

Apparent molar volumes and viscosity *B*-coefficients of some α -amino acids in aqueous solutions from 278.15 to 308.15 K

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Received 1 February 1998; received in revised form 5 May 1999; accepted 7 May 1999

Abstract

Viscosities and densities of aqueous solutions of glycine, DL-alanine, DL- α -amino-*n*-butyric acid, DL-valine, DL-leucine and L-serine have been measured as a function of amino acid concentration at 278.15, 288.15, 298.15 and 308.15 K. These data have been used to calculate the apparent molar volumes $V_{2,\phi}$ and viscosity *B*-coefficients. The calculated standard partial molar volumes $V_{2,\phi}^0$ and *B*-values were split into the contributions from the (NH₃⁺,COO⁻) and CH₂ groups by linear correlations. Free energies of activation, $\Delta\mu_2^{0\ddagger}$, of aqueous amino acids were obtained by application of the transition-state theory to the *B*-coefficient data, and the corresponding activation enthalpy $\Delta H_2^{0\ddagger}$ and entropy $\Delta S_2^{0\ddagger}$ were also given. On the basis of the contributions of (NH₃⁺, COO⁻) and CH₂ groups to $V_{2,\phi}^0$, *B*-coefficient and the activation parameters, comments on the effect of amino acids and their groups on the structure of water and the relative orderness of the ground and the transition state of these solutions have been made. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Viscosity *B*-coefficient; Apparent molar volume; α -Amino acid; Group additivity; Activation parameters

1. Introduction

Data on the thermodynamic and transport properties of amino acids in aqueous phase play a key role in the optimization and design of both the currently used and proposed industrial processes of biochemistry. On the other hand, amino acids have been quite useful as models for understanding the thermodynamic behaviour and the state of solvation of peptides and proteins in solution, especially in deriving simple additivity schemes for the prediction of the properties of biochemical systems.

Viscosity and apparent molar volume have been proven to be sensitive and accurate methods in solu-

tion studies [1]. The volumetric property of aqueous amino acid systems have been studied by a number of workers. Although there are some measurements of volumetric data for some amino acids as a function of temperature [2–10], viscosity data are extremely limited.

In the present work, densities and viscosities were measured for aqueous amino acids solutions as a function of temperature. These data were used to calculate the infinite-dilution apparent molar volumes $V_{2,\phi}^0$ and viscosity *B*-coefficients for the amino acids. The amino acids chosen in this work were glycine (Gly), DL- α -alanine (Ala), DL- α -amino-*n*-butyric acid (Abu), DL-valine (Val), DL-leucine (Leu) and L-serine (Ser). The use of the first five amino acids permits individual estimations of the zwitterionic end groups (NH₃⁺, COO⁻) and the CH₂ group contributions to

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$V_{2,\phi}^0$ and B -coefficient. L-serine was chosen to calculate the contribution of OH group in the alkyl chain of the amino acids. In addition, the thermodynamic activation parameters of the viscous flow for the amino acids and their groups in water are also given at different temperatures. Based on the transition-state theory, the activation parameters are discussed in terms of solute–solvent interactions and of solvent structure in ground and transition states.

2. Experimental

Glycine (Shanghai Chem.), DL- α -alanine (Shanghai Chem.), DL- α -amino-*n*-butyric acid (Shanghai Chem.), DL-valine (Fluka), DL-leucine (Baker) and L-serine (Beijing Chem.) were recrystallized twice from aqueous ethanol solutions as described by Jolicoeur et al., [11], and dried under vacuum at 348 K for 6 h. Thereafter, they were stored over P₂O₅ in a desiccator before use. Water of conductivity 1.2 $\mu\Omega^{-1} \text{cm}^{-1}$ was obtained by distilling deionized water from alkaline KMnO₄ to remove any organic matter. All solution were prepared freshly by weighing on the molarity scale.

Solution densities were measured to $\pm 3 \times 10^{-6} \text{g cm}^{-3}$ with an Anton Paar DMA 60/602 vibrating-tube digital densimeter that was calibrated at each investigated temperature using dry air and conductivity water daily. The densities of pure water at 278.15, 288.15, 298.15 and 308.15 K were taken from Kell's data [12].

Viscosity measurements were made with a suspended level Ubbelohde Viscometer which has a flow time of ca. 200 s for water at 298.15 K. The viscometer was calibrated at 278.15 and 308.15 K with water. The viscosities for water at different temperatures were taken from literature [13]. Flow-time measurements were performed using a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. Viscosity of solution, η , is given by the following equation

$$\eta/\rho = Ct - K/t \quad (1)$$

where ρ is the solution density, t the flow time, and C and K are the cell constants.

The densimeter and viscometer were thermostated using Schott thermostat units which have a thermal

stability of $\pm 0.005 \text{K}$. A thermistor probe was used to monitor the temperature of the density meter cell.

