

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA*

CRITICAL SURVEY OF THE STABILITY
CONSTANTS OF COMPLEXES OF ALIPHATIC
AMINO ACIDS[†]

(Technical Report)

Prepared for publication by

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[†]**Series Title: Critical Evaluation of Stability Constants of Metal Complexes in Solution**

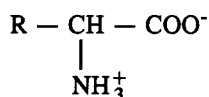
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Critical survey of the stability constants of complexes of aliphatic amino acids (Technical Report)

Abstract - Stability constants for the proton and metal ion complexation equilibria of aliphatic amino acids including α -alanine, valine, 2-aminopentanoic acid, leucine, isoleucine, 2-aminohexanoic acid and β -alanine were collected and critically evaluated. Data evaluation criteria involved the specification of the essential reaction conditions, the correctness of calibration techniques and calculation and the applicability of the methods used for the determination of stability constants. Recommended values for the proton and some metal ion complexes are collected in separate tables. Enthalpy values published on the protonation equilibria and metal ion complex formation processes of aliphatic amino acids were also surveyed.

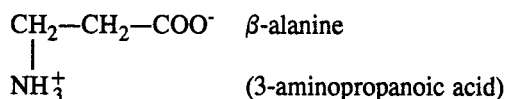
1. INTRODUCTION

Aliphatic amino acids are the most common α -amino-carboxylic acids, with the general formula:



where:	$\text{R} = -\text{CH}_3$	α -alanine (Ala) (2-aminopropanoic acid)
	$\begin{array}{c} -\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	valine (Val) (2-amino-3-methylbutanoic acid)
	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	2-aminopentanoic acid
	$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	leucine (Leu) (2-amino-4-methylpentanoic acid)
	$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	isoleucine (Ile) (2-amino-3-methylpentanoic acid)
	$-(\text{CH}_2)_3-\text{CH}_3$	2-aminohexanoic acid

β -Alanine is also an aliphatic amino acid, in which the amino group is present in the β -position:



The equilibrium data for the proton and metal ion complexes of the above mentioned ligands will be surveyed in this paper.

Except β -alanine the aliphatic amino acids (α -alanine, valine, 2-aminopentanoic acid (norvaline), leucine and 2-aminohexanoic acid (norleucine)) contain one chiral centre (asymmetric carbon atom), while two chiral centres are present in the molecule of isoleucine. Most of the data referred in this survey related to the L-enantiomers of the amino acids, but configuration of the α -carbon atom is not given in many publications. However, it should be taken into account that the absence of detectable

stereoselectivity has been demonstrated in the formation of bis complexes of most didentate amino acids (79PH). Consequently the stability constants of the species ML_2 are the same for both L- and racemic ligands.

It is characteristic of these aliphatic amino acids that they do not contain any donor group in the side chain, and thus their protonation and complexation equilibria are very similar to those of glycine. A critical survey on the stability constants of glycine complexes was published recently (91KS), and this paper serves here as a reference for the possible equilibrium processes of aliphatic amino acids.

All the ligands contain two donor groups (the amino and carboxylate groups), and therefore two hydrogen ions can dissociate from the fully protonated cations of the amino acids (H_2L^+). Dissociation of these protons occurs stepwise, but in well-separated processes, and the aliphatic amino acids can appear in three different forms in different pH ranges: the cationic (H_2L^+), the neutral or zwitterionic (HL) and the anionic (L^-) forms. Analogous to glycine, aliphatic amino acids generally act as didentate ligands, yielding mono, bis and tris complexes with most metal ions; these complexes contain 5-membered chelate rings formed via the coordination of amino-N and carboxylate-O donors. In the case of some metal ions (e.g. Ag^I , Hg^{II} or lanthanides), protonated species can also be formed, with monodentate coordination via the amino or carboxylate group. At high pH the formation of mixed hydroxo complexes is possible, but reliable stability constants are in general not available for these species. The presence of a side chain on the α -carbon atom of the amino acids does not generally result in new type of coordination, although it has some effect on the values of the stability constants. It is not the aim of this survey to discuss the various effects of the side chains on the thermodynamic and structural parameters of the amino acid complexes, but the reader can find an interpretation of this subject in a review published recently (90K).

β -Alanine is also a bidentate ligand, but the larger distance between the donor groups results in an increased basicity of the carboxylate and amino groups as compared to the situation in α -alanine or other aliphatic α -amino acids. On the other hand, β -alanine forms 6-membered chelate rings with metal ions, which results in the lower stability constants of the corresponding complexes and in an enhanced tendency to form mixed hydroxo complexes.

