Volumetric Properties of Some α,ω-Aminocarboxylic Acids in Aqueous Sodium Acetate and Magnesium Acetate Solutions at T = (288.15 to 318.15) K

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Densities, ρ, of glycine (GLY), 4-aminobutyric acid (4-ABA), and 6-aminocaproic acid (6-ACA) in water and in aqueous solutions of sodium acetate (SA) and magnesium acetate (MA) having a molality of (0.10, 0.25, 0.50 and 1.00) mol·kg^{-1} have been determined by using a vibrating-tube digital densimeter at T = (288.15 to 318.15) K. These data have been used to calculate the apparent molar volumes, V_ϕ, of the studied α,ω-aminocarboxylic acids. The partial molar volumes, $V_{2,m}{}^0$, at infinite dilution are evaluated and further used to obtain the corresponding transfer volumes, $\Delta_{tr}V_{2,m}{}^0$, for α,ω-aminocarboxylic acids from water to aqueous SA and MA solutions. Partial molar expansibilities, $V_E{}^0$, of α,ω-aminocarboxylic acids and interaction coefficients have been calculated. The $\Delta_{tr}V_{2,m}{}^0$ values for the α,ω-aminocarboxylic acids are positive, and these values increase with an increase in the concentration of SA and MA as well as with temperature. The results obtained have been rationalized in terms of various interactions taking place in these solutions.

Introduction

Proteins play a vital role in nearly all chemical and biological processes. They have well-defined physiochemical properties and functions in biological systems. These functions are mediated by their interactions with the environment which arise from various noncovalent forces, so it is important to understand the physical basis of these interactions.[1] Stability and denaturation of globular proteins in aqueous solutions involve a change from the native state, in which protein adopts its characteristic folded conformation, to the denatured state.[2,3] Because of the complex structure of proteins, direct investigations of solute−solvent effects are very challenging. Therefore, investigations on the behavior of simple low molecular weight model compounds of proteins like amino acids, peptides, and their derivatives are of great importance.

The presence of an electrolyte drastically affects the behavior of amino acids in solutions, and this fact has been used for their separation and purification. The volumetric properties of amino acids in aqueous electrolyte solutions provides excellent information about solute−solvent and solute−solute interactions.[4] A variety of thermodynamic and transport studies on amino acids and peptides are available in simple salt solutions,[5,6] but very few reports are available in the presence of organic salt solutions.[7−10] Earlier we have studied[11,12] the physicochemical properties of some α-amino acids in the presence of sodium acetate (SA) and magnesium acetate (MA) at 298.15 K only. However, to study the differences in the behavior of amino acids if the amino group is at the ω-position, we report the partial molar volumes, $V_{2,m}{}^0$ of glycine (GLY), 4-aminobutyric acid (4-ABA), and 6-aminocaproic acid (6-ACA) in water and in aqueous solutions of SA and MA at m_B = (0.10, 0.25, 0.50, and 1.00) mol·kg^{-1}, where m_B is the molality of the cosolutes, that is, SA and MA at (288.15 to 318.15) K. From these data, the partial molar volumes of transfer, $\Delta_{tr}V_{2,m}{}^0$, interaction coefficients, and partial molar expansibilities have been calculated.

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Experimental Section

GLY from the Sigma Chemical Co. and 4-ABA and 6-ACA from the Sisco Research Laboratory, India, all having a mass fraction purity of 0.99, were dried for 24 h in a vacuum oven before use. Analytical grade SA and MA procured from Thomas Baker, India, having a mass fraction purity of 0.98 were used as such after drying for 72 h in a vacuum desiccator at room temperature. Deionized, doubly distilled degassed water with a specific conductance less than $1.29\cdot10^{-6}$ $\Omega^{-1}\cdot$cm^{-1} was used for the preparation of all solutions. The solutions were prepared on the weight basis by using a Mettler balance having a precision of ± 0.01 mg. The densities of the solutions were measured by using a vibrating-tube digital densimeter (model DMA 60/602, Anton Paar, Austria) as reported earlier.[13] The maximum uncertainty in the measured values of densities comes out to be $3.70\cdot10^{-3}$ kg·m^{-3}.

Results and Discussion

Apparent molar volumes, V_ϕ, of selected α,ω-aminocarboxylic acids in water and in m_B = (0.10, 0.25, 0.50, and 1.00) mol·kg^{-1} aqueous SA and MA solutions at T = (288.15, 298.15, 308.15, and 318.15) K have been calculated as follows

$$V_\phi = M/\rho - [(\rho - \rho_0)/(m_A\rho\rho_0)] \quad (1)$$

where M and m_A are, respectively, the molar mass and the molality of the α,ω-aminocarboxylic acids, and ρ and ρ_0 are the densities of solution and the solvent, respectively.

The density and apparent molar volume data for GLY, 4-ABA, and 6-ACA in water and in aqueous solutions of both SA and MA are given in Tables 1, 2, and 3. The uncertainities in V_ϕ resulting from various experimentally measured quantities range from ($0.012\cdot10^{-6}$ to $0.002\cdot10^{-6}$) m^3·mol^{-1}.

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Table 1. Densities, ρ, and Apparent Molar Volumes, V_ϕ, of Some α,ω-Aminocarboxylic Acids in Water from T = (288.15 to 318.15) K

T/K = 288.15			T/K = 298.15			T/K = 308.15			T/K = 318.15		
m_A[a]	$\rho\cdot10^{-3}$	$V_\phi\cdot10^{6}$	m_A	$\rho\cdot10^{-3}$	$V_\phi\cdot10^{6}$	m_A	$\rho\cdot10^{-3}$	$V_\phi\cdot10^{6}$	m_A	$\rho\cdot10^{-3}$	$V_\phi\cdot10^{6}$
mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}
GLY in water											
(ρ_o = 999.129 kg·m^{-3})[b]			(ρ_o = 997.047 kg·m^{-3})			(ρ_o = 994.063 kg·m^{-3})			(ρ_o = 990.244 kg·m^{-3})		
0.14290	1.003762	42.46	0.14290	1.001557	43.35	0.14290	0.998477	43.85	0.14290	0.994636	44.27
0.27091	1.007854	42.50	0.27091	1.005539	43.39	0.27091	1.002401	43.89	0.27091	0.998503	44.35
0.38117	1.011334	42.54	0.38117	1.008928	43.42	0.38117	1.005733	43.94	0.38117	1.001794	44.39
0.41023	1.012232	42.58	0.41023	1.009802	43.46	0.41023	1.006593	43.98	0.41023	1.002635	44.45
0.48013	1.014396	42.63	0.48013	1.011917	43.49	0.48013	1.008665	44.03	0.48013	1.004670	44.52
0.57315	1.017272	42.65	0.57315	1.014710	43.52	0.57315	1.011414	44.06	0.57315	1.007374	44.56
4-ABA in Water											
0.04607	1.000545	72.31	0.04607	0.998428	73.16	0.04607	0.995406	73.45	0.04607	0.991616	73.65
0.09549	1.002049	72.35	0.09549	0.999894	73.20	0.09549	0.996864	73.51	0.09549	0.993071	73.71
0.11554	1.002652	72.39	0.11554	1.000482	73.25	0.11554	0.997447	73.56	0.11554	0.993654	73.76
0.18823	1.004829	72.44	0.18823	1.002606	73.29	0.18823	0.999542	73.61	0.18823	0.995747	73.86
0.16518	1.004133	72.48	0.16518	1.001928	73.32	0.16518	0.998889	73.69	0.16518	0.995086	73.89
0.22768	1.005987	72.52	0.22768	1.003732	73.38	0.22768	1.000665	73.78	0.22768	0.996868	73.96
6-ACA in Water											
0.05814	1.000758	103.08	0.05814	0.998622	104.17	0.05814	0.995592	104.68	0.05814	0.991793	105.16
0.09073	1.001657	103.14	0.09073	0.999493	104.21	0.09073	0.996454	104.73	0.09073	0.992649	105.20
0.17976	1.004088	103.17	0.17976	1.001843	104.25	0.17976	0.998775	104.79	0.17976	0.994956	105.26
0.19453	1.004479	103.21	0.19453	1.002219	104.30	0.19453	0.999147	104.84	0.19453	0.995328	105.30
0.26701	1.006409	103.25	0.26701	1.004082	104.35	0.26701	1.000989	104.89	0.26701	0.997158	105.35
0.35223	1.008641	103.28	0.35223	1.006234	104.39	0.35223	1.003120	104.92	0.35223	0.999270	105.40