3. Results and discussion

The density (g cm^{-3}) data measured for the aqueous amino acid solutions at 278.15, 288.15, 298.15 and 308.15 K are given in Table 1. The apparent molar volumes were calculated as

$$V_{2,\phi} = M/\rho - 10^3(\rho - \rho_0)/m\rho\rho_0 \quad (2)$$

where m is the molality of amino acid in water, M the molar mass of amino acid, ρ and ρ_0 the densities of the solution and water, respectively. The reported apparent molar volume data were found to be adequately represented by the linear equation

$$V_{2,\phi} = V_{2,\phi}^0 + S_v m \quad (3)$$

where $V_{2,\phi}^0$ is the infinite-dilution, apparent molar volume that has the same meaning as the standard partial molar volume, and S_v the experimental slope. The error in a solution molality is low (typically 0.03%) and its contribution to the uncertainty in $V_{2,\phi}$ is much smaller than that arising from the error in density. Considering only the error in density, the uncertainty $\delta V_{2,\phi}$ was calculated using:

$$\delta V_{2,\phi} = -(M + 1000/m)\delta\rho/\rho^2 \quad (4)$$

where $\delta\rho$ is the uncertainty in the solution density ($3 \times 10^{-6} \text{g cm}^{-3}$). Weighting factors, inversely proportional to $\delta V_{2,\phi}^2$ were included in the least-squares analysis. Eq. (3) was fitted to our calculated $V_{2,\phi}$ data (Table 1) using weighted least-squares regression analysis [14]. In those cases, where there was no dependence on m , $V_{2,\phi}^0$ was calculated by taking an average of all the data points. The obtained $V_{2,\phi}^0$ values for the amino acids at different temperatures are summarized, along with their standard deviations, and compared with available literature data [6,9,10,15–17] in Table 2. It can be seen that the obtained $V_{2,\phi}^0$ values for glycine, DL- α -alanine, DL- α -aminobutyric acid at 288.15 and 298.15 K, and L-serine at 298.15 K are generally in agreement with the literature values, considering the discrepancy of the published data from different sources, except for glycine at 278.15 and 308.15 K, DL- α -alanine at 308.15 K and L-serine at 288.15 K. We are unable to give a satisfactory

Table 1

Densities ρ and apparent molar volumes $V_{2,\phi}$ for aqueous amino acids solutions as functions of temperature and molarity of amino acid

278.15 K			288.15 K			298.15 K			308.15 K		
$m/$ (mol kg ⁻¹)	$\rho/$ (g cm ⁻³)	$V_{2,\phi}/$ (cm ³ mol ⁻¹)	$m/$ (mol kg ⁻¹)	$\rho/$ (g cm ⁻³)	$V_{2,\phi}/$ (cm ³ mol ⁻¹)	$m/$ (mol kg ⁻¹)	$\rho/$ (g cm ⁻³)	$V_{2,\phi}/$ (cm ³ mol ⁻¹)	$m/$ (mol kg ⁻¹)	$\rho/$ (g cm ⁻³)	$V_{2,\phi}/$ (cm ³ mol ⁻¹)
<i>Glycine</i>											
0.0000	0.999964	—	0.0000	0.999101	—	0.0000	0.997045	—	0.0000	0.994030	—
0.02973	1.000958	41.57	0.03220	1.000146	42.49	0.03099	0.998018	43.58	0.03220	0.995038	43.76
0.06101	1.001969	42.10	0.05964	1.001008	42.98	0.07072	0.999293	43.18	0.05964	0.995858	44.42
0.1013	1.003288	41.91	0.1003	1.002312	42.88	0.1080	1.000403	43.83	0.1003	0.997108	44.31
0.1520	1.004981	41.86	0.1511	1.003942	42.82	0.1551	1.001899	43.59	0.1511	0.998680	44.17
0.2005	1.006549	41.94	0.2043	1.005638	42.81	0.2039	1.003401	43.65	0.2043	1.000296	44.20
0.2519	1.008247	41.84	0.2571	1.007301	42.83	0.2732	1.005532	43.66	0.2571	1.001904	44.18
0.3023	1.009847	41.96	0.3024	1.008731	42.81	0.3137	1.006753	43.73	0.3024	1.003270	44.18
0.3533	1.011528	41.86	0.3479	1.010142	42.86	0.3639	1.008283	43.73	0.3479	1.004637	44.19
—	—	—	0.4457	1.013074	43.06	0.4048	1.009618	43.77	0.4457	1.007532	44.26
—	—	—	—	—	—	0.4937	1.012146	43.85	—	—	—
<i>DL-Alanine</i>											
0.02996	1.000841	59.77	0.03163	1.000020	59.88	0.03163	0.997957	60.23	0.03163	0.994923	60.99
0.05979	1.001755	59.02	0.05831	1.000801	59.80	0.05830	0.998714	60.14	0.05830	0.995635	61.65
0.1005	1.002930	59.39	0.1044	1.002085	60.31	0.1044	0.999965	61.01	0.1044	0.996906	61.55
0.1513	1.004409	59.43	0.1508	1.003440	60.06	0.1508	1.001290	60.75	0.1508	0.9982.07	61.31
0.2024	1.005886	59.47	0.2033	1.004930	60.08	0.2033	1.002753	60.75	0.2023	0.999658	61.25
0.2425	1.007237	59.51	0.2401	1.005954	60.15	0.2401	1.003715	60.84	0.2401	1.000634	61.37
0.3001	1.008699	59.46	0.2933	1.007442	60.16	0.2933	1.005212	60.84	0.2933	1.002082	61.34
0.3527	1.010176	59.52	0.3718	1.009619	60.18	0.3718	1.007344	60.85	0.3718	1.004119	61.34
—	—	—	0.4047	1.010506	60.24	0.4047	1.008224	60.88	0.4047	1.005064	61.35
<i>DL-Aminobutyric acid</i>											
0.03102	1.000845	74.64	0.03102	0.999969	75.31	0.03102	0.997887	75.99	0.03102	0.994862	76.53
0.05947	1.001650	74.64	0.05947	1.000783	74.69	0.05947	0.998661	75.94	0.05947	0.995640	76.21
0.09987	1.002807	74.44	0.09987	1.001890	74.99	0.09987	0.999790	75.55	0.09987	0.996743	76.03
0.1508	1.004268	74.26	0.1508	1.003270	75.19	0.1508	1.001157	75.67	0.1508	0.998102	76.10
0.2041	1.005766	74.26	0.2041	1.004719	75.19	0.2041	1.002547	75.85	0.2041	0.999472	76.33
0.2510	1.007076	74.26	0.2510	1.006002	75.14	0.2510	1.003807	75.80	0.2510	1.000707	76.30
0.3002	1.008420	74.32	0.3002	1.007313	75.18	0.3002	1.005079	75.88	0.3002	1.002009	76.23
0.3519	1.009869	74.24	0.3519	1.008708	75.13	0.3519	1.006503	75.67	0.3519	1.003363	76.18
<i>DL-Valine</i>											
0.03098	1.000802	90.01	0.03052	0.999930	89.86	0.03052	0.997862	90.43	0.03052	0.994812	91.84
0.05732	1.001507	90.09	0.05587	1.000618	89.87	0.05587	0.998527	90.65	0.05587	0.995483	91.39
0.09971	1.002680	89.67	0.09970	1.001756	90.30	0.09970	0.999627	91.19	0.09969	0.996555	91.99

