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Thermodynamics of dipeptides in water. V. calorimetric determination of enthalpy change values related to proton transfer processes of a series of dipeptides in water

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Abstract

We have made calorimetric determination of enthalpy change values related to proton dissociation processes (for a series of dipeptides having α-alanine as first common term) of the free α-amino groups belonging to the amino terminal residue (N-terminal) and of the free α-carboxyl groups belonging to the carboxyl terminal residue (C-terminal). These values were subsequently compared with those related to proton dissociation processes of the corresponding groups of alanyl–alanine and of the individual free α-amino acids. The results were interpreted in terms of reciprocal influence of the components of the dipeptides. © 1997 Elsevier Science B.V.

Keywords: Absolute scale; Acidity ; Basicity; Dipeptides; Enthalpy change values; Proton transfer; Relative scale

1. Introduction

Dipeptides which are compounds made up of two α-amino acids are the smallest part of proteic chains. For this reason dipeptides allow the mutual influence of different α-amino acids to be easily studied. Calorimetric study of this influence in two series of dipeptides having valine and glycine as first common component, has been the subject of previous papers [1,2].

This was achieved by means of calorimetric determination of enthalpy charge values related to proton transfer processes of the component of the series.

The aim of the present work was to study the reciprocal influence of the α-amino acids in a series of dipeptides, where the first common term is α-alanine. The dipeptides studied were alanyl–alanine (AlaAla), alanyl–glycine (AlaGly), alanyl–glutamic acid (AlaGlu), alanyl–isoleucine (AlaIle), alanyl–methionine (AlaMet), alanyl–aspartic acid (AlaAsp), alanyl–aspargine (AlaAsn), alanyl–lysine (AlaLys), alanyl–tyrosine (AlaTyr), alanyl–tryptophan (AlaTrp), alanyl–valine (AlaVal), alanyl–threonine (AlaThr), alanyl–phenylalanine (AlaPhe), alanyl–leucine (Ala-Leu), alanyl–serine (AlaSer), alanyl–proline (AlaPro).

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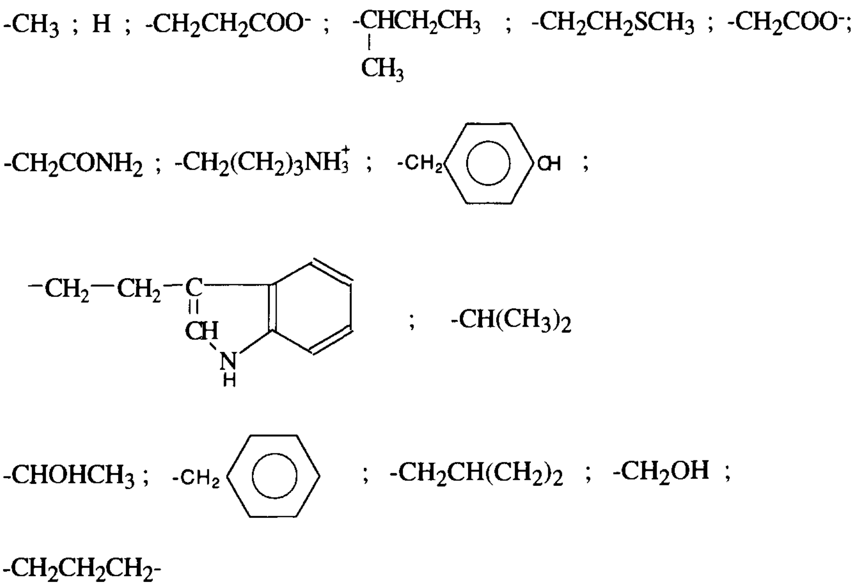
where R is $^-CH_3$ and R' is respectively:



Scheme 1.

This series is represented by

$NH_3^+CHRCONHCHR'COO$

where R is $-CH_3$ and R′ is respectively:Scheme 1

2. Experimental

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 make the measurements. The calorimeter vessel was a rapid response glass vacuum Dewar of capacity 100 cm^3. The thermostat was maintained, at 298.15 K, to 2×10^{-4} K during the calorimetric measurement by employing a Tronac P.T.C. 41 precision temperature controller.

