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Densities, Partial Molar Volumes, and Heat Capacities of Glycine, L-Alanine, and L-Leucine in Aqueous Magnesium Chloride Solutions at Different Temperatures

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The apparent molar volumes ($V_{2,\phi}$) have been determined for glycine, L-alanine, and L-leucine in water and in aqueous magnesium chloride solutions with concentrations ≈ (0.05 to 0.80) mol·kg^{-1} by measuring the densities at (288.15, 298.15, and 308.15) K. The apparent molar heat capacities ($C_{p2,\phi}$) have also been determined for glycine and L-alanine in aqueous magnesium chloride solutions with concentrations ≈ (0.05 to 0.40) mol·kg^{-1} by measuring heat capacities in the temperature range (298.15 to 328.15) K. These properties show a peculiar dependence upon the concentration of magnesium chloride. The standard partial molar volumes at infinite dilution (V_2^∞) obtained from these data have been used to calculate the partial molar volumes of transfer of amino acids from water to aqueous magnesium chloride solutions at infinite dilution ($\Delta_t V_2^\infty$), which are positive for the presently studied amino acids at all temperatures and concentrations. The partial molar expansibilities $(\partial V_2^\infty/\partial T)_P$ at infinite dilution and the $(\partial^2 V_2^\infty/\partial T^2)_P$ values have also been determined from the V_2^∞ data at various concentrations of the salt. The volumetric interaction parameters have been calculated from $\Delta_t V_2^\infty$ data. The results have been discussed in terms of various interactions operating in these systems.

Introduction

Despite the many publications on the structural and dynamical properties of proteins available in the literature, their thermodynamic properties in solutions remain unclear and demanding of further efforts.[1−3] The complex conformational and configurational factors affecting the structures of proteins in various solvents/cosolutes elude conclusive and direct interpretation of the results. This has led to the investigations of the behavior of model compounds, namely amino acids, peptides, and their derivatives. Some of these are directed at extracting thermodynamic properties of amino acid side chains and then checking the possibility of the additivity to estimate the properties of structurally more complicated molecules in the solution, such as of unfolded proteins.[4,5]

The interactions between charged biomolecules and ions can highly influence the behavior and conformation of the former in aqueous solutions. Consequently, salt solutions have been found to affect the solubility, denaturation, dissociation into subunits, and activity of enzymes.[6] Magnesium in biological chemistry has been branded as a Cinderella element because of its double behavior.[7] In light of the importance of magnesium in biology, the present paper reports the apparent molar volumes ($V_{2,\phi}^\infty$) of glycine (gly), L-alanine (ala), and L-leucine (leu) in aqueous solutions of magnesium chloride ($MgCl_2$) at (288.15, 298.15, and 308.15) K and the apparent molar heat capacities ($C_{p2,\phi}$) of glycine and L-alanine from (298.15 to 328.15) K obtained from precisely measured densities and specific heat capacities, respectively. The $V_{2,\phi}$ and $C_{p2,\phi}$ values of amino acids show an interesting dependence on the $MgCl_2$ concentrations. The partial molar volumes of the three amino acids obtained at infinite dilution ($V_{2,\phi}^\infty$) have been used to evaluate partial molar volumes of transfer ($\Delta_t V_2^\infty$) of these amino acids from water to aqueous $MgCl_2$ solutions. Interaction coefficients have been calculated using the McMillan Mayer approach. These, along with transfer data, have been rationalized in terms of various interactions.

Experimental Section

Glycine, L-alanine, and L-leucine (LR, Thomas Baker) were purified by recrystallization from a hot solution of 50% aqueous ethanol (EtOH). The large crystals formed were crushed, dried in a vacuum desiccator, and then used for density measurements. Magnesium chloride, $MgCl_2·6H_2O$ (AR, SD Fine Chemicals Ltd., India), was used as such and kept stored in a vacuum desiccator.

Water used to prepare solutions was obtained by distilling deionized water over alkaline $KMnO_4$, and it was thoroughly degassed prior to its use. All the solutions were prepared afresh on a molality scale. Weighings were done on a Mettler balance having an accuracy of ±0.01 mg. The estimated uncertainties in molalities are found to be ≤6 × 10^{-6} mol·kg^{-1}.

The densities of the solutions were measured by using a vibrating-tube digital densimeter (model DMA 60/602, Anton Paar, Austria). The details of its principles and working have been described elsewhere.[8] The temperature of the water flowing around the densimeter cell was controlled within ±0.01 K using an efficient temperature bath (Heto Birkerod/Denmark). The densimeter was cali-

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brated with dry air and water, and all the measurements were made relative to pure water. The working of the densimeter was checked by measuring the densities of aqueous NaCl solutions, which agree well with the literature values.[9]

The heat capacities of aqueous solutions of amino acids were measured using a microdifferential scanning calorimeter (SETARAM, France) employing cells of 1 cm^3 capacity. The masses of the sample and reference cells with or without the liquid of interest were always matched to within 0.1 mg. The instrument has a heat capacity resolution of 5×10^{-5} of the absolute value. To minimize the vapor space, the cell was always filled to 98% of the total volume. The amplitude of the deviation from equilibrium (A) is related to the specific heat capacity of the liquid by

$$A = m_s C_p \sigma \tag{1}$$

Here, m_s is the mass of the sample in the cell, C_p is the specific heat capacity of the sample, and σ is the scan rate of the instrument. The specific heat capacity (C_p) of the aqueous solution of $MgCl_2$ in the sample cell was determined against that of water of equal mass (m_s) in the reference cell. Corrections were applied to the values of A for the heat capacity difference arising due to any difference in the geometry of the cells by scanning both sample and reference cells empty and subtracting the resultant deviation. Sufficient equilibrium time was allowed before starting the temperature scanning at the rate 12 $K \cdot h^{-1}$. The C_p of the aqueous $MgCl_2$ solution was calculated by using the following relation:

$$C_p = \frac{A_{sample} - A_{water}}{A_{water}} C_p^\circ + C_p^\circ \tag{2}$$

Here $A_{sample} - A_{water}$ is the amplitude difference arising upon scanning the sample cell containing the solution of interest and the reference cell containing water. A_{water} is the amplitude obtained with water in the sample cell and an empty reference cell whereas A_{sample} is the amplitude obtained with sample in the sample cell and an empty reference cell. C_p° is the specific heat capacity of the reference water at the temperature of interest. The accuracy of the calorimeter was checked by measuring the apparent molar heat capacities of aqueous sodium chloride at several concentrations, which showed excellent agreement with the literature.[10] The apparent molar heat capacities of aqueous amino acids in the presence of $MgCl_2$ were calculated from the DSC scans at temperatures from (298.15 to 328.15) K at intervals of 5 K.

Results and Discussion

The apparent molar volumes ($V_{2,\phi}$) of the three amino acids glycine, L-alanine, and L-leucine and the apparent molar heat capacities ($C_{p2,\phi}$) of the two amino acids glycine and L-alanine in water and in various $MgCl_2$ (cosolute) aqueous solutions (having m_s molality of cosolute) have been obtained from the directly determined densities at (288.15, 298.15, and 308.15) K and the specific heat capacities from (298.15 to 328.15) K, employing the following equations, respectively

$$V_{2,\phi} = M/\rho - [(\rho - \rho_0)1000/m\rho\rho_0] \tag{3}$$

$$C_{p2,\phi} = MC_p - [(C_p^\circ - C_p)1000/m] \tag{4}$$

where M is the molar mass of the solute, m is the molality of the amino acid, ρ and ρ_0 denote the densities of the

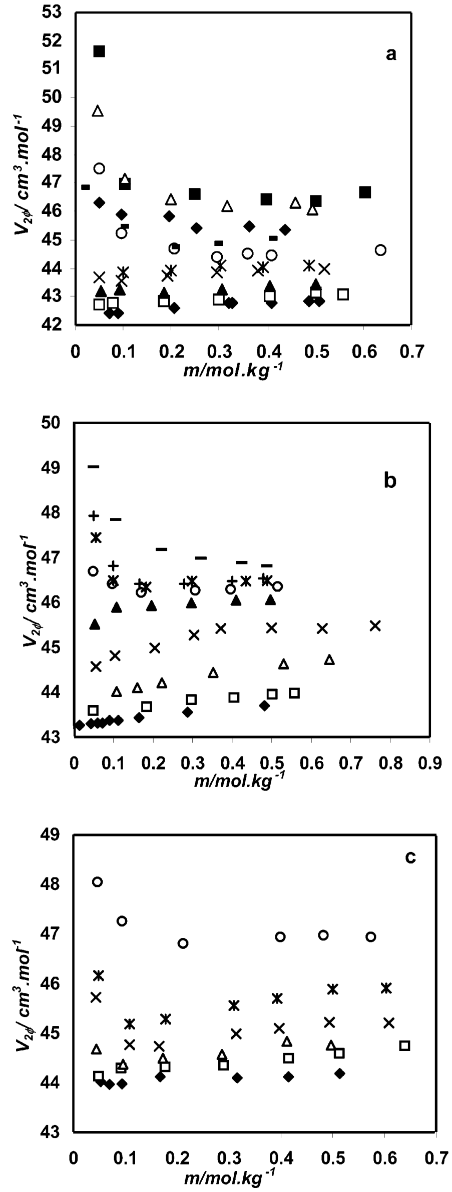

Figure 1. (a) Apparent molar volumes ($V_{2,\phi}$) of glycine vs molality of glycine (m) in (◆) water and aqueous $MgCl_2$ solutions (m_s = □, 0.05016; ▲, 0.10123; ×, 0.20109; ∗, 0.27158; ◇, 0.39699; −, 0.40466; ◆, 0.60742; ■, 0.81527; △, 0.81648) at 288.15 K. (b) Apparent molar volumes ($V_{2,\phi}$) of glycine vs molality of glycine (m) in (◆) water and aqueous $MgCl_2$ solutions (m_s = □, 0.05027; △, 0.09990; ×, 0.40358; ▲, 0.71553; ◇, 0.76311; +, 0.81462; ∗, 0.81468; −, 0.91811) at 298.15 K. (c) Apparent molar volumes ($V_{2,\phi}$) of glycine vs molality of glycine (m) in (◆) water and aqueous $MgCl_2$ solutions (m_s = □, 0.05255; △, 0.10105; ×, 0.20259; ∗, 0.40598; ○, 0.82218) at 308.15 K.

solution and the solvent, and C_p and C_p° are the specific heats of the solution and solvent, respectively.

