Densities, Apparent Molar Volumes, and Apparent Molar Heat Capacities of *l*-Arginine, *l*-Proline and *d*,*l*-Methionine in Water at 288.15, 298.15, 313.15, and 328.15 K

Andrew W. Hakin,* Alyson K. Copeland, Jin Lian Liu, Robert A. Marriott, and Kathryn E. Preuss

Department of Chemistry, University of Lethbridge, 4401 University Drive, Lethbridge, Alberta T1K 3M4, Canada

Relative densities, $(\rho - \rho_1^\circ)$, and heat capacity ratios, $c_p\rho/c_{p1}^\circ\rho_1^\circ - 1$, for *l*-arginine, *l*-proline, and *d*,*l*-methionine in water have been measured at 288.15, 298.15, 313.15 and 328.15 K. These data have been used to calculate apparent molar volumes and apparent molar heat capacities. Calculated standard state volumes and heat capacities have been compared to available literature data. Standard state expansibilities have been calculated from the temperature dependences of standard state volume data.

Introduction

The volumetric and thermochemical properties of aqueous amino acid systems have been studied by several authors. Although there is a wide selection of volumetric data as a function of temperature at ambient pressure, heat capacity data at temperatures removed from the standard condition of 298.15 K are extremely limited. Our most recent work has focused on the collection of volumetric and thermochemical data for aqueous amino acid systems as a function of temperature at ambient pressure (Hakin *et al.*, 1994a,b 1995; Duke *et al.*, 1994). These data have been utilized in the construction of group additivity schemes which are based on the standard state property, semiempirical modeling procedures described by Helgeson *et al.* (1981). Once a complete data base of thermodynamic data for the amino acid systems has been collected, it is our intention to apply our group additivity analyses to the prediction of thermodynamic properties of structurally more complicated peptide, and perhaps protein, systems.

To expand our data base of volumetric and thermochemical data for aqueous amino acid systems, this paper reports relative densities, $(\rho - \rho_1^\circ)$, and heat capacity ratios, $c_p\rho/c_{p1}^\circ\rho_1^\circ - 1$, for *l*-arginine, *l*-proline, and *d*,*l*-methionine in water at 288.15, 298.15, 313.15, and 328.15 K.

Experimental Section

l-Arginine, *l*-proline, and *d*,*l*-methionine were obtained from Sigma Chemical Co. (catalog numbers A 5006, P 0380, and M 9500, respectively). These compounds were recrystallized several times from ethanol + water mixtures, and their purities were checked by comparing their NMR spectra (obtained using a 250 MHz Brüker Instrument) to those contained in the literature (Pouchert and Campbell, 1974). In addition, the purity of each recrystallized amino acid was confirmed by elemental analyses (Galbraith Laboratories, Knoxville, TN). *d*,*l*-Methionine found: C, 40.43; H, 7.62; N, 9.40; S, 21.60. *Cf.* Calcd: C, 40.25; H, 7.43; N, 9.39; S, 21.49. *l*-Proline found: C, 52.50; H, 8.00; N, 12.17. *Cf.* Calcd: C, 52.16; H, 7.88; N, 12.17. *l*-Arginine found: C, 41.00; H, 8.38; N, 31.76. *Cf.* Calcd: C, 41.37; H, 8.1; N, 32.16. The purified anhydrous compounds were dried and stored in a vacuum oven over silica gel at 323.15 K. Water used in these investigations was obtained from an Osmonics model Aries High-purity D.I. Loop that can polish water to a resistance of 18.3 MΩ. All solutions were made by mass on the molality concentration scale and were stored in an unbuffered state in sealable 100 mL Nalgene bottles. Uncertainties in solution concentrations were assumed to be negligible in all of our calculations.

Density measurements were made with a Sodev Inc. O2D vibrating tube densimeter that was calibrated at each investigated temperature using a stream of high-purity N_2 gas and water. All densities were measured relative to water. Relative densities were calculated using the equation

$$(\rho - \rho_1^\circ) = K(\tau^2 - \tau_1^{\,2}) \qquad (1)$$

In this equation K defines the temperature dependent calibration constant of the densitometer, τ_1^2 and τ^2 are the squares of the time periods of oscillation of the vibrating tube containing pure water and solution, respectively, ρ_1° is the density of pure water (Kell, 1967), and ρ is the density of the solution. The uncertainty in the density, $\delta\rho$, is assigned a value of (5×10^{-6}) g cm^{-3}.

Heat capacity measurements for the amino acid solutions were made relative to pure water using a Picker flow microcalorimeter. Output from this instrument is in the form of a voltage signal recorded from a HP-3456A digital voltmeter. An IBM computer interfaced to the voltmeter facilitates the automatic (time stamped) collection of data. Heat capacity ratios were calculated from voltage versus time plots using a commercial data visualization program. The specific heat capacities for pure water, c_{p1}°, which are required in the calculation of amino acid specific heat capacities, were taken from the compilations of Kell (1972). The uncertainty in a measured specific heat capacity, δc_p, is estimated to be (7×10^{-5}) J K^{-1} g^{-1}. The heat loss correction factor, or *f* factor, associated with our calorimeter was determined prior to the start of our investigations using standard solutions of sodium chloride in water (Desnoyers *et al.*, 1976). A value of $f = 0.9967$ has been used in our calorimetric calculations at all temperatures.