Table 1 (Continued)

278.15 K			288.15 K			298.15 K			308.15 K		
m/ (mol kg ⁻¹)	ρ / (g cm ⁻³)	$V_{2,\phi}$ / (cm ³ mol ⁻¹)	m/ (mol kg ⁻¹)	ρ / (g cm ⁻³)	$V_{2,\phi}$ / (cm ³ mol ⁻¹)	m/ (mol kg ⁻¹)	ρ / (g cm ⁻³)	$V_{2,\phi}$ / (cm ³ mol ⁻¹)	m/ (mol kg ⁻¹)	ρ / (g cm ⁻³)	$V_{2,\phi}$ / (cm ³ mol ⁻¹)
0.1511	1.004059	89.69	0.1473	1.003009	90.29	0.1473	1.000916	90.69	0.1473	0.997780	91.73
0.2010	1.005400	89.63	0.1939	1.004251	90.16	0.1939	1.002058	91.01	0.1399	0.998961	91.65
0.2542	1.006840	89.48	0.2526	1.005756	90.24	0.2526	1.003551	90.98	0.2526	1.000428	91.63
0.3097	1.008316	89.44	0.3034	1.009067	90.22	0.3034	1.004837	90.94	0.3034	1.001668	91.67
0.3485	1.009304	89.52	0.3385	1.007990	90.14	0.3385	1.005725	90.91	0.3385	1.002575	91.52
—	—	—	0.3666	1.008665	90.25	0.3666	1.006384	91.02	0.3666	1.003186	91.73
—	—	—	0.3982	1.009746	90.20	0.3982	1.007180	90.96	0.3982	1.004000	91.59
—	—	—	0.4483	1.011582	90.25	0.4483	1.009238	91.00	0.4483	1.006007	91.67
<i>DL-Leucine</i>											
0.03123	1.000757	105.63	0.03162	0.999878	106.42	0.03162	0.997798	107.39	0.03162	0.994737	109.18
0.04287	1.001037	105.97	0.04287	1.000132	106.95	0.04287	0.998046	107.85	0.04287	0.995002	108.84
0.04502	1.001078	106.23	0.04669	1.000202	107.41	0.04669	0.998111	108.37	0.4669	0.995102	108.53
0.05219	1.001264	106.06	0.05219	1.000351	107.04	0.05219	0.998285	107.95	0.05219	0.995210	108.88
0.06061	1.001464	106.20	0.05419	1.000384	107.32	0.05419	0.998329	107.48	0.05419	0.995386	109.13
0.06112	1.001488	106.02	0.06069	1.000553	107.18	0.06069	0.998411	108.68	0.06112	0.995403	109.01
0.07032	1.001716	106.01	0.06112	1.000558	107.14	0.06112	0.998450	108.19	0.07032	0.995606	109.11
0.07634	1.001832	106.45	0.07032	1.000776	107.14	0.07032	0.998655	108.26	0.08050	0.995857	109.34
0.08050	1.001958	106.13	0.07451	1.000849	107.50	0.07451	0.998738	108.44	0.08624	0.995944	109.22
0.08103	1.001990	105.89	0.08050	1.001017	107.14	0.08050	0.998883	108.31	—	—	—
0.08624	1.002085	106.29	0.08624	1.001135	107.35	0.08624	0.999012	108.31	—	—	—
<i>L-Serine</i>											
0.02966	1.001264	59.18	0.02953	1.000429	59.93	0.02953	0.998349	60.81	0.02953	0.995311	61.73
0.06519	1.002818	59.16	0.05602	1.001609	60.13	0.05602	0.999527	60.64	0.05602	0.996429	62.22
0.1007	1.004520	59.57	0.1004	1.003529	60.68	0.1004	1.001444	61.02	0.1004	0.998309	62.29
0.1519	1.006826	59.50	0.1640	1.006354	60.42	0.1640	1.004232	60.87	0.1640	1.001034	62.06
0.2039	1.009142	59.53	0.1990	1.007865	60.52	0.1990	1.005655	61.34	0.1990	1.002500	62.12
0.2524	1.011312	59.45	0.2507	1.010120	60.46	0.2507	1.007840	61.41	0.2507	1.004673	62.08
0.3016	1.013500	59.40	0.3001	1.012230	60.55	0.3001	1.009939	61.38	0.3001	1.006702	62.20
0.3506	1.015667	59.36	0.3520	1.014410	60.68	0.3520	1.012071	61.53	0.3520	1.008870	62.13
—	—	—	0.4019	1.016541	60.65	0.4019	1.014524	61.53	0.4019	1.010903	62.18