The uncertainty[11] in the determination of $V_{2,\phi}$ has been evaluated and is on the order of (0.06 and 0.003) $cm^3 \cdot mol^{-1}$ in the lower ($\leq 0.05m$) and higher concentration ranges, respectively. The uncertainty in the $C_{p2,\phi}$ values lies within 2%. The $V_{2,\phi}$ and $C_{p2,\phi}$ values obtained for the various systems have been summarized in Tables 1 and 2 and illustrated (representative plots of $V_{2,\phi}$ or $C_{p2,\phi}$ versus m at different molalities (m_s) of $MgCl_2$ at various temperatures are given for glycine only) in Figures 1 and 2. The apparent molar volume at infinite dilution ($V_{2,\phi}^\infty$) (which is also equal to V_2^∞, the partial molar volume of the solute at

Table 1. Densities (ρ) and Apparent Molar Volumes ($V_{2\phi}$) of Some Amino Acids in Water and in Aqueous Magnesium Chloride Solutions at (288.15, 298.15, and 308.15) K

288.15 K

glycine

m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2\phi}$ / cm^3·mol^{-1}
m_s/mol·kg^{-1} = 0.0		
0.071 99	1.001 440	42.40
0.088 29	1.001 969	42.44
0.205 85	1.005 721	42.62
0.205 91	1.005 725	42.61
0.318 77	1.009 266	42.75
0.327 86	1.010 953	42.78
0.406 86	1.012 019	42.77
0.486 94	1.014 475	42.84
0.507 47	1.015 099	42.86
m_s/mol·kg^{-1} = 0.050 16 (ρ = 1.003 127 g·cm^{-3})		
0.048 10	1.004 679	42.69
0.079 84	1.005 692	42.80
0.183 41	1.008 989	42.82
0.297 18	1.012 561	42.89
0.404 99	1.015 875	43.01
0.500 67	1.018 769	43.11
0.557 78	1.020 528	43.09
m_s/mol·kg^{-1} = 0.101 23 (ρ = 1.007 082 g·cm^{-3})		
0.052 59	1.008 749	43.21
0.093 16	1.010 027	43.25
0.185 69	1.012 945	43.16
0.304 81	1.016 626	43.26
0.406 01	1.019 695	43.37
0.502 58	1.022 602	43.42
m_s/mol·kg^{-1} = 0.201 09 (ρ = 1.014 915 g·cm^{-3})		
0.049 21	1.016 448	43.65
0.096 69	1.047 930	43.57
0.192 48	1.020 863	43.72
0.294 24	1.023 917	43.88
0.381 42	1.026 527	43.91
0.518 76	1.030 587	43.96
m_s/mol·kg^{-1} = 0.271 58 (ρ = 1.020 094 g·cm^{-3})		
0.100 54	1.023 191	43.85
0.200 27	1.026 222	43.92
0.302 85	1.029 258	44.12
0.391 41	1.031 933	44.01
0.488 09	1.034 743	44.12
m_s/mol·kg^{-1} = 0.396 69 (ρ = 1.030 165 g·cm^{-3})		
0.049 61	1.031 498	47.49
0.096 71	1.032 992	45.21
0.205 91	1.036 262	44.71
0.295 87	1.038 983	44.41
0.359 59	1.040 817	44.50
0.408 48	1.042 261	44.45
0.635 22	1.048 673	44.62
m_s/mol·kg^{-1} = 0.404 66 (ρ = 1.030 233 g·cm^{-3})		
0.015 32	1.030 655	46.86
0.096 64	1.033 028	45.49
0.202 13	1.036 210	44.75
0.291 02	1.038 769	44.86
0.404 86	1.041 965	45.05
m_s/mol·kg^{-1} = 0.607 42 (ρ = 1.045 416 g·cm^{-3})		
0.048 41	1.047 676	46.28
0.097 36	1.048 160	45.90
0.194 34	1.020 887	45.81
0.253 35	1.052 636	45.42
0.362 34	1.055 337	45.48
0.437 05	1.057 794	45.36
m_s/mol·kg^{-1} = 0.815 27 (ρ = 1.060 203 g·cm^{-3})		
0.048 39	1.061 245	51.61
0.101 69	1.062 916	46.95
0.248 72	1.066 885	46.61
0.397 95	1.070 903	46.42
0.502 09	1.073 665	46.36
0.603 13	1.076 115	46.64
m_s/mol·kg^{-1} = 0.816 48 (ρ = 1.059 478 g·cm^{-3})		
0.045 21	1.060 556	49.55
0.101 50	1.062 165	47.15
0.197 34	1.064 838	46.42
0.316 36	1.068 111	46.17
0.457 61	1.071 824	46.28
0.493 97	1.072 886	46.09

L-alanine

m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2\phi}$ / cm^3·mol^{-1}
m_s/mol·kg^{-1} = 0.0		
0.057 42	1.000 779	59.72
0.079 81	1.001 428	59.78
0.096 07	1.001 905	59.73
0.184 06	1.004 435	59.81
0.319 72	1.008 254	59.93
0.421 89	1.011 586	60.05
m_s/mol·kg^{-1} = 0.050 17 (ρ = 1.003 116 g·cm^{-3})		
0.059 61	1.004 847	59.86
0.090 31	1.005 727	59.92
0.182 93	1.008 359	60.02
0.263 21	1.010 593	60.14
0.347 58	1.012 918	60.20
0.494 15	1.016 863	60.34
0.576 63	1.019 053	60.39
m_s/mol·kg^{-1} = 0.100 39 (ρ = 1.007 108 g·cm^{-3})		
0.053 45	1.008 626	60.38
0.104 57	1.010 064	60.41
0.202 99	1.012 818	60.39
0.291 84	1.015 266	60.41
0.353 03	1.016 936	60.42
0.451 40	1.019 599	60.43
0.593 22	1.023 310	60.56
m_s/mol·kg^{-1} = 0.403 39 (ρ = 1.030 418 g·cm^{-3})		
0.051 02	1.031 714	62.47
0.102 08	1.033 065	61.88
0.210 58	1.035 877	61.72
0.288 25	1.037 809	61.87
0.369 05	1.039 895	61.71
0.483 63	1.042 736	61.74
0.598 41	1.045 535	61.76
m_s/mol·kg^{-1} = 0.404 17 (ρ = 1.030 491 g·cm^{-3})		
0.059 44	1.031 990	62.61
0.097 11	1.032 907	62.88
0.204 17	1.035 743	61.91
0.288 22	1.037 895	61.82
0.415 10	1.041 178	61.57
0.525 76	1.043 795	61.91
0.568 04	1.044 795	61.88
m_s/mol·kg^{-1} = 0.813 65 (ρ = 1.060 342 g·cm^{-3})		
0.050 08	1.061 456	64.16
0.092 69	1.062 429	63.86
0.164 33	1.064 165	63.10
0.296 69	1.067 214	63.01
0.378 61	1.068 995	63.18
0.489 43	1.071 561	62.97
0.533 05	1.072 512	62.99

L-leucine

m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2\phi}$ / cm^3·mol^{-1}
m_s/mol·kg^{-1} = 0.0		
0.008 47	0.999 305	106.73
0.020 55	0.999 600	106.75
0.036 34	0.999 985	106.74
0.043 95	1.000 168	106.78
0.056 36	1.000 467	106.80
0.087 70	1.001 225	106.78
0.100 05	1.001 518	106.80
m_s/mol·kg^{-1} = 0.050 16 (ρ = 1.003 167 1 g·cm^{-3})		
0.009 52	1.003 389	107.92
0.019 09	1.003 618	107.23
0.037 38	1.004 056	107.05
0.046 97	1.004 238	107.09
0.070 15	1.004 822	107.14
0.079 56	1.005 039	107.18
0.110 57	1.005 781	106.99
m_s/mol·kg^{-1} = 0.100 57 (ρ = 1.007 117 g·cm^{-3})		
0.010 02	1.007 316	110.56
0.018 52	1.007 511	109.27
0.040 33	1.008 025	107.97
0.048 79	1.008 235	107.56
0.064 81	1.008 594	107.62
0.078 25	1.008 913	107.44
0.101 21	1.009 452	107.26
m_s/mol·kg^{-1} = 0.403 35 (ρ = 1.030 525 g·cm^{-3})		
0.009 45	1.030 683	111.52
0.021 27	1.030 917	109.91
0.047 41	1.031 442	108.99
0.070 16	1.031 914	108.51
0.087 34	1.032 246	108.56
0.092 79	1.032 358	108.50
m_s/mol·kg^{-1} = 0.812 97 (ρ = 1.060 669 g·cm^{-3})		
0.012 61	1.060 825	112.65
0.017 95	1.060 918	111.33
0.036 64	1.061 236	109.86
0.048 31	1.061 437	109.46
0.070 67	1.061 783	109.54
0.090 61	1.062 097	109.52
0.094 55	1.062 159	109.51

Table 1. (Continued)