The densimeter and the calorimeter were thermostated using Sodev Inc. programmable circulating thermostat units which have a working range of 273.15 K to 348.15 K and a thermal stability of ±0.001 K.

* Tel. (403) 329-2083. Fax (403) 329-2057.

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Table 1. Relative Densities, ($\rho - \rho_1^\circ$), Apparent Molar Volumes, $V_{2,\phi}$, Heat Capacity Ratios, [$c_p\rho/c_{p1}^\circ\rho_1^\circ - 1$], and Apparent Molar Heat Capacities, $C_{p2,\phi}$, of Aqueous Solutions of *l*-Arginine at (288.15, 298.15, 313.15, and 328.15) K[a]

m/mol kg^{-1}	$(\rho - \rho_1^\circ)$/ g cm^{-3}	$V_{2,\phi}$/cm^3 mol^{-1}	$10^3(c_p\rho/c_{p1}^\circ\rho_1^\circ - 1)$	$C_{p2,\phi}$/J K^{-1} mol^{-1}
		$T = 288.15$ K		
0.289 4	1.4151×10^{-2}	123.62(0.02)	−17.932	265.7(0.3)
0.197 4	9.954×10^{-3}	122.62(0.03)	−12.018	253.6(0.4)
0.142 0	7.122×10^{-3}	123.25(0.04)	−8.546	260.1(0.5)
0.081 06	4.098×10^{-3}	123.20(0.06)	−4.985	256.1(0.9)
0.05826	2.967×10^{-3}	122.98(0.09)	−3.579	256.7(1.2)
0.029 59	7.219×10^{-3}	122.34(0.17)	−1.821	243.5(2.4)
0.030 18	1.607×10^{-3}	120.85(0.17)	−1.936	236.9(2.3)
		$T = 298.15$ K		
0.289 4	1.3862×10^{-2}	124.81(0.02)	−15.325	290.8(0.3)
0.197 4	9.579×10^{-3}	124.71(0.03)	−10.599	289.8(0.4)
0.142 0	6.968×10^{-3}	124.51(0.04)	−7.816	284.8(0.5)
0.081 06	4.012×10^{-3}	124.44(0.06)	−4.515	283.3(0.9)
0.058 26	2.902×10^{-3}	124.26(0.09)	−3.285	280.4(1.2)
0.029 59	1.487×10^{-3}	124.01(0.17)	−1.672	279.7(2.4)
0.030 18	1.581×10^{-3}	121.88(0.17)	−1.780	260.5(2.3)
		$T = 313.15$ K		
0.289 4	1.3573×10^{-2}	126.20(0.02)	−13.858	316.6(0.3)
0.197 4	9.369×10^{-3}	126.17(0.03)	−9.2895	322.2(0.4)
0.142 0	6.821×10^{-3}	125.92(0.04)	−6.873	317.0(0.5)
0.081 06	3.937×10^{-3}	125.74(0.06)	−3.990	314.2(0.9)
0.058 26	2.846×10^{-3}	125.59(0.09)	−2.867	314.2(1.2)
0.029 59	1.462×10^{-3}	125.21(0.17)	−1.467	311.9(2.4)
0.030 18	1.549×10^{-3}	123.25(0.17)	−1.572	293.3(2.3)
		$T = 328.15$ K		
0.289 4	1.3446×10^{-2}	127.18(0.02)	−11.614	350.9(0.3)
0.197 4	9.293×10^{-3}	127.08(0.03)	−8.238	345.6(0.4)
0.142 0	6.756×10^{-3}	126.90(0.04)	−6.199	338.0(0.5)
0.081 06	3.895×10^{-3}	126.77(0.06)	−3.306	350.8(0.9)
0.058 26	2.824×10^{-3}	126.47(0.09)	−2.579	335.5(1.2)
0.029 59	1.448×10^{-3}	126.19(0.17)	−1.008	369.3(2.4)
0.030 18	1.506×10^{-3}	125.19(0.17)	−1.367	326.6(2.3)

[a] Uncertainties are shown in parentheses.

Results and Discussion

Apparent molar volumes, $V_{2,\phi}$, were calculated from relative densities using the equation

$$V_{2,\phi} = \left(\frac{M}{\rho}\right) - \left(\frac{\rho - \rho_1^\circ}{m\rho\rho_1^\circ}\right) \tag{2}$$

where m is the molality of the investigated solution and M is the molar mass of the solute. In a similar fashion, apparent molar heat capacities, $C_{p2,\phi}$, were calculated from measured heat capacity ratios using the relationship

$$C_{p2,\phi} = Mc_p + (c_p - c_{p1}^\circ)/m \tag{3}$$

where c_p is the specific heat capacity of the solute. Apparent molar volumes, heat capacities, relative densities, heat capacity ratios, and concentration data for the investigated amino acid systems are reported in Tables 1−3 at each temperature.

