Supporting Information

Densities and speeds of sound of solutions of glycine, L-alanine and L-valine in aqueous ammonium dihydrogen phosphate at different temperatures

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Partial molar volume at infinite dilution

Partial molar volume at infinite dilution V_ϕ^o, is calculated by least squares fitting of apparent molar volume V_ϕ by using equation E1:

$$V_\phi = V_\phi^o + S_V^* m_A \quad \text{(E1)}$$

where S_V^* the experimental slope is the volumetric pair wise interaction coefficient or semi empirical solute-solute interaction parameter. The values of V_ϕ^o and S_V^* together with standard errors derived by least squares fitting of the V_ϕ values to Equation E1 are reported in Table S1

Partial molar volume of transfer

Transfer volume of amino acid from water to aqueous ADP solutions at infinite dilution have been calculated as

$$\Delta V_\phi^o = V_\phi^o \text{ (in aq. ADP) } - V_\phi^o \text{ (in water)} \quad \text{(E2)}$$

These values of ΔV_ϕ^0 are reported in Table S2.

Temperature dependent partial molar volume at infinite dilution

At infinite dilution, the variation of apparent molar volumes *i.e.* (V_ϕ^o) with the temperature can be expressed by the general polynomial equation as follows

$$V_\phi^o = a + b(T-T_{ref}) + c(T-T_{ref})^2 \quad \text{(E3)}$$

where T is the temperature in Kelvin, T_{ref} = 298.15 K. *a, b,* and *c* are the empirical constants.In aqueous ADP solutions, the value of these constants for amino acids are reported in Table S3. The V_ϕ^o values were also calculated by using empirical constants *A, B* and *C* reported in Table S3 of supporting information. In Table S3, we have also reported the standard deviations (σ) obtained from experimental V_ϕ^o and V_ϕ^o values obtained from empirical parameters using equations . The standard deviations (σ) are calculated as follows

$$\sigma = \left[\frac{\sum_{i=1}^{4} (x_{i,\exp} - x_{i,calc,eqn(4)})^2}{4-p} \right]^{1/2} \quad \text{(E4)}$$

where x stands for partial molar volume at infinite dilution and p is the number of adjustable parameters (p = 3 in this case).

The temperature dependence of apparent partial molar volume (V_ϕ^o) can be expressed in terms of the absolute temperature (T) by the following relation E5. The limiting apparent molar expansibilities are calculated as follows:

$$E_\phi^o = (\partial V_\phi^o / \partial T)_p = b + 2c(T-T_{ref}) \quad \text{(E5)}$$

The values of limiting apparent molar expansibilities E_ϕ^o are reported in Table S4.

Group contributions in amino acids

The separate contributions of polar (NH_3^+, COO^-) and non polar(CH_2) groups towards V_ϕ^o of amino acids in aqueous solutions of ADP is provided by the Equation E6, E7 and E8 as given below

$$V_\phi^o(CH_3) = 1.5V_\phi^o(CH_2) \quad \text{(E6)}$$

$$V_\phi^o(CH) = 0.5V_\phi^o(CH_2) \quad \text{(E7)}$$

These assumptions are used to carry out the linear regression analysis of V_ϕ^o as a function of n_C(number of carbon atoms) using relation

$$V_\phi^o = V_\phi^o(NH_3^+, COO^-) + n_C V_\phi^o(CH_2) \quad \text{(E8)}$$

where n_C is the number of carbon atoms in the alkyl side chain of the amino acids. The $V_\phi^o(NH_3^+, COO^-)$, the zwitterionic end groups and $V_\phi^o(CH_2-)$, the methylene group contributions at constant temperature is given by above equation. The mean contributions of CH– and CH_3– groups to V_ϕ^o of amino acids is characterized by the obtained values of $V_\phi^o(CH_2-)$. The contributions of other alkyl chains of the amino acids are calculated using Equations (E7) and (E8). The values are reported in Table S5.

