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Thermodynamics of dipeptides in water. VI. Calorimetric determination of enthalpy changes of dissociation processes in water of the free α-carboxyl and α-amino groups in a series of dipeptides. Comparison of these processes for two series of dipeptides

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Abstract

A calorimetric study has been made on the dissociation processes in water of the free α-amino group of the amino terminal residue and the free α-carboxyl groups of the carboxyl terminal residue in a series of dipeptides having valine as first common term. These values have been compared with those of the proton dissociation processes related to the same groups of the corresponding single α-amino acids. The results of this series have also been considered in relation to those from another series of dipeptides, previously studied, in an effort to compare the effects of different chains on the dissociation processes of the free α-carboxyl and free α-amino groups. © 1998 Elsevier Science B.V.

Keywords: Acidity and basicity variations; Calorimetry; Dipeptides; Heat of dissociation; Heat of neutralization; Heat of protonation

1. Introduction

Much work concerning the thermodynamics of dipeptides in water has been carried out mainly in the last 20 years [1–8]. In particular, the stereoselectivity in the proton complex formation of L–L or L–D pairs of dipeptides has been investigated by means of calorimetric technique in aqueous solution [9–16]. On the basis of the results obtained, it was possible to assess the role played by two different non-covalent interactions, namely the electrostatic interaction (between COO^- and NH_3^+ groups) and the solvophobic interaction (between the side chains) on the thermodynamic stereoselectivity in the proton-complex formation. To study these interactions, the difference in proton-dissociation processes of some series of dipeptides and the corresponding single α-amino acids has been the subject of an extended research in our laboratory [17–21].

This study is based on the calorimetric determination of the enthalpy changes of the dissociation processes of the free α-amino group belonging to the

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amino terminal residue (N-terminal) and the free α-carboxyl group belonging to the carboxyl terminal residuum (C-terminal). These values are compared with those of the proton-dissociation processes related to the same groups of the corresponding single α-amino acids.

The aim of this work is to study this difference for a series of L-L dipeptides, where the first common term is L–leucine. The dipeptides studied were: leucyl–leucine (Leu–Leu), leucyl–isoleucine (Leu–Ile), leucyl–valine (Leu–Val), leucyl–glycine (Leu–Gly), leucyl–alanine (Leu–Ala), leucyl–tyrosine (Leu–Tyr), leucyl–phenylalanine (Leu–Phe), leucyl–proline (Leu–Pro), leucyl–tryptophan (Leu–Trp), leucyl–aspartic-acid (Leu–Asp), leucyl–aspargine (Leu–Asn), leucyl–serine (Leu–Ser).

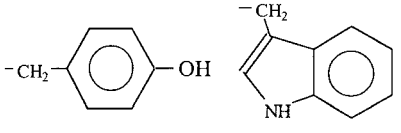
Using some compounds of a series of L–L dipeptides previously studied [17], with valine as the common first term. an attempt to compare the different influences of isopropyl and isobutyl chains on the α-free carboxyl and free-amino groups dissociation processes of the two series is made.

The pairs considered are Leu–Tyr/Val–Tyr, Leu–Trp/Val–Trp, Leu–Val/Val–Val, Leu–Leu/Val–Leu, Leu–Ser/Val–Ser and Leu–Pro/Val–Pro.

(structure 1)

R for the first series is $(CH_3)_2CHCH_2$– and for the second $(CH_3)_2CH$–.

For both series R′ is, respectively:



-CH(CH$_3$)$_2$ -CH$_2$CH(CH$_3$)$_2$ -CH$_2$OH -CH$_2$CH$_2$CH$_2$-

2. Experimental and procedure

The compounds (Calbiochem) were weighed and handled in a nitrogen-filled dry box.

The purity of all compounds is between 99% and 100% and was checked by means of DSC purity method using Stenton–Redcroft 625 simultaneous TG-DSC (with dynamic purity program supplied by P.L. Thermal Sciences) and, subsequently, by potentiometric titrations.

