Study of Interactions between Amino Acids and Zinc Chloride in Aqueous Solutions through Volumetric Measurements at T = (288.15 to 318.15) K

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Densities, ρ, of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine, and L-leucine in aqueous and in mixed aqueous solutions of zinc chloride, (0.1, 0.5, 1.0, and 1.5) mol·kg^{-1}, have been determined by using a vibrating-tube digital densimeter at (288.15, 298.15, 308.15, and 318.15) K. These data have been used to calculate the apparent molar volumes, $V_{2,\phi}$, of the studied amino acids. The partial molar volumes, V_2^0, at infinite dilution are evaluated and further used to obtain the corresponding transfer volumes, $\Delta_t V^0$ for amino acids from water to aqueous zinc chloride solutions. Partial molar expansibilities, V^0_E, hydration numbers, n_H, interaction coefficients, and side chain group contributions of amino acids have also been calculated. The $\Delta_t V^0$ values for the studied amino acids are positive, and these values increase with an increase in the concentration of zinc chloride as well as with temperature. The parameters obtained from the volumetric study are used to understand various mixing effects due to the interactions between amino acids and zinc chloride in aqueous solutions.

Introduction

Globular proteins form a class of macromolecules which have well-defined physicochemical properties and functions in biological systems. They have a marginally stable native structure that results from a fine balance among various noncovalent forces: ionic and dipolar interactions, hydrogen bonding, and hydrophobic forces, etc.[1] The process of denaturation of a globular protein in aqueous solutions involves a change from the native state, in which the protein adopts its characteristic folded conformation, to the denatured state where the protein is predominantly in an extended form.[2,3] During this process, substantial changes in protein solvation will occur, and these changes will make an important contribution to the energetics of protein denaturation. The study of these protein–solvent interactions is difficult because of the complexity of the interactions in such a large molecule. However, one useful approach, which can be of help in our understanding of these interactions, is to study simple compounds such as amino acids and peptides, which model some specific aspects of the protein structure. A survey of the literature shows that there are many studies on the physicochemical properties of amino acids in the presence of salts of alkali and alkaline earth metals, but there are only a few studies in aqueous solutions of transition metal salts.[4–12] Transition metals ions (zinc, copper, iron, manganese, and cobalt) play a vital role in life systems, because of their natural presence in vitamins, enzymes, and protein. Zinc ions are very important for a number of biological functions in the human body.[13] Therefore, we planned to carry out volumetric studies on amino acids in aqueous solutions of salts of transition metal ions having some biological importance. Volumetric properties are useful for the elucidation of noncovalent interactions occurring in solutions and characterizing the structure and properties of solutions.[14] In continuation of our studies on the amino acids, in this paper we report the partial molar volumes V_2^0 of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine, and L-leucine, in water and in aqueous solutions of (0.1, 0.5, 1.0, and 1.5) mol·kg^{-1} $ZnCl_2$ at (288.15, 298.15, 308.15, and 318.15) K. From these data, the partial molar volumes of transfer, $\Delta_t V^0$, hydration numbers, n_H, interaction coefficients, and side chain contributions have been calculated. These results have been rationalized in terms of various interactions occurring in these solutions.

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Experimental Section

Glycine (G-7126, 99 %), DL-α -alanine (A-7502, 99 %), DL-α-amino-*n*-butyric acid (A-1754, 98 %), L-valine (V-0500, 99 %), and L-leucine (L-8000, 98 %) were obtained from the Sigma Chemical Co. and were dried for 24 h in a vacuum oven before use. Analytical grade zinc chloride procured from Thomas Baker having a purity of 98 % was 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 $1.29 \cdot 10^{-6}$ $\Omega^{-1} \cdot cm^{-1}$ 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) having a precision of $\pm\ 1 \cdot 10^{-3}$ kg·m^{-3} and an accuracy of $\pm\ 3 \cdot 10^{-3}$ kg·m^{-3}. The temperature of water around the densimeter cell was controlled within ± 0.01 K using a thermostat. The densimeter was calibrated with dry air and pure water and was checked by measuring the densities of aqueous sodium chloride solutions [presently measured densities for aqueous solutions of sodium chloride are: (1005.594, 1010.434, 1017.310, 1036.665, 1054.954, 1071.250, and 1087.547) kg·m^{-3} at (0.20900, 0.33112, 0.50650, 1.01279, 1.51000, 1.97014, and 2.44845) mol·kg^{-1} of sodium chloride, respectively] which agree well with the literature values[15] [literature values of density are: (1005.571, 1017.344, 1036.690, 1054.672, 1071.353, and 1087.608) kg·m^{-3} at (0.20918, 0.50653, 1.01279,

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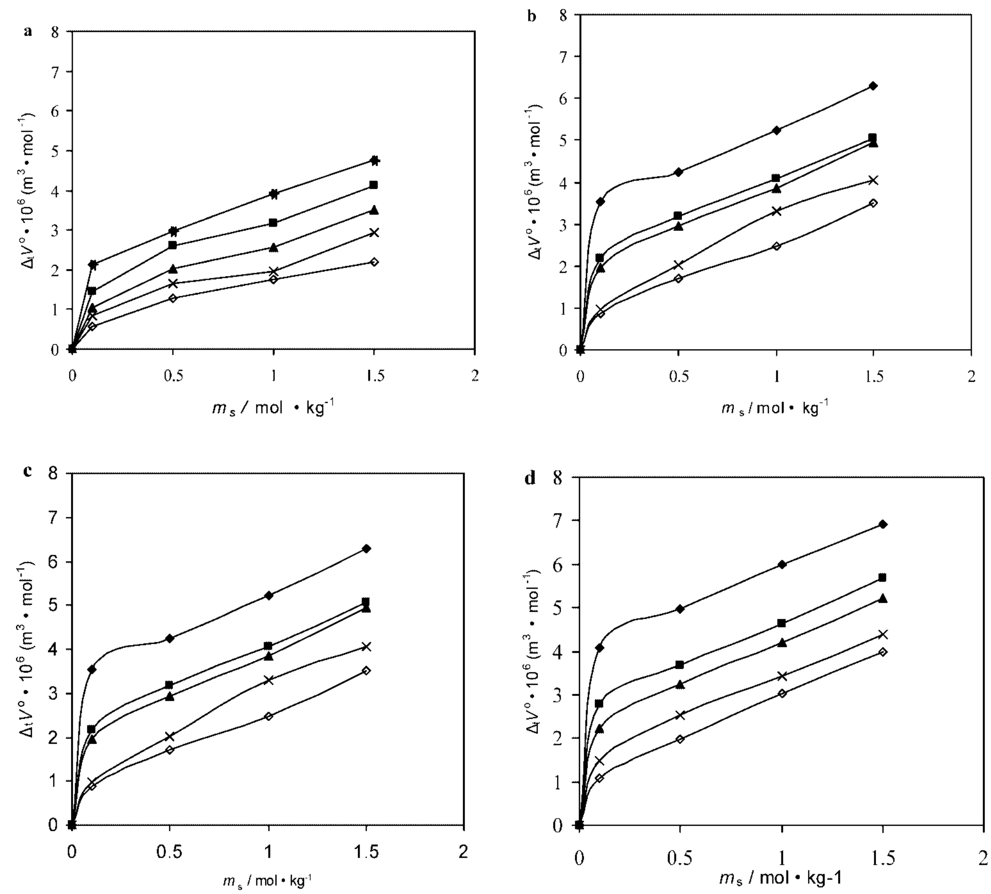

Figure 1. Partial molar volumes of transfer $\Delta_t V^0$ of some amino acids vs m_S: ◆, glycine; ■, DL-α-alanine; ▲, DL-α-amino-*n*-butyric acid; ×, L-valine; ◇, L-leucine at (a) 288.15 K; (b) 298.15 K; (c) 308.15 K; and (d) 318.15 K.

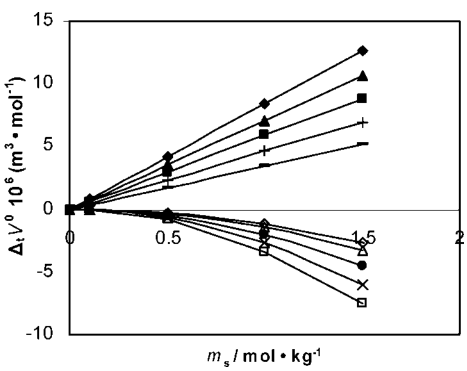

Figure 2. Contribution of the interaction coefficients to the partial molar transfer volumes, $\Delta_t V^0$, of the amino acids vs m_S of aqueous $ZnCl_2$ solutions at 298.15 K. The symbol for the pair is V_{XY} and for the triplet is V_{XYY}. Symbol for the glycine: ◆, V_{XY}; □, V_{XYY}. Symbol for the DL-α-alanine: ▲, V_{XY}; ×, V_{XYY}. Symbol for the DL-α-amino-*n*-butyric acid: ■, V_{XY}; ●, V_{XYY}. Symbol for the L-valine: +, V_{XY}; Δ, V_{XYY}. Symbol for the L-leucine: −, V_{XY}; ◇, V_{XYY}.

1.50262, 1.97403, and 2.44952) mol·kg^{-1} of sodium chloride, respectively] at 298.15 K.

