

Volumetric studies of some amino acids in binary aqueous solutions of MgCl₂·6H₂O at 288·15, and 308·15 K

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Abstract. Densities (ρ) of glycine, L-alanine, and L-valine in aqueous solutions of MgCl₂·6H₂O (0·1–0·8 mol kg⁻¹) have been measured at 288·15, and 308·15 K. Apparent molar volumes (V_F), and limiting partial molar volumes (V_F^0) of each amino acid have been calculated. These data were combined with the earlier reported V_F^0 values of glycine, L-alanine, and L-valine in aqueous MgCl₂·6H₂O solutions at 298·15 K in order to describe the temperature dependence behaviour of partial molar quantities. Group contributions to partial molar volumes have been determined for the amino acids. The trends of transfer volumes (ΔV_F^0) have been interpreted in terms of solute–cosolute interactions on the basis of a cosphere overlap model. Pair and triplet interaction coefficients have also been calculated from transfer parameters.

Keywords. Amino acids; transfer functions; cosphere overlap model; interaction coefficients.

1. Introduction

It is well known that electrolytes can influence the solubility behaviour of amino acids. Consequently, study of the volumetric properties of amino acids in aqueous salt solutions is very useful to obtain information^{1–5} about various types of interactions in solutions. There have been some recent studies^{6–8} on volumetric properties of amino acids in dilute electrolyte solutions though there are very few in concentrated electrolyte solutions.^{9,10}

In this work, we report the apparent molar volumes (V_F), limiting partial molar volumes (V_F^0), transfer volumes at infinite dilution (ΔV_F^0) and the infinite dilution partial molar expansibilities (f_E^0) of glycine, L-alanine, and L-valine in aqueous magnesium chloride solutions (0·1–0·8 mol kg⁻¹), at 288·15 and 308·15 K. These results are expected to highlight the role of amino acids in presence of aqueous magnesium chloride solutions and the influence of temperature on them.

2.1 Experimental

2.1 Materials

The amino acids used in this study, glycine, L-alanine, and L-valine, were analytical grade reagents and were used without further treatment. Analytical reagent grade magnesium chloride was used after drying at 250°C for 3 h and then *in vacuo* over P₂O₅ at room temperature for a minimum of 48 h. The water used (specific conductivity $\sim 10^{-6}$ S cm⁻¹) in these experiments was deionized and distilled, and was degassed prior to making solutions. Solutions were prepared on a molality concentration scale with a precision of $\pm 1 \times 10^{-4}$ g on a Dhona balance (India, Model 200D). Uncertainties in solution concentration were estimated at $\pm 2 \times 10^{-5}$ mol kg⁻¹ in calculations. The concentrations of amino acids were in the range of 0·03–0·20 mol kg⁻¹, while that of the salt varied from 0·1–0·8 mol kg⁻¹.

2.2 Apparatus and procedure

The densities (ρ) of solutions were measured using a single stem pycnometer of total volume 8 cm³ and capillary internal diameter about 0·1 cm. Details pertaining to calibration, experimental set-up and

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operational procedure have been previously described.¹¹ An average of three measurements were taken into account. Reproducibility in the density measurements was better than $\pm 3 \times 10^{-2} \text{ kg m}^{-3}$. A thermostatically controlled well-stirred water bath whose temperature was controlled to $\pm 0.01 \text{ K}$ was used for all the measurements.

3. Results and discussion

The measured densities (ρ) at 288.15, and 308.15 K are shown in table 1 at different concentrations of amino acids and electrolyte.