[a] m_A: molality (mol·kg^{-1}) of α,ω-aminocarboxylic acids in water. [b] ρ_o: density (kg·m^{-3}) of solvent (water).

The apparent molar volume data have been represented by the linear equation

$$V = V_{2,m}{}^0 + S_V m_A \quad (2)$$

where S_V is the experimental slope. The $V_{2,m}{}^0$ values along with standard deviations are summarized in Tables 4 and 5. The $V_{2,m}{}^0$ values of α,ω-aminocarboxylic acids in water[13−20] and both in SA[10,11] and MA[12] agree well with literature data except in case of GLY at 308.15 K where the literature values are slightly lower than the present values.

As already reported,[11,12] SA and MA, being salts of a weak acid and strong base, undergo hydrolysis and give basic solutions. The pH values for the aqueous solutions of cosolutes are less than the pK_a values for the α,ω-aminocarboxylic acids studied. Thus, the α,ω-aminocarboxylic acids mainly exist in zwitterionic form in water as well as in aqueous solutions of SA and MA.

Partial molar volumes of transfer, $\Delta_{tr}V_{2,m}{}^0$, at infinite dilution from water to aqueous SA/MA solutions have been calculated as follows

$$\Delta_{tr}V^0_{2,m} = V^0_{2,m}(\text{in aqueous SA/MA}) - V^0_{2,m}(\text{in water}) \quad (3)$$

The $\Delta_{tr}V_{2,m}{}^0$ values for the studied α,ω-aminocarboxylic acids in aqueous solutions of both cosolutes (i.e., SA and MA) are positive and increase with an increase of the molality of both cosolutes (the increase is sharp in the lower concentration range) as well as with temperature in all cases (Figures 1 and 2). The $\Delta_{tr}V_{2,m}{}^0$ values for various α,ω-aminocarboxylic acids have also been plotted against the concentration of cosolutes at different temperatures in the same plot (plots are not shown). Almost the same inference can be drawn as from Figures 1 and 2, except that the increasing $\Delta_{tr}V_{2,m}{}^0$ values slightly decrease with the rise of temperature at higher concentrations of the cosolute.

It is interesting to note that the $\Delta_{tr}V_{2,m}{}^0$ values in the present study, that is, for α,ω-aminocarboxylic acids increase with the increase in the molar mass of α,ω-aminocarboxylic acids (i.e., GLY < 4-ABA < 6-ACA), whereas for α-amino acids, as reported earlier,[11] the $\Delta_{tr}V_{2,m}{}^0$ values decrease with an increase in the side chain of amino acids. This indicates that the zwitterionic end groups in the case of α-amino acids modulates the physicochemical properties to a greater extent than the ω-amino acids.

In the presently studied (α,ω-aminocarboxylic acids + SA/MA + water) ternary systems, the following types of interactions

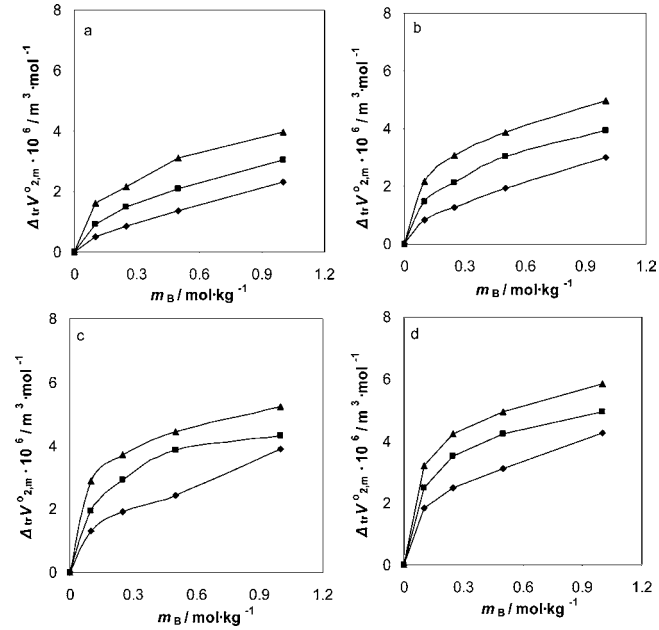

Figure 1. Partial molar volumes of transfer ($\Delta_{tr}V_{2,m}{}^0$) of some α,ω-aminocarboxylic acids vs different molalities m_B of aqueous SA solutions at: (a) 288.15 K; (b) 298.15 K; (c) 308.15 K; (d) 318.15 K: ♦, GLY; ■, 4-ABA; ▲, 6-ACA.

Table 2. Densities, ρ, and Apparent Molar Volumes, V_ϕ, of Some α,ω-Aminocarboxylic Acids in Aqueous SA Solutions as a Function of Concentration of α,ω-Aminocarboxylic Acids and SA from T = (288.15 to 318.15) K