Potential versus time measurements were made using a Fluke 88100 model digital voltmeter. The unbalance (volts) of the bridge of the calorimeter was fed into Hitachi 561-1000 2/P strip chart recorder and into 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 [3]. All the steps of the measurements (calibration curve, cooling curve, reaction curve and equilibrium temperature) were also described [3]. Data obtained using the chart record 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 29.712 kJ mol^{-1} ±0.31 and was compared with that obtained in the literature [4] of 29.744 kJ mol^{-1}. The average percentage deviation of the former relative to the latter is 0.11%.

The proton ionization of the free α-carboxyl group and of the free α-amino group of a generic dipeptide

Table 1
Partial molar enthalpy or 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	29.400
0.132	29.538
0.144	30.028
0.787	29.922
0.981	29.700
0.775	30.100
0.123	29.300

can be represented as:

$$NH_3^+CHRCONHCHR'COOH(aq) \rightarrow NH_3^+CHRCONHCHR'COO^-(aq) + H^+(aq) \qquad (1)$$

and

$$NH_3^+CHRCONHCHR'COO^-(aq) \rightarrow NH_2CHRCONHCHR'COO^-(aq) + H^+(aq) \qquad (2)$$

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

$$NH_3^+CHRCONHCHR'COO^-(cr) \rightarrow NH_3^+CHRCONHCHR'COO^-(aq) \qquad (3)$$

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 about 50 times larger than those of dipeptides. So no variation of 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 HCl solution

$$NH_3^+CHRCONHCHR'COO^-(cr) + H + (aq) \rightarrow NH_3^+CHRCONHCHR'COOH(aq) \qquad (4)$$

Results of at least six determinations of heats of solution of the various compounds (concentrations from 10^{-4} to 10^{-3} molal) 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 of Eq. (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 one mole of $NH_3^+CHRCONHCHR'COOH$ at infinite dilution in water, yielding one mole of $NH_3^+CHRCONHCHR'COO^-$ and one mole of protons.

For compound containing carboxyl and amino groups, the dissociation processes in water are complicated by tautomeric equilibria and zwitterion formation [5,6].

While 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 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 [7–9]. 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 at infinite dilution ΔH_2^0 of the second proton dissociation process of $NH_3^+CHRCONHCHR'COO^-$ is obtained by measuring the molar enthalpy of the neutralization of the crystalline compound in 2×10^{-2} m NaOH solution.

$$NH_3^+CHRCONHCHR'COO^-(cr) + OH^-(aq) \rightarrow NH_2CHRCONHCHR'COO^-(aq) + H_2O(l) \qquad (5)$$

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

If the solution process enthalpy values ΔH_3^0 and the ΔH_6^0 value in water ([10], value 55.94 kJ mol^{-1}) related to the Eq. (6)

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad (6)$$

are subtracted from ΔH_5^0 values, then the relation

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

These values refer to the proton dissociation of one mole of $NH_3^+CHRCONHCHR'COO^-$ at infinite dilution in water, yielding one mole of $NH_2CHRCONHCHR'COO^-$ and one mole of protons.

It has been noted that Eq. (6) occurs in basic solution so that only the $NH_2CHRCONHCHR'COO^-$ form is present.

Finally it was noted that in Eq. (5) the second free amino group of alanyl–lysine and the hydroxyl group of alanyl–tyrosine are converted respectively to amide and to ester of trifluoroacetate because the heat of neutralization of Eq. (5) must be referred only to one amino-group.

Next all the values are the total uncertainties (calorimetric, chemical and extrapolation).