Results and Discussion

Apparent molar volumes, $V_{2,\phi}$ of selected amino acids in water and in (0.1, 0.5, 1.0, and 1.5) mol·kg^{-1} $ZnCl_2$ solutions at (288.15, 298.15, 308.15, and 318.15) K, have been calculated using the following relationship

$$V_{2,\phi} = (M/\rho) - [(\rho - \rho_0) \cdot 1000/(m_A \cdot \rho \cdot \rho_0)] \qquad (1)$$

where M and m_A are, respectively, the molar mass and the molality of amino acids, and ρ and ρ_0 are the densities of solution and the solvent, respectively.

The densities of solutions and apparent molar volumes of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine, and L-leucine as a function of temperature and concentration of the amino acids in aqueous and in mixed aqueous solutions of zinc chloride are given in Table 1.

The uncertainties in $V_{2,\phi}$ resulting from various experimentally measured quantities have been calculated. It comes out to be $0.003 \cdot 10^{-6}$ at high and $0.039 \cdot 10^{-6}$ m^3·mol^{-1} at low concentration of amino acids in water as well as cosolute solutions over the studied temperature range.

The apparent molar volume data were found to be adequately represented by the linear equation

$$V_{2,\phi} = V_2^0 + S_v m \qquad (2)$$

where V_2^0 is the apparent molar volume at infinite dilution and it has the same meaning as that of the standard partial molar volume, and S_v is the experimental slope. The V_2^0 values along with standard deviations are summarized in Table 2. The V_2^0 values of amino acids in water agree well with literature data.[16–20]

Partial molar volumes of transfer, $\Delta_t V^0$ at infinite dilution from water to aqueous $ZnCl_2$ solutions have been calculated as follows

$$\Delta_t V^0 = V_2^0 \text{ (in aqueous } ZnCl_2 \text{ solutions)} - V_2^0 \text{ (in water)} \qquad (3)$$

$ZnCl_2$, being a salt of strong acid and weak base, undergoes hydrolysis and gives acidic solutions. The measured values of pH of aqueous solutions of $ZnCl_2$ are 6.60, 5.72, 5.32, and 5.22 at (0.1, 0.5, 1.0, and 1.5) mol·kg^{-1}. As $ZnCl_2$ aqueous solutions

Table 1. Densities, ρ, and Apparent Molar Volumes, $V_{2,\phi}$, of Some Amino Acids in Water and in Aqueous $ZnCl_2$ Solutions as a Function of Concentration of Amino Acids and $ZnCl_2$ from T = (288.15 to 318.15) K

m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})	m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})
		T/K = 288.15			
		Glycine in Water			
0.07326	1.001512	42.45	0.28243	1.008213	42.53
0.14584	1.003852	42.49	0.32774	1.009639	42.56
0.23257	1.006629	42.51	0.43706	1.013065	42.60
		Glycine in Aqueous $ZnCl_2$ Solutions			
		$^a m_s$ = 0.1 mol·kg^{-1} ($^b\rho_0$ = 1.011641)			
0.06663	1.013656	44.57	0.36244	1.022423	44.66
0.13040	1.015570	44.59	0.39769	1.023439	44.70
0.24609	1.019008	44.63	0.48260	1.025895	44.72
		m_s= 0.5 mol·kg^{-1} (ρ_0 = 1.058861)			
0.11002	1.061984	45.44	0.41810	1.070508	45.55
0.22574	1.065224	45.48	0.50466	1.072842	45.58
0.31256	1.067624	45.51	0.55541	1.074202	45.60
		m_s = 1.0 mol·kg^{-1} (ρ_0 = 1.113881)			
0.12123	1.117020	46.39	0.44819	1.125235	46.50
0.18534	1.118660	46.41	0.57973	1.128444	46.54
0.31260	1.121875	46.45	0.62616	1.129550	46.57
		m_s = 1.5 mol·kg^{-1} (ρ_0 = 1.160530)			
0.05547	1.161833	47.19	0.43625	1.170513	47.29
0.18617	1.164862	47.23	0.54264	1.172846	47.33
0.33435	1.168237	47.26	0.59038	1.173874	47.36
		DL-α-Alanine in Water			
0.05564	1.000747	59.95	0.22567	1.005607	60.02
0.10087	1.002052	59.97	0.31414	1.008092	60.05
0.16819	1.003978	60.00	0.36431	1.009483	60.08
		DL-α-Alanine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.06032	1.013282	61.39	0.29557	1.019537	61.48
0.10343	1.014444	61.41	0.40428	1.022362	61.50
0.17327	1.016310	61.45	0.46157	1.023817	61.55
		m_s = 0.5 mol·kg^{-1}			
0.05102	1.060093	62.53	0.29729	1.065890	62.63
0.10376	1.061353	62.57	0.41255	1.068525	62.67
0.19790	1.063578	62.60	0.44515	1.069257	62.69
		m_s = 1.0 mol·kg^{-1}			
0.05398	1.115007	63.10	0.29035	1.119809	63.19
0.10237	1.116005	63.14	0.37792	1.121536	63.22
0.19284	1.117851	63.16	0.46615	1.123253	63.25
		m_s = 1.5 mol·kg^{-1}			
0.04682	1.161328	64.06	0.36449	1.166555	64.16
0.15673	1.163173	64.10	0.45462	1.167964	64.21
0.26621	1.164976	64.12	0.52800	1.169106	64.23
		DL-α-Amino-*n*-butyric Acid in Water			
0.04917	1.000525	74.64	0.34792	1.008736	74.81
0.11882	1.002478	74.70	0.45036	1.011457	74.84
0.20732	1.004927	74.74	0.50298	1.012829	74.88
0.26862	1.006597	74.78			
		DL-α-Amino-*n*-butyric Acid in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.04984	1.012973	75.69	0.26342	1.018544	75.79
0.10145	1.014340	75.72	0.32206	1.020030	75.83
0.18582	1.016544	75.76	0.41816	1.022443	75.86
		m_s = 0.5 mol·kg^{-1}			
0.05450	1.060121	76.66	0.19554	1.063313	76.74
0.10848	1.061354	76.69	0.28784	1.065354	76.78
0.14625	1.062207	76.72	0.37856	1.067325	76.81
		m_s = 1.0 mol·kg^{-1}			
0.05367	1.114899	77.20	0.34119	1.120160	77.29
0.12957	1.116319	77.22	0.45087	1.122083	77.33
0.24081	1.118358	77.26	0.50249	1.122963	77.36
		m_s = 1.5 mol·kg^{-1}			
0.04687	1.161201	78.17	0.30925	1.164810	78.27
0.11187	1.162117	78.20	0.39579	1.165953	78.30

give a large amount of gelatinous white precipitate, which was presumably zinc hydroxide and zinc oxychloride, it is common to clear the turbid solutions by acidifying until the precipitate disappears. The pH values upon acidification of $ZnCl_2$ are 6.40, 5.52, 5.11, and 5.00 at (0.1, 0.5, 1.0, and 1.5) mol·kg^{-1}, respectively. Thus, upon acidification of the $ZnCl_2$ aqueous solutions, the pH changed by only about 0.2 units which is almost negligible. At the maximum concentration of the $ZnCl_2$ solutions (m_s = 1.5 mol·kg^{-1}), a decrease in pH values from 5.00 to 4.12 has been observed upon the addition of the amino

Table 1 Continued

m_A (mol·kg^{-1})	ρ·10^{-3} (kg·m^{-3})	$V_{2,\phi}$·10^6 (m^3·mol^{-1})	m_A (mol·kg^{-1})	ρ·10^{-3} (kg·m^{-3})	$V_{2,\phi}$·10^6 (m^3·mol^{-1})
		T/K = 288.15			
0.21503	1.163544	78.23	0.47731	1.167005	78.33
		L-Valine in Water			
0.01605	0.999563	90.09	0.04154	1.000246	90.17
0.02610	0.999833	90.12	0.04841	1.000429	90.19
0.03552	1.000085	90.15	0.05751	1.000658	90.20
		L-Valine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.01202	1.011946	90.92	0.04359	1.012739	91.05
0.02234	1.012207	90.95	0.05747	1.013084	91.09
0.03382	1.012495	91.00	0.06618	1.013300	91.11
		m_s = 0.5 mol·kg^{-1}			
0.01369	1.059150	91.72	0.05399	1.059991	91.83
0.02040	1.059291	91.74	0.06512	1.060220	91.86
0.03039	1.059500	91.78	0.06876	1.060294	91.88
		m_s = 1.0 mol·kg^{-1}			
0.01413	1.114109	92.08	0.03601	1.114458	92.17
0.02045	1.114211	92.10	0.04420	1.114586	92.21
0.02832	1.114336	92.14	0.05055	1.114685	92.24
		m_s = 1.5 mol·kg^{-1}			
0.01692	1.160708	93.06	0.04612	1.161008	93.17
0.02888	1.160833	93.09	0.05953	1.161144	93.20
0.03813	1.160928	93.13	0.06473	1.161194	93.23
		L-Leucine in Water			
0.01030	0.999379	106.84	0.03379	0.999945	106.95
0.01763	0.999557	106.86	0.04222	1.000146	106.97
0.02334	0.999694	106.90	0.04786	1.000279	107.02
0.02875	0.999824	106.93			
		L-Leucine in Aqueous $ZnCl_2$ Solutions			
		m_s= 0.1 mol·kg^{-1}			
0.01130	1.011897	107.42	0.04119	1.012567	107.53
0.02029	1.012099	107.46	0.04897	1.012739	107.57
0.03259	1.012375	107.49	0.05745	1.012926	107.60
		m_s = 0.5 mol·kg^{-1}			
0.01144	1.059062	108.10	0.04163	1.059585	108.22
0.01979	1.059208	108.15	0.04980	1.059724	108.26
0.03022	1.059389	108.18	0.06315	1.059950	108.31
		m_s = 1.0 mol·kg^{-1}			
0.02434	1.114155	108.61	0.05128	1.114449	108.72
0.03158	1.114234	108.64	0.06312	1.114577	108.74
0.04251	1.114355	108.67	0.06919	1.114643	108.75
		m_s = 1.5 mol·kg^{-1}			
0.02413	1.160656	109.07	0.04869	1.160776	109.19
0.03089	1.160689	109.12	0.05524	1.160806	109.23
0.03743	1.160721	109.16	0.06609	1.160857	109.27
		(T/K = 298.15)			
		Glycine in Water			
0.07547	0.999434	43.39	0.30202	1.006469	43.50
0.15357	1.001881	43.42	0.34694	1.007838	43.53
0.25279	1.004960	43.46	0.45933	1.011252	43.56
		Glycine in Aqueous $ZnCl_2$ Solutions			
		$^a m_s$ = 0.1 mol·kg^{-1} ($^b\rho_0$ = 1.009376)			
0.11677	1.012715	46.15	0.46809	1.022506	46.24
0.19879	1.015033	46.18	0.66300	1.027786	46.27
0.29186	1.017652	46.16	0.78829	1.031105	46.32
		m_s = 0.5 mol·kg^{-1} (ρ_0 = 1.055445)			
0.10403	1.058242	46.86	0.56213	1.070148	46.99
0.36099	1.065010	46.91	0.67266	1.072919	47.03
0.39549	1.065916	46.89	0.67684	1.073019	47.04
0.45605	1.067467	46.93			
		m_s = 1.0 mol·kg^{-1} (ρ_0 = 1.106551)			
0.13249	1.109796	47.70	0.44819	1.117311	47.77
0.18543	1.111085	47.67	0.57973	1.120329	47.84
0.31260	1.114128	47.72	0.64058	1.121716	47.85

