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Short Communication

ENTHALPY CHANGES IN PROTOLYTIC EQUILIBRIA OF GLYCYL-β-ALANINE IN AN AQUEOUS SOLUTION

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Reaction enthalpy changes were measured with the use of calorimetric method for the protonation and neutralization of glycyl-β-alanine at 298.15 K and ionic strengths 0.5, 1.0, 1.5 mol L^{-1} (KNO_3), and the corresponding standard thermodynamic parameters were evaluated. The results obtained were compared with the literature data on related compounds.

Keywords: *dipeptide, enthalpy, ionic strength, protolytic equilibria*

Introduction

Glycyl-β-alanine stepwise protonation constants have been published in several works [1–5]. The log*K* values were determined against various background electrolytes, and the results obtained were in close agreement. No data on the enthalpy changes in protolytic equilibria of this dipeptide have been found. Therefore, the aim of this work was calorimetric determination of enthalpy changes in protonation and neutralization reactions for glycyl-β-alanine and the evaluation of the corresponding standard thermodynamic parameters.

Experimental

Glycyl-β-alanine (pure for analysis, Reanal, Hungary) was used. Nitric acid and potassium hydroxide solutions were prepared from reagent grade samples. Potassium nitrate (pure for analysis) was twice crystallized from bidistilled water.

The calorimetric measurements were performed in an isothermal jacket calorimeter equipped with a KMT-14 thermistor. Enthalpy changes in reactions of protonation and neutralization of glycyl-β-alanine were determined at 298.15 K and ionic strengths of 0.5, 1.0, and 1.5 mol L^{-1}. Potassium nitrate was used as background electrolyte. The heats of mixing for 0.8514 M glycyl-β-alanine solution with 0.0996–0.1001 M nitric acid and 0.0100–0.0107 M potassium hydroxide solutions were measured. The heats of dilution for the dipeptide solution with a background electrolyte at the corresponding ionic strengths were also measured applying necessary corrections.

Results and discussion

The stepwise dissociation constants of glycyl-β-alanine differ considerably from one another. It allows to measure the enthalpies of the corresponding processes independently. The enthalpy change in the reaction of protonation of HL species ($\Delta_{prot}H$) was calculated by the equation

$$\Delta_{prot}H=\Delta_{mix}H_H-\Delta_{dil}H \quad (1)$$

where $\Delta_{mix}H_H$ is the heat of mixing the dipeptide solution with HNO_3 solution, $\Delta_{dil}H$ is the heat of dilution of the dipeptide solution with the background electrolyte solution. The enthalpy changes in reactions of neutralization ($\Delta_{neut}H$) and dissociation ($\Delta_{dis}H$) of the betaine proton of glycyl-β-alanine were calculated by the equations

$$\Delta_{neut}H=\Delta_{mix}H_{OH}-\Delta_{dil}H \quad (2)$$

$$\Delta_{dis}H=\Delta_{neut}H-\Delta_wH \quad (3)$$

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Table 1 The enthalpy changes in protolytic equilibria of glycyl-β-alanine at 298.15 K

Process	$-\Delta H$/kJ mol^{-1}		
	I=0.5 M	I=1.0 M	I=1.5 M
$H^+ + HL \leftrightarrow H_2L^+$	1.76±0.18	2.28±0.18	2.62±0.17
$2H^+ + L^- \leftrightarrow H_2L^+$	46.04±0.48	47.07±0.31	48.25±0.33
$H^+ + L^- \leftrightarrow HL$	44.28±0.44	44.79±0.25	45.63±0.28
$HL + OH^- \leftrightarrow L^- + H_2O$	12.62±0.20	11.95±0.20	11.16±0.20
$H^+ + OH^- \leftrightarrow H_2O$ [6]	56.90±0.40	56.74±0.15	56.79±0.20

Table 2 The standard thermodynamic parameters for dissociation of glycyl-glycine, glycyl-β-alanine and glycyl-γ-aminobutyric acid (I=0, T=298.15 K)

Dipeptide	$-\log K^0$	ΔG^0/kJ mol^{-1}	ΔH^0/kJ mol^{-1}	ΔS^0/J mol^{-1} K^{-1}
		$H_2L^+ \leftrightarrow H^+ + HL$		
glycyl-glycine [7]	3.16±0.01	18.04±0.06	0.61±0.14	58.5±0.5
glycyl-β-alanine	4.04±0.05	23.06±0.29	1.36±0.18	72.8±1.1
glycyl-γ-aminobutyric acid [8]	4.22±0.02	24.09±0.12	1.64±0.06	75.3±0.3
		$HL \leftrightarrow H^+ + L^-$		
glycyl-glycine [7]	8.31±0.01	47.43±0.06	44.19±0.33	10.9±1.1
glycyl-β-alanine	8.37±0.06	47.78±0.34	42.97±0.28	16.1±1.5
glycyl-γ-aminobutyric acid [8]	8.34±0.01	47.60±0.06	42.62±0.45	16.7±1.5
		$H_2L^+ \leftrightarrow 2H^+ + L^-$		
glycyl-glycine [7]	11.47±0.01	65.47±0.09	44.80±0.36	69.4±1.2
glycyl-β-alanine	12.41±0.08	70.84±0.44	44.33±0.33	88.9±1.9
glycyl-γ-aminobutyric acid [8]	12.56±0.02	71.69±0.12	44.26±0.45	92.0±1.5

where $\Delta_{mix}H_{OH}$ is the heat of mixing the dipeptide solution with KOH solution, and $\Delta_w H$ is the enthalpy change in the reaction of neutralization of HNO_3 by KOH at the corresponding temperature, ionic strength and background electrolyte. The relevant $\Delta_w H$ values were taken from [6]. The results obtained for the protolytic equilibria of glycyl-β-alanine are shown in Table 1.

The reaction enthalpy changes at zero ionic strength were determined by extrapolating the ΔH values found at the fixed ionic strengths using one-parameter equation [6].

$$\Delta H - \Delta z^2 \Psi(I) = \Delta H^0 + bI \qquad (4)$$

where ΔH, ΔH^0 denote the enthalpy changes at the finite and zero ionic strengths, respectively; b is an empirical coefficient; Δz^2 is the difference between the squared charges of the reaction products and reacting species; and $\Psi(I)$ was a function of ionic strength deduced theoretically [6]. The corresponding standard thermodynamic constants were evaluated using the following equation [6].

$$\log K^0 = \log K - A_\gamma \Delta z^2 [I^{1/2}/(1+1.6I^{1/2}) - 0.05I] - 0.05I \qquad (5)$$

where $\log K^0$, $\log K$ denote the thermodynamic and stoichiometric protonation constants, respectively; A_γ is the Debye parameter. The $\log K$ values are 4.04±0.05 and 8.17±0.06 at 298.15 K and ionic strength 0.1 mol L^{-1} as the averages of the results obtained previously [1–5]. The standard thermodynamic parameters for the stepwise and cumulative dissociation processes of glycyl-β-alanine are presented in Table 2. This table also contains the corresponding parameters of glycyl-glycine [7] and glycyl-γ-aminobutyric acid [8] being obtained in this laboratory using the same procedure.

These data shows that the thermodynamic parameters ($\log K^0$, ΔG^0, ΔH^0, ΔS^0) for the betaine group dissociation of glycyl-β-alanine are close with the parameters of glycyl-γ-aminobutyric acid. The release of proton from carboxylic groups is characterized by an endothermic effect, the value increases continuously in the series of glycyl-glycine<<glycyl-β-alanine<glycyl-γ-aminobutyric acid. This can be attributed to strengthening O–H bond on growing positive induction effect of their alkylene chains.

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