A Tronac (Model 458) instrument was used to carry out the measurements. The calorimeter vessel was a rapid response glass vacuum Dewar flask of 100 cm^3 capacity. The thermostat was maintained at $298.15\pm2\times10^{-4}$ K, during the calorimetric measurement, by employing a Tronac P.T.C. 41 precision temperature controller.

Potential vs. time measurements were made using a Fluke 88100 model digital voltmeter. The voltage differential of the bridge of the calorimeter was fed into Hitachi 561-1000 2/P strip chart recorder and a digital voltmeter connected to an Olivetti M24 computer.

Data were acquired by the computer via a data-acquisition system and, subsequently, read and converted into enthalpy values using a basic program run on the Olivetti M24 computer [22]. All the steps of the measurements (calibration curve, cooling curve, reaction curve and equilibrium temperature) were also described [22]. Data obtained using the chart recording may be slightly different from those obtained using the computer and they also give the shape of the thermograms expressed as temperature vs. time curves.

Standard chemical test system used to check calorimetric system was the standard thermochemical reaction values between solid *tris* (hydroxymethyl) amino methane and 0.1 M HCl at 298.15 K in water. The value obtained (see Table 1) is 29.71 ± 0.31 kJ mol^{-1}

Table 1
Partial molar enthalpy of reaction ΔH between solid *tris* (hydroxymethyl) amino methane and 0.1 M $HCl_{(aq)}$ in water at 298.15 K

tris/g	$-\Delta H$/(kJ mol^{-1})
0.098	29.40
0.132	29.54
0.144	30.03
0.787	29.92
0.981	29.70
0.775	30.10
0.123	29.30

and was compared with that obtained in the literature [23] as 29.744 kJ mol^{-1}. The average percentage deviation of the former relative to the latter is 0.11%.

The proton dissociation of the free α-carboxyl group and of the free α-amino group of a generic dipeptide can be represented as:

$$NH_3^+CHRCONHCHR'COOH_{(aq)} \rightarrow NH_3^+CHRCONHCHR'COO^-_{(aq)} + H^+_{(aq)} \quad (1)$$

and

$$NH_3^+CHRCONHCHR'COO^-_{(aq)} \rightarrow NH_2CHRCONHCHR'COO^-_{(aq)} + H^+_{(aq)} \quad (2)$$

The molar enthalpy of dissociation, at infinite dilution, ΔH_1^0, for the free carboxyl groups in water, is obtained by measuring the following quantities:

(a) The molar enthalpy of solution of the crystalline (cr) $NH_3^+CHRCONHCHR'COO^-$ zwitterion form in water at pH close to the isoelectric value

$$NH_3^+CHRCONHCHR'COO^-_{(cr)} \rightarrow NH_3^+CHRCONHCHR'COO^-_{(aq)} \quad (3)$$

pH 5.99±0.12 is the mean of the isoelectric pH values; a buffer solution at pH 6.00±0.02 (Carlo Erba RPE at 298.15 K) formed by KH_2PO_4 and Na_2HPO_4 was used. The concentrations of these salts are in the ratio of 1/10 and ca. 50 times larger than those of dipeptides. Thus, no variation in pH values, for the dissolution of the dipeptides, can be hypothesized.

(b) The molar enthalpy of protonation of the same compound in 0.02 m of HCl solution

$$NH_3^+CHRCONHCHR'COO^-_{(cr)} + H^+_{(aq)} \rightarrow NH_3^+CHRCONHCHR'COOH_{(aq)} \quad (4)$$

Results of at least six determinations of heats of solution of the various compounds (concentrations from 10^{-4} to 10^{-3} mol) have been extrapolated vs. the square root of concentrations, to infinite dilution ΔH_3^0.

Again, results of at least six determinations of heats of protonation were extrapolated vs. the square root of concentrations of the protonated dipeptide.

The molar enthalpy change of process (1) ΔH_1^0 at infinite dilution can be obtained by subtracting ΔH_4^0 from ΔH_3^0.

These values refer to the proton dissociation of 1 mol of $NH_3^+CHRCONHCHR'COOH$ at infinite dilution in water, yielding 1 mol of $NH_3^+CHRCONHCHR'COO^-$ and 1 mol of protons.