T/K = 288.15			T/K = 298.15			T/K = 308.15			T/K = 318.15		
m_A[a]	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$
mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}
GLY in Aqueous SA Solutions											
m_B = 0.10 mol·kg^{-1} [b]											
(ρ_o = 1003.458 kg·m^{-3})[c]			(ρ_o = 1001.312 kg·m^{-3})			(ρ_o = 998.243 kg·m^{-3})			(ρ_o = 994.384 kg·m^{-3})		
0.10023	1.006662	42.93	0.10681	1.004600	44.12	0.10681	1.001431	45.10	0.10681	0.997842	46.02
0.14254	1.008003	42.95	0.15911	1.006196	44.14	0.15911	1.002977	45.13	0.15911	0.998984	46.04
0.23015	1.010762	42.98	0.26101	1.009278	44.18	0.26101	1.005969	45.15	0.26101	1.001891	46.06
0.33025	1.013885	43.01	0.36150	1.012293	44.19	0.36150	1.008884	45.18	0.36150	1.004720	46.10
0.46002	1.017888	43.04	0.46417	1.015335	44.22	0.46417	1.011836	45.20	0.46417	1.007580	46.13
0.61257	1.022513	43.17	0.64640	1.020668	44.25	0.64640	1.016995	45.24	0.64640	1.012586	46.17
m_B = 0.25 mol·kg^{-1}											
(ρ_o = 1009.600 kg·m^{-3})			(ρ_o = 1007.387 kg·m^{-3})			(ρ_o = 1004.268 kg·m^{-3})			(ρ_o = 1000.347 kg·m^{-3})		
0.11256	1.013150	43.26	0.10543	1.010576	44.57	0.10543	1.007341	45.71	0.10543	1.003327	46.66
0.16024	1.014639	43.29	0.16648	1.012404	44.60	0.16648	1.009104	45.73	0.16648	1.005034	46.69
0.32568	1.019758	43.32	0.34275	1.017626	44.63	0.34275	1.014131	45.77	0.34275	1.009912	46.71
0.39851	1.021979	43.35	0.38864	1.018969	44.64	0.38864	1.015420	45.79	0.38864	1.011162	46.73
0.54216	1.026326	43.37	0.56075	1.023961	44.66	0.56075	1.020218	45.82	0.56075	1.015812	46.76
0.70236	1.031093	43.41	0.71964	1.028488	44.69	0.71964	1.024572	45.85	0.71964	1.020024	46.80
m_B = 0.50 mol·kg^{-1}											
(ρ_o = 1019.378 kg·m^{-3})			(ρ_o = 1017.068 kg·m^{-3})			(ρ_o = 1013.888 kg·m^{-3})			(ρ_o = 1009.850 kg·m^{-3})		
0.10452	1.022604	43.80	0.10327	1.020107	45.23	0.10327	1.016828	46.21	0.10327	1.012682	47.31
0.25370	1.027152	43.82	0.24626	1.024262	45.25	0.24626	1.020848	46.23	0.24626	1.016554	47.33
0.31256	1.028921	43.85	0.34658	1.027143	45.26	0.34658	1.023624	46.27	0.34658	1.019230	47.36
0.43562	1.032593	43.88	0.42567	1.029389	45.28	0.42567	1.025798	46.28	0.42567	1.021319	47.38
0.47256	1.033676	43.91	0.43257	1.029571	45.31	0.43257	1.025978	46.30	0.43257	1.021492	47.40
0.57264	1.036611	43.94	0.56986	1.033427	45.33	0.56986	1.029698	46.33	0.56986	1.025072	47.43
m_B = 1.00 mol·kg^{-1}											
(ρ_o = 1037.220 kg·m^{-3})			(ρ_o = 1034.760 kg·m^{-3})			(ρ_o = 1031.540 kg·m^{-3})			(ρ_o = 1027.230 kg·m^{-3})		
0.11256	1.040548	44.75	0.12347	1.038207	46.32	0.12347	1.034817	47.68	0.12347	1.030417	48.47
0.21456	1.043525	44.79	0.23466	1.041274	46.33	0.23466	1.037730	47.70	0.23466	1.033248	48.49
0.35215	1.047495	44.81	0.34215	1.044203	46.35	0.34215	1.040514	47.71	0.34215	1.035956	48.50
0.41256	1.049220	44.82	0.40246	1.045827	46.37	0.40246	1.042057	47.73	0.40246	1.037459	48.51
0.48725	1.051324	44.86	0.49653	1.048338	46.40	0.49653	1.044441	47.76	0.49653	1.039782	48.53
0.57124	1.053668	44.90	0.58653	1.050726	46.41	0.58653	1.046695	47.79	0.58653	1.041974	48.56
4-ABA in Aqueous SA Solutions											
m_B = 0.10 mol·kg^{-1}											
0.03426	1.004474	73.21	0.03913	1.002422	74.60	0.03913	0.999330	75.32	0.03913	0.995450	76.06
0.08216	1.005885	73.23	0.08697	1.003767	74.63	0.08697	1.000648	75.35	0.08697	0.996742	76.08
0.11254	1.006772	73.26	0.11110	1.004440	74.65	0.11110	1.001307	75.37	0.11110	0.997387	76.12
0.13526	1.007429	73.30	0.14391	1.005351	74.67	0.14391	1.002201	75.38	0.14391	0.998262	76.13
0.19254	1.009079	73.34	0.21453	1.007296	74.70	0.21453	1.004104	75.42	0.21453	1.000129	76.16
0.27154	1.011332	73.37	0.25557	1.008414	74.72	0.25557	1.005197	75.45	0.25557	1.001202	76.18
m_B = 0.25 mol·kg^{-1}											
0.04023	1.010760	73.74	0.04144	1.008522	75.27	0.04144	1.005366	76.30	0.04144	1.001421	77.09
0.05631	1.011220	73.78	0.05813	1.008975	75.30	0.05813	1.005805	76.32	0.05813	1.001850	77.11
0.10235	1.012532	73.80	0.11702	1.010567	75.33	0.11702	1.007346	76.35	0.11702	1.003358	77.12
0.16523	1.014305	73.84	0.17698	1.012169	75.36	0.17698	1.008898	76.37	0.17698	1.004876	77.14
0.20156	1.015318	73.87	0.21995	1.013307	75.38	0.21995	1.009999	76.39	0.21995	1.005951	77.17
0.28427	1.017604	73.91	0.25327	1.014177	75.42	0.25327	1.010843	76.42	0.25327	1.006779	77.19
m_B = 0.50 mol·kg^{-1}											
0.06582	1.021198	74.40	0.07609	1.019041	76.16	0.07609	1.015788	77.25	0.07609	1.011722	77.82
0.11256	1.022477	74.42	0.14399	1.020780	76.17	0.14399	1.017462	77.27	0.14399	1.013373	77.83
0.21536	1.025255	74.45	0.20453	1.022314	76.18	0.20453	1.018937	77.29	0.20453	1.014829	77.84
0.26541	1.026586	74.48	0.24827	1.023410	76.20	0.24827	1.019993	77.30	0.24827	1.015868	77.86
0.29359	1.027328	74.50	0.28323	1.024281	76.21	0.28323	1.020829	77.32	0.28323	1.016692	77.88
0.32156	1.028058	74.53	0.31251	1.025003	76.23	0.31251	1.021523	77.34	0.31251	1.017369	77.92
m_B = 1.00 mol·kg^{-1}											
0.04256	1.038319	75.32	0.04354	1.035809	77.05	0.04354	1.032567	77.70	0.04354	1.028230	78.53
0.08264	1.039343	75.37	0.09752	1.037098	77.07	0.09752	1.033830	77.71	0.09752	1.029459	78.54
0.12658	1.040458	75.39	0.14654	1.038255	77.10	0.14654	1.034964	77.73	0.14654	1.030563	78.56
0.20146	1.042337	75.42	0.19870	1.039476	77.12	0.19870	1.036160	77.75	0.19870	1.031728	78.57
0.23514	1.043169	75.45	0.21436	1.039839	77.13	0.21436	1.036513	77.77	0.21436	1.032072	78.59
0.27136	1.044058	75.48	0.24657	1.040582	77.15	0.24657	1.037243	77.78	0.24657	1.032778	78.62
6-ACA in Aqueous SA Solutions											
m_B = 0.10 mol·kg^{-1}											
0.03013	1.004246	104.70	0.03465	1.002168	106.31	0.03465	0.999065	107.55	0.03465	0.995189	108.35
0.07259	1.005345	104.73	0.08653	1.003435	106.33	0.08653	1.000282	107.56	0.08653	0.996382	108.37
0.15624	1.007482	104.75	0.14356	1.004812	106.34	0.14356	1.001602	107.59	0.14356	0.997678	108.38
0.21305	1.008909	104.77	0.19456	1.006026	106.36	0.19456	1.002767	107.61	0.19456	0.998820	108.40
0.25861	1.010036	104.80	0.23136	1.006890	106.39	0.23136	1.003597	107.63	0.23136	0.999634	108.42
0.29532	1.010927	104.85	0.27235	1.007845	106.41	0.27235	1.004513	107.65	0.27235	1.000532	108.44

