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Thermodynamic Characteristics of Protolytic Equilibria of D,L-Alanyl-D,L-leucine in Aqueous Solution

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Abstract—Previously unknown thermal effects of the stepwise dissociation of D,L-alanyl-D,L-leucine were determined by direct calorimetric measurements. The standard thermodynamic characteristics of the dissociation equilibria were calculated. The results were compared with the published data for related compounds.

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Published data on the thermal effects of stepwise dissociation of D,L-alanyl-D,L-leucine (HL) are lacking. We found the corresponding data [1] only for L-alanyl-L-leucine at ***I*** 0.1 (KNO_3) and T 298.15 K: $\Delta_{dis}H(H_2L^+) = -1.0$, $\Delta_{dis}H(HL) = 44.68$ kJ mol^{-1}.

The lack of this important information makes it necessary to study calorimetrically the protolytic equilibria of D,L-alanyl-D,L-leucine. The goal of this study is measurement of the thermal effects of the dissociation of this dipeptide at several values of the ionic strength and determination of the standard thermodynamic characteristics of the corresponding equilibria.

The speciation diagram (see figure) shows that the thermal effects of the dissociation of H_2L^+ and HL can be found as differences between the corresponding heats of mixing and dilution:

$$\Delta_{dis}H = -(\Delta_{mix}H - \Delta_{dil}H)/\alpha, \quad (1)$$

where $\Delta_{mix}H$ is the thermal effect of mixing of an HNO_3 solution with a solution of D,L-alanyl-D,L-leucine in the presence of a supporting electrolyte in the appropriate pH range; $\Delta_{dil}H$, thermal effect of dilution of an HNO_3 solution in the supporting electrolyte at the same ionic strength; and α, degree of protonation of HL and L^-. The obtained thermal effects of the dissociation of D,L-alanyl-D,L-leucine at 298.15 K and I 0.1, 0.5, and 1.0 (KNO_3) are given in Table 1.

From $\Delta_{dis}H$ at fixed ionic strengths it is possible to calculate the standard thermodynamic characteristics of the equilibria in question. To extrapolate the concentration thermal effect to zero ionic strength we used an equation with one individual parameter [2]:

$$\Delta_{dis}H - \Delta z^2\Psi(I) = \Delta_{dis}H^0 + bI, \quad (2)$$

where $\Delta_{dis}H^0$ and $\Delta_{dis}H$ are the enthalpies of the reaction at finite and zero ionic strengths, respectively; b, empirical coefficient; Δz^2, difference between the squared charges of the reaction products and reacting species; and $\Psi(I)$, function of the ionic strength,

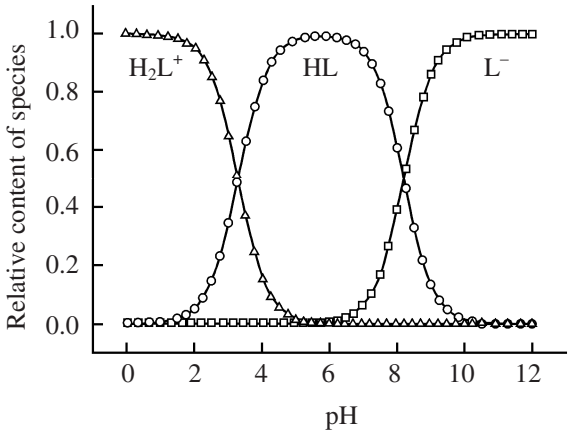

Diagram of protolytic equilibria of D,L-alanyl-D,L-leucinein aqueous solution at 298.15 K and I 0.5 (KNO_3).

Table 1. Thermal effects of dissociation of D,L-alanyl-D,L-leucine at 298.15 K and I 0.1–1.0 (KNO_3)

Process	ΔH, Jmol^{-1}		
	I 0.1	*I* 0.5	*I* 1.0
$H_2L^+ = H^+ + HL$	–1495±163	–1184±168	–912±172
$HL = H^+ + L^-$	46451±230	47323±210	47900±216
$H_2L^+ = 2H^+ + L^-$	44956±282	46139±269	46988±276

calculated theoretically [2]. The corresponding thermodynamic constants of dissociation of D,L-alanyl-D,L-leucine were calculated by Vasil'ev's equation [2]:

$$pK^0 = pK + A\Delta z^2[I^{1/2}/(1 + 1.6I^{1/2}) - 0.05I] + 0.05I, \quad (3)$$

where K^0 and K are the thermodynamic and concentration dissociation constants, respectively; A, constant of the Debye–Hückel theory. The concentration dissociation constants of the dipeptide were found in [3]. The standard thermodynamic characteristics of the dissociation of D,L-alanyl-D,L-leucine are given in Table 2. Also the results are given of calorimetric studies of D,L-alanyl-D,L-valine, D,L-alanyl-D,L-alanine, D,L-alanylglycine, and D,L-alanine, performed previously [4–7] in our laboratory.