Let us consider Eq. (1) for alanyl–alanine compound:

$$\begin{aligned} &NH_3^+CHCH_3CONHCHCH_3COOH(aq) \\ &\quad \rightarrow NH_3^+CHCH_3CONHCHCH_3COO^-(aq) \\ &\qquad + H^+(aq) \end{aligned} \tag{1a}$$

subtracting Eq. (1a) from Eq. (1) gives the following transfer proton process:

$$\begin{aligned} &NH_3^+CHRCONHCHR'COOH(aq) \\ &\quad + NH_3^+CHCH_3CONHCHCH_3COO^- \\ &\qquad = NH_3^+CHRCONHCHR'COO^- \\ &\quad + NH_3^+CHCH_3CONHCHCH_3COO(aq) \end{aligned} \tag{7}$$

Similarly, the proton transfer process related to the second proton dissociation can be written as:

$$\begin{aligned} &NH_3^+CHRCONHCHR'COO^-(aq) \\ &\quad + NH_2CHCH_3CONCHCH_3COO^-(aq) \\ &\qquad = NH_2CHRCONHCHR'COO^-(aq) \\ &\quad + NH_3^+CHCH_3CONHCHCH_3COO^-(aq) \end{aligned} \tag{8}$$

The change of enthalpy related to Eqs. (7) and (8) can be written as:

$$\delta\Delta H_1^0 = \Delta H_1^0(\text{Ala–Sub}) - \Delta H_1^0(\text{Ala–Ala})$$

and

$$\delta\Delta H_2^0 = \Delta H_2^0(\text{Ala–Sub}) - \Delta H_2^0(\text{Ala–Ala})$$

where $\Delta H_1^0(\text{Ala–Sub})$ and $\Delta H_1^0(\text{Ala–Ala})$ are related to the first ionization process of dipeptides and of alanyl–alanine whereas $\Delta H_2^0(\text{Ala}-\text{Sub})$ and $\Delta H_2^0(\text{Ala}-\text{Ala})$ are the values of the second ionization process for the same compounds.

3. Results and discussion

The enthalpy values of 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 ionization enthalpy values for the free carboxyl groups ΔH_1^0 and for the free amino groups ΔH_2^0 of the dipeptides.

Alanyl–alanine, which has a symmetrical structure, is chosen as reference compound to study the reciprocal influence of α-alanine and other α-amino acids in the series of dipeptides. The quantities $\delta\Delta H_1^0$ and $\delta\Delta H_2^0$ are reported in Table 3.

Thus dissociation processes of the carboxyl and amino groups of the studied dipeptides were compared with the dissociation processes of the corresponding groups of alanyl–alanine. Using alanyl–alanine as reference compound, it is possible to observe that the proton transfer process at the carboxyl group varies as a function of the alanine influence, so that the enthalpy contribution to a relative scale of acidity, can be found.

The scale for the dissociation processes of the carboxyl groups is AlaPro > AlaTrp > AlaMet > AlaTyr > AlaIle > AlaVal > AlaAla > AlaLeu > AlaLys > AlaPhe > AlaSer > AlaGly = AlaGlu > AlaAsp > AlaAsn > AlaThr.

This sequence can be explained by considering the scales for relative solvation of zwitterions $\delta\Delta H_3^0 = \delta\Delta H_3^0(\text{Ala}-\text{Sub}) - \Delta H_3^0(\text{Ala}-\text{Ala})$ and for the undissociated molecules $\delta\Delta H_4^0 = \delta\Delta H_4^0(\text{Ala}-\text{Sub}) - \Delta H_4^0(\text{Ala}-\text{Ala})$ (Table 2). For the zwitterions the order of solvation is: AlaPro > AlaLeu > AlaIle > AlaAla > AlaVal > AlaThr > AlaLys > AlaPhe > AlaGlu > AlaSer > AlaGly > AlaMet > AlaAsp > AlaTrp > AlaAsn > AlaTyr. For the undissociated molecules, the order becomes: AlaPro > AlaLeu > AlaIle > AlaAla > AlaThr > AlaVal > AlaLys > AlaPhe > AlaGlu > AlaSer > AlaGly > AlaAsp > AlaMet > AlaAsn > AlaTrp > AlaTyr.