Apparent molar volumes $V_F (\text{m}^3 \text{ mol}^{-1})$ was calculated from the solution densities using the standard expression:

$$V_F = M/\rho - \{1000 \cdot (\rho - \rho_0)/m \cdot \rho \cdot \rho_0\}, \quad (1)$$

where m is the molality (mol kg^{-1}) of the solution, M is the relative molar mass of the solute (kg mol^{-1}), and ρ_0 , and ρ are the densities (kg m^{-3}) of solvent and solution respectively. The resulting values of the apparent molar volumes (V_F) and the molal concentrations (m) of amino acids in different concentrations of magnesium chloride at 288.15, and 308.15 K are reported in table 1. Comparison with our earlier results¹⁰ at 298.15 K shows that the values increase with increasing temperature at each concentration of electrolyte. It is also found that V_F increases linearly with increase in size of the alkyl chain of the amino acid and also increases with increase in the concentration of magnesium chloride in solution. It indicates that the solute–solvent interactions increase with increasing concentration of magnesium chloride, size of the alkyl side chain of amino acids and temperature. The variation of the apparent molar volumes with the molal concentration can be adequately represented by the relation,

$$V_F = V_F^0 + S_V \cdot m, \quad (2)$$

where V_F^0 is the limiting value of the apparent molar volume (equal to the partial molar volume at infinite dilution) and S_V is the experimental slope. The values of V_F^0 , and S_V obtained by least squares fitting of the V_F values to (2) for various amino acids at different concentrations of magnesium chloride are reported in table 2, together with the standard errors. Plots of V_F against m are linear in all cases. A sample plot for glycine in 0.4 mol kg^{-1} of magnesium chloride

solution at different temperatures is shown in figure 1. It is evident from table 2 and our data at 298.15 K in reference¹⁰ that the values of the slope S_V for all the amino acids in different concentrations of magnesium chloride at different temperatures are negative suggesting weak solute–solvent interactions in the system.

Transfer volumes of different amino acids, ΔV_F^0 from solutions in water to aqueous magnesium chloride solutions are calculated as,

$$\Delta V_F^0 = V_F^0 (\text{in aqueous magnesium chloride solution}) - V_F^0 (\text{in water}). \quad (3)$$

and the values are illustrated in figure 2. Experimental values of V_F^0 for the amino acids in water are reported in our previous papers.^{11,12} The more positive values of ΔV_F^0 for glycine, and L-alanine (except at lower concentration of magnesium chloride and at lower temperatures) indicate the dominance of the charged end groups, NH_3^+ and COO^- , while negative ΔV_F^0 in case of L-valine indicates the effect of hydrophobic parts. That is, the interactions between the magnesium chloride and zwitterionic centre of amino acids (in case of glycine and L-alanine) increase both on increasing magnesium chloride concentration and temperature. This leads to an increase in the structure-breaking tendency of the ion and a reduction in the electrostriction of the water caused by these ions. For L-valine, the interactions between the non-polar group of L-valine and magnesium chloride are predominant. It decreases with increasing temperature.

The variation of V_F^0 with temperature can be expressed as:

$$V_F^0 = a + bT + cT^2, \quad (4)$$

where T is the temperature in Kelvin.

The partial molar expansibilities at infinite dilution can be obtained by differentiating (5) with respect to temperature,

$$f_E^0 = (\partial V_F^0 / \partial T)_P = b + 2 \cdot cT. \quad (5)$$

f_E^0 values of different amino acids at different temperatures are recorded in table 3. It is found that f_E^0 values of glycine (at higher concentrations of magnesium chloride) and L-valine (except at 0.4 mol kg^{-1} magnesium chloride) increase with rising temperature. This behaviour is contrary to that observed

Table 1. Densities (ρ), and apparent molar volumes (V_f) of glycine, L-alanine, and L-valine in binary aqueous solutions of $MgCl_2 \cdot 6H_2O$ at 288.15, and 308.15 K.