Table 2. Continued

T/K = 288.15			T/K = 298.15			T/K = 308.15			T/K = 318.15		
m_A[a]	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$
mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}
					$m_B = 0.25$ mol·kg^{-1}						
0.06002	1.011101	105.26	0.06149	1.008814	107.22	0.06149	1.005639	108.39	0.06149	1.001678	109.37
0.14653	1.013228	105.28	0.14812	1.010790	107.24	0.14812	1.007538	108.40	0.14812	1.003522	109.39
0.19315	1.014354	105.31	0.18391	1.011594	107.25	0.18391	1.008311	108.41	0.18391	1.004272	109.40
0.25631	1.015860	105.34	0.24274	1.012900	107.27	0.24274	1.009566	108.43	0.24274	1.005490	109.42
0.32105	1.017379	105.37	0.30821	1.014333	107.29	0.30821	1.010942	108.45	0.30821	1.006826	109.44
0.37817	1.018694	105.41	0.35586	1.015357	107.32	0.35586	1.011932	108.46	0.35586	1.007783	109.46
					$m_B = 0.50$ mol·kg^{-1}						
0.03521	1.020199	106.18	0.03466	1.017817	108.03	0.03466	1.014608	109.12	0.03466	1.010549	110.08
0.09852	1.021657	106.21	0.08653	1.018925	108.05	0.08653	1.015674	109.13	0.08653	1.011583	110.09
0.12541	1.022260	106.24	0.12465	1.019731	108.06	0.12465	1.016448	109.15	0.12465	1.012334	110.11
0.17259	1.023328	106.27	0.15478	1.020361	108.08	0.15478	1.017053	109.17	0.15478	1.012921	110.13
0.21035	1.024169	106.29	0.19565	1.021207	108.11	0.19565	1.017867	109.19	0.19565	1.013711	110.15
0.27156	1.025517	106.31	0.24354	1.022188	108.13	0.24354	1.018810	109.21	0.24354	1.014626	110.17
					$m_B = 1.00$ mol·kg^{-1}						
0.05236	1.038309	107.05	0.04326	1.035574	109.14	0.04326	1.032331	109.91	0.04326	1.027990	110.98
0.09254	1.039134	107.07	0.07659	1.036194	109.15	0.07659	1.032934	109.93	0.07659	1.028569	111.01
0.11256	1.039539	107.10	0.10462	1.036712	109.16	0.10462	1.033437	109.95	0.10462	1.029052	111.02
0.17259	1.040747	107.13	0.15623	1.037655	109.18	0.15623	1.034353	109.97	0.15623	1.029932	111.04
0.20146	1.041320	107.15	0.18643	1.038199	109.20	0.18643	1.034879	110.00	0.18643	1.030440	111.06
0.25366	1.042348	107.17	0.23326	1.039034	109.23	0.23326	1.035689	110.03	0.23326	1.031220	111.08

[a] m_A: molality (mol·kg^{-1}) of α,ω-aminocarboxylic acids in solution. [b] m_B: molality (mol·kg^{-1}) of SA in water. [c] ρ_o: density (kg·m^{-3}) of solvent.

may occur: (i) ion−ion interactions between the cosolutes (i.e., Na^+/ Mg^{2+}, CH_3COO^- ions) and α,ω-aminocarboxylic acids zwitterionic (COO^-, NH_3^+) end groups. (ii) ion−nonpolar group interactions occurring between ions of the cosolutes and the nonpolar parts of α,ω-aminocarboxylic acids. According to the cosphere overlap model,[21] the first type of interactions contributes positively, and the second type contributes negatively to $\Delta_{tr}V_{2,m}^0$. The presently observed positive $\Delta_{tr}V_{2,m}^0$ values indicate the dominance of the ion−ion interactions, and these interactions further increase with an increase in the molality of both cosolutes.

The modified equation of Shahidi and Farrell[22] gives the limiting partial molar volume $V_{2,m}^0$ as

$$V_{2,m}^0 = V_{vw} + V_{void} - V_{shrinkage} \quad (4)$$

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 that arises from the electrostriction of the solvent caused by the hydrophilic groups present in the solute. Assuming that V_{vw} and V_{void}[23] are not significantly affected by the presence of cosolutes, positive $\Delta_{tr}V_{2,m}^0$ values can, therefore, be attributed to a decrease in the shrinkage volume in both cosolutes. Because of the stronger interactions between zwitterionic end groups (COO^- and NH_3^+) of the α,ω-aminocarboxylic acids and ions of the cosolutes (Na^+/Mg^{2+}, CH_3COO^-), noncovalent ion pairs will be formed, and thus the electrostriction of neighboring water molecules due to these charged centers will be reduced, which will result in an increase in the apparent molar volumes. A comparison of $\Delta_{tr}V_{2,m}^0$ values of the studied α,ω-aminocarboxylic acids in aqueous solutions of SA and MA suggest that the values are higher in the presence of MA than in case of SA. This may be explained in terms of the charged density of the metal ions and ionic strength of cosolutes. The Mg^{2+} ion being smaller in size and having higher charged density as compared with the Na^+ ion may interact more strongly with the COO^- terminal of α,ω-aminocarboxylic acids. This may also be due to the higher ionic strength in the case of the Mg^{2+} ion when the molalities of divalent and monovalent salts are the same. Hence, a 1:2 electrolyte (MA) influences the $\Delta_{tr}V_{2,m}^0$ values (for both α-amino acids as well as α,ω-aminocarboxylic acids) to a greater extent than a 1:1 electrolyte (SA).