Using alanyl–alanine again, as reference compound, it can be observed that the proton transfer

Table 2
Enthalpy values (kJ mol^{-1}) of process (1), (2), (3), (4) and (5) for some dipetides having α-alanine as the first common term, in water at 298.15 K

Compounds	ΔH_1^0	ΔH_2^0	ΔH_3^0	ΔH_4^0	ΔH_4^0
AlaGu	0.87±0.16	47.61±0.59	1.46±0.14	0.59±0.08	−6.87±0.70
AlaGly	0.87±0.17	45.24±0.31	3.39±0.06	2.51±0.06	−7.31±0.27
AlaAla	−1.62±0.15	45.53±0.05	−7.93±0.03	−6.32±0.18	−18.31±0.04
AlaIle	−1.93±0.33	45.56±0.03	−11.23±0.03	−11.23±0.03	−19.61±0.01
AlaMet	−2.36±0.33	46.62±0.64	4.37±0.23	6.73±0.24	−5.15±0.67
AlaAsP	1.01±0.16	37.44±0.46	6.82±0.08	5.81±0.14	−11.68±0.57
AlaAsn	1.23±0.20	46.72±0.64	11.65±0.13	10.42±0.16	2.43±0.16
AlaLys	−0.21±0.06	47.07±0.52	−2.97±0.01	−2.76±0.08	−11.85±0.13
AlaTyr	−1.99±0.22	33.33±0.11	24.13±0.13	26.12±0.19	1.91±0.01
AlaTrp	−2.74±0.06	34.09±0.16	11.06±0.03	13.80±0.06	−10.80±0.19
AlaVal	−1.62±0.04	63.08±0.04	−4.44±0.01	−2.82±0.04	−2.70±0.04
AlaThr	2.01±0.02	43.08±0.16	−3.68±0.02	−5.69±0.01	−16.57±0.21
AlaPhe	0.34±0.03	49.20±0.75	0.41±0.04	0.07±0.01	−12.64±0.01
AlaLeu	−1.40±0.53	45.87±0.41	−17.45±0.45	−16.05±0.31	−27.52±0.05
AlaSer	0.76±10.00	45.83±0.18	1.64±0.12	0.88±0.02	−8.47±0.13
AlaPro	−2.96±0.45	42.58±0.45	−19.49±0.26	−16.52±0.38	−32.85±0.31

Table 3
Difference in enthalpy values (kJ mol^{-1}) of processes (1), (2), (3), (4) and (5) for some dipeptides with respect of the same processes for alanyl–alanine

Compounds	ΔH_1^0	ΔH_2^0	ΔH_3^0	ΔH_4^0	ΔH_4^0
AlaGu	2.49	2.08	9.39	6.91	11.47
AlaGly	2.49	0.29	11.32	8.83	11.03
AlaAla	0	0	0	0	0
AlaIle	−0.31	2.03	−3.30	−2.98	−1.27
AlaMet	−0.74	1.09	12.30	13.05	13.19
AlaAsP	2.63	−8.09	14.75	12.13	6.66
AlaAsn	2.85	1.19	19.58	16.74	20.77
AlaLys	1.41	1.54	4.96	3.56	6.49
AlaTyr	−0.37	−12.20	32.06	32.44	20.25
AlaTrp	−1.12	−11.44	18.99	20.12	7.54
AlaVal	−0.01	17.55	3.49	3.50	15.64
AlaThr	3.63	−2.45	4.25	0.63	1.77
AlaPhe	1.96	3.67	8.34	6.39	5.70
AlaLeu	0.22	0.34	−9.52	−9.73	−9.18
AlaSer	2.38	0.30	9.57	7.20	9.87
AlaPro	−1.34	−2.95	−11.50	−10.20	−14.51

process at the free amino group, in this series of dipeptides, varies as a function of the second component, and supplies the enthalpic contribution to a relative scale of basicity.