acids. At low concentration, zinc chloride seems to behave as a 2:1 electrolyte, indicating the presence of the $ZnCl^+$ or $ZnCl_3^-$ species.[21] Their conductance behavior shows that there is no appreciable complex formation in $ZnCl_2$ at low concentration (< 0.1 M), but at high concentration (> 1 M), complex formation takes place.[21] The pH values for ternary mixtures are greater than the pK_1 (COOH) and less than the pK_2 (NH_2) values of the studied amino acids. Thus, the amino acids mainly exist in zwitterionic form in water as well as aqueous $ZnCl_2$ solutions. However, if we consider the solutions as an equilibrium mixture of the zwitterionic and protonated forms, for a particular pH, the hydrogen ion [H^+] concentrations can be used to obtain the

Table 1 Continued

m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})	m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})
		T/K = 298.15			
		m_s = 1.5 mol·kg^{-1} (ρ_0 = 1.152820)			
0.08772	1.154756	48.43	0.43625	1.162245	48.47
0.22742	1.157793	48.46	0.61351	1.165859	48.58
0.33435	1.160074	48.49	0.64155	1.166416	48.60
		DL-α-Alanine in Water			
0.05593	0.998652	60.40	0.31414	1.005855	60.61
0.10173	0.999953	60.44	0.36909	1.007348	60.65
0.17053	1.001892	60.48	0.44962	1.009523	60.68
0.22628	1.003443	60.53			
		DL-α-Alanine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.05684	1.010868	62.40	0.42365	1.020200	62.51
0.09966	1.011982	62.43	0.53484	1.022967	62.48
0.21969	1.015070	62.47	0.63752	1.025425	62.56
		m_s = 0.5 mol·kg^{-1}			
0.09675	1.057696	63.39	0.38125	1.064123	63.46
0.21691	1.060444	63.42	0.45968	1.065836	63.49
0.25937	1.061408	63.41	0.60593	1.068975	63.55
		m_s = 1.0 mol·kg^{-1}			
0.09382	1.108392	64.38	0.47064	1.115487	64.48
0.15553	1.109584	64.41	0.55102	1.116923	64.53
0.29949	1.112338	64.39	0.72149	1.119939	64.58
0.40998	1.114391	64.44			
		m_s = 1.5 mol·kg^{-1}			
0.09583	1.154340	65.26	0.37919	1.158660	65.36
0.17965	1.155646	65.28	0.43456	1.159497	65.34
0.23392	1.156494	65.25	0.63443	1.162346	65.44
		DL-α-Amino-*n*-butyric Acid in Water			
0.05001	0.998427	75.54	0.35993	1.006688	75.73
0.12090	1.000359	75.59	0.46996	1.009506	75.79
0.20922	1.002733	75.64	0.52310	1.010840	75.83
0.27551	1.004485	75.68			
		DL-α-Amino-*n*-butyric Acid in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.05326	1.010730	77.07	0.20617	1.014544	77.14
0.08257	1.011469	77.10	0.29239	1.016652	77.16
0.10801	1.012111	77.08	0.48026	1.021135	77.21
		m_s = 0.5 mol·kg^{-1}			
0.05786	1.056705	78.04	0.23719	1.060516	78.12
0.10440	1.057707	78.07	0.33368	1.062511	78.15
0.14952	1.058677	78.04	0.48931	1.065633	78.24
0.16918	1.059094	78.05			
		m_s = 1.0 mol·kg^{-1}			
0.05790	1.107549	79.03	0.27931	1.111252	79.09
0.11766	1.108564	79.06	0.39199	1.113071	79.12
0.16203	1.109315	79.04	0.48025	1.114472	79.14
0.23294	1.110493	79.07	0.52034	1.115082	79.17
		m_s = 1.5 mol·kg^{-1}			
0.05530	1.153518	79.89	0.23103	1.155660	79.99
0.07459	1.153759	79.90	0.31198	1.156620	80.00
0.12394	1.154367	79.94	0.35030	1.157083	79.98
0.17983	1.155046	79.97			
		L-Valine in Water			
0.01627	0.997478	90.76	0.04207	0.998155	90.86
0.02615	0.997738	90.81	0.05513	0.998496	90.88
0.03594	0.997995	90.84	0.06596	0.998777	90.90
		L-Valine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.02873	1.010082	91.82	0.05513	1.010724	91.88
0.03927	1.010338	91.88	0.06596	1.010986	91.90
0.04573	1.010494	91.91	0.07704	1.011251	91.95
		m_s = 0.5 mol·kg^{-1}			
0.03000	1.056049	92.81	0.06928	1.056830	92.88
0.03869	1.056223	92.84	0.08109	1.057061	92.92
0.04979	1.056442	92.88	0.08741	1.057183	92.95

concentration of zwitterionic and protonated forms. In the extreme case of neutralization of all [H^+] ions by the amino acids, the molarities of zwitterionic forms change from 1 to 8 units at the fifth decimal place, which results in a change in V_2^0 values by 0.02 cm^3·mol^{-1}. This is within uncertainty limits of the measurements, so the effect of pH can be neglected. Thus, partial molar volumes result from the zwitterionic forms of amino acids.

Table 1 Continued

m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})	m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})
		T/K = 298.15			
0.06104	1.056668	92.86			
		m_s = 1.0 mol·kg^{-1}			
0.02725	1.106952	93.77	0.05741	1.107391	93.80
0.03535	1.107069	93.81	0.07067	1.107577	93.88
0.04759	1.107249	93.79	0.07731	1.107669	93.92
		m_s = 1.5 mol·kg^{-1}			
0.03458	1.153140	94.59	0.06184	1.153385	94.65
0.04191	1.153204	94.65	0.07399	1.153486	94.75
0.05451	1.153321	94.62	0.07837	1.153527	94.73
		L-Leucine in Water			
0.01051	0.997295	107.76	0.03474	0.997858	107.91
0.01799	0.997469	107.85	0.04395	0.998071	107.94
0.02418	0.997614	107.84	0.04875	0.998181	107.97
0.02931	0.997733	107.86			
		L-Leucine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.01123	1.009623	108.29	0.06599	1.010813	108.35
0.02200	1.009859	108.30	0.07001	1.010899	108.37
0.02931	1.010018	108.31	0.09920	1.011523	108.41
0.03248	1.010087	108.32			
		m_s = 0.5 mol·kg^{-1}			
0.02464	1.055858	109.13	0.07975	1.056761	109.27
0.04929	1.056266	109.18	0.08481	1.056846	109.24
0.05530	1.056363	109.21	0.09804	1.057053	109.32
0.05886	1.056424	109.19			
		m_s = 1.0 mol·kg^{-1}			
0.03100	1.106874	109.93	0.06193	1.107188	110.01
0.03845	1.106951	109.95	0.07191	1.107288	110.03
0.04910	1.107058	109.99	0.08923	1.107458	110.08
0.05861	1.107152	110.04			
		m_s = 1.5 mol·kg^{-1}			
0.00924	1.152863	110.25	0.04300	1.153011	110.37
0.02249	1.152924	110.23	0.06687	1.153116	110.36
0.04016	1.153003	110.28	0.07775	1.153157	110.43
		(T/K = 308.15)			
		Glycine in Water			
0.07746	0.993053	43.83	0.30173	0.999939	43.93
0.15072	0.995322	43.86	0.34658	1.001291	43.97
0.25338	0.998473	43.90	0.45862	1.004653	44.00
		Glycine in Aqueous $ZnCl_2$ Solutions			
		[a]m_s = 0.1 mol·kg^{-1} ([b]ρ_0 = 1.005927)			
0.06666	1.007761	47.35	0.36244	1.015727	47.44
0.13040	1.009500	47.38	0.39769	1.016651	47.47
0.24609	1.012627	47.41	0.43611	1.017652	47.50
		m_s = 0.5 mol·kg^{-1} (ρ_0 = 1.047950)			
0.05247	1.049303	48.08	0.27804	1.054988	48.26
0.10056	1.050534	48.12	0.39769	1.057929	48.33
0.18412	1.052652	48.17	0.43611	1.058847	48.38
		m_s = 1.0 mol·kg^{-1} (ρ_0 = 1.097590)			
0.05060	1.098768	49.02	0.31260	1.104697	49.21
0.13249	1.100651	49.08	0.44819	1.107681	49.25
0.18533	1.101842	49.16	0.57973	1.110495	49.34
		m_s = 1.5 mol·kg^{-1} (ρ_0 = 1.142537)			
0.05053	1.143564	50.08	0.30050	1.148495	50.25
0.10486	1.144655	50.14	0.40299	1.150464	50.29
0.21551	1.146849	50.19	0.50561	1.152404	50.32
		DL-α-Alanine in Water			
0.05765	0.992260	61.06	0.33370	0.999847	61.22
0.10610	0.993618	61.07	0.36909	1.000796	61.24
0.18686	0.995856	61.12	0.48750	1.003946	61.28
0.24133	0.997342	61.18			
		DL-α-Alanine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.06032	1.007469	63.21	0.29557	1.013323	63.37
0.10343	1.008558	63.26	0.40428	1.015958	63.41