glycine			L-alanine			L-leucine		
m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2\phi}$ / cm^3·mol^{-1}	m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2\phi}$ / cm^3·mol^{-1}	m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2\phi}$ / cm^3·mol^{-1}
				298.15 K				
m_s/mol·kg^{-1} = 0.0			m_s/mol·kg^{-1} = 0.0			m_s/mol·kg^{-1} = 0.0		
0.013 87	0.997 485	43.27	0.057 42	0.998 691	60.37	0.011 05	0.997 306	107.62
0.043 14	0.998 413	43.30	0.079 81	0.999 327	60.43	0.026 55	0.997 674	107.60
0.059 19	0.998 920	43.31	0.096 07	0.999 788	60.44	0.047 09	0.998 155	107.69
0.071 99	0.999 324	43.32	0.184 06	1.002 261	60.51	0.060 09	0.998 468	107.66
0.089 07	0.999 859	43.37	0.319 72	1.006 146	60.48	0.087 36	0.999 093	107.74
0.111 49	1.000 563	43.38	0.421 89	1.008 869	60.44	0.089 83	0.999 151	107.73
0.164 30	1.002 213	43.43						
0.286 85	1.005 980	43.56						
0.481 72	1.011 801	43.70						
m_s/mol·kg^{-1} = 0.050 27 (ρ = 1.001 018 g·cm^{-3})			m_s/mol·kg^{-1} = 0.050 28 (ρ = 1.001 018 g·cm^{-3})			m_s/mol·kg^{-1} = 0.050 27 (ρ = 1.001 02 g·cm^{-3})		
0.048 10	1.002 528	46.59	0.059 61	1.002 685	60.97	0.009 52	1.001 247	108.11
0.183 41	1.006 726	43.68	0.090 31	1.003 548	60.88	0.019 09	1.001 471	107.82
0.297 18	1.010 175	43.84	0.182 93	1.006 121	60.85	0.037 38	1.001 886	108.05
0.404 99	1.013 418	43.89	0.263 21	1.008 298	60.94	0.046 97	1.002 110	107.93
0.500 67	1.016 251	43.96	0.347 58	1.010 578	60.97	0.070 15	1.002 644	107.88
0.557 78	1.017 938	43.98	0.494 15	1.014 454	61.04	0.079 56	1.002 855	107.93
			0.576 63	1.016 269	61.13	0.110 57	1.003 569	107.83
m_s/mol·kg^{-1} = 0.099 90 (ρ = 1.004 890 g·cm^{-3})			m_s/mol·kg^{-1} = 0.100 61 (ρ = 1.004 956 g·cm^{-3})			m_s/mol·kg^{-1} = 0.100 79 (ρ = 1.004 959 g·cm^{-3})		
0.108 12	1.008 224	44.02	0.053 45	1.006 434	61.18	0.010 02	1.005 165	110.25
0.160 60	1.009 818	44.10	0.104 57	1.007 869	60.88	0.018 52	1.005 368	108.65
0.222 60	1.011 712	44.21	0.202 99	1.015 460	61.04	0.040 33	1.005 856	108.43
0.352 20	1.015 520	44.44	0.298 14	1.012 763	61.10	0.048 79	1.006 048	108.34
0.530 50	1.020 656	44.64	0.353 03	1.014 542	61.18	0.064 81	1.006 407	108.27
0.646 00	1.023 929	44.73	0.451 40	1.017 199	61.23	0.078 25	1.006 704	108.27
			0.593 22	1.020 779	61.28	0.101 21	1.007 206	108.33
m_s/mol·kg^{-1} = 0.403 58 (ρ = 1.027 856 g·cm^{-3})			m_s/mol·kg^{-1} = 0.404 38 (ρ = 1.027 998 g·cm^{-3})			m_s/mol·kg^{-1} = 0.404 33 (ρ = 1.028 123 g·cm^{-3})		
0.055 58	1.029 523	44.57	0.051 02	1.029 251	63.35	0.009 45	1.028 247	115.12
0.102 88	1.030 908	44.82	0.102 08	1.030 579	62.58	0.021 27	1.028 456	112.72
0.204 17	1.033 847	44.99	0.210 58	1.033 335	62.36	0.047 41	1.029 004	109.72
0.303 15	1.036 621	45.28	0.288 25	1.035 240	62.45	0.051 49	1.029 084	109.84
0.371 20	1.038 525	45.42	0.369 05	1.037 265	62.34	0.070 16	1.029 462	109.40
0.499 36	1.042 085	45.44	0.483 63	1.039 999	62.45	0.087 34	1.029 794	109.31
0.628 04	1.049 279	45.42	0.598 41	1.042 749	62.44	0.092 79	1.029 885	109.45
0.762 02	1.049 278	45.48						
m_s/mol·kg^{-1} = 0.711 55 (ρ = 1.050 170 g·cm^{-3})			m_s/mol·kg^{-1} = 0.405 14 (ρ = 1.028 128 g·cm^{-3})			m_s/mol·kg^{-1} = 0.818 09 (ρ = 1.054 509 g·cm^{-3})		
0.052 16	1.051 659	45.52	0.059 44	1.029 494	64.81	0.010 08	1.054 584	117.65
0.107 10	1.053 177	45.89	0.097 11	1.030 516	63.24	0.020 44	1.054 715	115.30
0.195 49	1.055 639	45.93	0.204 17	1.033 149	63.07	0.030 82	1.054 881	113.50
0.296 19	1.058 379	45.99	0.288 22	1.035 242	62.86	0.041 38	1.055 008	112.01
0.410 00	1.061 447	46.05	0.415 10	1.038 389	62.64	0.048 22	1.055 158	112.22
0.197 10	1.063 782	46.06	0.527 59	1.041 059	62.68	0.065 59	1.055 546	110.10
			0.568 04	1.042 321	62.16	0.077 86	1.055 744	110.00
m_s/mol·kg^{-1} = 0.763 11 (ρ = 1.054 226 g·cm^{-3})			m_s/mol·kg^{-1} = 0.815 84 (ρ = 1.057 703 g·cm^{-3})					
0.048 39	1.055 542	46.69	0.050 08	1.058 686	66.62			
0.096 08	1.056 862	46.41	0.092 69	1.059 672	65.11			
0.169 89	1.058 905	46.22	0.164 33	1.061 358	64.12			
0.306 67	1.062 599	46.27	0.296 69	1.064 351	63.80			
0.396 16	1.064 991	46.29	0.378 61	1.066 157	63.78			
0.515 09	1.068 103	46.35	0.489 43	1.068 567	63.73			
			0.533 05	1.069 579	63.60			
m_s/mol·kg^{-1} = 0.814 62 (ρ = 1.057 683 g·cm^{-3})								
0.049 03	1.058 944	47.93						
0.099 91	1.060 372	46.82						
0.165 49	1.062 194	46.41						
0.278 40	1.065 228	46.42						
0.400 85	1.068 512	46.48						
0.479 64	1.070 489	46.54						
m_s/mol·kg^{-1} = 0.814 68 (ρ = 1.057 542 g·cm^{-3})								
0.055 37	1.058 964	47.45						
0.099 48	1.060 255	46.49						
0.182 02	1.063 515	46.34						
0.298 21	1.065 599	46.47						
0.434 23	1.069 196	46.48						
0.488 21	1.070 604	46.49						
m_s/mol·kg^{-1} = 0.918 11 (ρ = 1.064 977 g·cm^{-3})								
0.048 62	1.066 158	49.02						
0.105 45	1.067 670	47.85						
0.220 27	1.070 737	47.18						
0.320 67	1.073 394	46.98						
0.423 26	1.076 073	46.89						
0.487 21	1.064 977	46.82						

Table 1. (Continued)

glycine			L-alanine			L-leucine		
m	ρ	$V_{2\phi}$	m	ρ	$V_{2\phi}$	m	ρ	$V_{2\phi}$
$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$
			308.15 K					
$m_s/mol \cdot kg^{-1} = 0.0$			$m_s/mol \cdot kg^{-1} = 0.0$			$m_s/mol \cdot kg^{-1} = 0.0$		
0.052 41	0.995 657	44.02	0.052 30	0.995 507	60.94	0.020 55	0.994 505	108.52
0.069 46	0.996 187	43.97	0.070 40	0.996 019	60.91	0.036 34	0.994 863	108.65
0.093 36	0.996 929	43.98	0.107 56	0.997 055	60.97	0.043 95	0.995 035	108.72
0.167 57	0.999 091	44.12	0.203 06	0.999 689	61.08	0.056 36	0.995 379	108.87
0.315 73	1.003 698	44.10	0.266 55	1.001 415	61.13	0.087 70	0.996 009	108.91
0.415 03	1.006 676	44.12	0.388 05	1.004 619	61.26	0.100 05	0.996 261	109.15
0.513 43	1.009 576	44.19	0.415 84	1.005 418	61.21			
			0.482 77	1.007 157	61.31			
$m_s/mol \cdot kg^{-1} = 0.052\ 55$ ($\rho = 0.998\ 143\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.050\ 43$ ($\rho = 0.997\ 978\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.050\ 42$ ($\rho = 0.997\ 997\ g \cdot cm^{-3}$)		
0.048 03	0.999 627	44.13	0.059 61	0.999 649	61.03	0.009 52	0.998 210	108.86
0.091 65	1.000 956	44.29	0.090 31	1.000 493	61.16	0.019 09	0.998 425	108.89
0.176 52	1.003 533	44.32	0.182 93	1.003 036	61.20	0.037 38	0.998 825	109.10
0.289 06	1.006 915	44.35	0.263 07	1.005 195	61.28	0.046 97	0.999 039	109.05
0.414 74	1.010 605	44.49	0.347 58	1.007 441	61.36	0.070 15	0.999 539	109.20
0.512 36	1.013 428	44.59	0.494 15	1.011 311	61.36	0.079 56	0.999 742	109.22
0.639 27	1.017 006	44.74	0.576 63	1.013 280	61.67	0.110 57	1.000 401	109.35
$m_s/mol \cdot kg^{-1} = 0.101\ 05$ ($\rho = 1.004\ 798\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.100\ 92$ ($\rho = 1.001\ 907\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.101\ 09$ ($\rho = 1.002\ 010\ 5\ g \cdot cm^{-3}$)		
0.095 89	1.004 691	44.37	0.053 45	1.003 348	61.98	0.010 02	1.005 165	110.25
0.172 72	1.006 999	44.49	0.104 57	1.004 751	61.65	0.018 52	1.005 368	108.65
0.286 30	1.010 376	44.57	0.202 99	1.007 392	61.67	0.040 33	1.005 856	108.43
0.411 39	1.013 976	44.83	0.291 84	1.009 739	61.70	0.048 79	1.006 048	108.34
0.496 55	1.016 470	44.76	0.353 03	1.011 334	61.74	0.064 81	1.006 407	108.27
			0.451 40	1.013 877	61.77	0.078 25	1.006 704	108.27
			0.593 22	1.017 479	61.81	0.101 21	1.007 206	108.33
$m_s/mol \cdot kg^{-1} = 0.202\ 59$ ($\rho = 1.009\ 543\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.104\ 42$ ($\rho = 1.002\ 150\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.405\ 60$ ($\rho = 1.0250\ 11\ g \cdot cm^{-3}$)		
0.042 99	1.010 793	45.72	0.053 51	1.003 599	61.76	0.009 45	1.025 155	113.42
0.108 12	1.012 788	44.77	0.097 65	1.004 789	61.78	0.021 27	1.025 379	111.44
0.165 58	1.014 507	44.73	0.200 47	1.007 529	61.83	0.047 41	1.025 871	110.61
0.313 79	1.018 801	44.99	0.266 92	1.009 284	61.83	0.051 49	1.025 940	110.69
0.397 01	1.021 178	45.09	0.404 99	1.012 879	61.84	0.070 16	1.026 294	110.43
0.494 15	1.023 892	45.22	0.463 62	1.014 735	61.92	0.087 34	1.026 599	110.49
0.607 91	1.027 115	45.21	0.487 97	1.014 955	61.97	0.093 79	1.026 696	110.51
$m_s/mol \cdot kg^{-1} = 0.405\ 98$ ($\rho = 1.024\ 752\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.203\ 46$ ($\rho = 1.009\ 698\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.818\ 21$ ($\rho = 1.054\ 368\ g \cdot cm^{-3}$)		
0.048 76	1.026 138	46.16	0.046 79	1.010 902	62.93	0.012 61	1.054 501	116.92
0.108 32	1.027 929	45.18	0.103 87	1.012 409	62.46	0.017 95	1.054 582	114.59
0.177 53	1.029 925	45.28	0.233 25	1.015 809	62.15	0.036 64	1.054 850	112.53
0.309 25	1.033 618	45.56	0.290 17	1.017 263	62.20	0.048 31	1.055 000	112.58
0.392 12	1.035 893	45.70	0.396 90	1.019 973	62.21	0.070 67	1.055 305	112.40
0.500 15	1.038 796	45.89	0.465 18	1.021 670	62.25	0.090 61	1.055 557	112.49
0.603 45	1.041 607	45.91	0.622 41	1.025 548	62.28	0.094 55	1.055 614	112.43
$m_s/mol \cdot kg^{-1} = 0.822\ 18$ ($\rho = 1.053\ 952\ g \cdot cm^{-3}$)			$m_s/mol \cdot kg^{-1} = 0.405\ 87$ ($\rho = 1.024\ 354\ g \cdot cm^{-3}$)					
0.045 91	1.055 131	48.31	0.051 02	1.025 564	64.31			
0.093 96	1.053 441	47.26	0.102 08	1.026 869	63.34			
0.211 59	1.059 634	46.81	0.210 58	1.029 567	63.06			
0.398 59	1.064 496	46.94	0.288 25	1.031 443	63.10			
0.481 82	1.066 633	46.97	0.369 05	1.033 405	63.04			
0.574 16	1.069 012	46.94	0.482 63	1.036 050	63.20			
			0.598 41	1.038 730	63.19			
			$m_s/mol \cdot kg^{-1} = 0.406\ 48$ ($\rho = 1.024\ 855\ g \cdot cm^{-3}$)					
			0.059 44	1.026 285	63.93			
			0.097 11	1.027 209	63.71			
			0.204 17	1.029 915	63.02			
			0.288 22	1.031 984	62.44			
			0.415 10	1.035 047	62.93			
			0.527 59	1.037 698	62.96			
			0.568 00	1.038 643	62.97			
			$m_s/mol \cdot kg^{-1} = 0.819\ 11$ ($\rho = 1.053\ 787\ g \cdot cm^{-3}$)					
			0.050 08	1.054 638	69.18			
			0.092 69	1.055 637	66.45			
			0.164 33	1.057 572	65.23			
			0.296 69	1.060 206	64.66			
			0.378 61	1.062 037	64.41			
			0.489 43	1.064 289	64.57			
			0.533 05	1.065 361	64.28			

