ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1155–1160. © Pleiades Publishing, Ltd., 2008.
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Thermodynamic Characteristics of Solution and Viscous Flow of Amino Acids in Water at 298.15 K

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Received June 29, 2007

Abstract—Thermodynamic and transport properties of aqueous solutions of 13 amino acids at 298.15 K are analyzed in relation to the structure of the side chains of the biomolecules on the basis of the newly obtained and published data. The standard enthalpies of solution ($\Delta_{sol}H^0$), partial molar volumes ($V^0_{2,\varphi}$), and partial molar contributions to the molar Gibbs free energy of activation of the viscous flow ($\Delta\mu_2^{0\neq}$) were determined for the amino acids in water. Correlation equations were suggested to describe the relationship between the enthalpy characteristics of hydration of amino acids, viscous flow parameters, and bulk properties of their aqueous solutions.

DOI: 10.1134/S1070363208060091

Determination of the thermodynamic and transport properties of amino acids in the aqueous phase is very important for designing and optimizing industrial biochemical processes, developing procedures for the synthesis, purification, and separation of amino acids, and describing principles of their transfer through biological membranes [1]. It is known that the reactivity and biological activity of proteins in aqueous medium depends on the hydration of their structural fragments, amino acid residues [2]. Amino acids show both hydrophilic and hydrophobic behavior in interaction with solvents [3]. The zwitterionic main chain of each amino acid [NH_3^+–CH(R)–COO^-, where R is a side radical] is hydrophilic, exhibiting structure-breaking properties in solution. Hydrophobic side chains exert an ordering effect, and polar and ionic side chains of amino acids, mainly a disordering effect on the solvent structure [1]. It was interesting to examine how the structure of amino acids containing various side substituents affects the enthalpy characteristics of hydration of the amino acids, bulk properties of their aqueous solutions, and thermodynamic parameters of activation of the viscous flow of the aqueous solutions. These properties are sensitive to changes in interparticle interactions in solution. In addition, we made an attempt to describe the enthalpy characteristics of amino acids at infinite dilution via activation parameters of viscous flow of their aqueous solutions.

The limiting enthalpies of solution ($\Delta_{sol}H^0$) and limiting partial molar volumes ($V^0_{2,\varphi}$) of amino acids at 298.15 K are given in Table 1 [4–11]. As can be seen, the dissolution of the amino acids in water is endothermic (the $\Delta_{sol}H^0$ values are positive). With an increase in the size of the solute molecule, the dissolution tends to become less endothermic. From the experimentally found enthalpies of solution $\Delta_{sol}H^0$ and sublimation ($\Delta_{subl}H$) [12–17] (Table 1), we calculated the enthalpy of hydration ($\Delta_{hydr}H^0$) of the amino acids by Eq. (1):

$$\Delta_{hydr}H^0 = \Delta_{sol}H^0 - \Delta_{subl}H. \quad (1)$$

With an increase in the length of the side substituent, the hydration of amino acids becomes more exothermic. The ratio of $\Delta_{hydr}H^0$ to the partial molar volume at infinite dilution ($V^0_{2,\varphi}$) characterizes the specific volume enthalpy of hydration of a substance ($\Delta_{hydr}H^0/V^0_{2,\varphi}$). The use of this quantity is preferable when performing comparative thermodynamic analysis of different compounds [4, 18]. The relative error of this quantity for the amino acids under consideration did not exceed 3.7%. The values of $\Delta_{hydr}H^0/V^0_{2,\varphi}$ increase (become less negative) in the

Table 1. Limiting partial molar volumes ($V^0_{2,\varphi}$) and enthalpies of solution ($\Delta_{sol}H^0$), sublimation ($\Delta_{subl}H$), and hydration ($\Delta_{hydr}H^0$) of amino acids at T 298.15 K