A comparison of the present transfer volumes (Table 6) with the available literature data[11,12,23,24] shows that, in general, the $\Delta_{tr}V_{2,m}^0$ values decrease for amino acids in the presence of various salts as follows

$$MgCl_2 > Mg(CH_3COO)_2 > CH_3COONa > NaCl$$

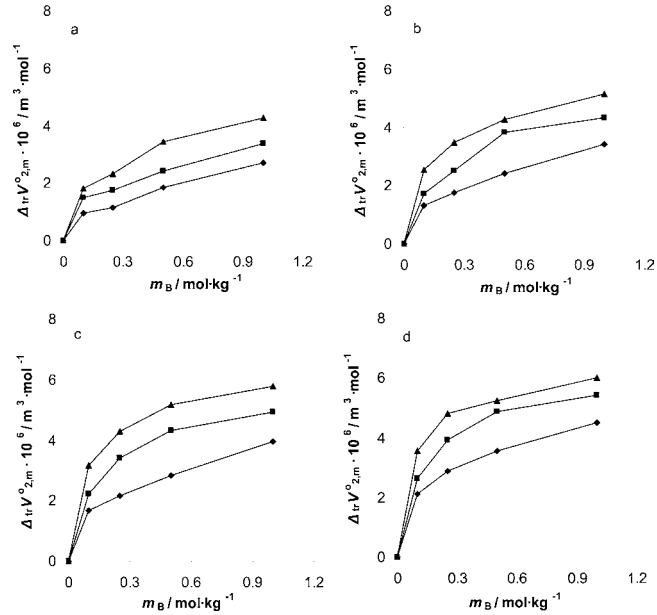

Figure 2. Partial molar volumes of transfer ($\Delta_{tr}V_{2,m}^0$) of some α,ω-aminocarboxylic acids vs different molalities m_B of aqueous MA solutions at: (a) 288.15 K; (b) 298.15 K; (c) 308.15 K; (d) 318.15 K: ♦, GLY; ■, 4-ABA; ▲, 6-ACA.

Table 3. Densities, ρ, and Apparent Molar Volumes, V_ϕ, of Some α,ω-Aminocarboxylic Acids in Aqueous MA Solutions as a Function of Concentration of α,ω-Aminocarboxylic Acids and MA from T = (288.15 to 318.15) K

T/K = 288.15			T/K = 298.15			T/K = 308.15			T/K = 318.15		
m_A[a]	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$	m_A	$\rho \cdot 10^{-3}$	$V_\phi \cdot 10^6$
mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}
GLY in Aqueous MA Solutions											
m_B = 0.10 mol·kg^{-1} [b]											
(ρ_o = 1007.015 kg·m^{-3})[c]			(ρ_o = 1004.898 kg·m^{-3})			(ρ_o = 1001.842 kg·m^{-3})			(ρ_o = 998.062 kg·m^{-3})		
0.15632	1.011922	43.38	0.11430	1.008352	44.63	0.11430	1.005204	45.47	0.11430	1.001338	46.29
0.15324	1.011825	43.39	0.16438	1.009850	44.65	0.16438	1.006665	45.48	0.16438	1.002759	46.31
0.25142	1.014867	43.41	0.24329	1.012199	44.66	0.24329	1.008950	45.50	0.24329	1.004987	46.32
0.34625	1.017778	43.43	0.33437	1.014886	44.68	0.33437	1.011564	45.52	0.33437	1.007533	46.34
0.43652	1.020523	43.45	0.42686	1.017584	44.71	0.42686	1.014194	45.54	0.42686	1.010090	46.37
0.52145	1.023076	43.48	0.54350	1.020951	44.74	0.54350	1.017471	45.57	0.54350	1.013280	46.40
m_B = 0.25 mol·kg^{-1}											
(ρ_o = 1018.199 kg·m^{-3})			(ρ_o = 1016.051 kg·m^{-3})			(ρ_o = 1012.893 kg·m^{-3})			(ρ_o = 1009.151 kg·m^{-3})		
0.09214	1.021069	43.56	0.09463	1.018854	45.07	0.09463	1.015614	45.96	0.09463	1.011771	47.08
0.15246	1.022932	43.58	0.17653	1.021256	45.09	0.17653	1.017945	45.99	0.17653	1.014016	47.10
0.33514	1.028514	43.60	0.32466	1.025557	45.10	0.32466	1.022115	46.01	0.32466	1.018027	47.13
0.38241	1.029940	43.61	0.39456	1.027559	45.12	0.39456	1.024052	46.04	0.39456	1.019890	47.16
0.45215	1.032021	43.65	0.46533	1.029566	45.15	0.46533	1.025997	46.07	0.46533	1.021766	47.18
0.57214	1.035580	43.68	0.56436	1.032352	45.18	0.56436	1.028703	46.09	0.56436	1.024363	47.21
m_B = 0.50 mol·kg^{-1}											
(ρ_o = 1035.440 kg·m^{-3})			(ρ_o = 1033.147 kg·m^{-3})			(ρ_o = 1030.053 kg·m^{-3})			(ρ_o = 1026.240 kg·m^{-3})		
0.10542	1.038615	44.27	0.10036	1.036018	45.73	0.10036	1.032833	46.65	0.10036	1.028912	47.75
0.21456	1.041866	44.29	0.22488	1.039539	45.75	0.22488	1.036240	46.67	0.22488	1.032183	47.78
0.32564	1.045137	44.31	0.33469	1.042608	45.76	0.33469	1.039202	46.70	0.33469	1.035031	47.80
0.40352	1.047410	44.32	0.41113	1.044719	45.78	0.41113	1.041243	46.72	0.41113	1.036991	47.82
0.47215	1.049393	44.34	0.46236	1.046115	45.81	0.46236	1.042592	46.75	0.46236	1.038286	47.85
0.52364	1.050862	44.37	0.51309	1.047493	45.83	0.51309	1.043913	46.79	0.51309	1.039560	47.88
m_B = 1.00 mol·kg^{-1}											
(ρ_o = 1064.680 kg·m^{-3})			(ρ_o = 1061.743 kg·m^{-3})			(ρ_o = 1059.650 kg·m^{-3})			(ρ_o = 1055.190 kg·m^{-3})		
0.10125	1.067580	45.12	0.10069	1.064451	46.73	0.10069	1.062248	47.75	0.10069	1.057694	48.69
0.20425	1.070499	45.13	0.21470	1.067480	46.75	0.21470	1.065153	47.77	0.21470	1.060492	48.72
0.29588	1.073066	45.15	0.30226	1.069778	46.77	0.30226	1.067360	47.78	0.30226	1.062614	48.74
0.36352	1.074938	45.18	0.38656	1.071972	46.78	0.38656	1.069456	47.81	0.38656	1.064636	48.76
0.46253	1.077661	45.20	0.45624	1.073765	46.80	0.45624	1.071174	47.83	0.45624	1.066290	48.78
0.53214	1.079554	45.22	0.52478	1.075508	46.83	0.52478	1.072837	47.87	0.52478	1.067896	48.81
4-ABA in Aqueous MA Solutions											
m_B = 0.10 mol·kg^{-1}											
0.04425	1.008295	73.76	0.04568	1.006174	74.85	0.04568	1.003090	75.60	0.04568	0.999290	76.22
0.09246	1.009678	73.79	0.09930	1.007658	74.87	0.09930	1.004542	75.62	0.09930	1.000720	76.23
0.13256	1.010820	73.80	0.14327	1.008865	74.88	0.14327	1.005721	75.64	0.14327	1.001881	76.25
0.18245	1.012227	73.83	0.19553	1.010288	74.90	0.19553	1.007110	75.67	0.19553	1.003248	76.28
0.23652	1.013740	73.85	0.22335	1.011037	74.92	0.22335	1.007842	75.69	0.22335	1.003969	76.30
0.29352	1.015317	73.88	0.28340	1.012642	74.96	0.28340	1.009413	75.72	0.28340	1.005518	76.32
m_B = 0.25 mol·kg^{-1}											
0.05123	1.019640	74.03	0.05306	1.017460	75.64	0.05306	1.014247	76.81	0.05306	1.010480	77.51
0.09241	1.020788	74.05	0.09643	1.018602	75.66	0.09643	1.015344	76.83	0.09643	1.011553	77.54
0.15245	1.022447	74.07	0.14358	1.019832	75.68	0.14358	1.016527	76.84	0.14358	1.012712	77.55
0.18325	1.023292	74.08	0.19862	1.021258	75.69	0.19862	1.017893	76.87	0.19862	1.014050	77.58
0.23524	1.024704	74.11	0.22349	1.021890	75.73	0.22349	1.018504	76.89	0.22349	1.014646	77.61
0.28315	1.025993	74.14	0.29962	1.023825	75.78	0.29962	1.020363	76.92	0.29962	1.016465	77.64
m_B = 0.50 mol·kg^{-1}											
0.06215	1.037090	74.69	0.06343	1.034686	76.94	0.06343	1.031551	77.72	0.06343	1.027702	78.46
0.10234	1.038146	74.71	0.11356	1.035889	76.97	0.11356	1.032722	77.74	0.11356	1.028844	78.49
0.15324	1.039475	74.72	0.16899	1.037205	76.99	0.16899	1.034002	77.77	0.16899	1.030095	78.51
0.20145	1.040719	74.75	0.22480	1.038250	77.00	0.22480	1.035278	77.79	0.22480	1.031343	78.52
0.27145	1.042506	74.78	0.28735	1.039882	77.03	0.28735	1.036603	77.82	0.28735	1.032636	78.55
0.35214	1.044540	74.81	0.36512	1.041756	77.06	0.36512	1.038424	77.85	0.36512	1.034418	78.57
m_B = 1.00 mol·kg^{-1}											
0.05314	1.065951	75.65	0.05433	1.062941	77.45	0.05433	1.060803	78.31	0.05433	1.056316	79.01
0.09125	1.066852	75.68	0.09832	1.063902	77.47	0.09832	1.061727	78.33	0.09832	1.057217	79.04
0.15246	1.068290	75.69	0.13348	1.064664	77.48	0.13348	1.062459	78.35	0.13348	1.057931	79.06
0.18324	1.069004	75.71	0.18320	1.065732	77.50	0.18320	1.063483	78.38	0.18320	1.058932	79.08
0.27145	1.071032	75.74	0.22004	1.066515	77.52	0.22004	1.064235	78.40	0.22004	1.059667	79.10
0.34125	1.072611	75.77	0.26479	1.067458	77.54	0.26479	1.065144	78.41	0.26479	1.060552	79.12
6-ACA in Aqueous MA Solutions											
m_B = 0.10 mol·kg^{-1}											
0.04125	1.008072	104.90	0.04325	1.005936	106.68	0.04325	1.002841	107.84	0.04325	0.999037	108.71
0.08514	1.009185	104.93	0.08787	1.006995	106.71	0.08787	1.003859	107.87	0.08787	1.000031	108.74
0.15262	1.010874	104.95	0.16325	1.008759	106.73	0.16325	1.005558	107.88	0.16325	1.001690	108.75
0.21456	1.012401	104.97	0.20358	1.009688	106.75	0.20358	1.006452	107.90	0.20358	1.002563	108.77
0.25417	1.013362	105.00	0.24524	1.010639	106.77	0.24524	1.007364	107.93	0.24524	1.003453	108.80
0.30142	1.014496	105.03	0.29863	1.011841	106.80	0.29863	1.008520	107.96	0.29863	1.004581	108.83