[a] m_s = molality of $MgCl_2$ in water.

Table 2. Heat Capacities (C_p) and Apparent Heat Capacities ($C_{p2,\phi}$) of Glycine and L-Alanine in Water and in Aqueous Magnesium Chloride Solutions at (298.15 to 328.15) K[a]

glycine						L-alanine					
m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]
mol·kg^{-1}	J·K^{-1}·g^{-1}	J·K^{-1}·mol^{-1}	mol·kg^{-1}	J·K^{-1}·g^{-1}	J·K^{-1}·g^{-1}	mol·kg^{-1}	J·K^{-1}·g^{-1}	J·K^{-1}·mol^{-1}	mol·kg^{-1}	J·K^{-1}·g^{-1}	J·K^{-1}·g^{-1}
298.15 K											
m_s/mol·kg^{-1} = 0.050 65 (C_p = 4.149 984 J·K^{-1}·g^{-1})						m_s/mol·kg^{-1} = 0.050 65					
0.054 91	4.137 778	88	0.958 91	3.921 351	56	0.048 10	4.141 335	189	0.149 20	4.117 028	146
0.095 50	4.127 489	74	1.459 10	3.826 006	65	0.064 91	4.138 127	186	0.188 90	4.107 089	139
0.196 86	4.101 858	63	1.924 10	3.747 191	72	0.065 11	4.135 964	153	0.475 90	4.041 875	133
0.477 11	4.031 064	53				0.146 50	4.118 144	150	0.994 71	3.957 759	140
						0.149 00	4.116 539	142	1.932 30	3.788 342	150
m_s/mol·kg^{-1} = 0.079 55 (C_p = 4.131 553 J·K^{-1}·g^{-1})						m_s/mol·kg^{-1} = 0.079 55					
0.045 36	4.124 970	77	0.393 96	4.034 746	57	0.047 39	4.123 635	200	0.376 10	4.052 033	149
0.068 71	4.114 611	62	0.580 49	3.990 492	57	0.067 37	4.119 555	189	0.946 84	3.943 472	154
0.098 01	4.107 144	59	0.963 31	3.907 169	60	0.094 37	4.112 018	159	1.457 04	3.863 607	160
0.198 39	4.082 112	57				0.198 87	4.089 546	153	1.892 90	3.794 459	160
m_s/mol·kg^{-1} = 0.099 39 (C_p = 4.118 668 J·K^{-1}·g^{-1})						m_s/mol·kg^{-1} = 0.099 39					
0.057 41	4.105 509	79	0.536 75	3.989 524	59	0.050 00	4.108 930	171	0.473 84	4.021 286	153
0.101 36	4.095 460	78	1.108 16	3.870 171	66	0.107 74	4.097 551	169	0.960 78	3.930 186	154
0.197 59	4.130 956	62	1.872 44	3.731 252	73	0.194 65	4.078 180	155	1.971 20	3.773 119	160
m_s/mol·kg^{-1} = 0.385 97 (C_p = 3.941 273 J·K^{-1}·g^{-1})						m_s/mol·kg^{-1} = 0.385 97					
0.050 38	3.930 879	89	0.188 76	3.900 041	74	0.075 00	3.929 839	198	0.361 04	3.877 866	170
0.062 09	3.928 453	88	0.378 80	3.861 928	80	0.095 43	3.923 603	164	0.942 33	3.784 662	171
0.070 32	3.926 548	85	0.563 52	3.826 240	83	0.186 05	3.907 837	168	1.883 03	3.651 958	171
0.098 23	3.919 168	70	1.872 44	3.750 706	83						
303.15 K											
m_s/mol·kg^{-1} = 0.050 65											
0.054 91	4.137 433	98	0.958 91	3.925 521	62	0.048 10	4.140 039	181	0.149 20	4.116 173	146
0.095 50	4.126 460	73	1.459 10	3.830 195	69	0.064 91	4.136 136	169	0.188 90	4.106 572	141
0.196 86	4.102 286	70	1.924 10	3.751 328	75	0.065 11	4.134 004	165	0.475 90	4.043 479	138
0.477 11	4.032 849	59				0.146 50	4.118 299	157	0.994 71	3.961 045	145
						0.149 00	4.115 865	144	1.932 30	3.801 048	159
m_s/mol·kg^{-1} = 0.079 55											
0.045 36	4.119 268	76	0.393 96	4.035 648	63	0.047 39	4.121 692	195	0.376 10	4.050 324	149
0.068 71	4.112 988	63	0.580 49	3.992 301	63	0.067 37	4.117 255	180	0.946 84	3.944 176	155
0.098 01	4.105 650	61	0.963 31	3.914 824	71	0.094 37	4.110 565	162	1.457 04	3.861 921	160
0.198 39	4.081 383	62				0.198 87	4.088 346	157	1.892 90	3.805 605	168
m_s/mol·kg^{-1} = 0.099 39											
0.057 41	4.104 474	78	0.536 75	3.991 066	64	0.050 00	4.107 905	170	0.473 84	4.022 292	157
0.101 36	4.094 351	77	1.108 16	3.885 722	82	0.107 74	4.096 513	168	0.960 78	3.931 016	156
0.197 59	4.071 052	70	1.872 44	3.734 944	76	0.194 65	4.077 880	159	1.971 20	3.774 887	162
m_s/mol·kg^{-1} = 0.385 97											
0.050 38	3.932 038	86	0.188 76	3.902 128	79	0.075 00	3.931 358	201	0.361 04	3.880 206	173
0.062 09	3.929 488	84	0.378 80	3.864 402	84	0.095 43	3.924 900	164	0.942 33	3.788 949	175
0.070 32	3.927 755	84	0.563 52	3.830 414	89	0.186 05	3.909 606	171	1.883 03	3.660 476	176
0.098 23	3.919 972	64	1.872 44	3.756 641	88						
308.15 K											
m_s/mol·kg^{-1} = 0.050 65											
0.054 91	4.138 208	116	0.958 91	3.930 429	67	0.048 10	4.140 046	195	0.149 20	4.116 194	147
0.095 50	4.135 837	83	1.459 10	3.838 232	75	0.064 91	4.139 210	167	0.188 90	4.107 309	146
0.196 86	4.103 812	79	1.924 10	3.758 060	79	0.065 11	4.134 701	160	0.475 90	4.046 745	146
0.477 11	4.035 321	65				0.146 50	4.117 330	151	0.994 71	3.965 571	152
						0.149 00	4.116 161	147	1.932 30	3.809 837	164
m_s/mol·kg^{-1} = 0.079 55											
0.045 36	4.119 418	84	0.393 96	4.036 488	66	0.047 39	4.121 793	199	0.376 10	4.051 202	152
0.068 71	4.113 466	71	0.580 49	3.994 020	66	0.067 37	4.117 914	191	0.946 84	3.949 211	161
0.098 01	4.106 310	69	0.963 31	3.915 772	72	0.094 37	4.110 891	166	1.457 04	3.870 628	167
0.198 39	4.082 468	68				0.198 87	4.088 680	158	1.892 90	3.802 077	166
m_s/mol·kg^{-1} = 0.099 39											
0.057 41	4.103 642	90	0.536 75	3.993 584	69	0.050 00	4.108 165	178	0.473 84	4.024 072	161
0.101 36	4.095 433	89	1.108 16	3.889 724	86	0.107 74	4.096 606	171	0.960 78	3.933 948	159
0.197 59	4.070 139	66	1.872 44	3.743 985	82	0.194 65	4.078 380	162	1.971 20	3.785 864	169
m_s/mol·kg^{-1} = 0.385 97											
0.050 38	3.936 245	88	0.188 76	3.906 116	78	0.075 00	3.935 530	202	0.361 04	3.883 760	172
0.062 09	3.933 115	76	0.378 80	3.867 939	82	0.095 43	3.928 644	161	0.942 33	3.791 240	172
0.070 32	3.931 739	82	0.563 52	3.832 513	85	0.186 05	3.913 339	169	1.883 03	3.659 518	174
0.098 23	3.924 173	65	1.872 44	3.757 534	83						
313.15 K											
m_s/mol·kg^{-1} = 0.050 65											
0.054 91	4.139 147	131	0.958 91	3.934 330	71	0.048 10	4.139 938	180	0.149 20	4.117 250	154
0.095 50	4.127 589	85	1.459 10	3.841 142	77	0.064 91	4.136 085	169	0.188 90	4.109 182	155
0.196 86	4.104 572	82	1.924 10	3.721 129	81	0.065 11	4.135 031	160	0.475 90	4.048 264	149
0.477 11	4.037 727	70				0.146 50	4.118 007	155	0.994 71	3.968 576	151
						0.149 00	4.117 415	155	1.932 30	3.813 153	166