Amino acid	$V^0_{2,\varphi}$, cm^3 mol^{-1}	$\Delta_{sol}H^0$, kJ mol^{-1}	$\Delta_{subl}H$, kJ mol^{-1}	$-\Delta_{hydr}H^0$, kJ mol^{-1}
Glycine (Gly)	43.3±0.1	14.25±0.14	136.5±2 [12]	122
DL-Alanine (*DL*-Ala)	60.5±0.1	9.34±0.09	144.8±4 [13]	135
β-Alanine (β-Ala)	58.3±0.2 [4]	9.50±0.09 [4]	157±7 [14]	148
DL-Valine (Val)	90.4±0.1 [5]	5.34±0.06 [10]	162±7 [14]	157
DL-Leucine (Leu)	107.3±0.1 [5]	2.93±0.12 [10]	150.6±6 [14]	147
L-Serine (Ser)	60.5±0.1 [4]	11.49±0.11	151±6 [14]	139
L-Threonine (Thr)	76.3±0.2 [6]	9.61±0.12 [9]	162±7 [14]	153
L-Proline (Pro)	81.6±0.2 [6]	–3.09±0.06 [10]	149±4 [15]	152
L-Phenylalanine (Phe)	128.5±0.2 [6]	8.31±0.08 [10]	153.9±0.9 [16]	145
L-Arginine (Arg)	120.4±0.3 [7]	24.85±0.33 [10]	131.8±5 [14]	107
2-Aminobutanoic acid (2-Abu)	75.7±0.1 [5]	6.64±0.14 [11]	132.0±2 [13]	125
4-Aminobutanoic acid (4-Abu)	72.5±0.2 [8]	–0.64±0.2 [11]	142.7±6 [17]	143
6-Aminohexanoic acid (6-Ahx)	103.6±0.2 [8]	–14.20±0.22 [11]	117.6±5[17]	132

following series of amino acids: Gly < β-Ala < Ser < *DL*-Ala < 4-Abu < Thr < Pro < *DL*-Val < 2-Abu < *DL*-Leu < 6-Ahx < Phe < Arg. The results obtained confirm the conclusions made previously [19] on the basis of ultrasonic measurements that the surrounding of a solute molecule in solution is less compressible than bulk water and that the compressibility of the hydration sphere of a biomolecule increases with an increase in the length of its side chain.

An increase in the number of carbon atoms (N_C) in the side chain (R–) of an amino acid molecule is accompanied by an increase in the partial molar volume of the amino acid in water $V_2{}^0{}_{,\varphi}$. The correlation is linear with a correlation coefficient r_{corr} 0.954:

$$V^0_{2,\varphi} = V^0_2(NH_3^+,COO^-) + V^0_2(CH_2)N_C. \quad (2)$$

To a first approximation [5], the slope $V^0_2(CH_2)$ 14.1±0.9 cm^3 mol^{-1} can be considered as the volume contribution of the CH_2 group, and the portion intercepted on the ordinate, $V^0_2(NH_3^+, COO^-)$ 46.3 ± 3 cm^3 mol^{-1}, as the volume contribution of zwitterionic groups in the amino acid molecule (which is close to the limiting partial molar volume of glycine).

The concentration dependence of the viscosity of the amino acid solutions under consideration can be described using a Jones–Doll type equation [20]:

$$\eta_r = \eta/\eta_0 = 1 + B_\eta C, \quad (3)$$

where η_r is the relative viscosity of the solution; η and η_0, dynamic viscosity coefficients of the solution and solvent, respectively; and C, solution concentration (M). The viscosity coefficients B_η at T 298.15 K, given in Table 2 [5–8, 21, 22], increase in the order Gly < β-Ala < Ser < *DL*-Ala < Pro < 4-Abu < Thr < 2-Abu < *DL*-Val < *DL*-Leu < 6-Ahx ≤ Arg < Phe. It is known [20] that coefficients B_η in Eq. (3) reflect the solvation interactions of zwitterions and their effects on the solvent structure in the nearest surrounding of solute particles. As the charged groups (NH_3^+, COO^-) are similar for all the amino acids under consideration, irrespective of whether the amino acids are linear or branched, the observed changes in B_η can be attributed to the effects of side groups. By analogy with Eq. (2), we obtained linear relationship (4) (r_{corr} 0.951, n 13):

