Apparent Molar Volumes of L-Glycine, L-Alanine, and L-Serine in Water + Dimethylformamide Mixtures at 298.15 K

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Densities of L-glycine, L-alanine, and L-serine have been measured with an oscillating-tube densimeter at 298.15 K in water + dimethylformamide (DMF) mixtures ranging from pure water to 45% DMF by mass. From these densities, apparent molar volumes and limiting apparent molar volumes of the three amino acids in the mixtures have been calculated. Transfer volumes were interpreted in terms of the structure-making or structure-breaking effects of these amino acids in the mixtures.

Introduction

Amino acids are monomers that constitute proteins and are considered to be the model compounds of proteins. There are extensive volumetric and thermochemical property studies of aqueous amino acid systems, but few in aqueous mixed solvents (Jolicoeur et al., 1986; Belibagli and Ayranci, 1990; Wadi and Goyal, 1992). Water + dimethylformamide (DMF) mixtures have proved to be the most interesting owing to the strong hydrogen-bond interactions of DMF with water. The present work reports the apparent molar volumes of some amino acids in H_2O + DMF mixtures.

Experimental Section

Analytical reagent grade L-glycine, L-alanine, and L-serine were recrystallized two times from ethanol + water mixtures. The materials were used after drying at 100 °C for 6 h and then in vacuo over silica gel at room temperature for a minimum of 24 h. Analytical reagent grade DMF was dried by storage over 0.4 nm molecular sieves for 2 days and then was distilled under reduced pressure. The refracting prism of the collected cut was $n_D^{25} = 1.4282$ (1.428 17 in the work of Riddick and Bunger (1970)). Freshly prepared twice-distilled water was used in all experiments. H_2O + DMF mixtures were prepared by mass. The mass percentage of DMF in these mixtures ranged in 10% increments from 5% to 45%. Solutions of amino acids were made by mass on the molality concentration scale. They were stored in sealable vials prior to use. Uncertainties in solution concentrations were estimated at ±0.000 02 mol·kg^{-1} in calculations.

The sample densities were measured with an Anton Paar DMA 55 densimeter thermostated to better than ±0.01 °C. The temperature inside the densimeter cell was monitored with an Anton Paar DT 100−20 digital thermometer. The densimeter was calibrated with twice-distilled water and dry air. The accuracy of density values was $\pm 10^{-5}$ g·cm^{-3}. The density of pure water at 298.15 K was taken as 0.997 05 g·cm^{-3} (Kell, 1975).

Results and Discussion

Densities for solutions of L-glycine, L-serine, and L-alanine in H_2O + DMF mixtures are shown in Tables 1−3. For the variation of densities of H_2O + DMF mixtures with DMF content, the result obtained in this work is in good agreement with those of Chittleborough et al. (1988) and Chu et al. (1990). Our measured density of pure DMF is 0.944 01, the density in the work of Chu et al. (1990) is 0.944 061, and it is 0.943 89 in the work of Chittleborough et al. (1988). Apparent molar volumes V_ϕ are calculated from these data using the equation (Millero, 1972)

$$V_\phi = \frac{1}{m}\left[\frac{1000 + mM}{d} - \frac{1000}{d_0}\right] \quad (1)$$

where m is the molality, M is the molecular weight of solute, and d_0 and d are the densities of solvent and solute, respectively. Calculated apparent molar volumes for amino acids are also listed in Tables 1−3. The results can be fitted by the equation

$$V_\phi = V_\phi^\circ + b_v m \quad (2)$$

where V_ϕ° is the apparent molar volume at infinite dilution and b_v is an experimentally determined parameter.

V_ϕ° and b_v values of eq 2 have been evaluated by the least-squares method and are listed in Table 4.

The agreement between V_ϕ° values in water obtained in this work and those reported in the literature is good (for L-serine, in Yang et al. (1993), Jolicoeur and Boileau (1978); for L-alanine, in Dipaola and Belleau (1978), Wadi and Goyal (1992); for L-glycine, in Belibagli and Ayranci (1990), Yang et al. (1993)).