Table 2. (Continued)

glycine						L-alanine					
m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]
mol·kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.mol^{-1}	mol.kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.g^{-1}	mol.kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.mol^{-1}	mol.kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.g^{-1}
313.15 K (Continued)											
m_s/mol·kg^{-1} = 0.079 55											
0.045 36	4.120 906	95	0.393 96	4.014 653	70	0.047 39	4.122 956	206	0.376 10	4.056 890	165
0.068 71	4.114 685	77	0.580 49	3.998 962	73	0.067 37	4.118 931	194	0.946 84	3.951 567	163
0.098 01	4.107 609	74	0.963 31	3.918 325	74	0.094 37	4.112 184	171	1.457 04	3.872 246	168
0.198 39	4.084 208	73				0.198 87	4.091 449	168	1.892 90	3.806 419	168
m_s/mol·kg^{-1} = 0.099 39											
0.057 41	4.104 154	93	0.536 75	3.996 196	79	0.050 00	4.108 799	182	0.473 84	4.026 439	165
0.101 36	4.096 116	91	1.108 16	3.878 189	75	0.107 74	4.097 928	179	0.960 78	3.940 125	166
0.197 59	4.071 902	72	1.872 44	3.749 049	84	0.194 65	4.080 138	169	1.971 20	3.790 229	171
m_s/mol·kg^{-1} = 0.385 97											
0.050 38	3.937 337	101	0.188 76	3.908 347	88	0.075 00	3.936 845	212	0.361 04	3.888 857	185
0.062 09	3.934 815	96	0.378 80	3.872 182	93	0.095 43	3.930 294	173	0.942 33	3.803 690	187
0.070 32	3.933 079	95	0.563 52	3.839 067	96	0.186 05	3.915 881	181	1.883 03	3.676 922	184
0.098 23	3.925 807	77	1.872 44	3.767 003	95						
318.15 K											
m_s/mol·kg^{-1} = 0.050 65											
0.054 91	4.139 954	134	0.958 91	3.938 305	75	0.048 10	4.141 121	191	0.149 20	4.117 585	152
0.095 50	4.128 283	86	1.459 10	3.848 180	82	0.064 91	4.136 355	163	0.188 90	4.108 831	150
0.196 86	4.104 617	79	1.924 10	3.767 131	84	0.065 11	4.135 902	157	0.475 90	4.051 773	155
0.477 11	4.040 102	74				0.146 50	4.118 233	152	0.994 71	3.972 670	165
						0.149 00	4.117 941	153	1.932 30	3.820 623	170
m_s/mol·kg^{-1} = 0.079 55											
0.045 36	4.122 176	102	0.393 96	4.042 202	77	0.047 39	4.124 023	208	0.376 10	4.058 663	168
0.068 71	4.115 987	82	0.580 49	4.001 307	76	0.067 37	4.119 875	193	0.946 84	3.957 710	169
0.098 01	4.109 214	80	0.963 31	3.918 325	79	0.094 37	4.113 265	172	1.457 04	3.880 438	173
0.198 39	4.086 045	77				0.198 87	4.092 688	169	1.892 90	3.812 389	171
m_s/mol·kg^{-1} = 0.099 39											
0.057 41	4.104 675	100	0.536 75	3.998 313	77	0.050 00	4.109 248	185	0.473 84	4.026 849	166
0.101 36	4.097 055	98	1.108 16	3.891 302	87	0.107 74	4.098 676	183	0.960 78	3.942 538	168
0.197 59	4.073 415	79	1.872 44	3.756 728	89	0.194 65	4.080 030	167	1.971 20	3.798 884	176
m_s/mol·kg^{-1} = 0.385 97											
0.050 38	3.941 073	102	0.188 76	3.913 260	95	0.075 00	3.940 911	218	0.361 04	3.891 628	183
0.062 09	3.938 992	105	0.378 80	3.877 639	98	0.095 43	3.933 756	171	0.942 33	3.805 096	184
0.070 32	3.937 821	111	0.563 52	3.843 482	98	0.186 05	3.919 767	182	1.883 03	3.680 829	185
0.098 23	3.930 664	90	1.872 44	3.771 915	97						
323.15 K											
m_s/mol·kg^{-1} = 0.050 65											
0.054 91	4.141 747	136	0.958 91	3.944 938	81	0.048 10	4.142 228	179	0.149 20	4.119 788	155
0.095 50	4.130 367	90	1.459 10	3.853 556	85	0.064 91	4.138 381	169	0.188 90	4.111 295	154
0.196 86	4.107 158	84	1.924 10	3.774 696	88	0.065 11	4.137 740	166	0.475 90	4.055 194	152
0.477 11	4.044 295	79				0.146 50	4.121 231	161	0.994 71	3.978 257	159
						0.149 00	4.120 013	156	1.932 30	3.812 844	164
m_s/mol·kg^{-1} = 0.079 55											
0.045 36	4.124 244	112	0.393 96	4.045 745	82	0.047 39	4.125 653	208	0.376 10	4.062 726	171
0.068 71	4.118 059	89	0.580 49	4.006 335	82	0.067 37	4.121 392	192	0.946 84	3.962 119	172
0.098 01	4.111 363	86	0.963 31	3.929 758	84	0.094 37	4.115 433	178	1.457 04	3.890 028	180
0.198 39	4.088 679	82				0.198 87	4.094 446	170	1.892 90	3.835 880	185
m_s/mol·kg^{-1} = 0.099 39											
0.057 41	4.106 415	105	0.536 75	4.005 265	86	0.050 00	4.111 392	188	0.473 84	4.030 795	170
0.101 36	4.099 305	101	1.108 16	3.895 713	90	0.107 74	4.100 275	179	0.960 78	3.948 066	171
0.197 59	4.076 587	85	1.872 44	3.764 833	93	0.194 65	4.082 986	172	1.971 20	3.800 381	176
m_s/mol·kg^{-1} = 0.385 97											
0.050 38	3.945 169	119	0.188 76	3.919 700	109	0.075 00	3.944 829	221	0.361 04	3.900 251	197
0.062 09	3.943 162	112	0.378 80	3.886 051	111	0.095 43	3.938 562	183	0.942 33	3.821 530	199
0.070 32	3.941 927	116	0.563 52	3.854 686	112	0.186 05	3.925 566	194	1.883 03	3.702 985	196
0.098 23	3.934 333	89	1.872 44	3.789 424	112						
328.15 K											
m_s/mol·kg^{-1} = 0.050 65											
0.054 91	4.142 504	133	0.958 91	3.950 835	87	0.048 10	4.146 697	191	0.149 20	4.121 789	163
0.095 50	4.131 768	95	1.459 10	3.863 369	92	0.064 91	4.142 495	172	0.188 90	4.113 453	161
0.196 86	4.108 875	88	1.924 10	3.786 006	94	0.065 11	4.139 062	166	0.475 90	4.059 774	161
0.477 11	4.048 090	85				0.146 50	4.122 674	165	0.994 71	3.982 705	166
						0.149 00	4.121 979	164	1.932 30	3.838 108	179
m_s/mol·kg^{-1} = 0.079 55											
0.045 36	4.125 867	116	0.393 96	4.048 747	86	0.047 39	4.126 980	207	0.376 10	4.066 551	181
0.068 71	4.119 792	94	0.580 49	4.011 211	89	0.067 37	4.123 514	203	0.946 84	3.969 229	179
0.098 01	4.113 241	91	0.963 31	3.936 470	90	0.094 37	4.117 821	189	1.457 04	3.892 898	181
0.198 39	4.091 359	89				0.198 87	4.099 151	187	1.892 90	3.842 010	188

Table 2. (Continued)

glycine						L-alanine					
m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]	m	C_p	$C_{p2,\phi}$[b]
mol·kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.mol^{-1}	mol.kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.g^{-1}	mol.kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.mol^{-1}	mol.kg^{-1}	J.K^{-1}.g^{-1}	J.K^{-1}.g^{-1}
328.15 K (Continued)											
m_s/mol·kg^{-1} = 0.099 39											
0.057 41	4.107 729	109	0.536 75	4.007 721	89	0.050 00	4.112 617	189	0.473 84	4.033 287	173
0.101 36	4.100 540	101	1.108 16	3.907 406	100	0.107 74	4.101 658	181	0.960 78	3.951 336	175
0.197 59	4.078 687	90	1.872 44	3.776 414	99	0.194 65	4.084 725	175	1.971 20	3.809 961	181
m_s/mol·kg^{-1} = 0.385 97											
0.050 38	3.947 974	101	0.188 76	3.921 167	100	0.075 00	3.947 845	219	0.361 04	3.900 984	190
0.062 09	3.945 520	98	0.378 80	3.887 420	106	0.095 43	3.941 354	179	0.942 33	3.818 953	193
0.070 32	3.943 162	88	0.563 52	3.856 416	110	0.186 05	3.927 757	188	1.883 03	3.696 230	190
0.098 23	3.937 091	84	1.872 44	3.786 912	109						

[a] m_s = molality of $MgCl_2$ in water. [b] $C^{\infty}_{p2,\phi}$ of glycine in water = (28, 35, 42, 47, 52, 55, and 57) J·K^{-1}·mol^{-1}at (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K. $C^{\infty}_{p2,\phi}$ of L-alanine in water = (135, 140, 148, 153, 156, 157, and 158) J·K^{-1}·mol^{-1} at (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K.