Table 3. Continued

T/K = 288.15			T/K = 298.15			T/K = 308.15			T/K = 318.15		
m_A[a] / mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V_\phi\cdot10^{6}$ / m^3·mol^{-1}	m_A / mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V_\phi\cdot10^{6}$ / m^3·mol^{-1}	m_A / mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V_\phi\cdot10^{6}$ / m^3·mol^{-1}	m_A / mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V_\phi\cdot10^{6}$ / m^3·mol^{-1}
					m_B = 0.25 mol·kg^{-1}						
0.05432	1.019499	105.44	0.05543	1.017273	107.65	0.05543	1.014056	108.96	0.05543	1.010275	109.97
0.13251	1.021339	105.47	0.12469	1.018776	107.67	0.12469	1.015486	108.98	0.12469	1.011659	109.99
0.18635	1.022586	105.49	0.19842	1.020351	107.68	0.19842	1.016983	109.00	0.19842	1.013105	110.01
0.24635	1.023960	105.50	0.25800	1.021601	107.70	0.25800	1.018172	109.02	0.25800	1.014254	110.03
0.32152	1.025649	105.53	0.31041	1.022683	107.73	0.31041	1.019199	109.05	0.31041	1.015247	110.06
0.37145	1.026751	105.66	0.36432	1.023779	107.76	0.36432	1.020241	109.08	0.36432	1.016254	110.09
					m_B = 0.50 mol·kg^{-1}						
0.05682	1.036662	106.53	0.05532	1.034236	108.44	0.05532	1.031074	109.87	0.05532	1.027251	110.38
0.09142	1.037396	106.55	0.09465	1.034999	108.46	0.09465	1.031790	109.89	0.09465	1.027961	110.40
0.15324	1.038695	106.56	0.13465	1.035769	108.47	0.13465	1.032498	110.00	0.13465	1.028674	110.42
0.19354	1.039530	106.58	0.18694	1.036763	108.49	0.18694	1.033423	110.02	0.18694	1.029598	110.43
0.23586	1.040396	106.60	0.22547	1.037483	108.52	0.22547	1.034098	110.03	0.22547	1.030263	110.47
0.27468	1.041179	106.63	0.26024	1.038124	108.55	0.26024	1.034699	110.05	0.26024	1.030858	110.50
					m_B = 1.00 mol·kg^{-1}						
0.05286	1.065626	107.35	0.05536	1.062627	109.31	0.05536	1.060475	110.46	0.05536	1.055997	111.16
0.08756	1.066238	107.38	0.08963	1.063167	109.33	0.08963	1.060978	110.48	0.08963	1.056489	111.18
0.13658	1.067093	107.40	0.12864	1.063776	109.34	0.12864	1.061543	110.51	0.12864	1.057045	111.19
0.19852	1.068161	107.41	0.18644	1.064664	109.37	0.18644	1.062372	110.53	0.18644	1.057855	111.22
0.26541	1.069290	107.44	0.24327	1.065522	109.40	0.24327	1.063170	110.56	0.24327	1.058637	111.25
0.29358	1.069754	107.47	0.28965	1.066213	109.42	0.28965	1.063810	110.59	0.28965	1.059263	111.28

[a] m_A: molality (mol·kg^{-1}) of α,ω-aminocarboxylic acids in solution. [b] m_B: molality (mol·kg^{-1}) of MA in water. [c] ρ_0: density (kg·m^{-3}) of solvent.