Apparent partial molar isentropic compression

The variation of apparent molar isentropic compression $K_{\phi,s}$ with the molal concentration can be adequately represented by using equation

$$K_{\phi,s} = K_{\phi,s}^o + S_K^* m_A \quad \text{(E9)}$$

where $K_{\phi,s}^o$ is the apparent partial molar isentropic compression and S_K^* is the experimental slope indicative of solute–solute interactions. The value of $K_{\phi,s}^o$ and S_K^* together with standard errors derived by least squares fitting are reported in Table S6.

Apparentpartialmolar isentropic compression of transfer

The apparent partial molar isentropic compressions $\Delta K_{\phi,s}^o$ of each amino acid from water to aqueous ADP solutions at infinite dilution were calculated by using the equation:

$$\Delta K_{\phi,s}^o = K_{\phi,s}^o \text{(in aqueous ADP)} - K_{\phi,s}^o \text{(in water)} \quad \text{(E10)}$$

These values of $\Delta K_{\phi,s}^o$ are reported in Table S7.

Pair and triplet interaction coefficients

McMillan and Mayer[56] theory which was further discussed by Friedman and Krishnan[57] proposed a formalism to calculate the interaction coefficients, which permits the separation of effects due to interaction between the pair of solute molecules and those due to its interaction between two or more solute molecules. So, apparent partial molar volume of transfer and apparent partialmolar isentropic compression of transfer can be expressed as follows:

$$\Delta V_\phi^o \text{ (water to aqueous ADP solution)} = 2V_{AB} m_B + 3V_{ABB} m_B^2 \quad \text{(E11)}$$

$$\Delta K_{\phi,s}^o \text{ (water to aqueous ADP solution)} = 2K_{AB} m_B + 3K_{ABB} m_B^2 \quad \text{(E12)}$$

where *A* denotes amino acid, *B* denotes ADP and m_B is the molality of aqueous ADP solutions. The corresponding parameters V_{AB}, V_{ABB} for volume and K_{AB}, K_{ABB} for isentropic compression

denote pair and triplet interaction coefficients. These constants were calculated by fitting the ΔV_{ϕ}^{o} and $\Delta K_{\phi,s}^{o}$ values to the above equations and are reported in Table S8.

Table S1

Partial molar volumes, V_ϕ^o and experimental slopes, S_V^* of amino acids in aqueous solutions of ADP at different temperatures.

[a]m_B/ (mol·kg^{-1})	$V_\phi^o \times 10^6$ / (m^3·mol^{-1})				$S_V^* \times 10^6$ / (m^3·kg·mol^{-2})			
	T= 288.15 K	*T*= 298.15 K	*T*= 308.15 K	*T*= 318.15 K	*T*= 288.15 K	*T*= 298.15 K	*T*= 308.15 K	*T*= 318.15 K
				Glycine				
0.0	41.92[31]	42.62[31]	43.56[31]	44.38[31]				
0.5	44.55(±0.003)	44.87(±0.005)	45.14(±0.003)	45.38(±0.003)	3.74(±0.033)	3.82(±0.055)	3.85(±0.038)	3.88(±0.032)
1.0	45.78(±0.003)	46.05(±0.004)	46.31(±0.002)	46.63(±0.007)	3.71(±0.038)	3.68(±0.049)	4.42(±0.024)	4.20(±0.076)
1.5	47.00(±0.007)	47.21(±0.007)	47.43(±0.006)	47.74(±0.008)	3.75(±0.077)	3.83(±0.085)	3.97(±0.072)	4.03(±0.093)
2.0	48.24(±0.003)	48.43(±0.006)	48.62(±0.006)	48.88(±0.005)	4.21(±0.037)	3.89(±0.075)	4.26(±0.067)	4.39(±0.062)
				L- alanine				
0.0	58.99[31]	59.42[31]	59.97[31]	60.37[31]				
0.5	61.20(±0.002)	61.44(±0.005)	61.68(±0.008)	61.88(±0.005)	3.25(±0.028)	3.60(±0.059)	3.09(±0.092)	3.72(±0.054)
1.0	62.40(±0.004)	62.61(±0.003)	62.86(±0.007)	63.08(±0.004)	3.49(±0.045)	3.38(±0.031)	3.35(±0.077)	3.50(±0.051)
1.5	63.48(±0.002)	63.75(±0.003)	63.95(±0.003)	64.13(±0.003)	3.77(±0.024)	3.24(±0.035)	3.48(±0.037)	3.82(±0.033)
2.0	64.71(±0.006)	64.90(±0.007)	65.13(±0.004)	65.29(±0.003)	2.87(±0.069)	3.37(±0.054)	3.56(±0.045)	3.56(±0.031)
				L- valine				
0.0	89.47[31]	90.68[31]	91.30[31]	91.79[31]				
0.5	91.11(±0.008)	91.49(±0.006)	91.90(±0.005)	92.36(±0.004)	2.72(±0.097)	2.88(±0.071)	3.46(±0.060)	2.94(±0.046)
1.0	92.60(±0.007)	92.94(±0.004)	93.38(±0.004)	93.76(±0.003)	2.91(±0.079)	3.10(±0.048)	2.83(±0.044)	3.88(±0.031)
1.5	94.18(±0.011)	94.51(±0.003)	94.95(±0.004)	95.40(±0.006)	2.16(±0.128)	3.06(±0.037)	2.82(±0.042)	2.66(±0.074)
2.0	95.90(±0.004)	96.20(±0.004)	96.60(±0.006)	97.04(±0.007)	3.15(±0.046)	3.35(±0.046)	3.51(±0.071)	3.12(±0.082)