infinite dilution) of a solute in a given system was determined by least-squares fitting of the $V_{2,\phi}$ data to the equation

$$V_{2,\phi} = V_2^{\infty} + am + bm^2 \tag{5}$$

where a and b are fitting parameters. The $V_{2,\phi}$ data at concentrations of amino acids ≤ 0.05 mol·kg^{-1}, being associated with a larger uncertainty of the order of 0.06 cm^3·mol^{-1}, have not been taken into account for estimating the V_2^{∞} values. However, the $V_{2,\phi}$ versus m dependence was almost linear at the lower concentrations of $MgCl_2$, and only a first-order polynomial was sufficient to fit the data. The values of V_2^{∞} and the constants a and b, along with the standard deviations obtained for the various systems, are summarized in Table 3. The partial molar heat capacities at infinite dilution ($C^{\infty}_{p2,\phi}$) have not been calculated due to a complex dependence of $C_{p2,\phi}$ upon m. The V_2^{∞} values for amino acids in water determined presently agree very well with the literature values.[5,12–14] No data are available for comparison in $MgCl_2$ solutions. Plots of $V_{2,\phi}$ versus m_s (Figure 1) show a peculiar $V_{2,\phi}$ dependence on the change in concentration of $MgCl_2$ which has been confirmed by repeating the experiments in some cases at concentrations of $MgCl_2$ near $m_s \simeq 0.4$, where overlapping results have been obtained. It may further be seen that in the case of glycine in $MgCl_2$ solutions, for concentrations up to $\simeq 0.4m_s$ and at 288.15 K, $V_{2,\phi}$ values increase more or less linearly with the concentration of amino acid. The dependence flattens off with m_s, which is well exhibited by the values of the parameter a, which changes sign from positive to negative. Similar behavior is observed at the other two temperatures, but the reversal occurs now at higher $MgCl_2$ concentration. More or less similar behavior has been observed for the three amino acids at the three temperatures studied. The different concentrations of $MgCl_2$ where reversal of behavior occurs leads to the speculation that factors contributing to the $V_{2,\phi}$ variation with m_s of amino acids remains temperature and $MgCl_2$ concentration specific. Grossly, $V_{2,\phi}$ values of amino acids in most of the cases increase with the increase in concentration of amino acids for lower concentrations of $MgCl_2$ whereas a slight decrease has been observed at higher concentrations of the electrolyte. This is in contrast to the conclusion reached by Soto et al.[15] for $V_{2,\phi}$ of glycine in the presence of KCl, NaCl, KNO_3, and $NaNO_3$ over almost similar concentrations of electrolytes where the $V_{2,\phi}$ of glycine for all the four electrolytes increases as the concentration of either glycine or the electrolyte increases. The plots of $C_{p2,\phi}$ versus m for glycine and L-alanine (Figure 2) also show peculiar behavior of the $C_{p2,\phi}$ values of the amino acids around $\approx 0.40m_s$, as observed in the case of $V_{2,\phi}$ values. The changes again appear to be temperature and $MgCl_2$ concentration specific. These results suggest that the thermodynamic properties of the amino acids in the presence of individual electrolytes may show different behavior, and thus, experimental determination of such properties is a prerequisite to arrive at any generalization. From the partial molar volumes (V_2^{∞}) in water and in aqueous $MgCl_2$ solutions the corresponding partial volumes of transfer ($\Delta_t V_2^{\infty}$) have been calculated as follows:

$$\Delta_t V_2^{\infty}(\text{water} \rightarrow \text{aqueous } MgCl_2) = V_2^{\infty}(\text{in aqueous } MgCl_2) - V_2^{\infty}(\text{in water}) \tag{6}$$

The values for $\Delta_t V_2^{\infty}$ are summarized in Table 4 and illustrated in Figures 3−5. $\Delta_t V_2^{\infty}$ values are positive for all the amino acids and increase with the increase in the concentration of the cosolute. The transfer heat capacity values at infinite dilution ($C^{\infty}_{p2,\phi}$) have not been calculated, but however, on comparing the $C_{p2,\phi}$ values for glycine and L-alanine in various solutions of $MgCl_2$ with $C^{\infty}_{p2,\phi}$ values in water[16] (included in Table 2), it is clear that the $C^{\infty}_{p2,\phi}$ values are higher in the presence of $MgCl_2$ for these amino acids. It may be seen that the $\Delta_t V_2^{\infty}$ values decrease with temperature from (288.15 to 308.15) K for glycine, whereas L-alanine and L-leucine behave differently because of contributions characterized by an opposite temperature dependence.

Franks et al.[17] have shown that the partial molar volume of a nonelectrolyte is a combination of two types of contributions

$$V_{int} = V_{vw} + V_{void} \tag{7}$$

Shahidi et al.[18] further modified the above equation to

$$V_2^{\infty} = V_{vw} + V_{void} - V_{shrinkage} \tag{8}$$

where V_{vw} is the van der Waals volume, V_{void} is the volume associated with the void or empty space, and $V_{shrinkage}$ is the volume due to shrinkage caused by the interaction of hydrogen bonding groups present in the solute with water molecules. Assuming that V_{vw} and V_{void} are not significantly affected by the presence of $MgCl_2$, a positive $\Delta_t V_2^{\infty}$ can therefore be attributed to a decrease in the shrinkage

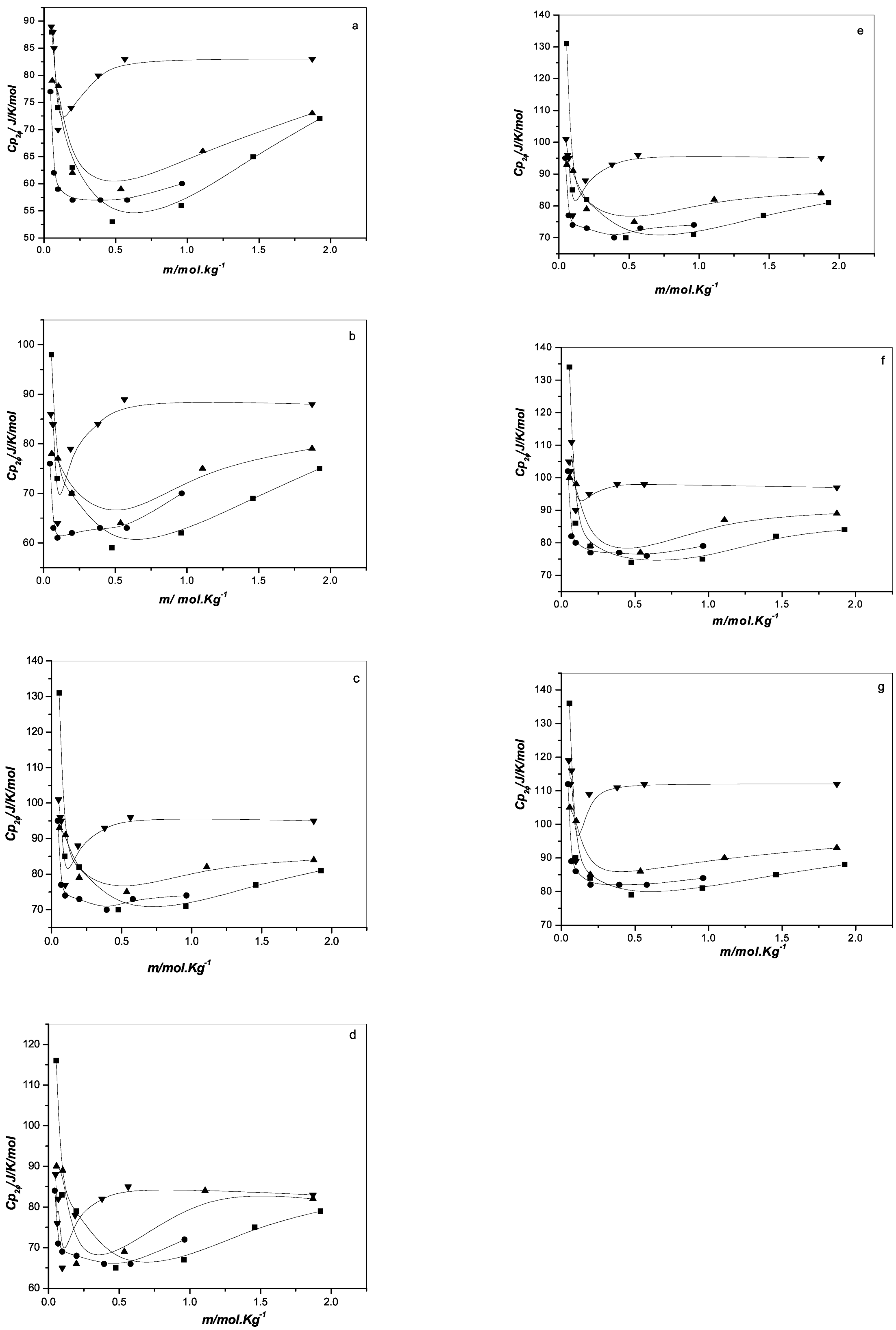

Figure 2. (a) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 298.15 K. (b) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 303.15 K. (c) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 308.15 K. (d) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 313.15 K. (e) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 318.15 K. (f) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 323.15 K. (g) Apparent molar heat capacity ($C_{p2,\phi}$) of glycine vs molality of glycine (m) in aqueous $MgCl_2$ solutions (m_s = ■, 0.05065; ●, 0.07955; ▲, 0.09939; ▼, 0.38597) at 328.15 K.