Table 2

The infinite-dilution apparent molar volume $V_{2,\phi}^0$ for aqueous amino acids solutions at 278.15, 288.15, 298.15 and 308.15 K using Eq. (3)

Amino acid	$V_{2,\phi}^0/(\text{cm}^3 \text{ mol}^{-1})$			
	278.15 K	288.15 K	298.15 K	308.15 K
Glycine	41.9(0.1) [41.07 ^b]	42.6(0.1) [42.56 ^c]	43.5(0.1) [43.39 ^d]	44.2(0.1) [43.81 ^b]
DL-Alanine	59.4(0.1)	60.0(0.1) [60.10 ^c]	60.7(0.2) [62.62 ^d]	61.4(0.1) [61.06 ^c]
DL-Aminobutyric acid	74.4(0.1)	75.1(0.1) [75.06 ^c]	75.8(0.1) [75.85 ^e]	76.2(0.2) [76.03 ^f]
DL-Valine	89.8(0.1)	90.2(0.1)	90.9(0.1)	91.7(0.1)
DL-Leucine	105.8(0.2)	106.7(0.3)	107.5(0.4)	108.4(0.3)
L-Serine	59.6(0.2)	60.3(0.1) [59.8 ^g]	60.9(0.1) [60.8 ^g]	62.1(0.1)

^a Values in parentheses represent standard deviation.^b Ref.[6].^c Ref.[15].^d Ref.[16].^e Ref.[17].^f Ref.[9].^g Ref.[10].

explanation for the origin of these discrepancies. In the literature, we could find no data available on $V_{2,\phi}^0$ for DL-valine and DL-leucine.

$V_{2,\phi}^0$ values were analyzed as a function of temperature using a least-squares routine, and the precise representation of the data was found to be

$$V_{2,\phi}^0 = a_1 + a_2(T - 293.15) + a_3(T - 293.15)^2 \quad (5)$$

When Eq. (5) is fitted to the experimental data of glycine, DL-alanine and DL-leucine using the least-

squares route, it is observed that a_3 values are very small and that their deviations are large. Therefore, for glycine, DL-alanine and DL-leucine the parameters were obtained from Eq. (5) in which the term containing a_3 was neglected. The coefficients a_1 , a_2 and a_3 for Eq. (5) are given in Table 3, together with their standard deviations and the standard deviations of the fit.

It is interesting to note that the $V_{2,\phi}^0$ values of this study vary linearly (average correlation coefficients $R \geq 0.9997$) with the number of carbon atoms in their alkyl chains at given temperatures. A similar linear correlation has been reported for the homologous

Table 3

Coefficients a_1 , a_2 and a_3 of Eq. (5) for α -amino acids in water

Amino Acid	$a_1^a/(\text{cm}^3 \text{ mol}^{-1})$	$a_2^a/(\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1})$	$a_3^a/(\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2})$	σ^b
Glycine	43.05(0.03)	0.078(0.003)	—	0.06
DL-Alanine	60.38(0.02)	0.067(0.002)	—	0.04
DL-Aminobutyric acid	75.46(0.04)	0.063(0.002)	-0.00070(0.0003)	0.05
DL-Valine	90.50(0.06)	0.063(0.003)	0.0010(0.0004)	0.07
DL-Leucine	107.10(0.02)	0.086(0.001)	—	0.03
L-Serine	60.55(0.16)	0.081(0.009)	0.0014(0.00001)	0.20

^a Values in parentheses are standard deviations.^b Standard deviations of the fit.

series of ω -amino acids in aqueous potassium thiocyanate solutions [18]. The alkyl chains of the homologous series of α -amino acids investigated in this work are as follows: CH_2 —(Gly), CH_3CH —(Ala), $\text{CH}_3\text{CH}_2\text{CH}$ —(Abu), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}$ —(Val) and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$ —(Leu). If we accept the assumptions

$$V_{2,\phi}^0(\text{CH}_3) = 1.5 V_{2,\phi}^0(\text{CH}_2) \quad (6)$$

$$V_{2,\phi}^0(\text{CH}) = 0.5 V_{2,\phi}^0(\text{CH}_2) \quad (7)$$

proposed by Hakin et al. [3,4] for the infinite-dilution apparent molar volumes of amino acids at all temperatures, the above linear relation could be reasonably represented by

$$V_{2,\phi}^0 = V_{2,\phi}^0(\text{NH}_3^+, \text{COO}^-) + n_c V_{2,\phi}^0(\text{CH}_2) \quad (8)$$