		288.15 K			308.15 K					288.15 K			308.15 K		
m (mol kg ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$V_f \times 10^6$ (m ³ mol ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$V_f \times 10^6$ (m ³ mol ⁻¹)	m (mol kg ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$V_f \times 10^6$ (m ³ mol ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$V_f \times 10^6$ (m ³ mol ⁻¹)	m (mol kg ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$V_f \times 10^6$ (m ³ mol ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$V_f \times 10^6$ (m ³ mol ⁻¹)	
<i>Glycine + 0.2 mol kg⁻¹ MgCl₂·6H₂O</i>					<i>L-Alanine + 0.6 mol kg⁻¹ MgCl₂·6H₂O</i>										
0.00000	1.01350		1.00800		0.00000	1.04269		1.03710		0.00000	1.04269		1.03710		
0.04834	1.01502	43.39	1.00941	45.70	0.04799	1.04397	60.84	1.03826	63.37	0.04799	1.04397	60.84	1.03826	63.37	
0.08076	1.01604	43.34	1.01036	45.61	0.08005	1.04482	60.83	1.03903	63.36	0.08005	1.04482	60.83	1.03903	63.36	
0.11320	1.01706	43.30	1.01131	45.56	0.10837	1.04558	60.75	1.03972	63.27	0.10837	1.04558	60.75	1.03972	63.27	
0.13697	1.01781	43.25	1.01200	45.55	0.13901	1.04640	60.68	1.04046	63.23	0.13901	1.04640	60.68	1.04046	63.23	
0.17036	1.01886	43.21	1.01297	45.54	0.16853	1.04719	60.62	1.04117	63.20	0.16853	1.04719	60.62	1.04117	63.20	
0.19902	1.01976	43.18	1.01381	45.48	0.20158	1.04807	60.58	1.04197	63.14	0.20158	1.04807	60.58	1.04197	63.14	
<i>Glycine + 0.4 mol kg⁻¹ MgCl₂·6H₂O</i>					<i>L-Alanine + 0.8 mol kg⁻¹ MgCl₂·6H₂O</i>										
0.00000	1.02943		1.02413		0.00000	1.05489		1.04883		0.00000	1.05489		1.04883		
0.04823	1.03089	44.30	1.02542	47.74	0.04947	1.05616	61.31	1.05000	63.37	0.04947	1.05616	61.31	1.05000	63.37	
0.07854	1.03181	44.23	1.02623	47.71	0.07982	1.05694	61.26	1.05072	63.30	0.07982	1.05694	61.26	1.05072	63.30	
0.10722	1.03268	44.18	1.02700	47.65	0.10829	1.05767	61.22	1.05140	63.21	0.10829	1.05767	61.22	1.05140	63.21	
0.13901	1.03364	44.16	1.02785	47.61	0.13907	1.05846	61.18	1.05214	63.11	0.13907	1.05846	61.18	1.05214	63.11	
0.16759	1.03450	44.15	1.02861	47.60	0.16925	1.05924	61.11	1.05286	63.05	0.16925	1.05924	61.11	1.05286	63.05	
0.19940	1.03547	44.08	1.02946	47.57	0.19954	1.06002	61.05	1.05359	62.97	0.19954	1.06002	61.05	1.05359	62.97	
<i>Glycine + 0.6 mol kg⁻¹ MgCl₂·6H₂O</i>					<i>L-Alanine + 0.1 mol kg⁻¹ MgCl₂·6H₂O</i>										
0.00000	1.04269		1.03710		0.00000	1.00638		1.00086		0.00000	1.00638		1.00086		
0.04862	1.04411	45.07	1.03831	49.19	0.03019	1.00729	86.57	1.00167	90.19	0.03019	1.00729	86.57	1.00167	90.19	
0.08084	1.04505	45.04	1.03911	49.17	0.04397	1.00771	86.43	1.00204	90.15	0.04397	1.00771	86.43	1.00204	90.15	
0.11001	1.04590	45.02	1.03984	49.10	0.05733	1.00812	86.29	1.00240	90.09	0.05733	1.00812	86.29	1.00240	90.09	