[a]m_B is the molality of aqueous solutions of ADP.

Table S2

Partial molar volume of transfer, ΔV_{ϕ}^{0} of amino acids in aqueous solutions of ADP at different temperatures.

[a]m_B/ (mol·kg^{-1})	$\Delta V_{\phi}^{0} \times 10^{6}$ (m^3·mol^{-1})			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
		Glycine		
0.5	2.63	2.25	1.58	1.00
1.0	3.86	3.43	2.75	2.25
1.5	5.08	4.59	3.87	3.36
2.0	6.32	5.81	5.06	4.50
		L- alanine		
0.5	2.21	2.02	1.71	1.51
1.0	3.41	3.19	2.89	2.71
1.5	4.49	4.33	3.98	3.76
2.0	5.72	5.48	5.16	4.92
		L- valine		
0.5	1.64	0.81	0.60	0.57
1.0	3.13	2.26	2.08	1.97
1.5	4.71	3.83	3.65	3.61
2.0	6.43	5.52	5.30	5.25

[a]m_B is the molality of aqueous solutions of ADP.

Table S3
Values of empirical parameters of Eq. (E3) and standard deviations (σ) for amino acids in aqueous ADP solutions.

[a]m_B / (mol·kg^{-1})	$A\times10^6$ / (m^3·mol^{-1})	$B\times10^6$ /(m^3·mol^{-1}·K^{-1})	$C\times10^6$/(m^3·mol^{-1}·K^{-2})	R^2	σ / (m^3·mol^{-1})
		Glycine			
0.5	44.87	0.030	-0.00019	0.9999	0.0003
1.0	46.04	0.027	0.00012	0.9999	0.0165
1.5	47.20	0.022	0.00024	0.9999	0.0199
2.0	48.42	0.019	0.00017	0.9999	0.0197
		L- alanine			
0.5	61.45	0.024	-0.00010	0.9999	0.0067
1.0	62.62	0.023	0.00010	0.9999	0.0145
1.5	63.75	0.024	-0.00022	0.9999	0.0113
2.0	64.92	0.021	-0.00007	0.9999	0.0240
		L- valine			
0.5	91.48	0.040	0.00021	0.9999	0.0056
1.0	92.97	0.039	0.00007	0.9999	0.0340
1.5	94.52	0.038	0.00030	0.9999	0.0231
2.0	96.21	0.035	0.00036	0.9999	0.0109

[a]m_B is the molality of aqueous solutions of ADP.

Table S4

Partial molar expansion E_ϕ^o for amino acids in aqueous ADP solutions at different temperatures.