Standard state volumes and heat capacities were determined from the concentration dependences of the relevant apparent molar properties. For the dilute concentration ranges investigated in the present study, the reported apparent molar data were found to be adequately modelled by equations of the form

$$Y_{2,\phi} = Y_{2,\phi}^\infty + A_Y m \tag{4}$$

In this equation Y represents the extensive thermodynamic property of interest, $Y_{2,\phi}$ defines an apparent molar property, $Y_{2,\phi}^\infty$ defines the value of the apparent molar property at infinite dilution, and A_Y is a constant obtained from the fit of the equation to the thermodynamic data. Partial molar properties, Y_2, may be related to apparent molar properties using the equation

$$Y_2 = Y_{2,\phi} + n_2\left(\frac{\partial Y_{2,\phi}}{\partial n_2}\right)_{T,p,n_1} \tag{5}$$

where n_1 and n_2 define the number of moles of solvent and solute, respectively. In the limit $n_2 \rightarrow 0$ the standard state property Y_2° is equal to the apparent molar property at infinite dilution, $Y_{2,\phi}^\infty$.

Standard state volumes and heat capacities were obtained by fitting the appropriate version of eq 4 to apparent molar volume and heat capacity data using a weighted regression analysis procedure. A weighted procedure is required because all of our measurements are performed relative to water. As our investigated solutions become more waterlike, the signal to noise ratio of our time period and voltage readings decreases. In other words, relative densities and heat capacity ratios can be measured with less precision for dilute solutions than for more concentrated solutions. To reflect this situation in our data analyses, we use a weighting factor of one over the square of the uncertainty in the apparent molar property of interest. Uncertainties in apparent molar volumes and heat capacities have been defined by eqs 6 and 7, respectively.

$$\delta V_{2,\phi} = -\left[M + \frac{1000}{m}\right]\frac{\delta\rho}{\rho^2} \tag{6}$$

$$\delta C_{p2,\phi} = \left(M + \frac{1000}{m}\right)\delta c_p \tag{7}$$

Calculated uncertainties have been included in parentheses

Table 2. Relative Densities, ($\rho - \rho_1^\circ$), Apparent Molar Volumes, $V_{2,\phi}$, Heat Capacity Ratios, [$c_p\rho/c_p^\circ\rho_1^\circ - 1$], and Apparent Molar Heat Capacities, $C_{p2,\phi}$, of Aqueous Solutions of *l*-Proline at (288.15, 298.15, 313.15, and 328.15) K[a]

