ± 0.002	0.903 ± 0.006
0.010	4.21	0.834 ± 0.003	0.889 ± 0.004
0.030	4.23	0.825 ± 0.001	0.850 ± 0.005
0.050	4.26	0.816 ± 0.004	0.821 ± 0.007
0.100	4.29	0.803 ± 0.002	0.798 ± 0.008
0.250	4.32	0.797 ± 0.001	0.775 ± 0.003
0.500	4.36	0.790 ± 0.003	0.748 ± 0.006
	T/K = 293.15		
0.005	4.65	0.763 ± 0.004	0.705 ± 0.004
0.010	4.67	0.755 ± 0.001	0.690 ± 0.007
0.030	4.69	0.747 ± 0.002	0.672 ± 0.006
0.050	4.72	0.740 ± 0.004	0.653 ± 0.002
0.100	4.75	0.731 ± 0.003	0.636 ± 0.009
0.250	4.78	0.720 ± 0.002	0.612 ± 0.005
0.500	4.82	0.710 ± 0.001	0.598 ± 0.003
	T/K = 293.15		
0.005	5.10	0.698 ± 0.003	0.585 ± 0.006
0.010	5.12	0.690 ± 0.002	0.570 ± 0.003
0.030	5.15	0.681 ± 0.004	0.556 ± 0.004
0.050	5.18	0.673 ± 0.001	0.542 ± 0.005
0.100	5.22	0.665 ± 0.002	0.531 ± 0.007
0.250	5.26	0.652 ± 0.003	0.517 ± 0.002
0.500	5.30	0.640 ± 0.001	0.500 ± 0.004
	T/K = 303.15		
0.005	5.52	0.615 ± 0.002	0.481 ± 0.007
0.010	5.55	0.606 ± 0.004	0.466 ± 0.002
0.030	5.58	0.598 ± 0.001	0.452 ± 0.003
0.050	5.62	0.590 ± 0.003	0.438 ± 0.004
0.100	5.66	0.582 ± 0.002	0.422 ± 0.005
0.250	5.70	0.573 ± 0.003	0.408 ± 0.001
0.500	5.75	0.562 ± 0.004	0.395 ± 0.006
	T/K = 308.15		
0.005	6.15	0.550 ± 0.003	0.376 ± 0.004
0.010	6.18	0.543 ± 0.002	0.358 ± 0.006
0.030	6.21	0.536 ± 0.004	0.342 ± 0.002
0.050	6.25	0.529 ± 0.001	0.328 ± 0.005
0.100	6.29	0.520 ± 0.003	0.311 ± 0.007
0.250	6.33	0.511 ± 0.002	0.296 ± 0.006
0.500	6.38	0.502 ± 0.001	0.282 ± 0.003
	T/K = 313.15		
0.005	6.82	0.491 ± 0.002	0.265 ± 0.006
0.010	6.84	0.483 ± 0.001	0.250 ± 0.003
0.030	6.88	0.475 ± 0.003	0.236 ± 0.005
0.050	6.91	0.466 ± 0.002	0.221 ± 0.007
0.100	6.94	0.458 ± 0.004	0.207 ± 0.008
0.250	6.97	0.450 ± 0.004	0.192 ± 0.004
0.500	7.02	0.441 ± 0.003	0.176 ± 0.002
	T/K = 318.15		
0.005	7.30	0.415 ± 0.001	0.152 ± 0.007
0.010	7.33	0.408 ± 0.004	0.136 ± 0.005
0.030	7.36	0.400 ± 0.002	0.121 ± 0.003
0.050	7.40	0.392 ± 0.004	0.103 ± 0.002
0.100	7.44	0.384 ± 0.002	0.090 ± 0.001
0.250	7.48	0.375 ± 0.003	0.076 ± 0.006
0.500	7.52	0.366 ± 0.001	0.061 ± 0.004

[a] Units: A $(mol \cdot dm^{-3})^{-1/2}$; B $(mol \cdot dm^{-3})^{-1}$; D $(mol \cdot dm^{-3})^{-2}$.

pure liquid.[31] Figure 7 allows us to examine the status and interactions of water molecules in ethanol, and it was found that Φ_K values of water are positive in ethanol. For alcohols like ethanol, the H-bonding with water causes the stiffening of structures, resulting in a loss of compressibility of water, and may be thought of in terms of the participation of water molecules in the chain-like structures of alcohols. On the basis of the sign and magnitude of the S_V parameter, we expect a similar behavior for the calculated S_K parameter ($S_K = B' + \beta_0 S_V$) accounting for effect due to solute−solute interaction.

The decrease in intermolecular free length (L_f) and increase in specific acoustic impedance (Z) with an increase in concentration indicate that there is a significant interaction between the solute and the solvent molecules, because of which the structural arrangement is considerably affected. This can be explained on the basis of hydrophobic interaction between solute and solvent molecules, which increases with the intermolecular distance, leaving relatively wider gaps between the molecules, and thus becomes the main cause of impediment to the propagation of ultrasound waves. A similar trend is observed in the case of aqueous ethanol mixture as well (Figures 8 and 9). The values of relative association (R_A) increase with increasing concentration. The increase in the values can be attributed to the fact that the solvation of ions increases with increasing solute concentration. At lower temperatures the molecular aggregation in the solution will be increased, and hence a considerable variation is observed. As the temperature increases, the process of relaxation of the molecules takes place, and hence the variation is proportionate. In the presence of a solvent such as ethanol, the relative association decreases (Figure 10) with an increase in the concentration of ethanol. This phenomenon can be explained by the fact that the surface of the solute molecules will be encompassed with the alcoholic molecules which hinders the solute−solvent interaction but favors solute−solute interactions. The values of solvation number in case one and two increase with an increase in concentration. The trends in solvation number over concentration and temperature somewhat mirror the trends of solvated ion sizes. The solvation number of water−ethanol solutions initially decreases with an increase in ethanol concentration to a minimum at about 30 % indicating a water-rich region where the molecules are highly hydrated from this region onward and then shows an increase with increasing ethanol concentration (Figure 11).[32] The solvation number is probably strongly influenced by the structure of the solvent, and that it has a maximum seems to be attributable to a difference in the structure of the solvent before and after the minimum solvation number.[33−35]

CONCLUSIONS

The results confirm that there is significant interaction between the solute and the solvent molecules in dilute solutions. The ion atmosphere causes a drag that retards the movement of the ion and indirectly diminishes the viscosity of the solution. The rise in the speed of sound signifies greater structural interaction with water and high molecular aggregation of solute components in the solution. The unusual behavior of the refractive index can be regarded as a measure of the relative extent of the polar domains and formation of close ion pairs. The solvation number has been strongly influenced by the structure of the solvent, and the maximum seems to be attributable to a difference in the structure of the solvent. Finally, the above results are in good agreement between observed and calculated values.

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