0.13854	1.04674	44.94	1.04055	49.07	0.07249	1.00858	86.25	1.00281	90.02	0.07249	1.00858	86.25	1.00281	90.02	
0.16719	1.04757	44.93	1.04153	49.05	0.08573	1.00898	86.24	1.00317	89.94	0.08573	1.00898	86.24	1.00317	89.94	
0.20051	1.04856	44.82	1.04209	49.01	0.10005	1.00942	86.15	1.00356	89.87	0.10005	1.00942	86.15	1.00356	89.87	
<i>Glycine + 0.8 mol kg⁻¹ MgCl₂·6H₂O</i>					<i>L-Alanine + 0.2 mol kg⁻¹ MgCl₂·6H₂O</i>										
0.00000	1.05489		1.04883		0.00000	1.01350		1.00800		0.00000	1.01350		1.00800		
0.05102	1.05625	47.15	1.05007	49.42	0.03013	1.01438	87.08	1.00879	90.34	0.03013	1.01438	87.08	1.00879	90.34	
0.08153	1.05706	47.14	1.05081	49.40	0.04380	1.01478	87.03	1.00915	90.28	0.04380	1.01478	87.03	1.00915	90.28	
0.11237	1.05788	47.12	1.05156	49.36	0.05816	1.01520	86.99	1.00953	90.19	0.05816	1.01520	86.99	1.00953	90.19	
0.13923	1.05860	47.05	1.05221	49.35	0.07187	1.01560	86.96	1.00989	90.17	0.07187	1.01560	86.96	1.00989	90.17	
0.17120	1.05945	47.02	1.05299	49.29	0.08596	1.01601	86.95	1.01026	90.14	0.08596	1.01601	86.95	1.01026	90.14	
0.19851	1.06018	46.98	1.05365	49.28	0.10057	1.01644	86.88	1.01065	90.05	0.10057	1.01644	86.88	1.01065	90.05	
<i>L-Alanine + 0.2 mol kg⁻¹ MgCl₂·6H₂O</i>					<i>L-Alanine + 0.3 mol kg⁻¹ MgCl₂·6H₂O</i>										
0.00000	1.01350		1.00800		0.00000	1.02318		1.01752		0.00000	1.02318		1.01752		
0.05072	1.01500	59.02	1.00933	62.49	0.03016	1.02397	89.41	1.01825	91.69	0.03016	1.02397	89.41	1.01825	91.69	
0.07625	1.01576	58.94	1.01000	62.44	0.04432	1.02434	89.39	1.01860	91.50	0.04432	1.02434	89.39	1.01860	91.50	
0.11026	1.01676	58.93	1.01089	62.41	0.05708	1.02468	89.26	1.01891	91.49	0.05708	1.02468	89.26	1.01891	91.49	
0.13997	1.01764	58.87	1.01167	62.35	0.07258	1.02509	89.19	1.01929	91.42	0.07258	1.02509	89.19	1.01929	91.42	
0.17044	1.01854	58.82	1.01247	62.30	0.08608	1.02545	89.11	1.01962	91.38	0.08608	1.02545	89.11	1.01962	91.38	
0.19958	1.01940	58.78	1.01323	62.27	0.10009	1.02582	89.07	1.01996	91.37	0.10009	1.02582	89.07	1.01996	91.37	
<i>L-Alanine + 0.4 mol kg⁻¹ MgCl₂·6H₂O</i>					<i>L-Alanine + 0.4 mol kg⁻¹ MgCl₂·6H₂O</i>										
0.00000	1.02943		1.02413		0.00000	1.02943		1.02413		0.00000	1.02943		1.02413		
0.05021	1.03088	59.21	1.02541	62.61	0.03092	1.03032	86.56	1.02485	92.12	0.03092	1.03032	86.56	1.02485	92.12	
0.07757	1.03167	59.16	1.02611	62.55	0.04461	1.03072	86.41	1.02517	92.07	0.04461	1.03072	86.41	1.02517	92.07	
0.10877	1.03257	59.12	1.02690	62.54	0.05894	1.03114	86.28	1.02551	91.95	0.05894	1.03114	86.28	1.02551	91.95	
0.13700	1.03339	59.04	1.02762	62.49	0.07184	1.03152	86.17	1.02581	91.94	0.07184	1.03152	86.17	1.02581	91.94	
0.16862	1.03430	59.01	1.02842	62.47	0.08556	1.03192	86.13	1.02613	91.92	0.08556	1.03192	86.13	1.02613	91.92	
0.19939	1.03519	58.95	1.02921	62.39	0.09939	1.03232	86.12	1.02646	91.83	0.09939	1.03232	86.12	1.02646	91.83	