$$B_\eta = B_\eta(NH_3^+,COO^-) + N_C B_\eta(CH_2), \quad (4)$$

where $B_\eta(NH_3^+, COO^-)$ 0.1183 ± 0.029 and $B_\eta(CH_2)$ 0.0648 ± 0.0073 are the contributions of the charged terminal groups and methylene group, respectively, to B_η.

The thermodynamic parameters of activation of the viscous flow of aqueous solutions of amino acids can be estimated on the basis of the modified Feakins transition state theory [23], initially developed for electrolyte solutions. In this approach, the partial Gibbs free energy of activation of the viscous flow of a solute at infinite dilution ($\Delta\mu_2^{0\neq}$) can be estimated by Eq. (5) [24]:

Table 2. Logarithms of the distribution ratios (log*P*'), viscosity coefficients (B_η), and partial molar Gibbs free energies of activation of viscous flow ($\Delta\mu_2^{0\neq}$) of amino acids in water at 298.15 K

Amino acid	Side substituent -R-	B_η, dm^3 mol^{-1}	$\Delta\mu_2^{0\neq}$, kJ mol^{-1}	log *P*'
Gly	–H	0.137±0.001 [23]	31.6	–3.58
DL-Ala	$-CH_3$	0.257±0.001 [5]	50.3	–3.45
β-Ala	$-CH_2-$	0.220±0.005 [8]	44.7	–3.25
Val	$-CH(CH_3)_2$	0.437±0.005 [5]	79.0	–2.58
Leu	$-CH_2-CH(CH_3)_2$	0.486±0.005 [5]	88.2	–2.48
Ser	$-CH_2-OH$	0.287±0.001 [6]	54.4	–3.76
Thr	$-CH_2(OH)-CH_3$	0.344±0.002 [23]	64.4	–3.88
Pro	$-(CH_2CH_2CH_2)-$	0.307±0.002 [23]	60.0	–2.05
Phe	$-CH_2-(C_6H_5)$	0.708±0.003 [24]	120.5	–3.57
Arg	$-(CH_2)_3-NH-C(=NH)NH_2$	0.476±0.005 [7]	88.1	–4.48
2-Abu	$-CH_2-CH_3$	0.351±0.003 [5]	65.2	–2.63
4-Abu	$-CH_2-CH_2-$	0.314±0.002 [8]	59.7	–2.64
6-Ahx	$-(CH_2)_4-$	0.513±0.003 [23]	91.3	–2.42

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + (RT/V_{1,\varphi}^0)[1000B_\eta - (V_{1,\varphi}^0 - V_{2,\varphi}^0)], \quad (5)$$

where $\Delta\mu_1^{0\neq}$ is the corresponding molar parameter of activation of the viscous flow of the pure solvent; $V_{2,\varphi}^0$, limiting partial molar volume of the solute; $V_{1,\varphi}^0$, molar volume of the pure solvent; *R*, universal gas constant; and *T*, temperature. According to the Feakins transition state theory [23, 24], $\Delta\mu_2^{0\neq}$ depends only on the difference between the solute–solvent interactions in the ground and transition states.

The quantities $\Delta\mu_2^{0\neq}$ calculated by Eq. (5) are given in Table 2. Assuming equal contribution to $\Delta\mu_2^{0\neq}$ from the interaction of the charged terminal groups (NH_3^+, COO^-) of different amino acids with water, an increase in $\Delta\mu_2^{0\neq}$ with increasing N_C can be attributed to differences in the interaction of the side substituents of the biomolecules with water dipoles:

$$\Delta\mu_2^{0\neq} = \Delta\mu_2^{0\neq}(NH_3^+, COO^-) + N_C\Delta\mu_2^{0\neq}(CH_2), \quad (6)$$

where $\Delta\mu_2^{0\neq}(NH_3^+, COO^-)$ 37.2 ± 3.2 kJ mol^{-1}, $\Delta\mu_2^{0\neq}(CH_2)$ 11.27 ± 1.0 kJ mol^{-1} (r_{corr} 0.958, standard deviation *SD* 5.8).