m/mol kg^{-1}	$(\rho - \rho_1^\circ)$/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	10^3 $(c_p\rho/c_p^\circ\rho_1 - 1)$	$C_{p2,\phi}$/ J K^{-1} mol^{-1}	m/mol kg^{-1}	$(\rho - \rho_1^\circ)$/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	10^3 $(c_p\rho/c_p^\circ\rho_1 - 1)$	$C_{p2,\phi}$/ J K^{-1} mol^{-1}
				$T = 288.15$ K					
0.005 212	1.74×10^{-4}	81.72(0.96)	−0.213	171.2(13.4)	0.101 3	3.354×10^{-3}	81.76(0.05)	−4.357	160.9(0.7)
0.007 473	2.51×10^{-4}	81.52(0.67)	−0.335	153.7(9.4)	0.203 3	6.662×10^{-3}	81.83(0.02)	−8.642	161.9(0.4)
0.009 422	3.21×10^{-4}	81.06(0.53)	−0.418	154.0(7.4)	0.333 4	1.0812×10^{-2}	81.83(0.02)	−14.048	161.6(0.2)
0.012 26	4.07×10^{-4}	81.91(0.40)	−0.456	152.0(5.7)	0.582 5	1.8437×10^{-2}	81.98(0.01)	−24.066	162.3(0.1)
0.017 59	5.89×10^{-4}	81.64(0.28)	−0.743	165.0(4.0)	0.697 9	2.1875×10^{-2}	82.01(0.01)	−28.622	162.1(0.1)
0.021 01	6.97×10^{-4}	81.90(0.23)	−0.871	169.1(3.3)	0.104 1	3.455×10^{-3}	81.69(0.05)	−4.499	159.7(0.7)
0.022 91	7.76×10^{-4}	81.19(0.21)	−0.954	165.4(3.1)	0.077 59	2.577×10^{-3}	81.75(0.06)	−3.354	160.4(0.9)
0.030 36	1.009×10^{-3}	81.83(0.17)	−1.268	167.5(2.3)	0.062 03	2.062×10^{-3}	81.77(0.08)	−2.673	161.2(1.1)
0.050 90	1.701×10^{-3}	81.58(0.10)	−2.168	162.7(1.4)	0.050 83	1.690×10^{-3}	81.79(0.10)	−2.170	163.2(1.4)
0.060 30	2.003×10^{-3}	81.77(0.08)	−2.574	163.0(1.2)	0.041 00	1.364×10^{-3}	81.78(0.12)	−1.784	159.9(1.7)
0.071 82	2.384×10^{-3}	81.76(0.07)	−3.094	161.1(1.0)	0.027 30	9.06×10^{-4}	81.91(0.18)	−1.188	160.5(2.6)
0.082 75	2.740×10^{-3}	81.81(0.06)	−3.562	161.3(0.9)	0.017 94	5.95×10^{-4}	81.96(0.28)	−0.766	164.3(3.9)
0.092 82	3.081×10^{-3}	81.69(0.05)	−3.992	160.9(0.8)	0.010 44	3.46×10^{-4}	81.97(0.50)	−0.452	162.2(6.7)
				$T = 298.15$ K					
0.005 212	1.70×10^{-4}	82.64(0.97)	−0.205	180.1(13.4)	0.101 3	3.278×10^{-3}	82.61(0.05)	−4.004	178.1(0.7)
0.007 473	2.44×10^{-4}	82.52(0.67)	−0.317	166.8(9.4)	0.203 3	6.510×10^{-3}	82.69(0.02)	−8.034	177.2(0.4)
0.009 422	3.07×10^{-4}	82.66(0.53)	−0.373	179.5(7.4)	0.333 4	1.0544×10^{-2}	82.75(0.02)	−12.955	178.5(0.2)
0.012 26	4.04×10^{-4}	82.24(0.41)	−0.495	174.4(5.7)	0.582 5	1.8012×10^{-2}	82.84(0.01)	−22.329	177.8(0.1)
0.014 64	4.84×10^{-4}	82.12(0.34)	−0.595	172.7(4.8)	0.697 9	2.1354×10^{-2}	82.89(0.01)	−26.448	178.4(0.1)
0.017 59	5.73×10^{-4}	82.61(0.29)	−0.730	171.1(4.0)	0.104 1	3.372×10^{-3}	82.60(0.05)	−4.155	176.4(0.7)
0.021 01	6.99×10^{-4}	81.90(0.24)	−0.855	171.5(3.3)	0.077 59	2.518×10^{-3}	82.62(0.07)	−3.068	178.5(0.9)
0.022 91	7.22×10^{-4}	83.67(0.22)	−0.909	183.0(3.1)	0.062 03	2.015×10^{-3}	82.63(0.08)	−2.453	178.8(1.1)
0.030 36	9.88×10^{-4}	82.63(0.17)	−1.220	176.4(2.3)	0.050 83	1.656×10^{-3}	82.57(0.10)	−1.981	181.1(1.4)
0.050 90	1.653×10^{-3}	82.63(0.10)	−2.058	175.2(1.4)	0.041 00	1.334×10^{-3}	82.64(0.12)	−1.555	185.9(1.7)
0.060 30	1.954×10^{-3}	82.69(0.08)	−2.406	177.5(1.2)	0.027 30	8.90×10^{-4}	82.61(0.18)	−1.076	179.6(2.6)
0.071 82	2.324×10^{-3}	82.70(0.07)	−2.864	177.5(1.0)	0.017 94	5.84×10^{-4}	82.67(0.28)		
0.082 75	2.678×10^{-3}	82.66(0.06)	−3.282	178.1(0.9)	0.010 44	3.38×10^{-4}	82.84(0.48)		
0.092 82	3.007×10^{-3}	82.60(0.05)	−3.639	179.6(0.8)					
				$T = 313.15$ K					
0.005 212	1.67×10^{-4}	83.45(0.97)	−0.194	190.5(13.4)	0.101 3	3.199×10^{-3}	83.65(0.05)	−3.675	194.4(0.7)
0.007 473	2.38×10^{-4}	83.64(0.67)	−0.272	194.9(9.4)	0.203 3	6.352×10^{-3}	83.73(0.03)	−7.172	197.8(0.4)
0.009 422	3.02×10^{-4}	83.43(0.54)	−0.350	191.1(7.4)	0.333 4	1.0299×10^{-2}	83.76(0.02)	−11.814	195.6(0.2)
0.012 26	3.95×10^{-4}	83.26(0.41)			0.582 5	1.7576×10^{-2}	83.87(0.01)	−20.338	195.3(0.1)
0.017 59	5.64×10^{-4}	83.40(0.29)	−0.648	192.2(4.0)	0.697 9	2.0848×10^{-2}	83.90(0.01)	−24.225	194.9(0.1)
0.021 01	6.70×10^{-4}	83.56(0.24)	−0.763	194.9(3.3)	0.104 1	3.290×10^{-3}	83.64(0.05)	−3.682	198.1(0.7)
0.022 91	7.35×10^{-4}	83.37(0.22)	−0.824	195.5(3.1)	0.07759	2.456×10^{-3}	83.68(0.07)	−2.732	199.3(0.9)
0.030 36	9.61×10^{-4}	83.76(0.17)	−1.086	197.8(2.3)	0.062 03	1.961×10^{-3}	83.76(0.08)	−2.242	196.0(1.1)
0.050 90	1.616×10^{-3}	83.62(0.10)	−1.842	195.3(1.4)	0.050 83	1.606×10^{-3}	83.80(0.10)	−1.838	196.2(1.4)
0.060 30	1.908×10^{-3}	83.70(0.08)	−2.130	199.1(1.2)	0.041 00	1.300×10^{-3}	83.73(0.12)	−1.443	200.0(1.7)
0.071 82	2.274×10^{-3}	83.66(0.07)	−2.549	198.1(1.0)	0.027 30	8.62×10^{-4}	83.89(0.19)	−0.946	203.1(2.6)
0.082 75	2.617×10^{-3}	83.66(0.06)	−2.964	196.6(0.9)	0.017 94	5.67×10^{-4}	83.87(0.28)	−0.612	205.3(3.9)
0.092 82	2.939×10^{-3}	83.59(0.05)	−3.248	199.7(0.8)	0.010 44	3.31×10^{-4}	83.78(0.49)	−0.356	205.3(6.7)
				$T = 328.15$ K					
0.050 90	1.597×10^{-3}	84.34(0.10)	−2.030	180.7(1.4)	0.082 75	2.573×10^{-3}	84.55(0.06)	−2.084	242.8(0.9)
0.060 30	1.876×10^{-3}	84.59(0.09)	−1.822	222.1(1.2)	0.092 82	2.882×10^{-3}	84.56(0.06)	−2.936	215.7(0.8)
0.071 82	2.237×10^{-3}	84.53(0.07)			0.101 3	3.150×10^{-3}	84.49(0.05)	−3.325	210.3(0.7)
0.082 75	2.578×10^{-3}	84.49(0.06)	−2.473	222.8(0.9)	0.203 3	6.250×10^{-3}	84.60(0.03)	−7.110	200.5(0.4)
0.092 82	2.894×10^{-3}	84.43(0.06)	−2.187	249.1(0.8)	0.333 4	1.0145×10^{-2}	84.58(0.02)	−8.572	238.5(0.2)
0.101 3	3.164×10^{-3}	84.35(0.05)	−1.891	269.2(0.7)	0.582 5	1.7311×10^{-2}	84.70(0.01)	−18.612	209.5(0.1)
0.203 3	6.260×10^{-3}	84.55(0.03)	−6.164	220.0(0.4)	0.697 9	2.0535×10^{-2}	84.72(0.01)	−22.190	209.0(0.1)
0.333 4	1.0170×10^{-2}	84.50(0.02)	−10.931	207.9(0.2)	0.104 1	3.249×10^{-3}	84.39(0.05)	−3.107	222.3(0.7)
0.582 5	1.7304×10^{-2}	84.71(0.02)	−19.706	201.3(0.1)	0.062 03	1.946×10^{-3}	84.35(0.08)	−2.114	204.9(1.1)
0.697 9	2.0573×10^{-2}	84.66(0.01)	−22.013	209.9(0.1)	0.050 83	1.601×10^{-3}	84.24(0.10)	−1.633	212.8(1.4)
0.050 90	1.594×10^{-3}	84.41(0.10)	−1.698	208.3(1.4)	0.041 00	1.288×10^{-3}	84.36(0.13)	−1.429	201.9(1.7)
0.060 30	1.881×10^{-3}	84.51(0.09)	−1.560	240.0(1.2)	0.027 30	8.59×10^{-4}	84.36(0.19)	−0.838	219.5(2.6)
0.071 82	2.230×10^{-3}	84.62(0.07)	−1.458	263.7(1.0)					