Table 2. Limiting partial molar volumes (V_f^0), and experimental slopes (S_V) of glycine, L-alanine, and L-valine in binary aqueous solutions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 288.15 and 308.15 K.

m_B (mol kg^{-1})	288.15 K		308.15 K	
	$V_f^0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	$S_V \times 10^6$ ($\text{m}^3 \text{L}^{1/2} \text{mol}^{-3/2}$)	$V_f^0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	$S_V \times 10^6$ ($\text{m}^3 \text{L}^{1/2} \text{mol}^{-3/2}$)
<i>Glycine</i>				
0.2	43.46 (± 0.01)	-1.42 (± 0.06)	45.73 (± 0.03)	-1.27 (± 0.21)
0.4	44.34 (± 0.02)	-1.29 (± 0.16)	47.79 (± 0.02)	-1.16 (± 0.12)
0.6	45.17 (± 0.03)	-1.59 (± 0.21)	49.25 (± 0.01)	-1.23 (± 0.11)
0.8	47.23 (± 0.02)	-1.23 (± 0.15)	49.48 (± 0.01)	-1.01 (± 0.09)
<i>L-Alanine</i>				
0.2	59.08 (± 0.02)	-1.53 (± 0.13)	62.56 (± 0.01)	-1.49 (± 0.07)
0.4	59.30 (± 0.01)	-1.75 (± 0.09)	62.67 (± 0.02)	-1.33 (± 0.14)
0.6	60.95 (± 0.02)	-1.87 (± 0.16)	63.46 (± 0.02)	-1.57 (± 0.15)
0.8	61.40 (± 0.01)	-1.71 (± 0.09)	63.51 (± 0.01)	-2.71 (± 0.09)
<i>L-Valine</i>				
0.1	86.68 (± 0.06)	-5.52 (± 0.90)	90.35 (± 0.02)	-4.70 (± 0.23)
0.2	87.15 (± 0.02)	-2.58 (± 0.24)	90.45 (± 0.03)	-3.84 (± 0.36)
0.3	89.58 (± 0.03)	-5.31 (± 0.47)	91.74 (± 0.06)	-4.14 (± 0.90)
0.4	86.71 (± 0.07)	-6.59 (± 1.02)	92.23 (± 0.04)	-4.01 (± 0.52)

Standard errors are given in parentheses

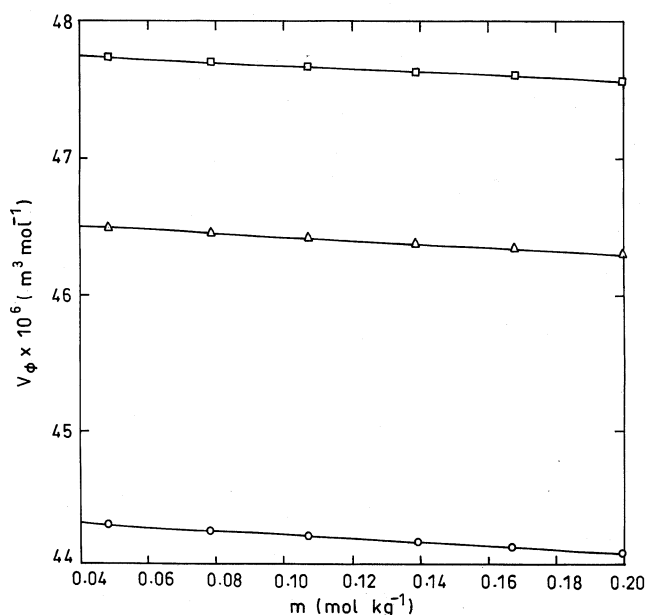


Figure 1. Plots of V_f vs m for glycine in 0.4 mol kg^{-1} $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at \circ – 288.15 K; \triangle – 298.15 K (ref. 10); and \square – 308.15 K.