where n_c is the number of carbon atoms in the alkyl chain of the amino acids. A linear regression analysis of $V_{2,\phi}^0$ values at constant temperature using Eq. (8) gives $V_{2,\phi}^0(\text{NH}_3^+, \text{COO}^-)$, the zwitterionic end groups and $V_{2,\phi}^0(\text{CH}_2)$, the methylene group contributions. The contributions of the other alkyl chains of the α -amino acids were calculated by Eqs. (6) and (7). That of the OH group of L-serine was obtained by

$$V_{2,\phi}^0(\text{OH}) = V_{2,\phi}^0(\text{serine}) - V_{2,\phi}^0(\text{NH}_3^+, \text{COO}^-) - V_{2,\phi}^0(\text{CH}_2) - V_{2,\phi}^0(\text{CH}) \quad (9)$$

These results are listed in Table 4. However, it should be pointed out that the $V_{2,\phi}^0(\text{CH}_2)$ value obtained here characterizes the mean contribution of CH and CH_3 groups to $V_{2,\phi}^0$ of the α -amino acids.

It can be seen from Table 4 that values of $V_{2,\phi}^0(\text{CH}_2)$ are constant over the studied temperature range within the experimental uncertainty. The $V_{2,\phi}^0(\text{CH}_2)$ value at 298.15 K reported in this work ($15.8 \text{ cm}^3 \text{ mol}^{-1}$) is in excellent agreement with the values of 15.7 and $15.8 \text{ cm}^3 \text{ mol}^{-1}$ given in literature [4,17]. The contribution of the OH group at 298.15 K reported by us ($8.9 \text{ cm}^3 \text{ mol}^{-1}$) is also very close to the values of 8.7 and $8.8 \text{ cm}^3 \text{ mol}^{-1}$ reported by Hakin et al., [3,4]. On the other hand, the end group contribution, $V_{2,\phi}^0(\text{NH}_3^+, \text{COO}^-)$, increases with increasing temperature. The thermal expansibility of hydrophobic CH_2 group is, therefore, very low like that of ice, and that of hydrophilic group ($\text{NH}_3^+, \text{COO}^-$) is high. This result is in agreement with the earlier observation [19] on thermal expansibilities of hydrophobic groups of alcohols.

The viscosity data for the amino acids in water at 278.15, 288.15, 298.15 and 308.15 K are collected in Table 5. The relative viscosities η_r can be represented by the relation [20,21]

$$\eta_r = \eta/\eta_0 = 1 + Bc \quad (10)$$

where η and η_0 are the viscosities of solution and water, respectively, c the molarity of amino acid in solution. The B -coefficients of the amino acids obtained by a least-squares procedure are given in Table 6. For the sake of comparison, B -coefficients of the amino acid available in the literature have also been included in Table 6. It can be seen that our B -values for glycine and DL-alanine at 288.15, 298.15 and 308.15 K are in good agreement with the literature values [1,18]. However, discrepancy is observed for glycine at 278.15 K between our value and that of

Table 4

Contributions to the infinite dilution apparent molar volume from the zwitterionic groups, CH_2 group and the other alkyl chains of amino acids in water at 278.15, 288.15, 298.15 and 308.15 K from Eqs. (6) and (9)

Groups	$V_{2,\phi}^0$ ^a /($\text{cm}^3 \text{ mol}^{-1}$)			
	278.15 K	288.15 K	298.15 K	308.15 K
($\text{NH}_3^+, \text{COO}^-$)	26.8(0.6)	27.4(0.6)	28.3(0.5)	28.7(0.5)
CH_2 —	15.8(0.2)	15.8(0.2)	15.8(0.2)	15.9(0.2)
CH_3CH —	31.6(0.3)	31.7(0.3)	31.6(0.3)	31.7(0.3)
$\text{CH}_3\text{CH}_2\text{CH}$ —	47.1(0.4)	47.5(0.4)	47(0.4)	47.6(0.4)
$(\text{CH}_3)_2\text{CHCH}$ —	63.2(0.4)	63.3(0.5)	63.3(0.4)	63.4(0.4)
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}$ —	79.0(0.5)	79.1(0.5)	79.1(0.5)	79.3(0.5)
OH—	9.1(0.7)	9.2(0.7)	8.9(0.6)	9.5(0.6)

^a Values in parentheses are standard deviations.

Table 5

Viscosity η of aqueous amino acid solutions as functions of temperature and molarity of amino acids