Transfer volumes of amino acids, ΔV_ϕ° from H_2O to H_2O + DMF mixtures are calculated from

$$\Delta V_\phi^\circ(H_2O \rightarrow H_2O + DMF) = V_\phi^\circ(\text{in } H_2O + DMF) - V_\phi^\circ(\text{in } H_2O) \quad (3)$$

The results are illustrated in Figure 1.

It can be found that transfer volumes of L-glycine are positive and increase with increasing DMF content in mixed solvent. This suggests that L-glycine is a structure breaker in H_2O + DMF mixtures. This structure-breaking effect increases with increasing DMF content in mixed solvents.

Up to 40 mass % of DMF, transfer volumes of L-alanine are negative, first decreasing to a minimum and then increasing rapidly. This indicates that L-alanine is an

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S0021-9568(98)00008-9 CCC: $15.00
Published on Web 07/11/1998

Table 1. Densities and Apparent Molar Volumes of L-Glycine in Water + DMF Mixtures at 298.15 K

m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}
	Gly + H_2O			Gly + 5% DMF			Gly + 15% DMF	
0	0.997 05		0	0.996 45		0	0.996 20	
0.024 94	0.997 86	42.59	0.007 38	0.996 69	42.57	0.007 45	0.996 44	42.89
0.051 32	0.998 71	42.68	0.010 16	0.996 78	42.61	0.010 25	0.996 53	42.90
0.075 14	0.999 47	42.79	0.025 26	0.997 27	42.61	0.025 20	0.997 01	42.93
0.101 21	1.000 29	42.95	0.050 32	0.998 06	43.04	0.050 38	0.997 80	43.29
0.124 58	1.001 03	42.98	0.075 11	0.998 85	43.05	0.075 23	0.998 58	43.37
0.150 38	1.001 83	43.11	0.100 96	0.999 66	43.18	0.101 10	0.999 38	43.52
0.203 62	1.003 46	43.35	0.124 13	1.000 37	43.36	0.125 09	1.000 10	43.77
	Gly + 25% DMF			Gly + 35% DMF			Gly + 45% DMF	
0	0.996 61		0	0.997 00		0	0.996 73	
0.007 51	0.996 85	43.14	0.007 35	0.997 23	43.80	0.007 69	0.996 95	46.51
0.010 03	0.996 93	43.19	0.010 24	0.997 32	43.84	0.010 14	0.997 02	46.52
0.025 18	0.997 41	43.30	0.025 05	0.997 78	43.94	0.025 13	0.997 45	46.44
0.050 22	0.998 19	43.58	0.050 21	0.998 54	44.37	0.050 09	0.998 17	46.31
0.075 19	0.998 96	43.76	0.075 15	0.999 29	44.54	0.075 21	0.998 89	46.31
0.100 86	0.999 74	43.94	0.100 55	1.000 04	44.74	0.100 73	0.999 62	46.30
0.125 11	1.000 46	44.17	0.123 68	1.000 70	45.03	0.127 31	1.000 39	46.21

Table 2. Densities and Apparent Molar Volumes of L-Serine in Water + DMF Mixtures at 298.15 K

m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}
	Ser + H_2O			Ser + 5% DMF			Ser + 15% DMF	
0	0.997 05		0	0.996 45		0	0.996 22	
0.010 09	0.997 50	60.51	0.010 07	0.996 90	60.43	0.010 11	0.996 67	60.61
0.025 08	0.998 17	60.41	0.025 11	0.997 57	60.47	0.025 19	0.997 34	60.62
0.050 23	0.999 29	60.41	0.050 42	0.998 69	60.58	0.050 29	0.998 44	60.87
0.075 25	1.000 41	60.28	0.075 78	0.999 81	60.60	0.075 58	0.999 54	61.02
0.100 99	1.001 56	60.21	0.101 28	1.000 93	60.64	0.100 93	1.000 63	61.19
0.126 53	1.002 70	60.14	0.126 57	1.002 02	60.80	0.126 67	1.001 74	61.24
			0.153 09	1.003 16	60.91			
	Ser + 25% DMF			Ser + 35% DMF			Ser + 45%DMF	
0	0.996 60		0	0.997 01		0	0.996 72	
0.024 99	0.997 69	61.47	0.025 00	0.998 08	62.28	0.009 99	0.997 13	64.10
0.050 39	0.998 79	61.56	0.050 21	0.999 15	62.39	0.025 18	0.997 75	64.19
0.075 63	0.999 87	61.71	0.075 36	1.000 21	62.49	0.050 30	0.998 77	64.28
0.100 96	1.000 95	61.80	0.100 59	1.001 26	62.63	0.075 52	0.999 78	64.45
0.126 68	1.002 04	61.87	0.126 37	1.002 33	62.72	0.101 02	1.000 80	64.52
0.152 34	1.003 12	61.95	0.151 93	1.003 38	62.82	0.126 62	1.001 81	64.64