[a]m_B / (mol·kg^{-1})	E_ϕ^o x10^6 / (m^3·mol^{-1}·K^{-1})			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
		Glycine		
0.5	0.0334	0.0295	0.0257	0.0218
1.0	0.0245	0.0270	0.0295	0.0320
1.5	0.0174	0.0222	0.0269	0.0316
2.0	0.0160	0.0194	0.0229	0.0263
		L- alanine		
0.5	0.0258	0.0238	0.0218	0.0199
1.0	0.0228	0.0229	0.0230	0.0231
1.5	0.0284	0.0238	0.0192	0.0146
2.0	0.0220	0.0205	0.0190	0.0175
		L- valine		
0.5	0.0355	0.0397	0.0438	0.0480
1.0	0.0371	0.0385	0.0400	0.0414
1.5	0.0321	0.0382	0.0443	0.0504
2.0	0.0273	0.0346	0.0418	0.0491

[a]m_B is the molality of aqueous solutions of ADP.

Table S5

Contributions to the partial molar volume from the zwitterionic groups (NH_3^+, COO^-), CH_2– groups and other alkyl chains of amino acids in aqueous solutions of ADP at different temperatures.

Groups	$V_\phi^o \times 10^6$ / ($m^3 \cdot mol^{-1}$)			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
		0.5 mol·kg^{-1} ADP		
(NH_3^+, COO^-)	29.60	29.84	30.03	30.14
$-CH_2-$	15.44	15.47	15.52	15.60
$-CH(CH_3)-$	30.88	30.94	31.04	31.20
$-CH(CH(CH_3)_2)-$	61.76	61.88	62.08	62.40
		1.0 mol·kg^{-1} ADP		
(NH_3^+, COO^-)	30.68	30.88	31.05	31.29
$-CH_2-$	15.53	15.56	15.63	15.66
$-CH(CH_3)-$	31.06	31.12	31.26	31.32
$-CH(CH(CH_3)_2)-$	62.12	62.24	62.52	62.64
		1.5 mol·kg^{-1} ADP		
(NH_3^+, COO^-)	31.65	31.83	31.93	32.10
$-CH_2-$	15.67	15.71	15.79	15.85
$-CH(CH_3)-$	31.34	31.42	31.58	31.70
$-CH(CH(CH_3)_2)-$	62.68	62.84	63.16	63.40
		2.0 mol·kg^{-1} ADP		
(NH_3^+, COO^-)	32.64	32.78	32.88	33.00
$-CH_2-$	15.85	15.88	15.96	16.03
$-CH(CH_3)-$	31.70	31.76	31.92	32.06
$-CH(CH(CH_3)_2)-$	63.40	63.52	63.84	64.12

Table S6

Partial molar isentropic compression, $K^{o}_{\phi,s}$ and experimental slopes, S^{*}_{K} for amino acids in aqueous solutions of ADP at different temperatures.