for L-alanine in binary aqueous solutions of magnesium chloride. It indicates that in case of L-alanine, the structure-breaking tendency of the ion increases with increase in concentrations of magnesium chloride. At lower concentrations of magnesium chloride

and at lower temperatures, the f_E^0 values of L-valine are negative, favouring solute-solvent interactions. The effect is that the charged end group of L-valine electrostatically influences the surrounding water molecules, the so-called electrostriction. As a result, electrostricted water may be released from the loose solvation layers of L-valine on the increase of temperature. The overall effect is that the removal of water molecules favours L-valine-magnesium chloride interactions, indicating the structure-making effect of L-valine at lower concentration of magnesium chloride and at lower temperature.

Franks and collaborators¹³ reported that the partial molar volume at infinite dilution of a non-electrolyte is a combination of two factors given by the following equation:

$$V_f^0 = V_{\text{int}} + V_S, \quad (6)$$

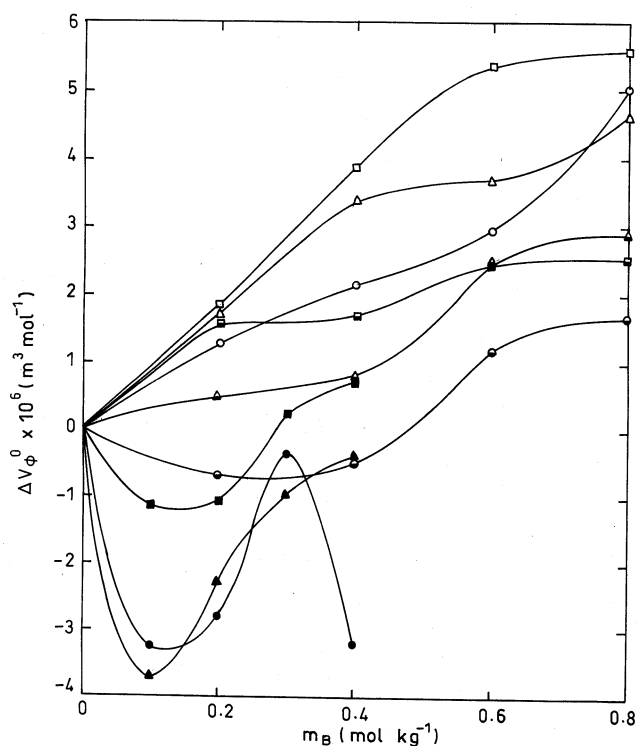
where V_{int} is the intrinsic molar volume of the non-hydrated solute, and V_S is the contribution due to the interaction of the solute with water. The intrinsic volume is made up^{14,15} of the following types of contributions:

$$V_{\text{int}} = V_{V,W} + V_{\text{void}}, \quad (7)$$

where $V_{V,W}$ is the van der Waals volume¹⁶ and V_{void} is the volume associated with the void or empty

Table 3. Limiting partial molar expansibilities (f_E^0) of glycine, L-alanine, and L-valine in binary aqueous solutions of $MgCl_2 \cdot 6H_2O$ at different temperatures.

m_B (mol kg ⁻¹)	288.15 K	298.15 K	308.15 K
	$f_E^0 \times 10^6$ (m ³ mol ⁻¹ K ⁻¹)	$f_E^0 \times 10^6$ (m ³ mol ⁻¹ K ⁻¹)	$f_E^0 \times 10^6$ (m ³ mol ⁻¹ K ⁻¹)
<i>Glycine</i>			
0.2	0.177	0.114	0.051
0.4	0.270	0.173	0.076
0.6	0.138	0.204	0.270
0.8	0.005	0.112	0.219
<i>L-Alanine</i>			
0.2	0.196	0.174	0.152
0.4	0.219	0.168	0.117
0.6	0.266	0.125	-0.016
0.8	0.277	0.106	-0.065
<i>L-Valine</i>			
0.1	-0.086	0.183	0.452
0.2	0.121	0.165	0.209
0.3	-0.040	0.108	0.256
0.4	0.478	0.276	0.074