278.15 K		288.15 K		298.15 K		308.15 K	
$c/(\text{mol l}^{-1})$	$\eta(\text{mPa s})$	$c/(\text{mol l}^{-1})$	$\eta(\text{mPa s})$	$c/(\text{mol l}^{-1})$	$\eta(\text{mPa s})$	$c/(\text{mol l}^{-1})$	$\eta(\text{mPa s})$
<i>Glycine</i>							
0.02969	1.525	0.03212	1.144	0.03085	0.895	0.03196	0.722
0.06085	1.531	0.05944	1.148	0.07029	0.900	0.05913	0.725
0.1009	1.539	0.09974	1.154	0.1071	0.905	0.09922	0.729
0.1511	1.548	0.1500	1.162	0.1536	0.910	0.1492	0.735
0.1988	1.557	0.2023	1.170	0.2015	0.916	0.2013	0.741
0.2493	1.566	0.2541	1.178	0.2692	0.925	0.2528	0.746
—	—	0.2983	1.185	0.3085	0.930	0.2967	0.751
<i>DL-Alanine</i>							
0.02990	1.532	0.03145	1.149	0.03148	0.897	0.03138	0.725
0.05958	1.545	0.05805	1.156	0.05793	0.903	0.05775	0.729
0.09986	1.563	0.1036	1.170	0.1034	0.913	0.1031	0.737
0.1499	1.583	0.1493	1.184	0.1490	0.924	0.1485	0.746
0.1999	1.604	0.2006	1.200	0.2002	0.936	0.1996	0.755
0.2459	1.625	0.2365	1.212	0.2359	0.945	0.2352	0.762
—	—	0.2879	1.228	0.2873	0.957	0.2864	0.771
<i>DL-Aminobutyric acid</i>							
0.03094	1.538	0.03092	1.152	0.03086	0.900	0.03076	0.727
0.05920	1.555	0.05915	1.164	0.05902	0.908	0.05885	0.734
0.09913	1.579	0.09903	1.181	0.09882	0.921	0.09853	0.743
0.1492	1.611	0.1490	1.203	0.1487	0.937	0.1482	0.755
0.2010	1.644	0.2008	1.226	0.2004	0.954	0.1997	0.768
<i>DL-Valine</i>							
0.03089	1.543	0.03041	1.155	0.03035	0.902	0.03026	0.728
0.05703	1.563	0.05554	1.168	0.05542	0.911	0.05525	0.735
0.09882	1.596	0.09872	1.194	0.09851	0.930	0.09820	0.749
0.1492	1.636	0.1452	1.217	0.1449	0.946	0.1444	0.762
0.1974	1.678	0.1904	1.243	0.1899	0.965	0.1893	0.775
0.2485	1.722	0.2467	1.276	0.2462	0.988	0.2454	0.793
—	—	0.2950	1.305	0.2944	1.009	0.2934	0.809
<i>DL-Leucine</i>							
0.03112	1.547	0.03148	1.158	0.03142	0.904	0.03132	0.729
0.04480	1.560	0.04642	1.167	0.04633	0.910	0.04618	0.734
0.06585	1.580	0.05383	1.172	0.05372	0.914	0.05355	0.737
0.07571	1.588	0.06024	1.176	0.06012	0.916	0.05993	0.739
0.08034	1.595	0.07385	1.184	0.07370	0.922	0.07347	0.743
—	—	0.07974	1.188	0.07957	0.925	0.07933	0.745
—	—	0.08537	1.192	0.08519	0.928	0.08492	0.747
<i>L-Serine</i>							
0.02961	1.530	0.02945	1.147	0.02939	0.896	0.02930	0.724
0.06493	1.542	0.05578	1.154	0.05566	0.901	0.05549	0.728
0.1001	1.554	0.09965	1.166	0.09944	0.911	0.09914	0.736
0.1505	1.573	0.1623	1.183	0.1619	0.924	0.1614	0.747
0.2015	1.592	0.1965	1.192	0.1960	0.932	0.1954	0.752
0.2487	1.610	0.2467	1.207	0.2461	0.943	0.2454	0.761
—	—	0.2945	1.220	0.2938	0.953	0.2929	0.770

Table 6
Viscosity B -coefficients from Eq. (10) of amino acids in water at different temperatures

Amino acid	$B^a/(\text{dm}^3 \text{ mol}^{-1})$			
	278.15 K	288.15 K	298.15 K	308.15 K
Glycine	0.1227(0.0004) [0.1164 ^d]	0.132(0.002) [0.129 ^c]	0.146(0.001) [0.1427 ^b ,0.143 ^c]	0.1466(0.0009) [0.148 ^c]
DL-Alanine	0.278(0.001)	0.269(0.001) [0.259 ^c]	0.258(0.002) [0.253 ^c]	0.250(0.001) [0.247 ^c]
DL-Aminobutyric acid	0.402(0.003)	0.379(0.002)	0.352(0.002)	0.3357(0.0005)
DL-Valine	0.526(0.005)	0.487(0.003)	0.447(0.003)	0.418(0.003)
DL-Leucine	0.599(0.005)	0.540(0.001)	0.487(0.002)	0.483(0.001)
L-Serine	0.2420(0.0008)	0.241(0.001)	0.238(0.001)	0.237(0.001)

^a Values in parentheses are standard deviation.

^b Ref.[1].

^c Ref.[18].

^d Ref.[20].

Tyrell and Kennerly [20]. The possible reasons are that: (1) the latter authors measured the efflux times and densities by a stop-watch and density bottle, respectively, which are not capable of the high precision; and (2) they determined B -coefficients using different equation.

It is noted that at any given temperature, B -coefficients increase in the following order:



The significance of this order is that B -values increase with increasing alkyl chain length of the α -amino acids. It is well established that B -coefficient is a measure of solute-solvent interactions, and is directly dependent on the size, shape and charge of the solute molecules. Since the charged groups of the amino acids studied here are the same, the observed order of viscosity B -coefficients may just be explained

in terms of the shape and size of alkyl groups of the amino acids. In fact, B -coefficients of the studied homologous series of α -amino acids vary linearly (average correlation coefficients $R \geq 0.990$) with the number of carbon atoms on their alkyl chains at given temperatures. Similar to Eq. (8), this linear relation can be represented by:

$$B = B(\text{NH}_3^+, \text{COO}^-) + n_c B(\text{CH}_2) \quad (11)$$

where $B(\text{NH}_3^+, \text{COO}^-)$ and $B(\text{CH}_2)$ are the contributions of the charged end group and the methylene group to B -values, respectively. The regression parameters $B(\text{NH}_3^+, \text{COO}^-)$ and $B(\text{CH}_2)$ are listed in Table 7.