[a] Uncertainties are shown in parentheses.

in Tables 1−3. Calculated standard state data are compared to available literature data in Table 4.

Our review of published standard state volume data for *l*-arginine in water indicates that previous investigations have been limited to two temperatures: 298.15 K and 308.15 K. At 298.15 K our value of (124.12 ± 0.28) cm^3 mol^{-1} agrees within the stated limits of experimental uncertainty with those values reported by Mishra and Ahluwalia (1984) and Jolicoeur *et al*. (1986). Our data appear to confirm that the earlier value of 127.34 cm^3 mol^{-1} reported by Millero *et al*. (1978) is too high. Iqbal and Ahmed's value of (131.10 ± 0.05) cm^3 mol^{-1} at 308.15 K (Iqbal and Ahmed, 1993) does not appear to agree with the temperature trends displayed by our data. Their value is approximately 6 cm^3 mol^{-1} greater than the value that may be estimated from our data set. The very large difference of approximately 7 cm^3 mol^{-1} between their standard state volume at 308.15 K and the value at 298.15 K (where there is a consensus of agreement between several studies) appears to be unlikely. In explaining this difference, we note that Iqbal and Ahmed's density measurements were performed using 20 mL pycnometer flasks which are not capable of the high precision offered by vibrating tube instruments.

Table 3. Relative Densities, ($\rho - \rho_1^\circ$), Apparent Molar Volumes, $V_{2,\phi}$, Heat Capacity Ratios, [$c_p\rho/c_p^\circ\rho_1^\circ - 1$], and Apparent Molar Heat Capacities, $C_{p2,\phi}$, of Aqueous Solutions of *d,l*-Methionine at (288.15, 298.15, 313.15, and 328.15) K[a]