The V_2^0 values for the studied amino acids in aqueous solutions of zinc chloride are higher than the values in water, which result in positive $\Delta_t V^0$ values. The plots of $\Delta_t V^0$ values as a function of concentration of zinc chloride are shown in Figure 1. These values increase with an increase of the molality of zinc chloride, and the increase is sharp in the lower concentration range. The transfer values also increase with temperature in all cases.

Table 1 Continued

m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})	m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})
		T/K = 308.15			
0.17327	1.010308	63.30	0.46157	1.017323	63.45
		m_s = 0.5 mol·kg^{-1}			
0.05401	1.049180	64.20	0.29729	1.054562	64.36
0.10376	1.050299	64.26	0.41255	1.057037	64.40
0.19790	1.052389	64.32	0.44616	1.057744	64.42
		m_s = 1.0 mol·kg^{-1}			
0.05038	1.098559	65.15	0.26529	1.102554	65.34
0.14848	1.100414	65.21	0.32885	1.103699	65.39
0.20811	1.101522	65.25	0.39023	1.104786	65.43
		m_s = 1.5 mol·kg^{-1}			
0.05271	1.143352	66.08	0.29917	1.147010	66.26
0.10863	1.144203	66.13	0.40663	1.148549	66.30
0.20260	1.145598	66.24	0.49406	1.149776	66.33
		DL-α-Amino-*n*-butyric Acid in Water			
0.05186	0.992026	76.58	0.35685	0.999947	76.75
0.12644	0.994002	76.66	0.45036	1.002299	76.77
0.20922	0.996164	76.70	0.50954	1.003754	76.81
0.27302	0.997812	76.72			
		DL-α-Amino-*n*-butyric Acid in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.05192	1.007179	78.57	0.25717	1.012005	78.66
0.09378	1.008178	78.59	0.31476	1.013323	78.69
0.16712	1.009909	78.63	0.41890	1.015681	78.72
		m_s = 0.5 mol·kg^{-1}			
0.05867	1.049158	79.54	0.38127	1.055556	79.64
0.10374	1.050075	79.57	0.46190	1.057088	79.67
0.20951	1.052195	79.61	0.55400	1.058809	79.71
		m_s = 1.0 mol·kg^{-1}			
0.05554	1.098485	80.48	0.21145	1.100929	80.58
0.10359	1.099250	80.51	0.28828	1.102100	80.62
0.15155	1.100001	80.55	0.34496	1.102946	80.65
		m_s = 1.5 mol·kg^{-1}			
0.05028	1.143105	81.54	0.20946	1.144845	81.63
0.10051	1.143664	81.57	0.30471	1.145856	81.66
0.15804	1.144293	81.60	0.41629	1.147007	81.69
		L-Valine in Water			
0.01502	0.991047	91.60	0.04346	0.991755	91.77
0.02637	0.991317	91.65	0.05081	0.991925	91.78
0.03597	0.991564	91.73	0.05769	0.992118	91.82
		L-Valine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.02847	1.006607	92.73	0.04821	1.007070	92.87
0.03793	1.006831	92.77	0.05365	1.007196	92.92
0.04495	1.006995	92.83	0.05995	1.007341	92.96
		m_s = 0.5 mol·kg^{-1}			
0.01369	1.048217	93.95	0.05399	1.048988	94.14
0.02039	1.048345	94.04	0.06512	1.049197	94.19
0.03039	1.048537	94.10	0.07106	1.049307	94.24
		m_s =1.0 mol·kg^{-1}			
0.01337	1.097780	94.86	0.04875	1.098273	94.99
0.02093	1.097886	94.91	0.06153	1.098448	95.04
0.03056	1.098021	94.96	0.06967	1.098557	95.08
		m_s =1.5 mol·kg^{-1}			
0.01158	1.142641	95.61	0.04036	1.142891	95.74
0.02073	1.142721	95.67	0.05079	1.142981	95.76
0.03072	1.142808	95.72	0.05828	1.143042	95.81
		L-Leucine in Water			
0.01051	0.990878	108.44	0.03753	0.991503	108.61
0.01847	0.991063	108.49	0.04534	0.991682	108.64
0.02445	0.991201	108.55	0.05226	0.991839	108.67
0.03091	0.991351	108.56			
		L-Leucine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.01126	1.006166	109.33	0.04191	1.006807	109.49

It has been observed that the $\Delta_t V^0$ values vary almost linearly with concentration of cosolute after a 0.1 mol·kg^{-1} $ZnCl_2$ concentration for all amino acids. It may also be noted that the behavior is more linear at low temperature, i.e., 288.15 K, than at the higher temperatures studied. These amino acids also do not show any saturation in $\Delta_t V^0$ values over the studied concentration range of cosolute. The $\Delta_t V^0$ values for the amino acids decrease with an increase in the hydrophobic part of the amino acids.

Table 1 Continued

m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})	m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})
		T/K = 308.15			
0.02274	1.006408	109.37	0.05294	1.007035	109.53
0.03141	1.006589	109.43	0.06244	1.007229	109.57
		m_s = 0.5 mol·kg^{-1}			
0.01141	1.048137	110.17	0.04163	1.048624	110.30
0.01979	1.048273	110.21	0.04980	1.048752	110.36
0.03033	1.048443	110.25	0.06312	1.048957	110.46
		m_s = 1.0 mol·kg^{-1}			
0.02431	1.097836	111.00	0.05128	1.098097	111.19
0.03158	1.097908	111.05	0.06312	1.098209	111.24
0.04251	1.098014	111.12	0.06919	1.098267	111.25
		m_s = 1.5 mol·kg^{-1}			
0.01235	1.142583	111.91	0.03427	1.142660	111.99
0.01859	1.142605	111.95	0.04537	1.142697	112.02
0.02835	1.142639	111.97	0.05946	1.142745	112.05
		(T/K = 318.15)			
		Glycine in Water			
0.07830	0.992665	44.17	0.30906	0.999679	44.26
0.15253	0.994942	44.19	0.36556	1.001362	44.30
0.25640	0.998093	44.24	0.48090	1.004790	44.31
		m_s = 0.1 mol·kg^{-1} (ρ_0 = 1.002031)			
0.06666	1.003811	48.24	0.45384	1.013830	48.45
0.13040	1.005497	48.28	0.52003	1.015501	48.47
0.24609	1.008520	48.34	0.54445	1.016113	48.48
0.36244	1.011514	48.40			
		m_s = 0.5 mol·kg^{-1} (ρ_0 = 1.043286)			
0.05313	1.044603	49.12	0.39549	1.052867	49.25
0.10403	1.045854	49.16	0.45605	1.054282	49.28
0.36099	1.052060	49.21	0.56213	1.056755	49.31
		m_s = 1.0 mol·kg^{-1} (ρ_0 = 1.090831)			
0.06448	1.092258	50.15	0.31260	1.097616	50.26
0.13249	1.093747	50.19	0.44819	1.100475	50.29
0.18533	1.094891	50.22	0.54311	1.102439	50.32
		m_s = 1.5 mol·kg^{-1} (ρ_0 = 1.135272)			
0.08772	1.136963	51.09	0.43625	1.143463	51.19
0.22743	1.139613	51.12	0.61351	1.146649	51.23
0.33435	1.141597	51.16	0.64741	1.147237	51.25
		DL-α-Alanine in Water			
0.06060	0.991936	61.38	0.33495	0.999401	61.52
0.10686	0.993217	61.41	0.37153	1.000364	61.56
0.18752	0.995427	61.46	0.49036	1.003484	61.61
0.24197	0.996902	61.49			
		DL-α-Alanine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.06032	1.003526	64.13	0.29557	1.009212	64.25
0.10343	1.004584	64.16	0.40428	1.011766	64.30
0.17327	1.006279	64.22	0.51845	1.014408	64.34
		m_s = 0.5 mol·kg^{-1}			
0.06305	1.044676	65.06	0.40135	1.051860	65.23
0.12439	1.046010	65.10	0.50055	1.053889	65.27
0.20495	1.047742	65.14	0.52068	1.054305	65.26
0.30372	1.049837	65.17			
		m_s = 1.0 mol·kg^{-1}			
0.07966	1.092307	66.01	0.39260	1.097890	66.13
0.15553	1.093691	66.04	0.44654	1.098808	66.17
0.29949	1.096262	66.10	0.54526	1.100489	66.20
		m_s = 1.5 mol·kg^{-1}			
0.05406	1.136065	67.05	0.38919	1.140768	67.19
0.14831	1.137425	67.09	0.50356	1.142309	67.22
0.27375	1.139194	67.13	0.56692	1.143118	67.27
		DL-α-Amino-n-butyric Acid in Water			
0.05233	0.991639	76.82	0.35685	0.999509	76.92
0.12654	0.993596	76.84	0.45112	1.001860	76.95
0.21116	0.995796	76.87	0.51084	1.003326	76.98
0.27302	0.997382	75.90			
		DL-α-Amino-n-butyric Acid in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.05192	1.003270	79.03	0.25717	1.008030	79.18
0.10738	1.004578	79.07	0.31476	1.009329	79.22
0.16712	1.005968	79.12	0.41890	1.011649	79.26