It is interesting that, for the aqueous amino acid solutions under consideration, B_η virtually linearly (r_{corr} 0.962) increases with increasing $V_{2,\varphi}^0$ of the amino acids:

$$B_\eta = (-0.053\pm0.033) + (0.0051\pm4\cdot10^{-4})V_{2,\varphi}^0. \quad (7)$$

A similar correlation was observed previously for aqueous electrolyte solutions [5]. We also revealed linear correlations of other parameters with the volume variable: $\Delta\mu_2^{0\neq} = f(V_{2,\varphi}^0)$ with r_{corr} 0.974 (*SD* 5.2) and $(\Delta_{hydr}H^0/V_{2,\varphi}^0) = f(V_{2,\varphi}^0)$ with r_{corr} 0.964 (*SD* 0.16).

The results obtained ($\Delta\mu_2^{0\neq} > 0$, $B_\eta > 0$) suggest that the ground state of water slightly resists the coordination of amino acid molecules. Then it can be assumed that, in the systems under consideration, the hydration is virtually complete in the ground state. Thus, amino acids (Table 2) exert an ordering effect on water, and their aqueous solutions will be more viscous than pure water (in contrast to aqueous solutions of electrolyte containing large K^+, Cs^+, Rb^+, I^-, and Br^- ions, which exhibit the effect of "negative" viscosity when dissolved in water).

Taking into account the additive character of $\Delta\mu_2^{0\neq}$ and B_η, we can expect the existence of potentially important correlations between these parameters and other additive properties (e.g., enthalpy, Gibbs free energy, and entropy of hydration, solvation, and transfer from one solvent into another) [20, 25]. Being structure-sensitive, the characteristics of viscous flow can serve as a basis for rational generalization of extensive thermochemical data for amino acids or peptides. The relationships between these parameters not only would allow estimation of unknown properties from other experimentally measured characteristics, but also would favor the development of theoretical concepts concerning the effect of intermolecular interactions on the character of transfer and dissolution of substances in liquid media.