Figure 2. Plots of ΔV_f^0 vs m_B for glycine at \circ – 288.15 K; \triangle – 298.15 K (ref. 10); \square – 308.15 K; L-alanine at \circ – 288.15 K; \square – 298.15 K (ref. 10); \blacksquare – 308.15 K; and L-valine at \bullet – 288.15 K; \blacktriangle – 298.15 K (ref. 10); \blacksquare – 308.15 K.

volume.¹⁷ This was modified by Shahidi *et al*¹⁵ in order to determine the contribution of one molecule to the partial molar volume of a hydrophobic solute as:

$$V_f^0 = V_{V,W} + V_{\text{void}} - V_{\text{shrinkage}}, \quad (8)$$

where $V_{\text{shrinkage}}$ is the volume due to shrinkage caused by interaction of hydrogen bonding sites with water molecules. Assuming that the $V_{V,W}$ and V_{void} remain of the same magnitude in water and aqueous magnesium chloride solutions, the positive ΔV_f^0 values for the amino acids can be attributed to the decrease in $V_{\text{shrinkage}}$. Electrostatic interaction of magnesium chloride with the zwitterionic centre of amino acids reduces the effect of electrostriction of water molecules lying in the vicinity of zwitterionic centres. This will lead to a reduction in $V_{\text{shrinkage}}$ and result in positive ΔV_f^0 values from water to aqueous magnesium chloride solutions.

The ΔV_f^0 values can also be explained on the basis of cosphere overlap model^{18,19} in terms of solute–cosolute interactions. According to this model, hydrophilic–ionic group interactions contribute positively, whereas hydrophilic–hydrophobic group interactions contribute negatively to the ΔV_f^0 values. For glycine, and L-alanine (at higher temperatures) in aqueous magnesium chloride solutions, the former

Table 4. Contribution of (NH₃⁺COO⁻), and (R) groups to the limiting partial molar volumes (V_f^0) of glycine, L-alanine, and L-valine in binary aqueous solutions of MgCl₂·6H₂O at 288·15 and 308·15 K.

m_B (mol kg ⁻¹)	$V_f^0 \times 10^6$ (m ³ mol ⁻¹)			
	NH ₃ ⁺ COO ⁻	-CH ₂	-CHCH ₃	-CHCH ₂ (CH ₃) ₂
288·15 K				
0·2	29·43 (± 1·04)	14·49	28·98	57·95
0·4	30·64 (± 0·82)	14·06	28·13	56·25
308·15 K				
0·2	31·79 (± 1·89)	14·77	29·54	59·08
0·4	33·01 (± 0·07)	14·81	29·62	59·23

Parentheses indicate standard errors

Table 5. Pair and triplet interaction coefficients for glycine, L-alanine, and L-valine in binary aqueous solutions of MgCl₂·6H₂O at 288·15 and 308·15 K.

Temperature	$V_{AB} \times 10^6$ (m ³ mol ⁻² kg)	$V_{ABB} \times 10^6$ (m ³ mol ⁻³ kg ²)
<i>Glycine</i>		
288·15 K	1·4217	2·5126
308·15 K	3·2100	3·1045
<i>L-Alanine</i>		
288·15 K	-1·3445	1·0467
308·15 K	1·7797	1·3713
<i>L-Valine</i>		
288·15 K	-9·2416	10·9032
308·15 K	-5·7334	11·5968

type of interactions are more predominant over the latter. The magnitude of ΔV_f^0 decreases from glycine to L-alanine to L-valine (table 3), indicating the building up of hydrophilic–hydrophobic group interactions. It may be noted from our previous finding^{12,20} that ΔV_f^0 values of L-alanine in presence of sucrose are less than those of glycine and L-valine. The increasing magnitude of ΔV_f^0 with the increasing concentration of magnesium chloride, as can be seen from figure 2 at any particular temperature (except L-valine), may also be attributed to the greater ion–hydrophilic interactions.