In the presently studied (amino acids + $ZnCl_2$ + water) ternary systems, the following types of interactions may occur; (1) ion−ion interactions between the Zn^{2+} and Cl^- ions of the cosolute and zwitterionic (COO^-, NH_3^+) groups; (2) ion−nonpolar group interactions occurring between ions of cosolute and the nonpolar group of amino acids. According to the cosphere overlap model,[22] the overlap of the cosphere of an ion with that of a hydrophobic group always results in a negative $\Delta_t V^0$

Table 1 Continued

		T/K = 318.15			
m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})	m_A (mol·kg^{-1})	$\rho \cdot 10^{-3}$ (kg·m^{-3})	$V_{2,\phi} \cdot 10^6$ (m^3·mol^{-1})
		m_s = 0.5 mol·kg^{-1}			
0.05185	1.044340	80.06	0.22242	1.047719	80.17
0.10688	1.045446	80.09	0.34147	1.050012	80.21
0.15247	1.046350	80.12	0.40389	1.051188	80.24
		m_s = 1.0 mol·kg^{-1}			
0.05106	1.091647	81.03	0.33925	1.096064	81.16
0.13440	1.092956	81.07	0.38586	1.096742	81.20
0.25879	1.094866	81.11			
		m_s = 1.5 mol·kg^{-1}			
0.08836	1.136262	82.05	0.34535	1.139014	82.14
0.12584	1.136672	82.08	0.42192	1.139784	82.19
0.28901	1.138430	82.11	0.51902	1.140757	82.22
		L-Valine in Water			
0.01602	0.990656	91.96	0.04383	0.991365	92.07
0.02637	0.990922	91.99	0.05048	0.991533	92.09
0.03619	0.991171	92.03	0.05901	0.991749	92.10
		L-Valine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.02847	1.002695	93.57	0.04821	1.003147	93.70
0.03793	1.002913	93.62	0.05361	1.003270	93.73
0.04491	1.003074	93.65			
		m_s = 0.5 mol·kg^{-1}			
0.01983	1.043668	94.52	0.04979	1.044234	94.67
0.03000	1.043861	94.58	0.06104	1.044444	94.71
0.03869	1.044025	94.63	0.06928	1.044595	94.76
		m_s = 1.0 mol·kg^{-1}			
0.02725	1.091216	95.43	0.05741	1.091631	95.56
0.03535	1.091329	95.48	0.06391	1.091719	95.60
0.04759	1.091497	95.53	0.07399	1.091856	95.62
		m_s = 1.5 mol·kg^{-1}			
0.01745	1.135425	96.35	0.04382	1.135648	96.46
0.02188	1.135462	96.38	0.05108	1.135708	96.49
0.03319	1.135558	96.43	0.05783	1.135763	96.52
		L-Leucine in Water			
0.01048	0.990480	109.39	0.03752	0.991082	109.51
0.01881	0.990667	109.41	0.04561	0.991262	109.52
0.02437	0.990791	109.43	0.05191	0.991401	109.53
0.03010	0.990918	109.47			
		L-Leucine in Aqueous $ZnCl_2$ Solutions			
		m_s = 0.1 mol·kg^{-1}			
0.01126	1.002261	110.48	0.04191	1.002879	110.59
0.02274	1.002494	110.51	0.05294	1.003098	110.64
0.03141	1.002669	110.54	0.06244	1.003287	110.67
		m_s = 0.5 mol·kg^{-1}			
0.01766	1.043560	111.40	0.04447	1.043966	111.54
0.02680	1.043699	111.47	0.05452	1.044118	111.56
0.03455	1.043816	111.51	0.06188	1.044226	110.61
		m_s = 1.0 mol·kg^{-1}			
0.02434	1.091054	112.46	0.05128	1.091293	112.57
0.03158	1.091118	112.51	0.06312	1.091396	112.61
0.04251	1.091216	112.53	0.06905	1.091446	112.64
		m_s = 1.5 mol·kg^{-1}			
0.02589	1.135341	113.40	0.05028	1.135401	113.48
0.03056	1.135352	113.43	0.06035	1.135423	113.52
0.04226	1.135382	113.45			

[a] m_s: molality (mol·kg^{-1}) of $ZnCl_2$ in water. [b] ρ_0: density (kg·m^{-3}) of $ZnCl_2$ in water.

value, and the overlap of cosphere of an ion with that of a hydrophilic group results in positive $\Delta_t V^0$ values. The presently observed positive $\Delta_t V^0$ values indicate the dominance of the ion−ion interactions, and these interactions further increase with an increase in the molality of $ZnCl_2$.

The modified equation of Shahidi and Farell[23] gives the limiting partial molar volume V_2^0

$$V_2^0 = V_{vw} + V_{void} - V_{shrinkage} \quad (4)$$

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} are not significantly affected by the presence of $ZnCl_2$, a positive $\Delta_t V^0$ can therefore be attributed to a decrease in the shrinkage volume in the presence of the aqueous solution of $ZnCl_2$. Because of the stronger interactions between zwitterionic groups (COO^- and NH_3^+) of the amino acids and ions of the cosolute (Zn^{2+}, Cl^-), noncovalent ion pairs will be formed and thus the electrostriction of neighboring water molecules due to these charged centers will be reduced, which result in the reduction of the volume of

Table 2. Partial Molar Volumes, V_2^0, of Some Amino Acids in Water and in Aqueous $ZnCl_2$ Solutions from T = (288.15 to 318.15) K

amino acids	$V_2^0 \cdot 10^6$ ($m^3 \cdot mol^{-1}$) 0.0[a] m_s	0.1 m_s	0.5 m_s	1.0 m_s	1.5 m_s
	T/K = 288.15				
glycine	42.42[b] ± 0.01, 42.48[c], 42.40[d]	44.54 ± 0.01	45.40 ± 0.03	46.35 ± 0.03	47.17 ± 0.03
DL-α-alanine	59.93[b] ± 0.01, 59.67[c], 59.90[d]	61.37 ± 0.01	62.52 ± 0.01	63.09 ± 0.03	64.04 ± 0.03
DL-α-amino-*n*-butyric acid	74.63[b] ± 0.01, 74.67[e]	75.67 ± 0.01	76.64 ± 0.01	77.18 ± 0.01	78.15 ± 0.03
L-valine	90.05[b] ± 0.01, 90.08[c]	90.88 ± 0.01	91.69 ± 0.02	92.01 ± 0.01	93.00 ± 0.01
L-leucine	106.79[b] ± 0.01, 106.81[f]	107.37 ± 0.01	108.0 ± 0.02	108.54 ± 0.02	108.97 ± 0.01
	T/K = 298.15				
glycine	43.35[b] ± 0.01, 43.26[c], 43.30[d], 43.24[g]	46.12 ± 0.02	46.80 ± 0.03	47.62 ± 0.03	48.39 ± 0.03
DL-α-alanine	60.37[b] ± 0.01, 60.47[c], 60.49[g]	62.38 ± 0.02	63.35 ± 0.01	64.33 ± 0.03	65.21 ± 0.03
DL-α-amino-*n*-butyric acid	75.51[b] ± 0.01, 75.51[e], 76.35[g]	77.06 ± 0.01	78.00 ± 0.03	79.01 ± 0.01	79.89 ± 0.02
L-valine	90.74[g] ± 0.03, 90.80[f], 90.98[g]	91.78 ± 0.02	92.75 ± 0.02	93.69 ± 0.03	94.48 ± 0.03
L-leucine	107.64[b] ± 0.03, 107.73[f], 107.77[g]	108.27 ± 0.02	109.06 ± 0.02	109.86 ± 0.02	110.20 ± 0.04
	T/K = 308.15				
glycine	43.79[b] ± 0.01, 43.80[d], 43.79[f]	47.33 ± 0.02	48.04 ± 0.03	49.02 ± 0.03	50.08 ± 0.03
DL-α-alanine	61.02[b] ± 0.01, 60.90[d], 61.01[g]	63.19 ± 0.02	64.20 ± 0.01	65.09 ± 0.03	66.08 ± 0.03
DL-α-amino-*n*-butyric acid	76.59[b] ± 0.01, 76.61[g]	78.55 ± 0.01	79.53 ± 0.03	80.45 ± 0.01	81.53 ± 0.02
L-valine	91.52[b] ± 0.01, 91.55[g]	92.49 ± 0.02	93.93 ± 0.02	94.83 ± 0.03	95.58 ± 0.03
L-leucine	108.39[b] ± 0.01, 108.41[g]	109.27 ± 0.02	110.10 ± 0.02	110.87 ± 0.02	111.89 ± 0.04
	T/K = 318.15				
glycine	44.14[b] ± 0.01, 44.17[g]	48.21 ± 0.01	49.11 ± 0.01	50.14 ± 0.03	51.06 ± 0.01
DL-α-alanine	61.35 ± 0.01, 61.31[g]	64.12 ± 0.02	65.04 ± 0.01	65.98 ± 0.01	67.03 ± 0.01
DL-α-amino-*n*-butyric acid	76.80[b] ± 0.01, 76.82[g]	79.01 ± 0.01	80.04 ± 0.01	81.00 ± 0.01	82.02 ± 0.01
L-valine	91.90[b] ± 0.03, 91.93[g]	93.38 ± 0.02	94.44 ± 0.01	95.33 ± 0.03	96.29 ± 0.01
L-leucine	109.35[b] ± 0.03, 109.38[g]	110.43 ± 0.02	111.34 ± 0.02	112.38 ± 0.02	113.32 ± 0.01