Several hundred papers have already been published in which the proton and metal complex formation equilibria of the aliphatic amino acids have been reported and discussed. Many different procedures (mainly electrochemical and spectroscopic methods) have been employed to determine the stability constants of the various complexes formed. The applicability of these methods is discussed in detail in various textbooks (e.g. 61RR, 69B, 89BN), and the problems associated with the use of these methods have already been considered in previous parts of this IUPAC series (77B, 82A, 82NT, 82SL, 83T, 84Pa, 84Pb, 87BO, 91KS). Taking into account the considerable similarity between the complex-forming abilities of glycine and aliphatic amino acids, it is not necessary to repeat the most important findings reported in the previous references.

It is obvious from a literature survey, however, that pH-metry (with a glass electrode, or with a H-electrode in the early works) has been applied most extensively for determination of the stability constants of the metal complexes of aliphatic amino acids. pH-metry (or other potentiometric procedures) is an accurate and sensitive method for the determination of stability constants, but its reproducibility requires appropriate calibration techniques. The details of this method and the recommended procedure for testing the potentiometric apparatus have already been reviewed elsewhere (82BD, 86BB, 87BO, 91KS).

Appropriate consideration of the effect of ionic strength on the value and constancy of the activity coefficients is one of the biggest problems during the determination of equilibrium data. Most studies have been carried out in media with constant ionic strength, attained through the use of different inert salts. The most common ionic strengths applied were 0.1, 0.2, 0.5, 1.0 and 3.0 mol dm^{-3} , mainly with 1:1 electrolytes, including KCl, KNO_3 , NaCl, $NaNO_3$ and $NaClO_4$. Stability constants for zero ionic strength were obtained either by extrapolation to infinite dilution of the constants determined at various ionic strengths, or by calculating the activity coefficients of the ions through the use of some theoretical or empirical formula (see e.g. 80SH).

In potentiometric titrations with a glass electrode, the calibration technique will govern the type of constants calculated. Concentration constants (C) can be determined by calibrating the electrode systems with solutions of known hydrogen ion concentration (e.g. $HClO_4$, HCl or HNO_3 solutions). When standard buffer solutions of known hydrogen ion activity are used (e.g. 0.05 mol dm^{-3} potassium hydrogenphthalate of pH=4.008 at 25 °C), mixed constants (M) are obtained, which include both activity

(for hydrogen ion) and concentration (for all other components) terms. The advantage of the use of concentration constants was discussed in detail earlier for glycine complexes (91KS). It was shown that mixed constants can cause particularly large errors in high ($pK > 11$) or low ($pK < 3$) pK values.

According to the van't Hoff relationship:

$$\partial(\ln K)/\partial T = \Delta H^\circ/RT^2$$

the equilibrium constant is a function of temperature. Most equilibrium measurements were performed at 25 °C, although other temperatures, such as 20 °C, 30 °C and 37 °C, or a range of temperatures, e.g. between 0 °C and 60 °C have also been employed.

The enthalpy changes accompanying protonation or metal complex formation can be obtained directly through calorimetric measurements, or indirectly from the temperature-dependence of the stability constants via the van't Hoff equation.

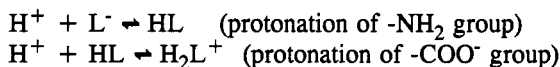
The accuracy of ΔH values based upon calorimetric measurements is generally higher than those based on the temperature-dependence of $\log K$ values, but many factors influence the reproducibility of calorimetric data (e.g. the enthalpy of dissociation of water, the dilution heat, the proton dissociation heat of the ligands, etc.) as has already been discussed by several authors (63HI, 70AM) and will be mentioned in Section 3.

Application of van't Hoff method generally requires the determination of very accurate stability constants over a rather wide temperature range. On the other hand, the wider the temperature range employed, the greater the uncertainty in the calculated values, because of the temperature dependence of the enthalpy values. If the temperature dependence of the enthalpy changes is neglected ($\Delta C_p \approx 0$), the stability constants for any temperatures can be calculated by using the equation:

$$\log K_{T_2} = \log K_{T_1} + \Delta H^\circ(T_2 - T_1)/(2.303 \cdot R \cdot T_1 \cdot T_2)$$

1.1 Presentation of the equilibrium data

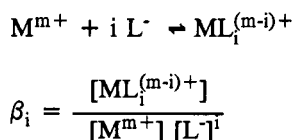
Stability constants (as association constants) are used for the presentation of equilibrium data throughout this paper, for both proton and metal ion complexes. The proton complex formation constants of amino acids are expressed as stepwise protonation constants. For the equilibria:



the constant K_{HL} relates to the first of these processes and $K_{\text{H}_2\text{L}}$ to the second one:

$$K_{\text{HL}} = \frac{[\text{HL}]}{[\text{H}^+][\text{L}^-]} \quad K_{\text{H}_2\text{L}} = \frac{[\text{H}_2\text{L}^+]}{[\text{H}^+][\text{HL}]}$$