For a compound containing carboxyl and amino groups, the dissociation processes in water are complicated by tautomeric equilibria and zwitterion formation [24,25].

Whereas a generic dipeptide in acid solution can be represented by the form $NH_3^+CHRCONHCHR'COOH$, in a solution approaching pH 7.00 the principal species are neutral molecules, which may be either in the $NH_2CHRCONHCHR'COOH_{(aq)}$ form or the zwitterion form.

Thus, only the $NH_3^+CHRCONHCHR'COOH$ form is represented in Eq. (4) for acid solution, while in Eq. (3) this is not the case. The isoelectric pH values for the compounds examined can be calculated by means of the dissociation constants [26,27]. Therefore, it can be assumed that in this solution the zwitterion form is predominant. In this way, the carboxyl proton dissociation enthalpy values can be calculated.

The molar enthalpy change at infinite dilution ΔH_2^0 of the second proton dissociation process of $NH_3^+CHRCONHCHR'COO^-$ is obtained by measuring the molar enthalpy change of the neutralization of the crystalline compound in 2×10^{-2} m NaOH solution.

$$NH_3^+CHRCONHCHR'COO^-_{(cr)} + OH^-_{(aq)} \rightarrow NH_2CHRCONHCHR'COO^-_{(aq)} + H_2O_{(l)} \quad (5)$$

The enthalpy change values of process (5) were extrapolated vs. the square root of concentrations of the anion form.

If the solution process enthalpy change values ΔH_3^0 and the ΔH_6^0 value in water (Ref. [28], value 55.94 kJ mol^{-1}) related to the process (6)

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \quad (6)$$

are subtracted from ΔH_5^0, then the relation

$\Delta H_5^0 - (\Delta H_3^0 + \Delta H_6^0)$ supplies the enthalpy change values of process (2).

These values refer to the proton dissociation of 1 mol of $NH_3^+CHRCONHCHR'COO^-$ at infinite dilution in water, yielding 1 mol of $NH_2CHRCONHCHR'COO^-$ and 1 mol of protons. It has been noted that process (5) occurs in basic solution so that only the $NH_2CHRCONHCHR'COO^-$ form is present. Finally, it was noted that in process (5) the second carboxyl group of leucyl–aspartic acid and the hydroxyl group of leucyl–tyrosine are converted to ester (methyl and trifluoro acetate) because the heat of neutralization of process (5) must be referred to the protonated amino group. In addition, all the values of the total uncertainties (calorimetric, chemical and extrapolationary) are given.

3. Results and discussion

The enthalpy change values for solution ΔH_3^0, protonation ΔH_4^0 and neutralization ΔH_5^0 of all the compounds cited are reported in Table 2. This table also gives the dissociation enthalpy changes for the free carboxyl group (ΔH_1^0) and for the free amino group (ΔH_2^0) of the dipeptides. A technique previously used [17–20] to study the differences in enthalpy changes for dissociations processes of dipeptides and single α-amino acids can be described by the following relations:

$$\Delta H_1^0(\text{LeuA}) - \Delta H_1^0(\text{A})/\Delta H_1^0(\text{A}) \quad (6a)$$

$$\Delta H_2^0(\text{LeuA}) - \Delta H_2^0(\text{A})/\Delta H_2^0(\text{A}) \quad (6b)$$

where ΔH_1^0 represents the dissociation process of the free carboxyl groups of dipeptides having leucine as first component, $\Delta H_1^0(\text{A})$ represents the dissociation process of the carboxyl groups of the corresponding single α-amino acids, ΔH_2^0 represents the dissociation process of the free amino group of leucine in the various dipeptides and $\Delta H_2^0(\text{A})$ is the enthalpy change for dissociation of the amino group of free leucine. The values of reactions (6a) and (6b) which are related to the effect of leucine upon the free carboxyl groups of dipeptides and to the effects of the various α-amino acids upon the free amino group of leucine (which is the first common term of the series considered) are given in Table 2.