[a] m_s: molality ($mol \cdot kg^{-1}$) of $ZnCl_2$ in water. [b] Present work. [c] Ref 16. [d] Ref 17. [e] Ref 18. [f] Ref 19. [g] Ref 20.

Table 3. Pair, V_{XY}, and Triplet, V_{XYY}, Interaction Coefficients of Studied Amino Acids in Aqueous $ZnCl_2$ Solutions from T = (288.15 to 318.15) K

amino acids	$V_{XY} \cdot 10^6$ ($m^3 \cdot mol^{-2} \cdot kg$)	$V_{XYY} \cdot 10^6$ ($m^3 \cdot mol^{-2} \cdot kg^2$)	$V_{XY} \cdot 10^6$ ($m^3 \cdot mol^{-2} \cdot kg$)	$V_{XYY} \cdot 10^6$ ($m^3 \cdot mol^{-2} \cdot kg^2$)
	288.15 K		298.15 K	
glycine	3.589 ± 1.198	−0.920 ± 0.605	4.215 ± 1.073	−1.117 ± 0.542
DL-α-alanine	2.629 ± 0.830	−0.498 ± 0.419	3.547 ± 1.073	−0.888 ± 0.542
DL-α-amino-*n*-butyric acid	2.144 ± 0.607	−0.453 ± 0.307	2.932 ± 0.827	−0.675 ± 0.417
L-valine	1.639 ± 0.545	−0.312 ± 0.27	2.330 ± 0.502	−0.492 ± 0.253
L-leucine	1.445 ± 0.215	−0.328 ± 0.221	1.732 ± 0.221	−0.397 ± 0.221
	308.15 K		318.15 K	
glycine	5.172 ± 2.133	−1.419 ± 1.077	6.121 ± 2.428	−1.755 ± 1.225
DL-α-alanine	3.729 ± 1.243	−0.941 ± 0.627	4.381 ± 1.629	−1.147 ± 0.822
DL-α-amino-*n*-butyric acid	3.401 ± 1.118	−0.810 ± 0.564	3.809 ± 1.259	−0.953 ± 0.635
L-valine	2.734 ± 0.431	−0.629 ± 0.218	2.906 ± 0.800	−0.664 ± 0.404
L-leucine	1.835 ± 0.471	−0.312 ± 0.238	2.282 ± 0.534	−0.439 ± 0.269

shrinkage. This increases the apparent molar volume of the studied amino acids in the presence of $ZnCl_2$. A comparison of $\Delta_t V^0$ values of the studied amino acids in $ZnCl_2$ solutions at 298.15 K with the values in the presence of aqueous NaCl[24] and $MgCl_2$[25] shows that the order of decrease of $\Delta_t V^0$ values of the amino acids in the three cosolutes is as follows: $MgCl_2 > ZnCl_2 >$ NaCl.

Transfer volumes $\Delta_t V^0$ of amino acids can also be expressed by the McMillan−Mayer theory[26] of solutions, which permit the formal separation of the effect due to interactions between the pair of solute molecules and those due to interactions between three or more solute molecules by the equation

$$\Delta_t V^0 = 2V_{XY} \cdot m_s + 3V_{XYY} \cdot m_s^2 + \ldots \tag{5}$$

where X stands for amino acids and Y for $ZnCl_2$. V_{XY} and V_{XYY} are the volumetric pair and triplet interaction coefficients, respectively, and these are presented in Table 3.

V_{XY} values are positive, whereas V_{XYY} values are negative in all cases. The large positive values of pair interaction coefficients suggest that interactions between amino acids and $ZnCl_2$ are mainly pairwise. These observations are in line with the conclusion drawn from the cosphere overlap model that solute−solute interactions dominate over solute−solvent interactions. The V_{XY} value decreases with an increase in the hydrophobic part, i.e., from glycine to L-leucine regularly, and increases with an increase in the temperature. The triplet interaction coefficients are negative for all amino acids and further decrease with an increase of temperature. As the interactions of zwitterionic end groups for different amino acids with $ZnCl_2$ are almost the same, this suggests that the alkyl side chain of amino acids plays an important role in modulating the volume of transfer and pair interaction coefficients. The amino acids with a longer hydrophobic alkyl side chain may undergo a stronger dehydration effect in the presence of $ZnCl_2$. As L-leucine has a longer alkyl chain, it will undergo a stronger dehydration effect and will give a smaller value of V_{XY}, whereas the reverse is true in the case of glycine which has a shorter alkyl chain.

The contribution of the relative weight of the pair and triplet interaction coefficients to $\Delta_t V^0$ may be better judged at various molalities of $ZnCl_2$ by plotting the contributions of the interaction coefficients versus m_s (plots of contributions of pair and triplet interaction coefficients versus m_s are shown in Figure 2). The relative weight for V_{XY} is positive and increases linearly

Table 4. Contribution to the Partial Molar Volumes, V_2^0, from Zwitterionic End Groups (NH_3^+, COO^-), and Other Alkyl Side Chains of Some Amino Acids in Water and in Aqueous $ZnCl_2$ Solutions from T = (288.15 to 318.15) K

	$V_2^0 \cdot 10^6$(m^3·mol^{-1})				
	[a]0.0 m_s	0.1 m_s	0.5 m_s	1.0 m_s	1.5 m_s
		T/K = 288.15			
NH_3^+, COO^-	27.11 ± 0.83	29.42 ± 0.87	30.52 ± 0.87	31.44 ± 0.85	32.50 ± 0.79
-CH_2	15.89 ± 0.25	15.52 ± 0.26	15.45 ± 0.26	15.33 ± 0.26	15.26 ± 0.24
-$CHCH_3$	31.78 ± 0.35	31.04 ± 0.33	30.90 ± 0.37	30.66 ± 0.37	30.52 ± 0.34
-$CHCH_2CH_3$	47.67 ± 0.43	46.56 ± 0.40	46.35 ± 0.45	45.99 ± 0.45	45.78 ± 0.42
-$CHCH(CH_3)_2$	63.56 ± 0.50	62.08 ± 0.46	61.80 ± 0.52	61.32 ± 0.52	61.04 ± 0.48
-$CHCHCH_2(CH_3)_2$	79.45 ± 0.56	77.60 ± 0.51	77.25 ± 0.58	76.65 ± 0.58	76.30 ± 0.54
		T/K = 298.15			
NH_3^+, COO^-	27.84 ± 0.68, 27.72[b]	31.82 ± 0.67	31.82 ± 0.67	32.75 ± 0.70	33.77 ± 0.73
-CH_2	15.90 ± 0.20, 15.99[b]	15.37 ± 0.19	15.39 ± 0.20	15.38 ± 0.21	15.29 ± 0.22
-$CHCH_3$	31.80 ± 0.28, 31.98[b]	30.74 ± 0.27	30.78 ± 0.28	30.76 ± 0.30	30.58 ± 0.31
-$CHCH_2CH_3$	47.70 ± 0.35	46.11 ± 0.33	46.17 ± 0.35	46.14 ± 0.36	45.87 ± 0.38
-$CHCH(CH_3)_2$	63.60 ± 0.40	61.48 ± 0.38	61.56 ± 0.40	61.52 ± 0.42	61.16 ± 0.44
-$CHCHCH_2(CH_3)_2$	79.50 ± 0.45, 79.95[b]	76.85 ± 0.42	76.95 ± 0.45	76.90 ± 0.47	76.45 ± 0.49
		T/K = 308.15			
NH_3^+, COO^-	28.35 ± 0.73	32.21 ± 0.74	33.01 ± 0.56	34.02 ± 0.50	35.10 ± 0.61
-CH_2	15.97 ± 0.22	15.32 ± 0.22	15.39 ± 0.17	15.34 ± 0.21	15.31 ± 0.22
-$CHCH_3$	31.94 ± 0.31	30.64 ± 0.31	30.78 ± 0.28	30.68 ± 0.30	30.62 ± 0.31
-$CHCH_2CH_3$	47.70 ± 0.38	45.96 ± 0.38	46.17 ± 0.35	46.02 ± 0.36	45.93 ± 0.38
-$CHCH(CH_3)_2$	63.87 ± 0.44	61.28 ± 0.44	61.56 ± 0.40	61.36 ± 0.42	61.24 ± 0.44
-$CHCHCH_2(CH_3)_2$	79.84 ± 0.49	76.60 ± 0.49	76.95 ± 0.45	76.70 ± 0.47	76.55 ± 0.49
		T/K = 318.15			
NH_3^+, COO^-	28.42 ± 0.75	32.92 ± 0.75	33.84 ± 0.69	34.82 ± 0.73	35.81 ± 0.75
-CH_2	16.10 ± 0.20	15.37 ± 0.19	15.39 ± 0.20	15.38 ± 0.21	15.38 ± 0.22
-$CHCH_3$	31.80 ± 0.28	30.68 ± 0.27	30.78 ± 0.28	30.76 ± 0.30	30.76 ± 0.31
-$CHCH_2CH_3$	48.29 ± 0.35	46.05 ± 0.33	46.17 ± 0.35	46.14 ± 0.36	46.14 ± 0.38
-$CHCH(CH_3)_2$	64.39 ± 0.40	61.36 ± 0.38	61.56 ± 0.40	61.52 ± 0.42	61.52 ± 0.44
-$CHCHCH_2(CH_3)_2$	80.49 ± 0.45	76.73 ± 0.42	76.95 ± 0.45	76.90 ± 0.47	76.90 ± 0.49