Table 3. Densities and Apparent Molar Volumes of L-Alanine in Water + DMF Mixtures at 298.15 K

m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	d/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}
	Ala + H_2O			Ala + 5% DMF			Ala + 15% DMF	
0	0.997 05		0	0.996 45		0	0.996 22	
0.007 41	0.997 26	60.84	0.005 01	0.996 60	59.25	0.002 50	0.996 30	57.19
0.009 90	0.997 33	60.90	0.007 36	0.996 67	59.30	0.004 81	0.996 37	58.01
0.025 16	0.997 77	60.53	0.010 04	0.996 75	59.31	0.007 39	0.996 45	58.06
0.050 21	0.998 49	60.43	0.025 14	0.997 20	59.33	0.009 77	0.996 52	58.48
0.074 95	0.999 22	60.11	0.050 19	0.997 92	59.83	0.024 33	0.996 96	58.75
0.101 51	1.000 01	59.85	0.075 28	0.998 65	59.85	0.048 88	0.997 67	59.46
0.123 27	1.000 67	59.61	0.100 93	0.999 38	60.00	0.075 34	0.998 44	59.61
			0.126 59	1.000 08	60.32	0.097 99	0.999 08	59.86
						0.123 81	0.999 72	60.74
						0.146 54	1.000 28	61.27
	Ala + 25% DMF			Ala + 35% DMF			Ala + 45% DMF	
0	0.996 62		0	0.997 00		0	0.996 71	
0.007 50	0.996 86	57.17	0.007 52	0.997 22	59.92	0.007 37	0.996 91	62.07
0.009 98	0.996 93	58.11	0.009 92	0.997 29	59.94	0.009 95	0.996 98	62.06
0.025 14	0.997 38	58.92	0.025 11	0.997 73	60.08	0.025 07	0.997 39	62.05
0.050 23	0.998 09	59.85	0.050 23	0.998 45	60.24	0.050 19	0.998 07	62.03
0.075 02	0.998 70	61.36	0.075 44	0.999 15	60.57	0.075 72	0.998 76	62.01
0.100 91	0.999 27	62.80	0.100 81	0.999 86	60.65	0.100 89	0.999 44	61.99
0.127 11	0.999 78	64.17	0.126 73	1.000 56	60.89			

effective structure maker in the region of rich water. The minimum in ΔV_ϕ° values at 25 mass % of DMF indicates maximum making of the solvent structure on addition of L-alanine. After 40 mass % of DMF, the transfer values become positive, indicating the structure-breaking effect of L-alanine in the region of rich DMF.

When the concentration of DMF is lower than 15 mass %, the variation of L-serine transfer volumes with DMF content is the same as that of L-alanine in the range 0−40 mass % of DMF, but the values are very small (Figure 1). This indicates the weaker structure-making effect by L-serine in this region. Maximum structure making of L-serine appears at 5 mass % of DMF. But as compared with L-alanine, the latter is a more effective structure maker.

When the concentration of DMF is equal to or higher than 15 mass %, the variation of L-serine transfer volumes with DMF content is the same as that of L-glycine. This indicates that L-serine is a structure breaker in this region. It is found that in the range 20−40 mass % of DMF,