Table 4. Partial Molar Volumes, $V_{2,m}^0$, of Some α,ω-Aminocarboxylic Acids in Water and in Aqueous SA Solutions from T = (288.15 to 318.15) K

	$V_{2,m}^0\cdot10^6$/m^3·mol^{-1}				
α,ω-aminocarboxylic acids	m_B = 0.00 mol·kg^{-1} [a]	m_B = 0.10 mol·kg^{-1}	m_B = 0.25 mol·kg^{-1}	m_B = 0.50 mol·kg^{-1}	m_B = 1.00 mol·kg^{-1}
		T/K = 288.15			
GLY	42.38[b] ± 0.01 42.40[c]	42.90 ± 0.02	43.24 ± 0.01	43.76 ± 0.02	44.71 ± 0.01
4-ABA	72.25[b] ± 0.02 72.20[d], 72.62[e]	73.18 ± 0.01	73.73 ± 0.02	74.36 ± 0.01	75.30 ± 0.01
6-ACA	103.06[b] ± 0.02 103.0[d], 102.96[e], 103.02[f]	104.68 ± 0.03	105.22 ± 0.01	106.16 ± 0.01	107.02 ± 0.02
		T/K = 298.15			
GLY	43.28[b] ± 0.01 43.26[c], 43.30[c], 43.24[c]	44.10 ± 0.01	44.56 ± 0.02	45.20 ± 0.01 44.82[g]	46.29 ± 0.03 46.06[g]
4-ABA	73.10[b] ± 0.01 73.60[e], 73.02[h], 73.50[i]	74.58 ± 0.01	75.25 ± 0.01	76.13 ± 0.02	77.03 ± 0.03
6-ACA	104.13[b] ± 0.01 104.18[e], 104.02[h], 104.17[j]	106.29 ± 0.02	107.19 ± 0.01	108.01 ± 0.03	109.11 ± 0.01
		T/K = 308.15			
GLY	43.76[b] ± 0.01 43.80[c], 43.79[c]	45.08 ± 0.01	45.69 ± 0.02	46.18 ± 0.01 44.90[k]	47.64 ± 0.01 45.91[k]
4-ABA	73.36[b] ± 0.01 74.37[e], 71.60[l]	75.30 ± 0.03	76.28 ± 0.02	77.22 ± 0.02	77.68 ± 0.02
6-ACA	104.65[b] ± 0.02 104.96[e], 104.88[f]	107.53 ± 0.02	108.37 ± 0.01	109.10 ± 0.02	109.88 ± 0.01
		T/K = 318.15			
GLY	44.16[b] ± 0.01 44.17[c]	45.99 ± 0.02	46.64 ± 0.01	47.27 ± 0.01	48.44 ± 0.03
4-ABA	73.56[b] ± 0.01	76.04 ± 0.03	77.07 ± 0.01	77.78 ± 0.02	78.50 ± 0.02
6-ACA	105.12[b] ± 0.02	108.33 ± 0.02	109.35 ± 0.01	110.06 ± 0.03	110.96 ± 0.01

[a] m_B: molality (mol·kg^{-1}) of SA in water. [b] Present work. [c] Ref 13. [d] Ref 14. [e] Ref 15. [f] Ref 16. [g] Ref 11. [h] Ref 17. [i] Ref 18. [j] Ref 19. [k] Ref 10. [l] Ref 20.

The methylene group contribution, $V_2^0(CH_2)$, of the studied α,ω-aminocarboxylic acids have been calculated (data not given) as follows

$$V_2^0(\text{4-ABA}) - V_2^0(\text{GLY}) = 2V_2^0(CH_2) \quad (5a)$$

$$V_2^0(\text{6-ACA}) - V_2^0(\text{GLY}) = 4V_2^0(CH_2) \quad (5b)$$

$$V_2^0(\text{6-ACA}) - V_2^0(\text{4-ABA}) = 2V_2^0(CH_2) \quad (5c)$$

It has been observed that $V_2^0(CH_2)$ values for the studied α,ω-aminocarboxylic acids in water are smaller than the corresponding values for α-amino acids[13] at all temperatures. Moreover, $V_2^0(CH_2)$ comes out to be slightly larger in the presence of cosolutes as compared to their values in water. It has been noted that, with an increase in temperature, $V_2^0(CH_2)$ values increase when these are calculated by using eq 5c in the presence of SA, but no trend has been observed in the presence of MA at all concentrations.

The $\Delta_{tr}V_{2,m}^0$ values of α,ω-aminocarboxylic acids can also be expressed by the McMillan−Mayer theory[25] 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

Table 5. Partial Molar Volumes, $V_{2,m}^0$, of Some α,ω-Aminocarboxylic Acids in Aqueous MA Solutions from T = (288.15 to 318.15) K

	$V_{2,m}^0 \cdot 10^6/m^3 \cdot mol^{-1}$			
α,ω-aminocarboxylic acids	m_B = 0.10 mol·kg^{-1} [a]	m_B = 0.25 mol·kg^{-1}	m_B = 0.50 mol·kg^{-1}	m_B = 1.00 mol·kg^{-1}
		T/K = 288.15		
GLY	43.35 ± 0.02	43.53 ± 0.02	44.24 ± 0.01	45.09 ± 0.01
4-ABA	73.74 ± 0.02	74.00 ± 0.03	74.66 ± 0.02	75.63 ± 0.02
6-ACA	104.88 ± 0.03	105.39 ± 0.01	106.50 ± 0.03	107.33 ± 0.01
		T/K = 298.15		
GLY	44.60 ± 0.01	45.04 ± 0.01	45.70 ± 0.02 45.76[b]	46.70 ± 0.03 47.04[b]
4-ABA	74.82 ± 0.03	75.60 ± 0.02	76.92 ± 0.01	77.43 ± 0.02
6-ACA	106.66 ± 0.02	107.62 ± 0.01	108.41 ± 0.02	109.28 ± 0.01
		T/K = 308.15		
GLY	45.44 ± 0.01	45.93 ± 0.02	46.60 ± 0.02	47.71 ± 0.03
4-ABA	75.57 ± 0.03	76.78 ± 0.02	77.69 ± 0.01	78.28 ± 0.01
6-ACA	107.82 ± 0.03	108.93 ± 0.01	109.83 ± 0.02	110.43 ± 0.01
		T/K = 318.15		
GLY	46.26 ± 0.02	47.05 ± 0.01	47.71 ± 0.01	48.66 ± 0.03
4-ABA	76.19 ± 0.01	77.48 ± 0.02	78.44 ± 0.02	78.99 ± 0.01
6-ACA	108.69 ± 0.02	109.94 ± 0.03	110.35 ± 0.02	111.13 ± 0.01

[a] m_B: molality (mol·kg^{-1}) of MA in water. [b] Ref 12.