[a]m_B / (mol·kg^{-1})	$K^{o}_{\phi,s} \times 10^6$ /(m^3·mol^{-1}·GPa^{-1})				$S^{*}_{K} \times 10^6$ / (kg· m^3·mol^{-2}·GPa^{-1})			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
				Glycine				
0.0	-45.21[46]	-43.25[46]	-41.92[46]	-40.99[46]				
0.5	-41.27(±0.61)	-39.79(±0.59)	-38.71(±0.58)	-37.95(±0.57)	-22.40(±7.04)	-21.71(±6.83)	-21.25(±6.69)	-20.99(±6.61)
1.0	-39.48(±0.57)	-38.21(±0.55)	-37.28(±0.54)	-36.63(±0.54)	-19.96(±6.53)	-19.43(±6.36)	-19.07(±6.25)	-18.88(±6.19)
1.5	-38.02(±0.42)	-36.94(±0.41)	-36.14(±0.41)	-35.59(±0.40)	-16.56(±4.88)	-16.17(±4.77)	-15.93(±4.70)	-15.79(±4.66)
2.0	-36.48(±0.40)	-35.56(±0.39)	-34.88(±0.39)	-34.41(±0.38)	-15.42(±4.59)	-15.12(±4.50)	-14.93(±4.45)	-14.84(±4.42)
				L- alanine				
0.0	-44.51[46]	-42.92[46]	-41.61[46]	-40.68[46]				
0.5	-41.39(±0.58)	-39.90(±0.56)	-38.81(±0.55)	-38.05(±0.54)	-21.32(±6.63)	-20.67(±6.43)	-20.24(±6.30)	-19.99(±6.22)
1.0	-39.57(±0.52)	-38.30(±0.51)	-37.36(±0.50)	-36.71(±0.49)	-19.04(±6.01)	-18.54(±5.86)	-18.21(±5.76)	-18.03(±5.70)
1.5	-37.85(±0.49)	-36.76(±0.48)	-35.97(±0.47)	-35.42(±0.47)	-18.05(±5.68)	-17.64(±5.55)	-17.38(±5.47)	-17.24(±5.43)
2.0	-36.44(±0.43)	-35.48(±0.42)	-34.80(±0.42)	-34.34(±0.41)	-15.99(±4.94)	-15.67(±4.84)	-15.48(±4.78)	-15.39(±4.76)
				L- valine				
0.0	-43.88[46]	-41.96[46]	-40.66[46]	-39.75[46]				
0.5	-41.36(±0.58)	-39.87(±0.56)	-38.78(±0.55)	-38.03(±0.55)	-21.47(±6.71)	-20.81(±6.52)	-20.36(±6.38)	-20.12(±6.31)
1.0	-39.58(±0.50)	-38.31(±0.48)	-37.38(±0.47)	-36.73(±0.47)	-18.64(±5.71)	-18.15(±5.55)	-17.82(±5.47)	-17.64(±5.42)
1.5	-37.98(±0.44)	-36.89(±0.43)	-36.10(±0.43)	-35.55(±0.42)	-16.63(±5.12)	-16.25(±5.01)	-16.01(±4.93)	-15.88(±4.96)
2.0	-36.44(±0.40)	-35.52(±0.40)	-34.84(±0.40)	-34.38(±0.40)	-15.38(±4.76)	-15.08(±4.67)	-14.90(±4.62)	-14.81(±4.59)

[a]m_B is the molality of aqueous solutions of ADP.

Table S7

Partial molar isentropic compression of transfer $\Delta K_{\phi,s}^{o}$ of amino acids in aqueous solution of ADP at different temperatures.

[a]m_B / (mol·kg^{-1})	$\Delta K_{\phi,s}^{o} \times 10^6$ (m^3·mol^{-1}·GPa^{-1})			
	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
		Glycine		
0.5	3.94	3.46	3.21	3.04
1.0	5.73	5.04	4.64	4.36
1.5	7.19	6.31	5.78	5.40
2.0	8.73	7.69	7.04	6.58
		L- alanine		
0.5	3.12	3.02	2.80	2.63
1.0	4.94	4.62	4.25	3.97
1.5	6.66	6.16	5.64	5.26
2.0	8.07	7.44	6.81	6.34
		L- valine		
0.5	2.52	2.09	1.88	1.72
1.0	4.30	3.65	3.28	3.02
1.5	5.90	5.07	4.56	4.20
2.0	7.44	6.44	5.82	5.37

[a]m_B is the molality of aqueous solutions of ADP.

Table S8

Pair and triplet interaction coefficients of amino acids in aqueous solutions of ADP at different temperatures.

T / (K)	$V_{AB} \times 10^6$ / ($m^3 \cdot mol^{-2} \cdot kg$)	$V_{ABB} \times 10^6$ / ($m^3 \cdot mol^{-3} \cdot kg^2$)	$K_{AB} \times 10^6$ / ($m^3 \cdot mol^{-2} \cdot kg \cdot GPa^{-1}$)	$K_{ABB} \times 10^6$ / ($m^3 \cdot mol^{-3} \cdot kg^2 \cdot GPa^{-1}$)
		Glycine		
288.15	2.45	-0.30	3.75	-0.54
298.15	2.10	-0.22	3.29	-0.47
308.15	1.52	-0.09	3.04	-0.44
318.15	1.07	-0.02	2.87	-0.43
		L- alanine		
288.15	2.07	-0.22	3.08	-0.36
298.15	1.92	-0.19	2.94	-0.37
308.15	1.65	-0.12	2.71	-0.35
318.15	1.49	-0.09	2.54	-0.33
		L- valine		
288.15	1.55	0.02	2.50	-0.22
298.15	0.82	0.19	2.08	-0.16
308.15	0.66	0.23	1.87	-0.14
318.15	0.60	0.25	1.71	-0.13