Table 3. Standard Partial Molar Volume (V_2^∞) for Amino Acids in Water and Aqueous Magnesium Chloride Solutions at (288.15, 298.15, and 308.15) K[a]

288.15 K				298.15 K				308.15 K			
m_s	V_2^∞			m_s	V_2^∞			m_s	V_2^∞		
mol·kg^{-1}	cm^3·mol^{-1}	*a*	*b*	mol·kg^{-1}	cm^3·mol^{-1}	*a*	*b*	mol·kg^{-1}	cm^3·mol^{-1}	*a*	*b*
					Glycine						
0.0	42.37[b] (0.04)	1.01		0.0	43.27[b] (0.02)	0.94		0.0	43.98[b] (0.04)	0.39	
	42.48[c]				43.26[c]				43.79[e]		
	42.54[d]				43.20[d]				43.80[d]		
0.050 16	42.69 (0.04)	0.77		0.050 27	43.56 (0.03)	0.80		0.052 55	44.14 (0.05)	0.90	
0.101 23	43.16 (0.06)	0.47		0.099 90	43.90 (0.04)	1.35		0.101 05	44.29 (0.07)	1.09	
0.201 09	43.57 (0.06)	0.83		0.403 58	45.10 (0.06)	0.83		0.202 59	44.63 (0.06)	1.07	
0.271 58	43.81 (0.07)	0.66		0.715 53	46.20 (0.08)	0.66		0.405 98	45.50 (0.37)	0.54	
0.396 69	44.96 (0.27)	−0.93		0.763 11	46.75 (0.11)	−3.34	5.15	0.822 18	47.05 (0.23)	−0.26	
0.404 66	45.33 (0.35)	−1.18		0.814 62	46.66 (0.18)	−0.43					
0.607 42	46.03 (0.13)	−1.60		0.841 68	46.93 (0.39)	−1.19					
0.815 27	47.40 (0.08)	−4.77	5.70	0.918 11	47.63 (0.44)	−1.93					
0.816 48	47.95 (0.16)	−9.64	12.40								
					L-Alanine						
0.0	59.67[b] (0.03)	0.86		0.0	60.42[b] (0.05)	0.14		0.0	60.88[b] (0.03)	0.89	
	59.67[c]				60.47[c]				61.01[e]		
	59.90[d]				60.40[d]				60.90[d]		
0.050 17	59.83 (0.03)	1.02		0.050 28	60.85 (0.06)	0.40		0.050 43	61.05 (0.09)	0.64	0.52
0.100 39	60.35 (0.04)	0.26		0.100 61	61.08 (0.27)	0.48		0.10092	61.77 (0.12)	−0.04	
0.403 39	61.94 (0.08)	−0.86	0.93	0.404 38	63.33 (0.23)	−5.28	6.60	0.104 42	61.77 (0.03)	0.04	0.64
0.404 17	61.82 (0.17)	0.01		0.405 14	63.44 (0.16)	−1.89		0.203 46	62.60 (0.22)	−0.08	
0.813 65	63.96 (0.33)	−2.36		0.815 84	65.75 (0.24)	−9.99	11.63	0.405 87	64.31 (0.29)	−6.96	8.88
								0.406 48	64.48 (0.25)	−9.84	13.03
								0.819 11	67.34 (0.26)	−14.60	16.84
					L-Leucine						
0.0	106.71[b] (0.02)	1.74	−9.47	0.0	107.59[b] (0.03)	1.65		0.0	108.40[b] (0.07)	6.93	
	106.71[f]				107.70[e]				108.41[e]		
					107.73[f]						
0.050 16	107.53 (0.27)	−5.64		0.050 27	108.02 (0.11)	−1.76		0.050 42	108.84 (0.04)	4.87	
0.100 57	109.10 (0.43)	−21.25	0.43	0.100 79	109.42 (0.58)	−14.94		0.101 09	110.45 (0.12)	−23.77	163.76
0.403 35	111.07 (0.06)	−62.10	374.76	0.404 33	112.52 (0.85)	−39.64		0.405 60	113.95 (0.39)	−105.57	752.70
0.812 97	113.78 (0.39)	−135.21	973.09	0.818 09	116.50 (0.62)	−91.05		0.818 21	118.24 (0.73)	−188.09	1373.66

[a] m_s = molality of $MgCl_2$; parentheses contain standard deviations. [b] Present work. [c] Reference 13. [d] Reference 5. [e] Reference 12. [f] Reference 14.

Table 4. Partial Molar Volume of Transfer ($\Delta_t V_2^\infty$) of Amino Acids from Water to Aqueous Magnesium Chloride Solutions at (288.15, 298.15, and 308.15) K

288.15 K		298.15 K		308.15 K	
m_s	$\Delta_t V_2^\infty$	m_s	$\Delta_t V_2^\infty$	m_s	$\Delta_t V_2^\infty$
mol·kg^{-1}	cm^3·mol^{-1}	mol·kg^{-1}	cm^3·mol^{-1}	mol·kg^{-1}	cm^3·mol^{-1}
		Glycine			
0.050 16	0.32	0.050 27	0.29	0.052 55	0.16
0.101 23	0.79	0.099 90	0.63	0.101 05	0.31
0.201 09	1.20	0.403 58	1.83	0.202 59	0.65
0.271 58	1.44	0.715 53	2.93	0.405 98	1.52
0.396 69	2.59	0.763 11	3.48	0.822 18	3.07
0.404 66	2.96	0.814 62	3.39		
0.607 42	3.66	0.814 68	3.66		
0.815 27	5.03	0.918 11	4.36		
0.816 48	5.58				
		L-Alanine			
0.050 17	0.16	0.050 28	0.43	0.050 43	0.17
0.100 39	0.68	0.100 61	0.66	0.100 92	0.89
0.403 39	2.27	0.404 38	2.91	0.104 42	0.89
0.404 17	2.15	0.405 14	3.02	0.203 46	1.72
0.813 65	4.29	0.815 84	5.33	0.405 87	3.43
				0.406 48	3.60
				0.819 11	6.46
		L-Leucine			
0.050 16	0.82	0.050 27	0.43	0.050 42	0.44
0.100 57	2.39	0.100 79	1.83	0.101 09	2.05
0.403 35	4.36	0.404 33	4.93	0.405 60	5.55
0.812 97	7.07	0.818 09	8.91	0.818 21	9.84

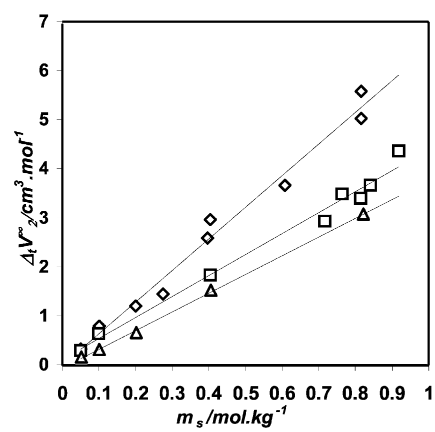

Figure 3. Standard volumes of transfer ($\Delta_t V_2^\infty$) of glycine vs molality (m_s) at different temperatures: ◇, 288.15 K; □, 298.15 K; △, 308.15 K.

volume in the presence of aqueous solutions of $MgCl_2$. Because of the stronger interactions of Mg^{2+} and Cl^- with COO^- and $NH^+{}_3$ in the amino acids, the electrostriction of neighboring water molecules due to these charged centers will be reduced, which will result in a reduction in the shrinkage volume.

The increase of V_2^∞ values with the increase in temperature may also be attributed to the reduction in electrostriction with temperature. This also gets support from the volumetric and compressibility studies of glycine and DL-alanine in aqueous sodium sulfate solutions by Wadi and Ramasami, who report that the hydration number of amino acids decreases with increasing temperature and concentration of sodium sulfate.[19] The increase in the positive V_2^∞ values of the studied amino acids with the increase in the

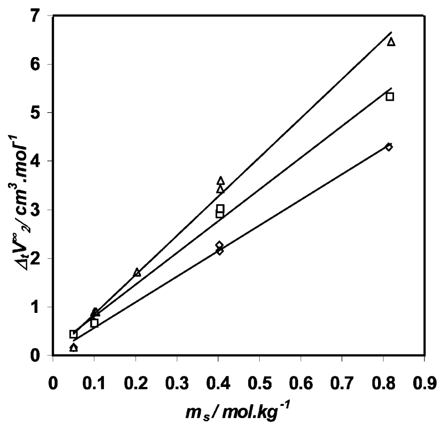

Figure 4. Standard volumes of transfer ($\Delta_t V_2^\infty$) of L-alanine vs molality (m_s) at different temperatures: ◇, 288.15 K; □, 298.15 K; △, 308.15 K.

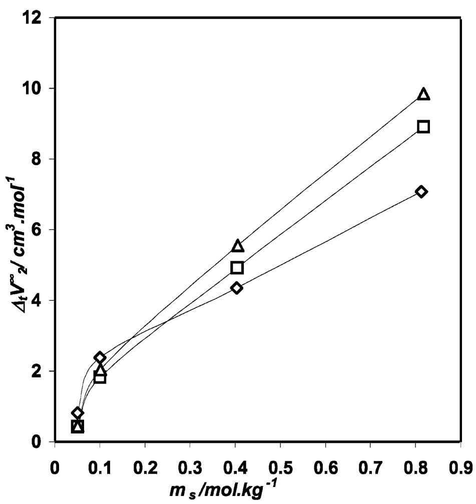

Figure 5. Standard volumes of transfer ($\Delta_t V_2^\infty$) of L-leucine vs molality (m_s) at different temperatures: ◇, 288.15 K; □, 298.15 K; △, 308.15 K.

concentration of $MgCl_2$ may further be attributed to the formation of noncovalent ion pairs between the charged groups of the amino acids and the cation (Mg^{2+}) and the anion (Cl^-) of the electrolyte. This increases the apparent molar volume of the amino acid and decreases the electrostriction of water around amino acids in the presence of $MgCl_2$. Further, the formation of the ion pairs also decreases the hydrophobicity of amino acid molecules arising from the interactions of the hydrocarbon portion of amino acids with water molecules.[15]

Apart from the ion-charged group interactions between Mg^{2+} and COO^- and between Cl^- and $NH^+{}_3$ centers as discussed above, another type of interactions such as ion−nonpolar group interactions between Mg^{2+} or Cl^- ions and nonpolar groups of the amino acids may occur in amino acid + magnesium chloride + water ternary systems. According to the cosphere overlap model developed by Gurney,[20] the ion-charged group interactions would lead to a positive $\Delta_t V_2^\infty$, whereas ion−nonpolar group interactions will result in negative $\Delta_t V_2^\infty$ values. Since positive $\Delta_t V_2^\infty$ values were observed for all the amino acids studied, we can conclude that the contributions of ion-charged group interactions to $\Delta_t V_2^\infty$ dominate over the second type of interactions especially for the infinitely dilute solutions. Owing to the higher charge and small size of Mg^{2+} ions, the $\Delta_t V_2^\infty$ values for the amino acids are higher than the corresponding values in aqueous NaCl solutions.[21] The higher $C_{p2,\phi}$ values for these amino acids in $MgCl_2$ than those in water are also indicative of strong interactions between charged centers of amino acids and ions of $MgCl_2$.