Table 6. Volumes of Transfer, $\Delta_{tr}V_{2,m}^0$, of Some α,ω-Aminocarboxylic Acids from Water to Aqueous Solutions of Various Electrolytes at T = 298.15 K

	CH_3COONa[a]	$(CH_3COO)_2Mg$[b]	$MgCl_2$[c]	NaCl[d]
α,ω-amino acids	m_B = 1 mol·kg^{-1} [e]	m_B = 1 mol·kg^{-1}	m_B = 0.92 mol·kg^{-1}	m_B = 1 mol·kg^{-1}
GLY	3.01	3.42	4.36	1.35
4-ABA	3.93	4.33	-	0.38
6-ACA	4.98	5.15	-	-
DL-α-alanine	1.95	2.98	5.33	0.78
L-leucine	1.02	1.69	8.91	0.44

[a] Ref 11. [b] Ref 12. [c] Ref 23. [d] Ref 24. [e] m_B: molality (mol·kg^{-1}) of cosolutes in water.

$$\Delta_{tr}V_{2,m}^0 = 2V_{AB}m_B + 3V_{ABB}m_B^2 + ... \quad (6)$$

where A stands for α,ω-aminocarboxylic acids and B for cosolutes (i.e., SA and MA). V_{AB} and V_{ABB} are the volumetric pair and triplet interaction coefficients, respectively, and these are presented in Table 7. V_{AB} values are positive, whereas V_{ABB} values are negative in all cases. The larger positive values of V_{AB} suggest that the interactions between α,ω-aminocarboxylic acids and cosolutes are mainly pairwise. The V_{AB} values increase with an increase in the hydrophobic part, that is, from GLY to 4-ABA to 6-ACA and temperature regularly in both cosolutes, whereas the reverse is true for the triplet interaction coefficients. As the interactions of zwitterionic end groups for different α,ω-aminocarboxylic acids with both SA and MA are almost the same, this suggests that the alkyl chain of α,ω-aminocarboxylic acids plays an important role in modulating the volume of transfer and pair interaction coefficients.

The partial molar expansibilities V_E^0 [$V_E^0 = (\partial V_{2,m}^0/\partial T)_P$] and $(\partial^2 V_{2,m}^0/\partial T^2)_P$ have been calculated (Table S1 of the Supporting Information with literature values[26]) by fitting the data using the method of least-squares as follows:

$$V_{2,m}^0 = a + bT + cT^2 \quad (7)$$

where a, b, and c are constants and T is the temperature. The V_E^0 values show a regular decrease with temperature but increase

Table 7. Pair, V_{AB}, and Triplet, V_{ABB}, Interaction Coefficients of Studied α,ω-Aminocarboxylic Acids in Aqueous SA/MA Solutions from T = (288.15 to 318.15) K

α,ω-aminocarboxylic acids	$V_{AB}\cdot 10^6$ m^3·mol^{-2}·kg	$V_{ABB}\cdot 10^6$ m^3·mol^{-2}·kg^2	$V_{AB}\cdot 10^6$ m^3·mol^{-2}·kg	$V_{ABB}\cdot 10^6$ m^3·mol^{-2}·kg^2
	In Aqueous SA Solutions			
	T/K = 288.15		T/K = 298.15	
GLY	1.794 ± 0.227	−0.426 ± 0.169	2.696 ± 0.403	−0.806 ± 0.299
4-ABA	3.133 ± 0.462	−1.086 ± 0.343	4.744 ± 0.757	−1.874 ± 0.562
6-ACA	4.886 ± 0.867	−1.959 ± 0.644	6.490 ± 1.293	−2.705 ± 0.960
	T/K = 308.15		T/K = 318.15	
GLY	3.784 ± 0.879	−1.257 ± 0.652	5.170 ± 1.167	−2.054 ± 0.866
4-ABA	6.473 ± 0.988	−2.904 ± 0.734	7.450 ± 1.530	−3.366 ± 1.135
6-ACA	7.983 ± 1.862	−3.633 ± 1.382	8.947 ± 2.112	−4.081 ± 1.568
	In Aqueous MA Solutions			
	T/K = 288.15		T/K = 298.15	
GLY	2.680 ± 0.542	−0.895 ± 0.402	3.791 ± 0.776	−1.408 ± 0.576
4-ABA	3.859 ± 0.944	−1.471 ± 0.701	5.952 ± 0.724	−2.541 ± 0.537
6-ACA	5.414 ± 0.968	−2.209 ± 0.718	7.450 ± 1.558	−3.296 ± 1.156
	T/K = 308.15		T/K = 318.15	
GLY	4.624 ± 1.053	−1.796 ± 0.782	6.095 ± 1.317	−2.603 ± 0.978
4-ABA	7.382 ± 1.195	−3.318 ± 0.887	8.482 ± 1.479	−3.889 ± 1.098
6-ACA	9.274 ± 1.951	−4.313 ± 1.448	9.921 ± 2.484	−4.687 ± 1.844

with the concentration of cosolutes up to 0.25 mol·kg^{-1}, but they do not follow any regular trend after this, which may be attributed to the competition between various types of interactions occurring in these solutions.

Hepler[27] proposed a method by which qualitative information on the hydration of a solute can be obtained from thermal expansion of aqueous solutions by using the thermodynamic relation

$$(\partial C^0_{p,2}/\partial P)_T = -T(\partial^2 V^0_{2,m}/\partial T^2)_P \quad (8)$$

It has been suggested that structure-breaking solutes are accompanied by positive $(\partial C^0_{p,2}/\partial P)_T$ and negative $(\partial^2 V_{2,m}{}^0/\partial T^2)_P$ values, while the reverse is true for structure-making solutes. The presently obtained $(\partial^2 V_{2,m}{}^0/\partial T^2)_P$ values are negative, and hence the studied α,ω-aminocarboxylic acids act as structure breakers in water as well as in both cosolutes; the same behavior has been observed for α-amino acids in water as well as in $ZnCl_2$[13] (except for L-leucine). The α-amino acids tend to be structure making with an increase in the side chain of amino acids.

Conclusion

Partial molar volumes, $V_{2,m}{}^0$, of GLY, 4-ABA, and 6-ACA in water and in aqueous solutions of SA and MA, m_B = (0.10, 0.25, 0.50, and 1.00) mol·kg^{-1}, have been determined at T = (288.15 to 318.15) K. From these data, transfer volumes, interaction coefficients, partial molar expansibilities, and methylene group contributions have been determined. The $\Delta_{tr}V_{2,m}{}^0$ values are positive for the studied α,ω-aminocarboxylic acids and increase with an increase in the concentration of both SA and MA and temperature. V_{AB} values are positive, and V_{ABB} values are negative in all cases, which suggest that interactions between α,ω-aminocarboxylic acids and cosolutes are mainly pairwise. These parameters suggest that ion−ion interactions between charged ends of α,ω-aminocarboxylic acids and ions of cosolutes dominate over the ion−hydrophobic interactions in these systems. The negative $(\partial^2 V_{2,m}{}^0/\partial T^2)_P$ values for the α,ω-aminocarboxylic acids suggest that these act as structure breakers in water as well as in aqueous solution of both cosolutes. A comparison of results shows that the zwitterionic end groups in the case of α-amino acids modulates the $\Delta_{tr}V_{2,m}{}^0$ values to a greater extent than the α,ω-aminocarboxylic acids.

Supporting Information Available:

Partial molar expansibilities of some α,ω-aminocarboxylic acids in water and in aqueous SA/MA acetate solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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