[a] m_s: molality (mol·kg^{-1}) of $ZnCl_2$ in water. [b] Ref 28.

with the increase in the molalities of $ZnCl_2$ in all cases. The relative weights for V_{XYY} are negative and almost zero up to ~ 0.5 mol·kg^{-1} of cosolute; thereafter, these decrease sharply with the increase in the molalities of $ZnCl_2$ for the studied amino acids. The contribution of pair interaction coefficients V_{XY} decreases, while triplet interaction coefficients V_{XYY} increase with an increase in the hydrophobic part of the amino acids.

A linear relationship has been observed between the V_2^0 of the amino acids and the number of carbon atoms, n_C, in their alkyl side chains which is represented[27] by

$$V_2^0 = V_2^0(NH_3^+, COO^-) + n_C V_2^0(CH_2) \qquad (6)$$

where V_2^0 (NH_3^+, COO^-) and V_2^0 (CH_2) represent the zwitterionic end group and (CH_2) group contributions to V_2^0, respectively. The calculated values for these contributions are summarized in Table 4.

The zwitterionic end group V_2^0 (NH_3^+, COO^-) and methylene group V_2^0 (CH_2) contributions, in water, agree well with literature values[28] (Table 4). The V_2^0 (NH_3^+, COO^-) group contribution for amino acids increases with an increase in the concentration of zinc chloride. The larger value of V_2^0 (NH_3^+, COO^-) in $ZnCl_2$ as compared to the value in water indicates that the interactions of the ions of $ZnCl_2$ with the zwitterionic end groups (NH_3^+, COO^-) of the amino acids are stronger and increase with the concentration of $ZnCl_2$.

The contributions of (NH_3^+, COO^-) groups and R groups (R = -CH_2, -$CHCH_3$, -$CHCH_2CH_3$, -$CHCH_2CH(CH_3)_2$) to $\Delta_t V^0$ values of amino acids from water to aqueous $ZnCl_2$ solutions have been calculated using an equation analogous to eq 3 and depicted in Figure 3. The $\Delta_t V^0$ (NH_3^+, COO^-) values are positive and increase sharply initially, and thereafter almost linear behavior is observed with increasing molality of $ZnCl_2$. The contributions of the R group to $\Delta_t V^0$ are negative and decrease slightly with an increase in the concentration of $ZnCl_2$ at all temperatures. Further, the negative contributions of R increase with an increase in the size of the nonpolar side chains of amino acids. As reported earlier,[28] the ratio of the effect of hydrophilic to the hydrophobic hydration is reflected in the partial specific quantities, while the partial molar quantities are a reflection of the net change in both types of hydration. The molar specific volume v_2^0 ($v_2^0 = V_2^0/M$ where M is the molar mass of the amino acids) for the studied amino acids in aqueous $ZnCl_2$ solutions is illustrated in Figure 4. The v_2^0 values increase from glycine to L-leucine with the increase in the size of the side chain of amino acids, but it may noted that the increase in v_2^0 becomes smaller and smaller with the increase in the size of the nonpolar side chains of amino acids from glycine to L-leucine. The effect of $ZnCl_2$ concentration on v_2^0 is more in glycine, which further decreases with the increase of alkyl side chain of the amino acids. The v_2^0 values of L-leucine are almost independent of the concentration of $ZnCl_2$, because the positive effect of the interactions of the ions of $ZnCl_2$ with the zwitterionic end group of amino acids is compensated by the negative effect due to the interactions of the ions of $ZnCl_2$ with the nonpolar side chain of the amino acids.

The hydration (n_H) for the amino acids has been calculated from the partial molar volumes V_2^0 by using the method reported by Millero et al.[29] The value of V_2^0 for the amino acids can be expressed[29] by

$$V_2^0 = V_2^0(\text{int}) + V_2^0(\text{elect}) \qquad (7)$$

where V_2^0(int) is the intrinsic partial molar volume of the amino acids and V_2^0(elect) is the electrostriction partial molar volume due to the hydration of amino acids. The V_2^0(int) further consists of two terms: van der Waals volume and volume due to a packing effect. Millero et al.[29] have obtained the values of V_2^0(int) for amino acids from their molar crystal volume by using the relationship[30]

$$V_2^0(\text{int}) = (0.7/0.634)V_2^0(\text{cryst}) \qquad (8)$$

where 0.7 is the packing density for the molecule in an organic crystal and 0.634 is the packing density for a random packing sphere. Millero et al.[29] reported a relationship between the

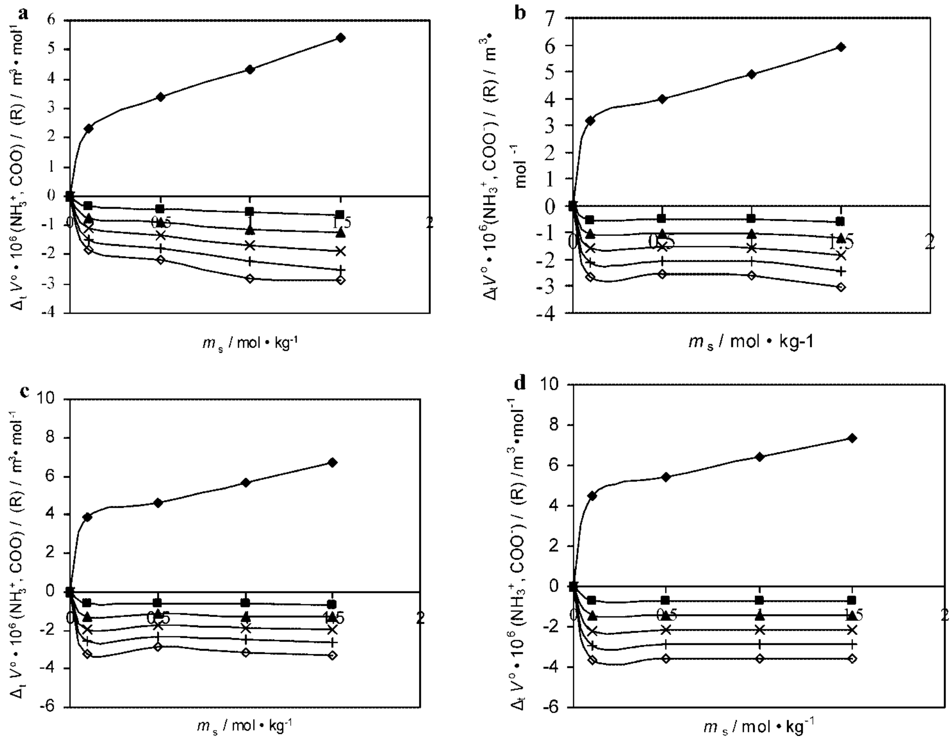

Figure 3. $\Delta_t V^0$ (NH_3^+, COO^-)/$\Delta_t V^0$ (R) vs m_s: ♦, NH_3^+, COO^-; ■, $-CH_2$; ▲, $CHCH_3$; ×, $-CHCH_2CH_3$; +, $-CHCH(CH_3)_2$; ◊, $-CHCHCH_2(CH_3)_2$ at (a) 288.15 K; (b) 298.15 K; (c) 308.15 K; and (d) 318.15 K.

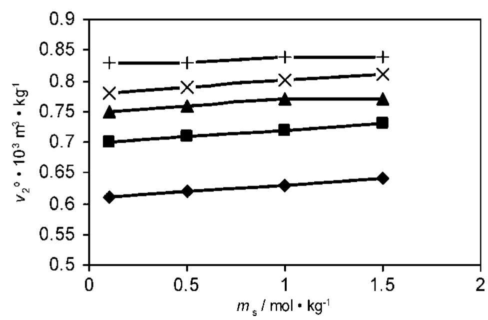

Figure 4. Partial specific volumes v_2^0 of some amino acids vs m_s: ♦, glycine; ■, DL-α-alanine; ▲, DL-α-amino-*n*-butyric acid; ×, L-valine; +, L-leucine at 298.15 K.

electrostriction volume and the hydration number of the nonelectrolyte as

$$V_{\text{elect}} = n_H(V_e^0 - V_b^0) \tag{9}$$

where V_e^0 is the molar volume of electrostricted water and V_b^0 is the molar volume of bulk water. For every water molecule taken from the bulk phase to the region near the amino acids, the volumes ($V_e^0 - V_b^0$) are (−2.9, −3.3, and −4.0) $cm^3 \cdot mol^{-1}$ at (288.15, 298.15, and 308.15) K, respectively.[31] The n_H values calculated for amino acids are given in Table 5. The hydration numbers of the studied amino acids are less in the presence of $ZnCl_2$ as compared to their values in water, and with a further increase in concentration of $ZnCl_2$ the hydration numbers decrease. These observations suggest that the interactions involving the (Zn^{2+}, Cl^-) ions with the charged centers of amino acids are strong, which weakens the electrostriction effect of the charged centers of the amino acids and exerts a dehydration effect. In the case of more polar amino acids, there is a large decrease in hydration numbers with concentration of $ZnCl_2$, but as the hydrophobic part of amino acids increases, the decrease becomes progressively smaller. The hydration numbers of all amino acids decrease with an increase in temperature.