Comparison of the thermodynamic characteristics of the protolytic equilibria shows that the reactions of dissociation of the betaine group are characterized by similar thermal effects $\Delta_{dis}H^0$(HL). At the same time, the thermal effects $\Delta_{dis}H^0$(HL) of dissociation of the carboxy group considerably changes in going from D,L-alanyl-D,L-leucine, D,L-alanyl-D,L-valine, and D,L-alanyl-D,L-alanine to D,L-alanylglycine and D,L-alanine. The exothermic nature of the carboxy group dissociation in D,L-alanyl-D,L-leucine, D,L-alanyl-D,L-

Table 2. Standard thermodynamic characteristics of dissociation of D,L-alanyl-D,L-leucine, D,L-alanyl-D,L-valine, D,L-alanyl-D,L-alanine, D,L-alanylglycine, and D,L-alanine in aqueous solution

Dipeptide	pK^0	$\Delta_{dis}G^0$, kJ mol^{-1}	$\Delta_{dis}H^0$, kJ mol^{-1}	$-\Delta_{dis}S^0$, Jmol^{-1} K^{-1}
		$H_2L^+ = H^+ + HL$		
D,L-Alanyl-D,L-leucine	3.24±0.01	18.49±0.06	–1.54±0.17	67.2±0.6
D,L-Alanyl-D,L-valine [4]	3.10±0.02	17.69±0.11	–2.23±0.24	66.8±1.0
D,L-Alanyl-D,L-alanine [5]	3.12±0.01	17.81±0.06	–1.72±0.11	65.5±0.5
D,L-Alanylglycine [6]	3.18±0.03	18.15±0.17	0.74±0.11	58.4±0.7
D,L-Alanine [7]	2.43±0.01	13.87±0.06	3.39±0.21	35.2±0.9
		$HL = H^+ + L^-$		
D,L-Alanyl-D,L-leucine	8.48±0.03	48.40±0.17	45.97±0.23	8.2±1.0
D,L-Alanyl-D,L-valine [4]	8.43±0.02	48.12±0.11	46.22±0.40	6.4±1.4
D,L-Alanyl-D,L-alanine [5]	8.54±0.01	48.75±0.06	45.89±0.56	9.6±1.9
D,L-Alanylglycine [6]	8.35±0.03	47.66±0.17	45.14±0.22	8.5±0.9
D,L-Alanine [7]	10.09±0.01	57.59±0.06	45.54±0.72	40.4±2.4
		$H_2L^+ = 2H^+ + L^-$		
D,L-Alanyl-D,L-leucine	11.72±0.03	66.90±0.18	44.43±0.29	75.4±1.1
D,L-Alanyl-D,L-valine [4]	11.53±0.03	65.81±0.16	43.99±0.47	73.2±1.7
D,L-Alanyl-D,L-alanine [5]	11.66±0.01	66.56±0.09	44.17±0.57	75.1±2.0
D,L-Alanylglycine [6]	11.53±0.04	65.81±0.24	45.88±0.25	66.9±1.1
D,L-Alanine [7]	12.52±0.01	71.46±0.09	48.93±0.75	75.6±2.5

valine, and D,L-alanyl-D,L-alanine is appa-rently due to the presence of hydrophobic substituents in both amino acid fragments of the dipeptide: Alkyl groups of these dipeptides form a medium with a low dielectric permittivity, thus enhancing the interaction of the ammonium cation with the carboxylate anion.

EXPERIMENTAL

We used chemically pure grade D,L-alanyl-D,L-leucine purchased from Reanal (Hungary). Solutions of the dipeptide were prepared by dissolving weighed portions of the compound in freshly prepared double-distilled water just before the experiment. Solutions of KOH and HNO_3 were prepared from chemically pure grade chemicals. The concentrations of the working solutions were determined by common titration methods. Analytically pure grade KNO_3 used for supporting the ionic strength was twice recrystallized two times from double-distilled water.

Calorimetric measurements were performed in an ampule calorimeter with an isothermal shell, equipped with a thermistor temperature sensor. Temperature variation with time was recorded automatically. At 298.15 K and ionic strengths of 0.1, 0.5, and 1.0 (KNO_3), we measured the thermal effects of mixing of an HNO_3 solution (0.9439 mol kg^{-1} solution) with 0.0051–0.0073 M solutions of the dipeptide in the pH ranges from 3.9 to 2.7 and from 8.7 to 7.7. To make the required corrections, we also determined the heats of dilution of HNO_3 in supporting electrolyte solution at the corresponding ionic strengths.

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