The results in Table 7 clearly reveal the structural features of these solutions. The positive dB/dT values for the zwitterion groups confirm that they are structure-breakers, i.e. as the water structure decreases with

Table 7
Contributions of the zwitterionic ($\text{NH}_3^+, \text{COO}^-$) and CH_2 groups of amino acids to viscosity B -coefficients at 278.15, 288.15, 298.15 and 308.15 K from Eq. (11)

Group	$B^a/(\text{dm}^3 \text{ mol}^{-1})$			
	278.15 K	288.15 K	298.15 K	308.15 K
($\text{NH}_3^+, \text{COO}^-$)	0.024(0.027)	0.052(0.029)	0.074(0.026)	0.089(0.023)
CH_2	0.120(0.008)	0.103(0.009)	0.088(0.007)	0.077(0.007)

^a Values in parentheses are standard deviations.

increasing temperature, these groups become less effective structure breakers and the B -coefficient increases. On the other hand, the hydrophobic structure-making CH_2 group shows negative dB/dT as expected. As seen from Table 6, glycine has a positive dB/dT value and the others have negative dB/dT values. This suggests that the effect of the charged end group ($\text{NH}_3^+, \text{COO}^-$) of glycine on water structure predominates that of the non-polar part of this amino acids, whereas, for the other amino acids, the reverse is true. According to Frank and Wen [22], when a molecule with non-polar and polar parts dissolves in water at room temperature, the water adjacent to the non-polar part becomes more ice-like than normal, and this effect increases with the size of the non-polar part of the molecule. Since the other five amino acids have bigger non-polar parts, the effect of structure-making hydrophobic groups becomes important.

It is interesting to note that there is a linear correlation between the B -coefficient and $V_{2,\phi}^0$ values for the α -amino acids in water.

$$B = A_1 + A_2 V_{2,\phi}^0 \quad (12)$$

The coefficients A_1 and A_2 obtained by a least-squares analysis are given in Table 8. A similar correlation for ω -amino acids in water was observed by Devine and Lowe [21].

Thermodynamic activation parameters of viscous flow for the amino acids were evaluated using the Feakins et al. [23] extension of Eyring transition-state theory

$$B = (V_{1,\phi}^0 - V_{2,\phi}^0)/1000 + (V_{1,\phi}^0/1000) \times (\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT \quad (13)$$

where $V_{1,\phi}^0$ and $V_{2,\phi}^0$ are the partial molar volumes of the solvent and solute at infinite dilution, respectively, $\Delta\mu_1^{0\neq}$ is the free energy of activation per mole of pure solvent, and is given by

$$\Delta\mu_1^{0\neq} = RT \ln (\eta_0 V_{1,\phi}^0 / h N_A) \quad (14)$$

where h is the Plank constant, N_A the Avagadro number. $\Delta\mu_2^{0\neq}$ is the contribution per mole of solute to the free energy of activation for viscous flow of the solution. Hence, Eq. (13) can be rearranged as follows

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + (RT/V_{1,\phi}^0)[1000B - (V_{1,\phi}^0 - V_{2,\phi}^0)] \quad (15)$$

$\Delta\mu_2^{0\neq}$ values thus obtained at different temperatures are recorded in Table 9.

Over the temperature range concerned, the entropy and enthalpy of activation for viscous flow of the amino acids were calculated by

$$\Delta S_2^{0\neq} = -\text{d}(\Delta\mu_2^{0\neq})/\text{dT} \quad (16)$$

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \quad (17)$$

The results are presented in Table 10.

As seen from Tables 9 and 10, values of $\Delta\mu_2^{0\neq}$ increase from glycine to leucine at given temperatures. Because the interactions of the charged end groups for different amino acids with water are the same, it can be deduced that the increasing $\Delta\mu_2^{0\neq}$ comes from the difference in interactions of the alkyl groups of the amino acids with water. In addition, the value of $\Delta\mu_2^{0\neq}$ for glycine increases with increasing temperature and gives negative $\Delta S_2^{0\neq}$ and smaller $\Delta H_2^{0\neq}$. The possible reason is that the effect of the solute-solvent bond for glycine is smaller in the ground state, a significant solute-solvent bond will be made in the transition state. The other amino acids have positive $\Delta S_2^{0\neq}$ and

Table 8
Coefficients A_1 and A_2 of Eq. (12) for α -amino acids in water

T/K	$A_1^a/(\text{dm}^3 \text{mol}^{-1})$	A_2^a	R^b	σ^c
278.15	-0.179(0.037)	7.61(0.48)	0.994	0.02
288.15	-0.128(0.048)	6.53(0.53)	0.990	0.03
298.15	-0.079(0.038)	5.51(0.47)	0.989	0.02
308.15	-0.055(0.037)	4.92(0.47)	0.987	0.02

^a Values in parentheses are standard deviation.