Table 5. Hydration Numbers, n_H, of Studied Amino Acids in Water and in Aqueous $ZnCl_2$ Solutions from T = (288.15 to 308.15) K

$^a m_s$	n_H					
($mol \cdot kg^{-1}$)	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K
		glycine			DL-α-Alanine	
0.0	3.26 ± 0.01	2.58 ± 0.01	2.02 ± 0.01	4.08 ± 0.01	3.45 ± 0.01	2.68 ± 0.01
0.1	2.53 ± 0.01	1.74 ± 0.02	1.14 ± 0.02	3.58 ± 0.01	2.84 ± 0.02	2.14 ± 0.02
0.5	2.23 ± 0.03	1.54 ± 0.03	0.96 ± 0.03	3.18 ± 0.01	2.55 ± 0.01	1.89 ± 0.01
1.0	1.90 ± 0.03	1.29 ± 0.03	0.71 ± 0.03	2.99 ± 0.03	2.25 ± 0.03	1.67 ± 0.03
1.5	1.62 ± 0.03	1.05 ± 0.03	0.45 ± 0.03	2.66 ± 0.03	1.98 ± 0.03	1.42 ± 0.03
		L-Valine			L- Leucine	
0.0	4.13 ± 0.01	3.42 ± 0.03	2.63 ± 0.01	5.94 ± 0.01	4.97 ± 0.03	3.91 ± 0.01
0.1	3.84 ± 0.01	3.11 ± 0.02	2.39 ± 0.02	5.74 ± 0.01	4.78 ± 0.02	3.69 ± 0.02
0.5	3.57 ± 0.02	2.82 ± 0.02	2.03 ± 0.02	5.51 ± 0.02	4.54 ± 0.02	3.23 ± 0.02
1.0	3.46 ± 0.01	2.53 ± 0.03	1.80 ± 0.03	5.34 ± 0.02	4.29 ± 0.02	3.29 ± 0.02
1.5	3.12 ± 0.01	2.29 ± 0.03	1.62 ± 0.03	5.19 ± 0.01	4.10 ± 0.04	3.04 ± 0.04

[a] m_s: molality ($mol \cdot kg^{-1}$) of $ZnCl_2$ in water.

To study the effect of temperature on the interactions between the studied amino acids in zinc chloride, partial molar expansibilities V_E^0 [$V_E^0 = (\partial V_2^0/\partial T)_P$] and $(\partial^2 V_2^0/\partial T^2)_P$ have been calculated by fitting the data using the method of least-squares into the following equation

$$V_2^0 = a + bT + cT^2 \qquad (10)$$

where a, b, and c are constants and T is the temperature. Values of $(\partial V_2^0/\partial T)_P$ and $(\partial^2 V_2^0/\partial T^2)_P$ have been obtained by differentiating the above equation, and their values are summarized in Table 6. The V_E^0 values show a regular decrease in the partial molar expansibilities with an increase of temperature for all amino acids except for L-leucine, where the expansibilities increase regularly with temperature as well as with concentration.

The effect of concentration of $ZnCl_2$ on V_E^0 values does not follow any regular trend except for L-leucine. At low temperature, i.e., 288.15 K, the V_E^0 values increase initially for glycine, DL-α-alanine, and DL-α-amino-*n*- butyric acid. At 0.5 m_s the V_E^0 values decrease, and with further increase in concentration, the V_E^0 values again increase regularly. In the case of L-valine, V_E^0 does not follow any regular trend with concentration.

With a further increase of temperature, i.e., 308.15 K, for glycine, DL-α-amino-*n*-butyric acid, and L-valine, the V_E^0 values increase regularly with concentration, but for DL-α-alanine, V_E^0 does not follow any regular trend. At higher temperature, i.e., 318.15 K, no regular trend has been observed except for L-leucine.

Hepler[32] proposed a method by which quantitative information on hydration of a solute can be obtained from thermal expansion of aqueous solutions by using the thermodynamic relation

$$(\partial C^{o}_{p,2}/\partial T)_P = -T(\partial^2 V_2^0/\partial T^2)_P \qquad (11)$$

It has been suggested that for a structure breaking solute, the left side of the equation should be positive, and therefore $(\partial^2 V_2^0/\partial T^2)_P$ values should be negative for structure breaking and positive for structure making solutes. This equation is useful for making a distinction between ionic or polar solutes and those for which hydrophobic hydration is dominant. The presently obtained $(\partial^2 V_2^0/\partial T^2)_P$ values are negative for all amino acids, except L-leucine, which suggests that studied amino acids are structure breakers while L-leucine acts as structure maker in water as well as in aqueous $ZnCl_2$ solutions.

Conclusion

Partial molar volumes, V_2^0, of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine, and L-leucine in aqueous and in mixed aqueous solutions of zinc chloride, (0.1, 0.5, 1.0, and 1.5) mol·kg^{-1}, have been determined at T = (288.15 to 318.15) K. From these data, transfer volumes, hydration numbers, and side chain contributions have been determined. The $\Delta_t V^0$ values are positive in all the cases, and these increase with an increase in the concentration of $ZnCl_2$ and temperature. V_{XY} values are positive, and V_{XYY} values are negative in all cases, which suggest that interactions between amino acids and $ZnCl_2$ are mainly pairwise. n_H values also decrease with concentration of $ZnCl_2$ and temperature. These parameters suggest that ion−ion interactions between charged ends of amino acids and ions of $ZnCl_2$ dominate over the ion−hydrophobic interactions in theses systems. The negative $(\partial^2 V_2^0/\partial T^2)_P$ values for all amino acids, except L-leucine, suggest that studied amino acids are structure breakers while L-leucine acts as structure maker in water as well as in aqueous $ZnCl_2$ solutions.

Table 6. Partial Molar Expansibilities, V_E^0, of Some Amino Acids in Water and in Aqueous $ZnCl_2$ Solutions from T = (288.15 to 318.15) K

$^a m_s$	$10^{-6}\ V_E^0$ (m^3·mol^{-1}·K^{-1})					$10^{-6}(\partial^2 V_2^0/\partial T^2)_P$
(mol·kg^{-1})	288.15 K	298.15 K	308.15 K	318.15 K	^{b}SD	(m^3·mol^{-1}·K^{-2})
		Glycine in Aqueous $ZnCl_2$ Solutions				
0.0	0.099	0.071, 0.063[c]	0.041	0.012	0.089	−0.0029
0.1	0.175	0.140	0.105	0.070	0.009	−0.0035
0.5	0.148	0.132	0.115	0.099	0.002	−0.0017
1.0	0.239	0.184	0.129	0.074	0.121	−0.0056
1.5	0.589	0.577	0.565	0.553	0.264	−0.0012
		DL-α-Alanine in Aqueous $ZnCl_2$ Solutions				
0.0	0.057	0.052, 0.062[c]	0.046	0.041	0.118	−0.0006
0.1	0.097	0.093	0.089	0.085	0.071	−0.0004
0.5	0.083	0.084	0.084	0.085	0.007	0.0001
1.0	0.120	0.103	0.086	0.068	0.136	−0.0018
1.5	0.121	0.110	0.099	0.088	0.085	−0.0011
		DL-α-Amino-*n*-butyric Acid in Aqueous $ZnCl_2$ Solutions				
0.0	0.126	0.093	0.059	0.026	0.239	−0.0034
0.1	0.185	0.138	0.092	0.045	0.252	−0.0047
0.5	0.181	0.139	0.096	0.053	0.266	−0.0043
1.0	0.225	0.161	0.097	0.033	0.111	−0.0064
1.5	0.224	0.163	0.102	0.041	0.200	−0.0061
		L-Valine in Aqueous $ZnCl_2$ Solutions				
0.0[a]	0.087	0.071, 0.080[c]	0.056	0.040	0.109	−0.0016
0.1	0.083	0.082	0.082	0.081	0.083	−0.0001
0.5	0.136	0.108	0.081	0.053	0.170	−0.0028
1.0	0.200	0.141	0.082	0.023	0.020	−0.0059
1.5	0.167	0.129	0.090	0.052	0.002	−0.0039
		L-Leucine in Aqueous $ZnCl_2$ Solutions				
0.0[a]	0.076	0.082, 0.084[c]	0.087	0.093	0.069	0.0006
0.1	0.082	0.095	0.108	0.121	0.134	0.0013
0.5	0.091	0.103	0.115	0.127	0.036	0.0012
1.0	0.111	0.121	0.130	0.140	0.181	0.0010
1.5	0.132	0.142	0.153	0.162	0.161	0.0010

[a] m_s: molality (mol·kg^{-1}) of $ZnCl_2$ in water. [b] SD: Standard deviation calculated using eq 10. [c] Ref 20.

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