In the first dissociation process of the dipeptides, the influence of leucine favours the dissociation, from the enthalpic point of view, of the free carboxyl groups, with respect to those of the corresponding single α-amino acids, for leucine, valine, tyrosine, glycine, proline, aspartic acid, aspargine and serine. For these compounds the carboxyl groups of the dipeptides show enthalpy changes for dissociation more exothermic or less endothermic than those of the corresponding free α-amino acids while for the other dipeptides considered the reverse is true.

The proton dissociation process of the free amino group of leucine is hindered by leucine and isoleucine while other α-amino acids favour it. The proton dissociation trends could be related to increase or decrease of the electron charge localized on the car-

Table 2
Enthalpy values (in kJ mol^{-1}) of processes (1), (2), (3), (4) and (5) and values obtained by using relations (6a) and (6b) for some dipeptides having leucine as the first common term, at 298.15 K in water

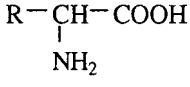
Compounds	ΔH_1^0	ΔH_2^0	ΔH_3^0	ΔH_4^0	ΔH_5^0	(6a)	(6b)
Leu–Leu	0.23±0.05	49.47±0.03	−8.75±0.02	−8.98±0.05	−15.23±0.02	−0.85	0.04
Leu–Ile	0.54±0.06	49.01±0.10	−16.56±0.02	−17.10±0.06	−23.43±0.10	7.51	0.03
Leu–Val	−1.75±0.18	46.61±0.25	−13.70±0.15	−11.95±0.10	−23.03±0.2	−3.46	−0.02
Leu–Gly	−0.01±0.01	44.25±0.20	−5.14±0.01	−5.13±0.01	−16.83±0.20	−1.00	−0.07
Leu–Ala	8.32±0.10	38.47±0.08	−5.66±0.06	−13.98±0.08	−23.13±0.05	2.41	−0.19
Leu–Tyr	−8.74±0.15	42.75±0.01	−9.77±0.15	−1.03±0.01	−23.16±0.01	−6.12	−0.10
Leu–Phe	1.00±0.01	47.33±0.04	0.1±0.01	−0.90±0.01	−8.51±0.04	0.69	−0.002
Leu–Pro	−7.31±0.02	−6.29±0.03	−3.11±0.01	4.20±0.02	−65.34±0.03	−26.21	−0.13
Leu–Trp	1.54±0.09	42.63±0.32	6.31±0.02	4.77±0.09	−7.00±0.32	2.08	−0.10
Leu–Asp	−0.58±0.09	42.56±0.23	2.74±0.09	3.32±0.01	−16.64±0.21	−1.17	−0.10
Leu–Asn	1.48±0.12	43.72±0.10	−2.01±0.09	−4.49±0.08	−15.33±0.05	−0.52	−0.08
Leu–Ser	−0.33±0.10	44.84±0.07	−6.90±0.07	−6.57±0.07	−18.00±0.02	−1.24	−0.05

Table 3
Hückel–McLachlan charge density distributions for some dipeptides in neutral form

Compounds	$CH^{(1)}$	NH_2	$CH^{(2)}$	COOH
Leu–Leu	0.56495	0.25422	0.57364	0.25288
Leu–Tyr	0.46150	0.19093	0.33573	0.06797
Leu–Asp	0.59843	0.27749	0.65410	0.37015
Leu–Asn	0.55524	0.24870	0.62262	0.32558
Leu–Ser	0.56487	0.25723	0.65180	0.32010
Leu–Ile	0.57239	0.25852	0.58767	0.24232
Leu–Ala	0.57301	0.25957	0.72889	0.51176
Leu–Val	0.55791	0.24914	0.49301	0.00000
Leu–Gly	0.53953	0.23664	0.48526	0.34287
Leu–Pro	0.56783	0.52790	0.20267	0.27718
Leu–Trp	0.78547	0.54467	0.70776	0.56436
Leu–Phe	0.44789	0.18538	0.36650	0.13135

Table 4
Hückel-McLachlan charge density distributions for some α-amino acids in neutral form