Table 4 shows the contributions of the various groups to the V_f^0 of glycine, L-alanine, and L-valine in aqueous magnesium chloride solutions at 288·15, and 308·15 K. The values of V_f^0 for CH₂-(glycine),

CH₃CH-(L-alanine), (CH₃)₂CHCH-(L-valine), and zwitterionic end groups (NH₃⁺COO⁻) were estimated by least squares fitting of V_f^0 of the amino acids containing the group vs the molecular weight of the hydrocarbon portion of the amino acid. The contribution of (NH₃⁺COO⁻) to V_f^0 is larger than the -CH₂ group and increases with the increase in the concentration of magnesium chloride at all temperatures. It may be inferred that the interactions between magnesium chloride and charged end groups (NH₃⁺COO⁻) of amino acids are much stronger than those between magnesium chloride and -CH₂ groups. However, the V_f^0 values for non-polar groups increase with the size of side chain of amino acids but decrease both with increasing concentration of magnesium chloride as well as increasing temperature, except at 0·4 mol kg⁻¹ of magnesium chloride and at higher temperatures. It indicates that the increased length of side chains of amino acids leads to increase in the hydrophilic–hydrophobic group interactions. This is very important in case of L-valine.

The McMillan–Mayer theory of solutions²¹ was proposed by Kozak *et al*²² and further discussed by Friedman and Krishnan²³ and Frank *et al*²⁴ in order to include the solute–cosolute interactions in solvation spheres. According to this treatment, at infinite dilution ΔV_f^0 can be expressed as:

$$\Delta V_f^0(\text{water to aqueous magnesium chloride solution}) = 2 \cdot V_{AB} \cdot m_B + 3 \cdot V_{ABB} \cdot m_B^2 + \dots, \quad (9)$$

where A stands for amino acids and B denotes magnesium chloride, and m_B is the molality of magnesium chloride (cosolute), and constants V_{AB} and V_{ABB} are pair and triplet interaction coefficients respectively.

ΔV_f^0 data have been fitted to (9) to obtain V_{AB} and V_{ABB} interaction coefficients, which are given in table 5.

Triplet interaction coefficients V_{ABB} are positive, whereas pair interaction parameters V_{AB} contribute positively in case of glycine and negatively as well as positively in case of L-alanine and L-valine at all temperatures. The magnitude of V_{AB} decrease with the size of alkyl chain of amino acids. V_{AB} has maximum values in case of glycine and minimum in case of L-valine which may be due to the shorter alkyl side chain in case of glycine and larger in case of L-valine respectively. The positive values of pair interaction coefficients of glycine and those of L-alanine (at higher temperatures) suggest that interactions occur due to the overlap of hydration spheres of the solute-cosolute molecules, which again supports the conclusions drawn from the cosphere overlap model.

4. Conclusion

In summary, we have shown ion-amino acid interaction parameters from the volumetric properties of glycine, L-alanine, and L-valine in aqueous solutions of magnesium chloride at 288.15 and 308.15 K. Limiting partial molar expansibilities f_E^0 of amino acids in aqueous solutions of magnesium chloride are calculated from the measured quantities. The transfer volume ΔV_f^0 behaviour for glycine and L-alanine are contrary to that observed for L-valine. In the case of glycine and L-alanine, the ΔV_f^0 values are positive (except at lower concentrations of magnesium chloride and at lower temperatures), indicating the dominance of charged end groups, NH_3^+ and COO^- , and negative in case of L-valine, indicating the effect of hydrophobic parts. The magnitude of ΔV_f^0 decreases from glycine to L-alanine to L-valine, indicating the building up of hydrophilic-hydrophobic group interactions. Also, group contributions calculated from V_f^0 suggest increase in hydrophilic-hydrophobic group interactions with increase of the side-chain length of the amino acids.

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