The transfer volumes of the amino acids can also be expressed by the McMillan Mayer theory[22] of solutions, which permits the formal separation of the effects due to interactions between the pairs of solute molecules and those due to interactions between three or more solute molecules by the following equation.

$$\Delta_t V_2^\infty = 2V_{AB}m_s + 3V_{ABB}{m_s}^2 + ... \quad (9)$$

where A stands for the amino acids and B stands for $MgCl_2$ .V_{AB} and V_{ABB} are the pair and triplet volumetric interaction parameters. Using the above equation, volumetric interaction parameters were calculated and are given in Table 5. The data reveal that all pair volumetric interaction parameters V_{AB} are positive for the three amino acids studied and are larger than the corresponding V_{ABB} values. This shows that the interactions between the amino acids and $MgCl_2$ are mainly pair interactions. Further, V_{AB} decreases from L-leucine to L-alanine to glycine at (298.15 and 308.15) K whereas the order is different at 288.15 K, that if, from L-leucine to glycine to L-alanine, which is again indicative of a different temperature dependence of the contributions to V_2^∞. It may also be seen that V_{AB} decreases with temperature in the case of glycine whereas it increases or remains almost constant in the cases of L-alanine and L-leucine, respectively.

The V_2^∞ values for the amino acids studied in water and in aqueous $MgCl_2$ solutions (at rounded molalities of $MgCl_2$ m_s = 0.1, 0.2, ...) at different temperatures were fitted by the method of least squares using the equation

$$V_2^\infty = \alpha + \beta T + \gamma T^2 \quad (10)$$

where α, β, and γ are constants and T is the temperature. The $(\partial V_2^\infty/\partial T)_P$ and $(\partial^2 V_2^\infty/\partial T^2)_P$ parameters were then determined from the above equation and are illustrated in Figures 6 and 7. The values of $(\partial V_2^\infty/\partial T)_P$ and $(\partial^2 V_2^\infty/\partial T^2)_P$ for the amino acids studied presently are 0.0805 cm^3·mol^{-1}·K^{-1}, −0.0019 cm^6·mol^{-2}· K^{-2} for glycine; 0.0605 cm^3·mol^{-1}·K^{-1}, −0.0029 cm^6·mol^{-2}·K^{-2} for L-alanine; and 0.0845 cm^3·mol^{-1}·K^{-1}, −0.0007 cm^6·mol^{-2}·K^{-2} for L-leucine, respectively, in water, which agree very well with the literature values[12] (0.0630 cm^3·mol^{-1}·K^{-1}, −0.0017 cm^6·mol^{-2}·K^{-2} for glycine; 0.0620 cm^3·mol^{-1}·K^{-1}, −0.0016 cm^6·mol^{-2}·K^{-2} for L-alanine; and 0.0840 cm^3·mol^{-1}·K^{-1}, −0.0003 cm^6·mol^{-2}·K^{-2} for L-leucine). It may be seen

Table 5. Pair and Triplet Interaction Coefficients for Some Amino Acids in Aqueous Magnesium Chloride Solutions at (288.15, 298.15, and 308.15) K

	V_{AB}/cm^3·mol^{-2}·kg			V_{ABB}/cm^3·mol^{-3}·kg^2		
amino acid	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K
glycine	3.155	2.0720	1.7096	0.0631	0.1309	0.1335
L-alanine	2.861	3.9899	4.5239	−0.1859	−0.5863	0.4589
L-leucine	7.561	7.0670	7.4857	−2.6806	−1.3342	−1.6199

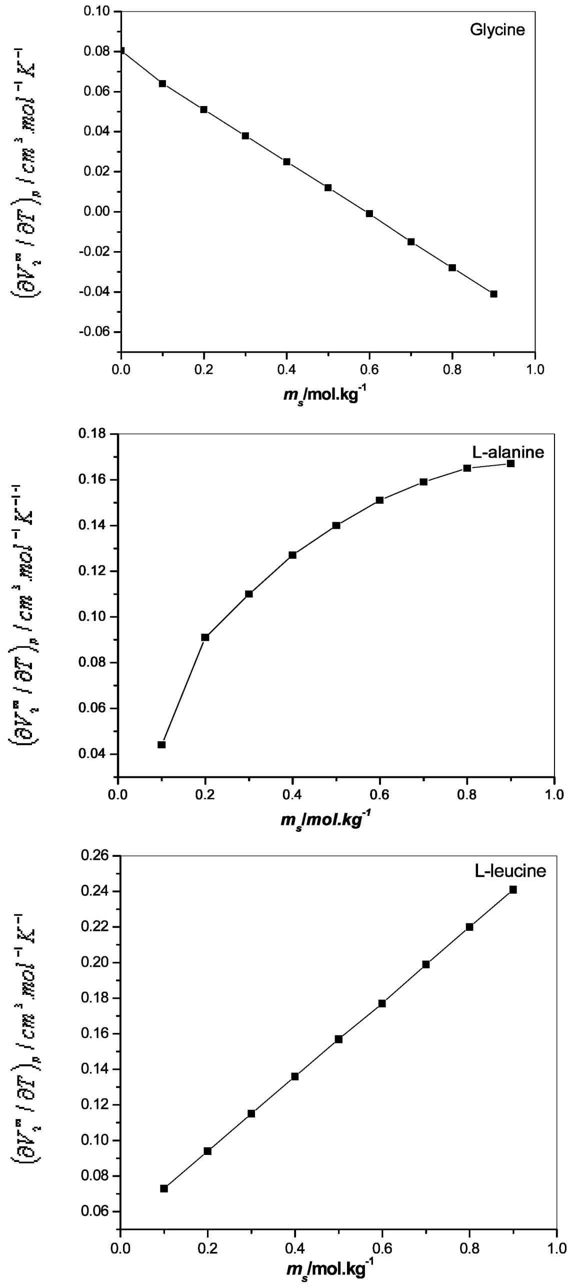

Figure 6. $(\partial V_2^\infty/\partial T)_P$ vs m_s for amino acids in aqueous magnesium chloride solutions at 298.15 K.

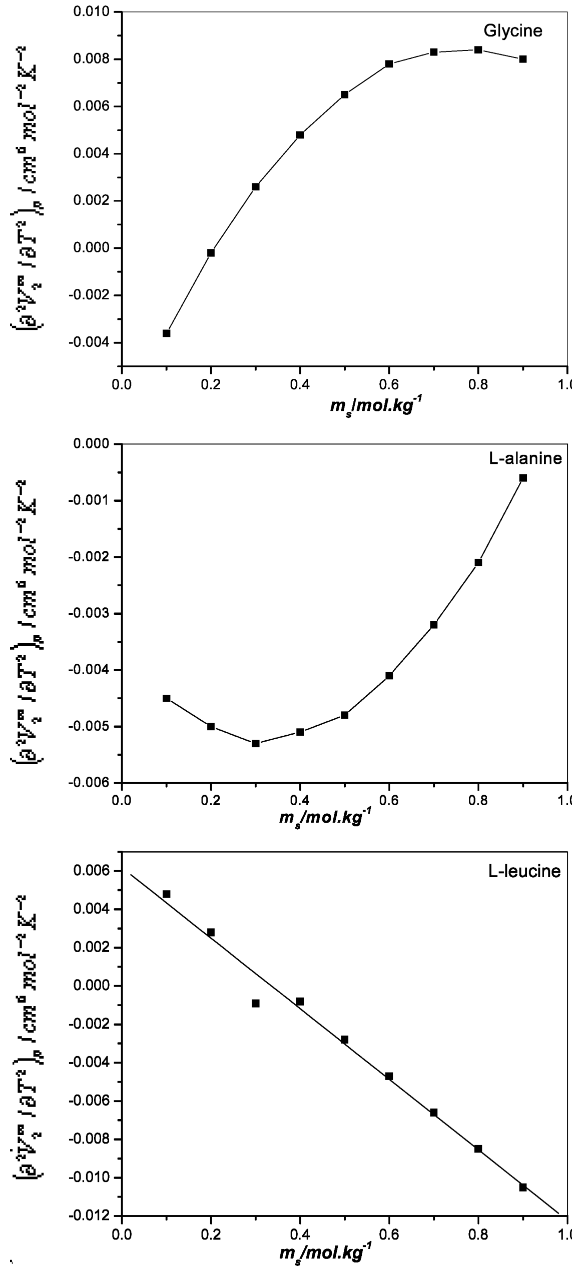

Figure 7. $(\partial^2 V_2^\infty/\partial T^2)_P$ vs m_s for amino acids in aqueous magnesium chloride solutions at 298.15 K.

(Figures 6 and 7) that $(\partial V_2^\infty/\partial T)_P$ for glycine decreases with m_s of $MgCl_2$ and becomes negative at $\approx 0.6 m_s$ while for both L-alanine and L-leucine it increases: the increase is nonlinear in the case of L-alanine and linear in the case of L-leucine. This may well be correlated with the increasing hydrophobicity from L-alanine to L-leucine molecules. The second-order dependence, that is, $(\partial^2 V_2^\infty/\partial T^2)_P$, is not much pronounced and it changes from the slightly negative side to the positive side for glycine and L-alanine while for L-leucine it shows the opposite behavior.

Hepler[23] proposed a method by which qualitative information on hydration of solutes could be obtained from the thermal expansion of aqueous solution by using the relation

$$(\partial C_{p2}^\infty/\partial P)_T = -T(\partial^2 V_2^\infty/\partial T^2)_P \tag{11}$$

According to this, the left side of the above equation should be positive for structure-breaking solutes, and therefore, structure-breaking solutes possess negative $(\partial^2 V_2^\infty/\partial T^2)_P$ values. Similarly, the positive values of $(\partial^2 V_2^\infty/\partial T^2)_P$ should be associated with the structure-making solutes. Although this method has its limitations, even then this equation is helpful for distinguishing between polar and ionic solutes and those for which hydrophobic hydration is dominant.[23] $(\partial^2 V_2^\infty/\partial T^2)_P$ values for the presently studied amino acids in water are negative, which suggests that these solutes are structure breakers. Thus, the negative values of $(\partial^2 V_2^\infty/\partial T^2)_P$ show the dominance of ionic $NH^+{}_3$ and COO^- functional groups in solute–water interactions in these amino acids. However, it is difficult to rationalize presently the sign and magnitude of $(\partial^2 V_2^\infty/\partial T^2)_P$ for the amino acids studied in the presence of $MgCl_2$.

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