m/mol kg^{-1}	$(\rho - \rho_1^\circ)$/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	10^3 ($c_p\rho/c_p^\circ\rho_1 - 1$)	$C_{p2,\phi}$/ J K^{-1} mol^{-1}	m/mol kg^{-1}	$(\rho - \rho_1^\circ)$/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	10^3 ($c_p\rho/c_p^\circ,\rho_1 - 1$)	$C_{p2,\phi}$/ J K^{-1} mol^{-1}
				$T = 288.15$ K					
0.043 41	1.949×10^{-3}	104.16(0.12)	−1.557	285.3(1.6)	0.049 75	2.254×10^{-3}	103.73(0.10)	−1.761	285.4(1.4)
0.050 88	2.284×10^{-3}	104.13(0.10)	−1.865	281.7(1.4)	0.045 57	2.056×10^{-3}	103.93(0.11)	−1.570	290.2(1.5)
0.054 53	2.452×10^{-3}	104.05(0.09)	−1.965	284.0(1.3)	0.049 86	2.247×10^{-3}	103.97(0.10)	−1.872	277.4(1.4)
0.061 62	2.759×10^{-3}	104.20(0.08)	−2.252	282.3(1.1)	0.054 83	2.470×10^{-3}	103.96(0.09)	−1.945	285.9(1.3)
0.067 57	3.026×10^{-3}	104.16(0.07)	−2.426	284.8(1.0)	0.060 21	2.708×10^{-3}	104.00(0.08)	−2.228	279.5(1.2)
0.074 50	3.341×10^{-3}	104.08(0.07)	−2.726	281.4(1.0)	0.066 64	3.001×10^{-3}	103.92(0.08)	−2.434	281.1(1.1)
0.084 40	3.775×10^{-3}	104.14(0.06)	−3.058	283.0(0.8)	0.075 87	3.413×10^{-3}	103.92(0.07)	−2.709	284.5(0.9)
0.093 20	4.168×10^{-3}	104.14(0.05)	−3.431	280.3(0.8)	0.077 02	3.459×10^{-3}	103.99(0.07)	−2.843	279.7(0.9)
0.097 29	4.339×10^{-3}	104.21(0.05)	−3.567	281.3(0.7)	0.0886 0	3.979×10^{-3}	103.94(0.06)	−3.200	282.6(0.8)
0.099 50	4.439×10^{-3}	104.19(0.05)	−3.698	279.1(0.7)	0.098 59	4.412×10^{-3}	104.06(0.05)	−3.563	282.9(0.7)
				$T = 298.15$ K					
0.043 41	1.908×10^{-3}	105.24(0.12)	−1.491	294.8(1.6)	0.044 69	1.969×10^{-3}	105.11(0.11)	−1.560	291.9(1.6)
0.050 88	2.231×10^{-3}	105.31(0.10)	−1.729	296.5(1.4)	0.051 02	2.237×10^{-3}	105.30(0.10)	−1.745	295.6(1.4)
0.054 53	2.382×10^{-3}	105.47(0.09)	−1.844	297.8(1.3)	0.056 43	2.471×10^{-3}	105.34(0.09)	−1.944	294.6(1.3)
0.061 62	2.689×10^{-3}	105.47(0.08)	−2.088	297.4(1.1)	0.063 72	2.789×10^{-3}	105.33(0.08)	−2.192	294.7(1.1)
0.067 57	2.948×10^{-3}	105.44(0.07)	−2.291	297.1(1.0)	0.067 75	2.963×10^{-3}	105.35(0.07)	−2.312	295.8(1.0)
0.074 50	3.245×10^{-3}	105.49(0.07)	−2.525	297.3(1.0)	0.072 16	3.156×10^{-3}	105.32(0.07)	−2.478	294.7(1.0)
0.084 40	3.677×10^{-3}	105.44(0.06)	−2.876	296.2(0.8)	0.079 97	3.491×10^{-3}	105.37(0.06)	−2.737	295.3(0.9)
0.093 20	4.053×10^{-3}	105.48(0.05)	−3.161	296.9(0.8)	0.083 63	3.651×10^{-3}	105.35(0.06)	−2.836	296.5(0.8)
0.097 29	4.229×10^{-3}	105.48(0.05)	−3.331	295.4(0.7)	0.089 88	3.919×10^{-3}	105.37(0.06)	−3.058	296.0(0.8)
0.099 50	4.325×10^{-3}	105.47(0.05)	−3.376	296.7(0.7)	0.103 2	4.492×10^{-3}	105.39(0.05)	−3.522	295.4(0.7)
				$T = 313.15$ K					
0.050 88	2.156×10^{-3}	107.11(0.10)	−1.552	316.3(1.4)	0.051 02	2.167×10^{-3}	107.00(0.10)	−1.646	308.5(1.4)
0.054 53	2.302×10^{-3}	107.25(0.09)	−1.738	311.1(1.3)	0.056 43	2.397×10^{-3}	106.98(0.09)	−1.790	310.7(1.3)
0.061 62	2.606×10^{-3}	107.14(0.08)	−1.906	314.5(1.1)	0.063 72	2.705×10^{-3}	106.97(0.08)	−2.015	310.9(1.1)
0.067 57	2.852×10^{-3}	107.19(0.08)	−2.172	309.5(1.0)	0.067 75	2.866×10^{-3}	107.11(0.08)	−2.146	311.2(1.0)
0.074 50	3.146×10^{-3}	107.15(0.07)	−2.417	308.0(1.0)	0.072 16	3.054×10^{-3}	107.05(0.07)	−2.328	310.7(1.0)
0.084 40	3.558×10^{-3}	107.17(0.06)	−2.643	312.8(0.8)	0.079 97	3.387×10^{-3}	106.99(0.06)	−2.554	309.4(0.9)
0.097 29	4.099×10^{-3}	107.14(0.05)	−3.064	311.7(0.7)	0.083 63	3.535×10^{-3}	107.06(0.06)	−2.676	309.4(0.8)
0.099 50	4.192×10^{-3}	107.13(0.05)	−3.031	315.9(0.7)	0.089 88	3.798×10^{-3}	107.04(0.06)	−2.854	310.2(0.8)
0.044 69	1.906×10^{-3}	106.86(0.11)	−1.429	309.2(1.6)	0.103 2	4.352×10^{-3}	107.07(0.05)	−3.293	309.5(0.7)
				$T = 328.15$ K					
0.054 53	2.258×10^{-3}	108.52(0.09)	−1.376	341.5(1.3)	0.054 53	2.261×10^{-3}	108.46(0.09)	−1.978	295.0(1.3)
0.061 62	2.551×10^{-3}	108.49(0.08)	−1.615	337.2(1.1)	0.061 62	2.547×10^{-3}	108.54(0.08)	−1.845	321.8(1.1)
0.067 57	2.802×10^{-3}	108.38(0.08)	−2.135	314.1(1.0)	0.067 57	2.790×10^{-3}	108.57(0.08)	−1.432	358.5(1.0)
0.074 50	3.081×10^{-3}	108.48(0.07)	−2.642	298.1(1.0)	0.074 50	3.078×10^{-3}	108.52(0.07)	−2.383	312.9(1.0)
0.084 40	3.485×10^{-3}	108.49(0.06)	−2.682	313.5(0.8)	0.084 40	3.480×10^{-3}	108.55(0.06)	−2.213	337.2(0.8)
0.093 20	3.828×10^{-3}	108.68(0.06)	−2.647	328.4(0.8)	0.093 20	3.839×10^{-3}	108.55(0.06)	−2.704	325.3(0.8)
0.097 29	4.007×10^{-3}	108.55(0.05)	−3.064	314.8(0.7)	0.097 29	4.023×10^{-3}	108.38(0.05)	−2.946	319.2(0.7)
0.099 50	4.092×10^{-3}	108.59(0.05)	−3.073	317.5(0.7)	0.099 50	4.106×10^{-3}	108.45(0.05)	−3.020	319.2(0.7)
0.050 88	2.106×10^{-3}	108.54(0.10)	−1.718	305.9(1.4)					