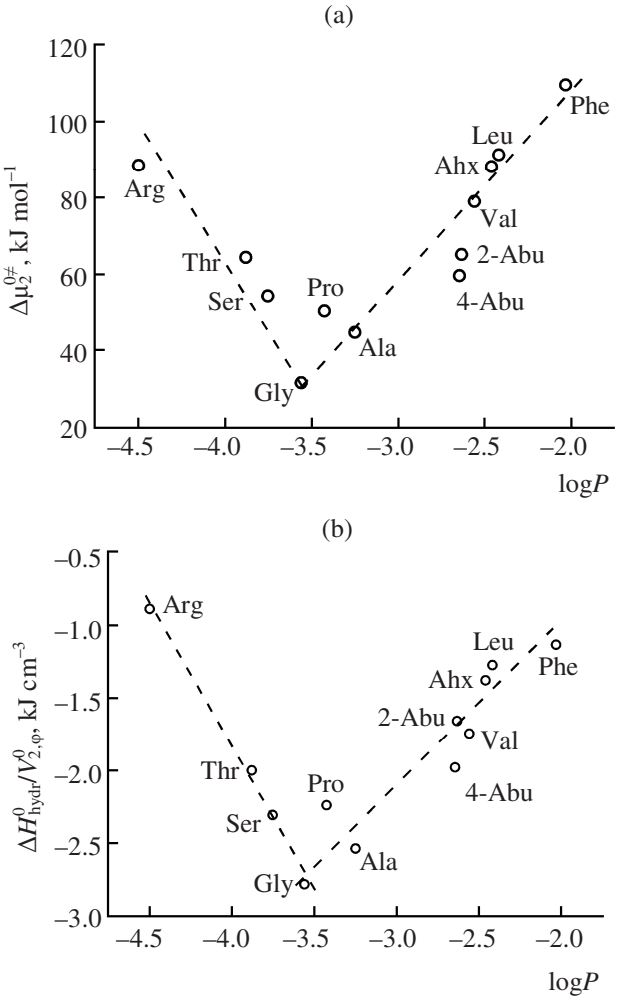

Fig. 1. (a) Partial molar Gibbs free energy of activation of viscous flow $\Delta\mu_2^{0\neq}$ and (b) specific volumetric enthalpy of hydration $\Delta_{hydr}H^0/V_2^0{}_{,\varphi}$ of amino acids in water as functions of the hydrophobicity parameter log$P$'.

Analysis of the variation of B_η and $(\Delta_{hydr}H^0/V^0_{2,\varphi})$ of the amino acids revealed linear correlation (8) with the correlation coefficient r_{corr} 0.953 (SD = 0.22, n 13).

$$(\Delta_{hydr}H^0/V^0_{2,\varphi}) = (-3.213\pm0.09) + (3.68\pm0.44)B_\eta. \quad (8)$$

As seen from Table 2, aqueous solutions of different amino acids under the same conditions resist the viscous flow differently. To evaluate the effect of hydrophobicity of the amino acid molecules on the enthalpy and viscosity characteristics of their aqueous solutions, we used the logarithm of the distribution ratio (log$P$') of a substance between water and 1-octanol [1]. The log$P$' values calculated using data from [26] are given in Table 2. The plots of $\Delta\mu_2^{0\neq} = f(\log P')$ and $(\Delta_{hydr}H^0/V^0_{2,\varphi}) = f(\log P')$, having a similar shape, are shown in Fig. 1. With an increase in the hydrophobicity of molecules of nonpolar amino acids, the contribution of hydrophobic hydration increases, which leads to an increase in the energy consumption for the transfer of solution particles in the direction of the action of the shear force from one equilibrium position to another. Amino acids with polar groups (OH–, NH–, NH_2–) in the side chain, capable of hydrogen bonding, break the intrinsic water structure to a greater extent, causing at the same time an increase in the solution ordering, which is accompanied by an increase in the free energy of activation of the viscous flow of their aqueous solutions. The results obtained show that, for the amino acid solutions under consideration, there is a correlation between $\Delta_{hydr}H^0/V^0_{2,\varphi}$ and $\Delta\mu_2^{0\neq}$:

$$\Delta_{hydr}H^0/V^0_{2,\varphi} = a + b\Delta\mu_2^{0\neq} \quad (9)$$

with a –3.49±0.20, b 0.0243±0.0027, r_{corr} 0.940, SD = 0.21 (n 13) (Fig. 2).

Thus, the existence of correlations (8) and (9) allows $\Delta\mu_2^{0\neq}$ and B_η to be considered as parameters from which it is possible to estimate the enthalpy characteristics of hydration of amino acids in water. The mean relative error of such estimation in our case was 9.7%. The existence of the linear correlations $(\Delta_{hydr}H^0/V^0_{2,\varphi}) = f(\Delta\mu_2^{0\neq})$, $(\Delta_{hydr}H^0/V^0_{2,\varphi}) = f(B_\eta)$, $\Delta\mu_2^{0\neq} = f(V^0_{2,\varphi})$, $B_\eta = f(V^0_{2,\varphi})$, and $(\Delta_{hydr}H^0/V^0_{2,\varphi}) = f(V_2^0{}_{,\varphi})$ offers wide opportunities, e.g., to evaluate from the viscosities of solutions the enthalpies of solvation and transfer of zwitterions of amino acids between aqueous-organic solvents for which the experimental thermochemical data are lacking.