Table 4. V_ϕ° and b_v Values for Amino Acids in Water + DMF Mixtures at 298.15 K

mass % DMF	V_ϕ°/cm^3·mol^{-1}	b_v/cm^3·mol^{-2}·kg	V_ϕ°/cm^3·mol^{-1}	b_v/cm^3·mol^{-2}·kg	V_ϕ°/cm^3·mol^{-1}	b_v/cm^3·mol^{-2}·kg
	L-Gly		L-Ala		L-Ser	
0	42.48 (0.02)[a]	4.26 (0.16)	60.92 (0.04)	−10.64 (0.63)	60.53 (0.02)	−3.07 (0.29)
5	42.54 (0.06)	6.75 (0.78)	59.22 (0.05)	8.49 (0.75)	60.39 (0.03)	3.17 (0.31)
15	42.82 (0.04)	7.42 (0.54)	57.90 (0.17)	22.98 (2.28)	60.54 (0.04)	6.01 (0.55)
25	43.10 (0.02)	8.59 (0.26)	57.25 (0.19)	54.72 (2.64)	61.39 (0.02)	3.84 (0.25)
35	43.74 (0.04)	10.47 (0.54)	59.87 (0.03)	8.15 (0.41)	62.17 (0.01)	4.31 (0.12)
45	46.51 (0.03)	−2.42 (0.38)	62.07 (0.00)	−0.81 (0.03)	64.06 (0.02)	4.61 (0.22)

[a] Entries in parentheses are the standard errors on each coefficient.

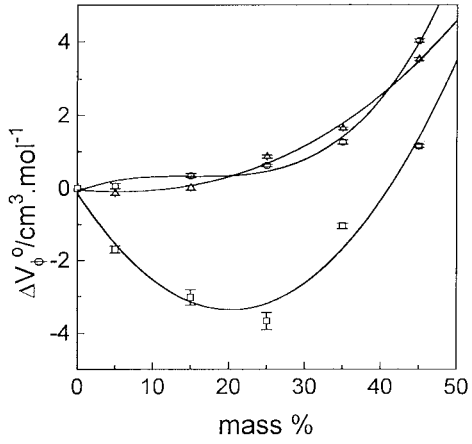

Figure 1. Transfer volumes ΔV_ϕ° of amino acids against mass % of DMF at 298.15 K: (○) L-Gly, (△) L-Ser, (□) L-Ala.

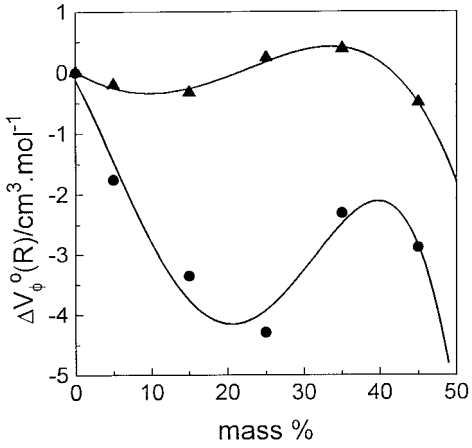

Figure 2. Contribution of R groups to transfer volumes ΔV_ϕ°(R) against mass % of DMF at 298.15 K: (▲) L-Ser, (●) L-Ala.

L-serine is even more effective as a structure breaker than L-glycine.

It is of interest to examine the contribution of R groups on the α-carbon of amino acids to transfer volumes. For this purpose, the V_ϕ° of L-glycine was subtracted from that of the other two amino acids

$$V_\phi^\circ(\mathrm{R}) = V_\phi^\circ(\text{amino acids}) - V_\phi^\circ(\text{glycine}) \qquad (4)$$

where V_ϕ°(R) is the R group contribution to V_ϕ°. In this calculation, it is being assumed that the volume contribution of −H in L-glycine can be neglected. The results are shown in Figure 2.

It can be seen that contributions of $-CH_3$ of L-alanine to transfer volumes are significant and negative. This indicates that $-CH_3$ is closely related to the structure making of L-alanine in H_2O−DMF mixtures. At 25 mass % of DMF, the ΔV_ϕ° ($-CH_3$) value is maximum, and the structure making of L-alanine is also maximum. The contributions of $-CH_2OH$ of L-serine to transfer volumes are smaller. In the range 20−40 mass % of DMF, the ΔV_ϕ° ($-CH_2OH$) values are positive, indicating that L-serine has stronger structure-breaking effect than L-glycine.

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Received for review January 20, 1998. Accepted May 1, 1998. This work was supported by the National Natural Science Foundation of China No. 29773041.

JE980008C