Compounds	CH	NH_2	COOH
Ala	0.06797	0.01034	1.9150
Tyr	0.76717	0.38818	0.43920
Trp	0.76885	0.39767	1.55808
Val	0.07216	0.01096	1.90376
Phe	0.02970	0.00280	1.96369
Leu	0.07630	0.01069	1.48889
Ser	0.07619	0.01155	1.47627
Pro	0.40291	0.78321	0.22140
Asp	0.07140	0.01085	1.89671
Asn	0.05359	0.00000	1.44529
Ile	0.07244	0.01100	1.90263
Gly	0.05355	0.00821	1.93824



boxyl and amino groups of the dipeptides with respect to the charge localized on the same groups of single α-amino acids. For the carboxyl groups, the trend of most of the components agrees with the results of the Hückel–McLachlan molecular orbital calculations which show the decrease of the electron charge density on the carboxyl groups of dipeptides (Table 3) with respect to the density charge localized on the carboxyl groups of the corresponding α-amino acids (Table 4).

The Hückel-McLachlan charge distribution was calculated by a computer program using the following values [29]:

$h_{\ddot{N}} = 0.5$ K_{CC}=0.8 K_{C-C}=0.8
$h_{\ddot{O}}$=2 $K_{C=0}$=1
$h_{\dot{O}} = 1$ K_{C-N}=0.8

where h is the Coulomb integral (interaction energy between each electron and its respective nucleus) increment and K is the bond integral which represents the energy of two atomic orbitals; C–C symbolizes a single bond, C=C a double bond and CC an aromatic bond.

Let us compare the results of relations (6a) and (6b) in Table 2 with the analogous relations (Table 5) relating to the series previously studied [17] with valine as the first common term.

Valine favours, from the enthalpic point of view, the dissociation processes related to the free carboxyl groups of tryptophan, valine, leucine, proline and hinders that of serine and tyrosine with respect to the dissociation processes of the corresponding single α-amino acids.

Tyrosine, tryptophan and proline favour the dissociation process related to the α-amino group of valine, while other α-amino acids hinder it.

Table 5
Enthalpy values (kJ mol^{-1}) of processes (1), (2), (3), (4) and (5) and values obtained by using relations (6a) and (6b) for some dipeptides having valine as first common term, at 298.15 K

Compounds	ΔH_1^0	ΔH_2^0	ΔH_3^0	ΔH_4^0	ΔH_5^0	(6a)	(6b)
Val–Tyr	2.38±0.02	32.17±0.23	2.68±0.02	0.29±0.01	−21.09±0.32	2.97	−0.05
Val–Trp	−2.43±0.02	27.82±0.35	16.61±0.02	19.04±0.01	−11.51±0.10	−0.70	−0.17
Val–Val	−1.80±0.17	47.66±0.14	−13.47±0.15	−11.67±0.09	−21.75±0.05	−3.53	0.41
Val–Leu	−1.59±0.35	45.90±0.43	−24.31±0.39	−22.72±0.10	−34.35±0.31	−2.05	0.38
Val–Ser	1.46±0.03	55.90±0.16	−10.51±0.02	−11.97±0.03	−11.25±0.20	0.09	0.66
Val–Pro	−3.43±0.07	−5.31±0.23	−2.26±0.01	1.17±0.09	−63.55±0.34	−12.83	−1.16

Table 6
Differences in enthalpy values (kJ mol^{-1}) of processes (1), (2), (3), (4) and (5) for two series of dipeptides having leucine and valine as the first common term

Compounds	$\delta\Delta H_1^0$	$\delta\Delta H_2^0$	$\delta\Delta H_3^0$	$\delta\Delta H_4^0$	$\delta\Delta H_5^0$
Leu–Tyr/Val–Tyr	−11.08	10.58	−12.45	−1.32	−2.07
Leu–Trp/Val–Trp	3.94	14.81	−10.30	−14.27	4.51
Leu–Val/Val–Val	0.05	−1.05	−0.23	−0.28	−1.28
Leu–Leu/Val–Leu	1.82	3.57	15.56	13.71	19.33
Leu–Ser/Val–Ser	−1.79	−11.06	3.60	5.40	−6.75
Leu–Pro/Val–Pro	−3.88	−0.98	−0.85	3.03	−1.79

Leucine and valine show the same influence on leucine, proline and valine, whereas an opposite influence on tyrosine, tryptophan and serine was found. Moreover, leucine and valine undergo the same effect from tyrosine, leucine, tryptophan and proline and the opposite influence from valine and serine.