[a] Uncertainties are shown in parentheses.

Table 4. Comparison of Calculated V_2° and C_{p2}° Data with Literature Data

T/K	V_2°/cm^3 mol^{-1}	A_V/cm^3 mol^{-2} kg	C_{p2}°/J K^{-1} mol^{-1}	A_{C_p}/J K^{-1} mol^{-2} kg
		l-Arginine		
288.15	122.29 ± 0.51	4.24 ± 2.14	247.2 ± 5.4	60.1 ± 22.4
298.15	124.12 ± 0.28 (127.34,[a] 123.86,[b] 123.7[c])	2.48 ± 1.18	279.5 ± 3.0 (279[c])	40.9 ± 12.3
313.15	125.51 ± 0.30	2.58 ± 1.25	317.3 ± 4.8	2.0 ± 20.1
328.15	126.51 ± 0.19	2.42 ± 0.80	336.3 ± 5.9	48.8 ± 24.4
		l-Proline		
288.15	81.71 ± 0.02 (81.57[d])	0.44 ± 0.03	161.4 ± 0.3	1.2 ± 0.5
298.15	82.61 ± 0.02 (82.50,[d] 82.5,[e] 82.83,[a] 82.63,[b] 82.65[c])	0.40 ± 0.03	177.9 ± 0.4 (172.3,[c] 170.3[f])	0.5 ± 0.7
313.15	83.64 ± 0.01 (83.6[e])	0.38 ± 0.02	197.6 ± 0.4	−4.0 ± 0.7
328.15	84.46 ± 0.03 (84.5[e])	0.37 ± 0.05	226.5 ± 6.7	−27.9 ± 11.0
		d,l-Methionine		
288.15	103.8 ± 0.11 (103.89[e], 104.0[d])	2.79 ± 1.37	286.3 ± 2.3	−53.6 ± 28.5
298.15	105.21 ± 0.07 (105.35,[a] 105.57,[b] 105.3,[c] 104.83,[d] 105.2[e])	2.33 ± 0.87	295.2 ± 1.1 (293[c])	9.7 ± 13.9
313.15	107.02 ± 0.09 (107.0[e])	0.85 ± 1.09	309.7 ± 2.8	18.4 ± 33.8
328.15	108.47 ± 0.11 (108.1[e])	0.60 ± 1.31	325.1 ± 18.9	−47.6 ± 220.9

[a] Millero *et al.* (1978). [b] Mishra and Ahluwalia (1984). [c] Jolicoeur *et al.* (1986). [d] Kikuchi *et al.* (1995). [e] Kharakoz *et al.* (1989). [f] Spink and Wadso (1975).

Only one previous investigation of the apparent molar heat capacities of *l*-arginine could be found in the literature (Jolicoeur *et al.*, 1986). Their reported standard state heat capacity of (279 ± 1) J K^{-1} mol^{-1} is in very good agreement with our value of (279.5 ± 3.0) J K^{-1} mol^{-1}.

Turning to standard state data for *l*-proline in water, there have been several volumetric investigations reported in the literature. Standard state volume data for these investigations together with data calculated from the current investigation have been summarized in Figure 1.

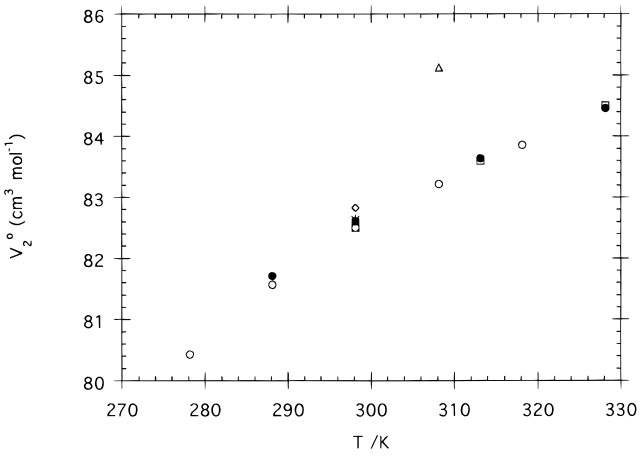

Figure 1. A comparison of standard state volume data contained in the literature with those calculated in the present study. (●) present study; (○) Kikuchi *et al*. (1995); (△) Iqbal and Ahmed (1993); (+) Jolicoeur *et al*. (1986); (×) Mishra and Ahluwalia (1984); (◇) Millero *et al*. (1978); (□) Kharakoz (1989).