The scale for the dissociation of the free amino groups of the dipeptides can be written as:

AlaTyr > AlaTrp > AlaAsp > AlaPro >
AlaThr > AlaGly > AlaAla > AlaSer >
AlaLeu > AlaMet > AlaAsn > AlaLys >
AlaIle > AlaGlu > AlaPhe > AlaVal.

This can be explained by considering solvation scales for the zwitterions and the anion form $NH_2CHRCONHCHR'COO^-$.

This last relative solvation scale $\delta\Delta H_5^0 = \delta\Delta H_5^0(\text{Ala-Sub}) - \Delta H_5^0(\text{Ala-Ala})$(Table 2) shows the sequence:

$$\text{AlaPro} > \text{AlaLeu} > \text{AlaIle} > \text{AlaAla} > \text{AlaThr} > \text{AlaPhe} > \text{AlaLys} > \text{AlaAsp} > \text{AlaTrp} > \text{AlaSer} > \text{AlaGly} > \text{AlaGlu} > \text{AlaMet} > \text{AlaVal} > \text{AlaTyr} > \text{AlaAsn}.$$

It can be observed that, as regard the first ionizaton process, AlaPro, AlaTrp, AlaMet, AlaTyr, AlaIle and AlaVal, dissociate, from the enthalpic point of view, more easily than alanyl–alanine does, by virtue of the greater solvation of the zwitterions with respect to the undissociated molecules. For the remaining compounds, the solvation of the undissociated molecules prevails with respect to that of the zwitterions.

In this scale, the carboxyl groups of Pro, Trp, Met, Tyr, Ile and Val dissociate easily than that of the α-alanine by virtue of the influence of the same α-alanine.

In the second process of ionization, AlaTyr, AlaTrp, AlaAsp, AlaPro, AlaThr and AlaGly are more dissociated, in the amino group, than alanyl–alanine. For these compounds the solvation of the ionic form prevails with respect to that of the zwitterions, while for the others the reverse is true.

Tyr, Trp, Asp, Pro, Thr, Gly decrease the enthalpic contribution to the basicity of α-alanine in the dipeptides with respect to that of the reference compound.

The first "relative" scale gives a measure of the effect of α-alanine upon the other α-amino acids, assuming AlaAla as reference compound, while the scale for the second ionization process, shows how α-amino acids can affect α-alanine.

For the corresponding free α-amino acids, the enthalpy values of the first and second ionization processes, in the aqueous phase have been calculated previously [11]. From these values and with the same procedure used for dipeptides the differences, with respect to α-alanine, in enthalpy values of the ionization processes of these α-amino acids in the aqueous phase are given in Table 4.

Table 4
Difference in enthalpy values (kJ mol^{-1}) of Eqs. (1) and (2), for some α-amino acids with respect of the same processes for α-alanine

Compounds	ΔH_1^0	ΔH_1^0
α-alanine	0	0
d,l-Valine	−1.72	−12.43
L(+) Leucine	−0.92	1.26
d,l-Isoleucine	−2.51	0.20
L(−) Proline	−2.14	−3.22
L(−) Methionine	0.16	−2.06
L(+) Tryptophan	−3.86	3.77
d,l-Phynylalanine	−1.84	−0.59
D(−) Serine	−1.09	−5.52
L(−) Threonine	0.88	−5.02
L(−) Glycine	1.50	−1.84
L(−) Aspargine	0.67	−4.94
L(−) Tyrosine	−3.64	−11.32
L(−) Lysine	−2.30	0.04
d,l-Aspartic Acid	0.92	18.46
L(+) Glutamic Acid	1.72	24.45

For the free α-amino acids in the aqueous phase the relative scale of the two proton transfer processes are respectively:

$$\text{Trp} > \text{Tyr} > \text{Ile} > \text{Lys} > \text{Pro} > \text{Phe} > \text{Val} = \text{Glu} > \text{Ser} > \text{Leu} > \text{Thr} > \text{Ala} > \text{Met} > \text{Asn} > \text{Asp} > \text{Gly}$$

and

$$\text{Val} > \text{Tyr} > \text{Ser} > \text{Thr} > \text{Asn} > \text{Pro} > \text{Met} > \text{Gly} > \text{Phe} > \text{Ala} > \text{Lys} > \text{Ile} > \text{Leu} > \text{Trp} > \text{Asp} > \text{Glu}$$