A further contribution to the comprehension of the reciprocal influence of leucine, valine and the other α-amino acids can be obtained in the following way. The quantities $\delta\Delta H_1^0 = \Delta H_1^0(\text{LeuA}) - \Delta H_1^0(\text{ValA})$ and $\delta\Delta H_2^0 = \Delta H_2^0(\text{LeuA}) - \Delta H_2^0(\text{ValA})$ are reported in Table 6, where ΔH_1^0(LeuA) and ΔH_1^0(ValA) are related to the first dissociation process values whereas ΔH_2^0(LeuA) and ΔH_2^0 (ValA) are related to the second ionization process values for the two series of dipeptides. It can be observed that, as regards the first dissociation process, Leu–Tyr, Leu–Ser and Leu–Pro are, from the enthalpy point of view, more dissociated, while Leu–Trp, Leu–Val and Leu–Leu are less dissociated with respect to the corresponding compounds of the series having valine as first common term. Thus, compared with valine, leucine makes the carboxyl groups of tyrosine, serine and proline more dissociated and those of tryptophan, valine and leucine less dissociated.

Valine, serine and proline, as the second component, increase the dissociation process of the free amino group of leucine with respect to that valine. This behaviour can be explained by considering (Table 6) the relative solvations of the undissociated molecules $\delta\Delta H_4^0 = \Delta H_4^0(\text{LeuA}) - \Delta H_4^0(\text{ValA})$ and those of the zwitterions $\delta\Delta H_3^0 = \Delta H_3^0(\text{LeuA}) - \Delta H_3^0$ (ValA) of the two series of dipeptides.

For Leu–Tyr/Val–Tyr, Leu–Ser/Val–Ser and Leu–Pro/Val–Pro pairs, the relative solvations of the zwitterions prevail over those of the undissociated molecules, while for Leu–Trp/Val–Trp, Leu–Val/Val–Val and Leu–Leu/Val–Leu pairs the relative solvations of the undissociated molecules play a major role. The second process can be explained by considering the relative solvations of the zwitterions $\delta\Delta H_3^0$ and the relative solvations of the anions forming $NH_2CHRCONHR'COO^-$ $\delta\Delta H_5^0 = \Delta H_5^0(\text{LeuA}) - \Delta H_5^0$ (ValA) (Table 6).

For Leu–Tyr/Val–Tyr, Leu–Trp/Val–Trp and Leu–Leu/Val–Leu the relative solvations of the zwitterions prevail over the relative solvations of the anions formed, so that the decrease of the dissociation process of the amino group of the first series is explained. In this way, it can be directly compared the isopropyl and isobutyl chains role in determining the dissociation processes of the carboxyl and amino groups for some dipeptides of the two series.

Some considerations can be made on ΔH_1 values for Leu–Ala, Leu–Tyr and Leu–Pro. For Leu–Ala the ΔH_1 high positive value is due to the high solvation of the undissociated molecule while for Leu–Tyr the high negative value of ΔH_1 is due to the high solvation of zwitterion. Finally, for Leu–Pro (as far as for Val–Pro), the ΔH_1 and ΔH_2 values, which greatly differ from those of other compounds, can be related to the particular structure of the proline that is an imino acid.

4. Conclusions

In a series of dipeptides, leucine favours the dissociation processes of the free carboxyl groups of most of the considered dipeptides with respect to the corresponding groups of simple α-amino acids. In a direct comparison of the two series, the effect of

leucine and valine on the dissociation processes can be directly compared in some dipeptides.

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