For the complex formation processes:

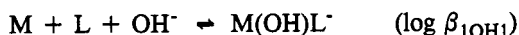


the overall stability constants $\beta_1, \beta_2, \dots, \beta_n$, or in some cases the stepwise stability constant, K , are used and the reaction concerned, is specified in brackets. For the formation of protonated, hydroxo or polynuclear species, the overall stability constants (β_{pqr}) are used:

$$\beta_{\text{pqr}} = \frac{[\text{M}_p\text{H}_q\text{L}_r]}{[\text{M}]^p[\text{H}]^q[\text{L}]^r}$$

Negative subscripts for $[\text{H}^+]$ refer to complex formation reactions in which a hydrogen ion is

eliminated. For metal complexes of aliphatic amino acids this hydrogen ion can originate only from a coordinated water molecule ($MH_{-1}L = M(OH)L$). In some publications stability constants of hydroxo complexes are represented by the equation:



$\log \beta_{1OH1}$ can be deduced from the overall stability constants ($\log \beta_{pqr}$) using the appropriate ionization constants of water (pK_w) (82H), e.g.

$$\log \beta_{1OH1} = \log \beta_{1-11} + pK_w$$

In the above equations, $[H^+]$ refers to either the concentration or the activity of hydrogen ion and thus the constants defined by them are referred to as "concentration" (C) or "mixed" (M) stability constants, respectively.

1.2 Data evaluation criteria

Stability constants for a particular system have been determined by several authors, using different experimental techniques and different conditions. The data reported in the literature were treated and grouped into various evaluation categories by considering the following general criteria:

- The specification and reliability of the essential reaction conditions (e.g. the purity of the ligands and other reactants, the temperature, the ionic strength, the nature of supporting electrolytes, etc.).
- The applicability of the experimental method used for the determination of stability constants (e.g. the application of pH-metry for complexes of very low or very high stability).
- The correctness of the calibration of the apparatus used (e.g. calibration of the electrode system, etc.).
- Details on the calculation methods used (data obtained by either graphical or computational methods of any kind were considered without any prejudice).
- Unambiguous definition of the equilibrium constants reported (e.g. concentration or mixed constants were calculated).
- Control of the constancy of temperature and ionic strength during the measurements.
- Reliable treatment of the experimental data (e.g. consideration of the formation of all possible species: mixed hydroxo complexes for the readily hydrolysable metal ions, tris complexes in the case of a large ligand excess, etc.).
- Correct selection of the auxiliary data from the literature (e.g. selection of the protonation constants of the ligand for calculation of the stability constants of metal ion complexes).

On the basis of these criteria, data were evaluated and grouped into four categories: recommended (R), tentative (T), doubtful (D) and rejected (Rj), according to the original guidelines put forward by IUPAC in 1975 (75CE). The data which passed the above-mentioned acceptance criteria were averaged and, depending on the standard deviation of the average values, were regarded as recommended ($s.d. \leq 0.05$ log units) or tentative ($0.05 < s.d. < 0.2$ log units). It should be noted, however, that this type of evaluation can be accepted only if a reasonable number of independent determinations are available in the literature for a particular system. For aliphatic amino acids the number of determinations is much lower than that for glycine complexes; consequently, recommended values were suggested if at least three different determinations have been reported for the system under the same experimental conditions.

With regard to the similarities in the complex formation abilities of the various aliphatic amino acids, the stability constants are collected and surveyed in the following groups:

- Protonation equilibria of the amino acids, in the sequence of α -alanine, valine, 2-aminopentanoic acid, leucine, 2-aminohexanoic acid, isoleucine and β -alanine.
- Recommended or tentative values for the protonation of the above mentioned ligands.
- Protonation enthalpy values of the amino acids.
- Stability constants of the metal ion complexes of the amino acids in the same sequence
- The enthalpy values reported for the metal ion complexes of the various aliphatic amino acids.

The greatest number of stability constant determinations has been reported for the complexes of

α -alanine, and in this case the metal ions are grouped as: main group elements, first row (3d) transition elements, second and third row (4d and 5d) transition elements, and f-block elements. The stability constants of the metal complexes of valine, leucine and β -alanine are included in two Tables, as: 3d transition elements and other elements. For 2-amino-pentanoic and -hexanoic acids and isoleucine the number of stability constant determinations is quite small, and all the stability constants for a given ligand are included in a common Table, containing the metal ions in alphabetical order.