EXPERIMENTAL

Experiments were performed with glycine (Sigma Ultra, main substance content >99%), *DL*-alanine (Reanal, Hungary, chromatographically homogeneous, main substance content >99%), and *L*-serine (Aldrich, >99%). The amino acids were dried in a vacuum oven at 323.15 K for 48 h and stored over P_2O_5 in a vacuum desiccator. Aqueous solutions were prepared gravimetrically using double-distilled water.

The enthalpies of solution of Gly, *DL*-Ala, and *L*-Ser in water were measured in a specially designed four-ampule calorimeter with an isothermal shell. The installation is described in detail elsewhere [27]. The temperature control accuracy in the course of calorimetric measurements was 0.001 K. The

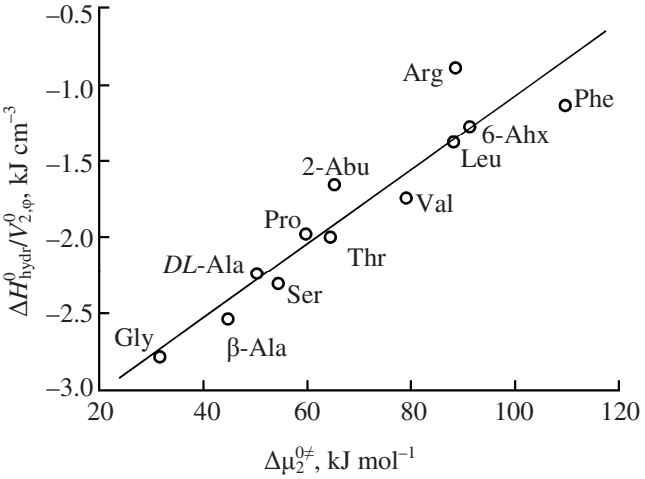

Fig. 2. Specific volumetric enthalpy of hydration $\Delta_{hydr}H^0/V^0_{2,\varphi}$ of amino acids as a function of the partial molar Gibbs free energy of activation of the viscous flow $\Delta\mu_2^{0\neq}$ of their aqueous solutions at 298.15 K.

temperature and energy sensitivities of the calorimeter were 2×10^{-4} K and 1×10^{-3} J per millimeter of the recorder scale. The thermal effect was compensated by the electric current. The maximal error of measuring the enthalpy of solution of amino acids was 0.5%. In the examined concentration range, 0.003–0.018 mol kg^{-1} H_2O, the measured values of $\Delta_{sol}H^m$ for all the systems are concentration-independent within the experimental error. Therefore, the standard enthalpies of solution $\Delta_{sol}H^0$ were found as weighted average values from a series of seven independent measurements.

The densities of aqueous solutions of Gly and *DL*-Ala were measured using a magnetic-float method. Its features and measurement procedure are described elsewhere [28]. The error of measuring the solution densities was $\pm 4.1 \times 10^{-5}$ g cm^{-3}. In the concentration range 0.008–0.12 mol kg^{-1} H_2O, we determined the apparent molar volumes ($V_{2,\varphi}$) of the amino acids in water and estimated the partial volumes at infinite dilution ($V^0_{2,\varphi}$). Data on the viscosities of aqueous solutions of amino acids were taken from [5–8, 21, 22]. The viscosities of these solutions were measured with an accuracy of $\pm 5 \times 10^{-6}$ g cm^{-1} s^{-1} on a modified Ubbelohde capillary viscometer with a suspended level.

The correlations were calculated by linear regression methods at a confidence level of 0.95. The correlations can be considered as satisfactory, with linear correlation coefficients in the range $0.95 < r_{corr} < 0.98$ [29]. As r_{corr} is a random quantity, we estimated its rms error by the formula $\sigma_r = (1 - r^2_{corr})/n$ [29]. We found that $|r_{corr}| > 3\sigma_r$, which confirms the existence of a linear correlation between the variables X and Y in the regression equation $Y = a + bX$.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 07-03-00369).

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