With the exception of the V_2° value at 308.15 K reported by Iqbal and Ahmed (1993), there is excellent agreement between literature data and those reported in this paper.

There are two previous standard state heat capacities for *l*-proline at 298.15 K reported in the literature. Spink and Wadso's (1975) value of (170.3 ± 3) J K^{-1} mol^{-1} was calculated from drop calorimetric measurements, whereas the value of (172.3 ± 0.9) J K^{-1} mol^{-1} obtained by Jolicoeur *et al*. (1986) was obtained using a Picker flow microcalorimeter. Our value of C_{p2}° = (177.7 ± 0.4) J K^{-1} mol^{-1} is in reasonable agreement with these values, although outside the limits of the combined experimental uncertainties. Our elemental anayses results confirm that we have not introduced a systematic error by failing to consider a change in water of crystallization; therefore, we are unable to fully explain this discrepancy.

Following the patterns in available data displayed by the two previous systems there are several sets of volumetric data for *d*,*l*-methionine in the literature but extremely limited heat capacity data. Indeed, we were able to locate only one previous standard state heat capacity determination (Jolicoeur *et al*., 1986), and this was for the levo isomer of methionine not the racemic mixture investigated in this study. However, Jolicoeur *et al*.'s value of (293 ± 29) J K^{-1} mol^{-1} is in good agreement with our reported value of (295.2 ± 1.1) J K^{-1} mol^{-1}. With respect to our standard state heat capacity data for *d*,*l*-methionine at 328.15 K, we acknowledge that the reported standard error on this value is large. This situation arises because of the low solubility of *d*,*l*-methionine in water compared to the solubilities of the other investigated systems and as a result of the increased noise in our calorimetric signal at this higher temperature.

With respect to standard state volumes, our values are in excellent agreement with the temperature dependence trends reported by Kharakoz (1989). Kikuchi *et al*. (1995) have recently reported standard state volume data for this system in the temperature range 278.15 K to 318.15 K. Although there is good agreement between this set and ours below 298.15 K, at higher temperatures Kikuchi's data are somewhat lesser in value than the values reported by both Kharakoz (1989) and ourselves. This discrepancy cannot be readily explained.

To further expand our growing data base of standard state properties of aqueous amino acid systems, we have combined the standard state volume data reported in this paper with those previously published in the literature to yield standard state expansibilities, E_2°. These data may be calculated from the first derivative of polynomial equations which model the temperature dependences of standard state volume data (see eq 8). Each data set was

$$V_2^\circ(T) = A_1 + A_2(T - 298.15) + A_3(T - 298.15)^2 \quad (8)$$

assigned unit weighting in our regression analysis procedure. Estimates of the A_i ($i = 1 \rightarrow 3$) constants together with their calculated standard errors are contained in Table 5 together with references to the standard state volume data utilized in each fitting procedure. Iqbal and Ahmed (1993) have reported E_2° based on a linear extrapolation between two standard state volumes obtained at 298.15 K and 308.15 K. Their values of (0.72 and 0.25) cm^3 mol^{-1} K^{-1} for *l*-arginine and *l*-proline, respectively, are in poor agreement with the values which may be calculated from the data contained in Table 5. This disagreement appears to be the result of Iqbal and Ahmed's unusually large standard state volumes at 308.15 K.

Table 5. Estimated Values for A_i Parameters to Eq 8 Which May Be Used To Calculate Standard State Expansibilities (Standard Errors on the A_i Parameters Are Shown in Parentheses)

A_1/cm^3 mol^{-1}	A_2/cm^3 mol^{-1} K^{-1}	A_3/cm^3 mol^{-1} K^{-2}	temp range/K	ref
		l-Arginine		
123.87 (0.09)	0.138 20 (0.011 90)	−0.001 69 (0.000 48)	288.15−328.15	*a*−*c*
		l-Proline		
82.57 (0.04)	0.086 28 (0.002 81)	−0.000 83 (0.000 13)	278.15−328.15	*a*−*e*
		d,*l*-Methionine[f]		
105.02 (0.20)	0.135 81 (0.012 25)	−0.001 19 (0.000 66)	278.15−328.15	*a*, *d*
		d,*l*-Methionine[g]		
105.17 (0.12)	0.135 95 (0.009 37)	−0.001 36 (0.000 45)	278.15−328.15	*a*−*e*

[a] Millero *et al*. (1978). [b] Mishra and Ahluwalia (1984). [c] Jolicoeur *et al*. (1986). [d] Kikuchi *et al*. (1995). [e] Kharakoz *et al*. (1989). [f] Data for only *d*,*l*-methionine. [g] Data for *d*,*l*-methionine and *l*-methionine combined.

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