^b Correlation coefficient.

^c Standard deviation of the fit.

Table 9

Activation free energies $\Delta\mu_2^{0\ddagger}$ from Eq. (15) for viscous flow of amino acids in water at 278.15, 288.15, 298.15 and 308.15 K

Amino acid	$\Delta\mu_2^{0\ddagger a}/(\text{kJ mol}^{-1})$			
	278.15 K	288.15 K	298.15 K	308.15 K
Glycine	28.61(0.05)	30.3(0.3)	32.7(0.1)	33.4(0.1)
DL-Alanine	50.8(0.1)	50.8(0.1)	50.4(0.3)	50.4(0.1)
DL-Aminobutyric acid	68.7(0.4)	67.4(0.3)	65.4(0.3)	64.64(0.07)
DL-Valine	86.6(0.6)	83.8(0.4)	80.6(0.4)	78.5(0.4)
DL-Leucine	98.0(0.6)	93.0(0.1)	88.3(0.3)	85.8(0.1)
L-Serine	46.2(0.1)	47.1(0.1)	47.7(0.1)	48.7(0.1)

^a Values in parentheses are the standard deviations.

Table 10

Activation enthalpy $\Delta H_2^{0\ddagger}$ from Eq. (17) and entropy $\Delta S_2^{0\ddagger}$ from Eq. (16) for viscous flow of the aqueous amino acids solutions

Amino acid	$\Delta H_2^{0\ddagger a}/(\text{kJ mol}^{-1})$	$\Delta S_2^{0\ddagger a}/(\text{J mol}^{-1})$
Glycine	17.6(6.9)	-167(24)
DL-Alanine	55.5(2.3)	16.7(7.8)
DL-Aminobutyric acid	107.5(5.9)	139(18)
DL-Valine	163.7(4.2)	277(14)
DL-Leucine	212.8(12.1)	415(41)
L-Serine	14.5(5.0)	112(17)

^a Values in parentheses are the standard deviations.

large $\Delta H_2^{0\ddagger}$ values owing to the effect of solute–solvent bond-breaking in the transition state.

The value of $\Delta\mu_2^{0\ddagger}$ varies linearly with the number of carbon atoms in the alkyl chains of α -amino acids. The linear regression of $\Delta\mu_2^{0\ddagger}$ vs. n_c using the equation

$$\Delta\mu_2^{0\ddagger} = \Delta\mu_2^{0\ddagger}(\text{NH}_3^+, \text{COO}^-) + n_c \Delta\mu_2^{0\ddagger}(\text{CH}_2) \quad (18)$$

gives $\Delta\mu_2^{0\ddagger}(\text{NH}_3^+, \text{COO}^-)$ and $\Delta\mu_2^{0\ddagger}(\text{CH}_2)$ as the respective contributions of $(\text{NH}_3^+, \text{COO}^-)$ and CH_2 groups. These results are given in Table 11. Using similar arguments as above, we can obtain the $\Delta H_2^{0\ddagger}$

Table 11

Contributions of $(\text{NH}_3^+, \text{COO}^-)$ and CH_2 groups of the amino acids to $\Delta\mu_2^{0\ddagger}$, $\Delta H_2^{0\ddagger}$ and $\Delta S_2^{0\ddagger}$ in water from Eqs. (16)–(18)

Group	$\Delta H_2^{0\ddagger a}/(\text{kJ mol}^{-1})$	$\Delta S_2^{0\ddagger a}/(\text{kJ mol}^{-1})$	$\Delta\mu_2^{0\ddagger a}/(\text{kJ mol}^{-1})$			
			278.15 K	288.15 K	298.15 K	308.15 K
$(\text{NH}_3^+, \text{COO}^-)$	-38.1(5.9)	-0.281(0.018)	14.2(3.6)	17.6(3.9)	21.0(3.4)	22.7(3.3)
CH_2	49.9(1.8)	0.142(0.005)	17.5(1.1)	15.8(1.2)	14.1(1.0)	13.3(1.0)

^a Values in parentheses are the standard deviations.

and $\Delta S_2^{0\ddagger}$ value for zwitterion $(\text{NH}_3^+, \text{COO}^-)$ and CH_2 groups. These results are also collected in Table 11.

It can be seen from Table 11 that with increasing temperature, values of $\Delta\mu_2^{0\ddagger}(\text{NH}_3^+, \text{COO}^-)$ increase, while those of $\Delta\mu_2^{0\ddagger}(\text{CH}_2)$ decrease, giving negative $\Delta H_2^{0\ddagger}$ and $\Delta S_2^{0\ddagger}$ for the $(\text{NH}_3^+, \text{COO}^-)$ group and positive $\Delta H_2^{0\ddagger}$ and $\Delta S_2^{0\ddagger}$ for the CH_2 group. These indicate that ground-state water is highly structured and thus resists the complete coordination of the solute, so additional solute–solvent bonds can be formed in the less rigid transition-state solvent with an increase in the coordination number of the solute. At the other extreme, the formation of the transition state for CH_2 groups of the amino acids is associated with bond-breaking and a decrease in order. This means that the solute is completely coordinated in the ground-state solvent.

Acknowledgements

Financial support from the Science Foundation of the State Education Commission of China and the Youth Science Foundation of Henan Province are gratefully acknowledged.

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