A further contribution to the comprehension of the reciprocal influence of α-alanine and other α-amino acids can be supplied from the following relations, which directly compare the two series in absolute scales and supply percentage values of the contribution of the enthalpy to the acidity and basicity of dipeptides:

$$\frac{\Delta H_1^0(\text{Ala-Sub}) - \Delta H_1^0)(\text{Sub})}{\Delta H_1^0(\text{Sub}))} \tag{9a}$$

and

$$\frac{\Delta H_2^0(\text{Ala-Sub}) - \Delta H_2^0)(\text{Ala})}{\Delta H_2^0(\text{Ala})} \tag{9b}$$

where $\Delta H_1^0(\text{Ala-Sub})$ represents the ionization

Table 5
Values from Eq. (9a) and (9b)

Compounds	(9a)	(9b)
AlaGu	0.22	0.03
AlaGly	−0.78	−0.02
AlaAla	2.50	−0.01
AlaIle	23.12	0.03
AlaMet	−1.91	0.01
AlaAsP	−0.70	−0.19
AlaAsn	−0.60	0.01
AlaLys	−2.67	0.02
AlaTyr	−0.64	−0.28
AlaTrp	0.91	−0.26
AlaVal	−3.28	0.37
AlaThr	0.30	−0.07
AlaPhe	−0.42	0.07
AlaLeu	−1.93	−0.01
AlaSer	−0.43	−0.01
AlaPro	−11.21	−0.08

process values for the carboxyl groups of the dipeptides, $\Delta H_1^0(\mathrm{Sub})$ represents the values of the dissociation process for carboxyl groups of the corresponding free α-amino acids, $\Delta H_2^0(\mathrm{Ala-Sub})$ represents the value of the dissociation for the free amino groups of dipeptides and $\Delta H_2^0(\mathrm{Ala})$ the values for the dissociation processes of the amino group of free α-alanine.

Values related to the "absolute" influence of α-alanine upon the free carboxyl groups of dipeptides and of the α-amino acids upon the amino group of α-alanine in the dipeptides, obtained using Eq. (9a) and Eq. (9b) are given in Table 5. These scales supply percentage values of the enthalpic contribution to the acidity and basicity variation in the dipeptides. It can be seen that in the first ionization process, the influence of α-alanine favours the dissociation of the free α-carboxyl groups with respect to those of the corresponding free α-amino acids, for Gly, Met, Asp, Asn, Lys, Val, Phe, Leu, Ser, Pro and hinders the same process for the other α-amino acids.

The influence of other α-amino acids on α-alanine was also studied from the second relation Eq. (9b).

The proton dissociation of the free amino group of α-alanine is favoured, in the dipeptides, by Gly, Ala, Asp, Tyr, Trp, Thr, Leu, Ser and Pro, while Ile, Met, Asn, Lys, Val and Phe hinder the proton dissociation of this group.

These values are close, indicating that the influence of the α-amino acids is similar.

4. Conclusions

Our experimental evidence supports the conclusion that the mutual influence of α-alanine and the other α-amino acids, in a series of dipeptides, can be considered from two points of view. This was achieved by using the proton transfer processes of these compounds in the aqueous phase. The enthalpy values for these proton transfer processes (with alanyl–alanine as reference compound) vary as function of the influence of α-alanine and of the second component, so that, two relative scales of acidity and basicity, in the aqueous phase, are found.

Two relationships, which compare the proton dissociation processes of the carboxyl and the free amino groups of the dipeptides with the same processes of the free α-amino acids, supply, on absolute scale, the enthalpic contribution to the basicity and acidity variation in the dipeptides.

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