The metal complexes of the aliphatic amino acids have been most extensively studied for the $3d^7$ - $3d^{10}$ transition elements in the divalent oxidation state (Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}). Thus, recommended or tentative values for the stability constants of these metal ions are given in separate Tables. The stability constants (standard deviation of the last digit in parentheses) are listed together with the most important information, such as: method, medium, type of constant, temperature, reference, and evaluation category.

The abbreviations used in the Tables are as follows:

cal	calorimetry
Cat	evaluation category
CD	circular dichroism
con	conductivity
dis	distribution between two phases
E	e.m.f. measurements (not specified)
elph	electrophoresis
ESR	electron spin resonance
gl	glass electrode (pH-metry)
H	hydrogen electrode (pH-metry)
ix	ion-exchange
kin	rate of reaction
M	metal electrode (e.m.f. measurements)
M/Hg	amalgam electrode (e.m.f. measurements)
NMR	nuclear magnetic resonance
ORD	optical rotatory dispersion
pol	polarography
red	redox electrode (e.m.f. measurements)
sol	solubility
sp	spectrophotometry
T	temperature-dependence

2. PROTON COMPLEXES OF ALIPHATIC AMINO ACIDS

2.1. Protonation constants

In aqueous solution, aliphatic amino acids exist as zwitterions (HL), the amino group being protonated ($-\text{NH}_3^+$), while the carboxyl group is deprotonated ($-\text{COO}^-$). In the case of the α -amino acids, deprotonation of the ammonium group occurs in slightly basic solutions (pH 9 to 10) to give the species (L^-). The carboxylate group undergoes protonation in acidic media (pH 2 to 3), and therefore the two dissociation processes of the fully protonated cationic form (H_2L^+) are completely separated. If the pH ranges of the protonation processes are considered it can be stated that $\log K_{\text{HL}}$ can be determined quite accurately because the protonation takes place within a very accessible pH range. Protonation of the carboxylate group occurs at low pH, however, where the accuracy of pH measurements and the accuracy of the constants obtained are lower.

Literature values for the protonation constants of α -alanine are listed in Table 2.1.

TABLE 2.1 Protonation Constants of α -Alanine (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
H	C	?	25	9.72	2.61	23B	D
H	C	→ 0.0	20	10.006	2.350	33NS	T
			25	9.870	2.340		
			30	9.740	2.332		
			35	9.615	2.327		
			40	9.494	2.324		
			45	9.378	2.322		
H	C	→ 0.0	1	10.586	2.426	37ST	T
			12.5	10.225	2.383		
			25	9.866	2.348		
			37.5	9.548	2.330		
			50	9.256	2.332		
H	C	0.1	25	9.75	2.40	40CH	D
H	M	→ 0.0	25	9.87	2.34	41KRa	T
gl	M	0.01	25	9.97	2.22	50A	D
gl	M	< 0.01	21	9.90		52P	D
gl	M?	0.15 (KNO ₃)	25.15	9.78		53TS	D
gl	M	< 0.01	25	9.90		54P	D
gl	M	1.0 (NaClO ₄)	20	9.79	2.49	58Pc	T
gl	M	1.0 (KCl)	20	9.79		59P	T
gl	C	0.0 (corr)	0	10.57	2.43	61IW	T
			10	10.30	2.39		
			20	10.04	2.37		
			30	9.78	2.36		
			40	9.48	2.36		
gl	M	0.3 (K ₂ SO ₄)	25	9.62(3)	3.0	61JW	D
gl	M	0.1 (KCl)	20	9.93	2.30	63IP	T
gl	C	1.0 (KNO ₃)	30	9.70(2)		64RSa	D
gl	C	0.1 (NaClO ₄)	25	9.59	2.53	65MO	D
gl	C	0.2 (KCl)	15	10.01	2.47	65SMb	T
			25	9.77	2.40		
			40	9.41	2.44		
gl	C	→ 0.0	10	10.29	2.40	66AN	T
			25	9.89	2.37		
			40	9.51	2.35		
gl	C	0.1 (KCl)	20	9.84	2.20	66GI	T
gl	M	0.37 (NaNO ₃)	20	9.93	2.54	66SW	T
gl	M	0.5 (KCl)	25	9.83	2.44	66LHa	T
gl	C	→ 0.0	10	10.29	2.60	67AG	T
			25	9.89	2.63		
			40	9.51	2.65		
gl	?	0.6	25	9.88(3)		67AM	Rj
gl	M	0.5 (NaClO ₄)	25	9.84	2.39	67RP	T
gl	C	0.15 (KNO ₃)	37	9.502(3)		69CP	T
gl	M	0.2 (NaClO ₄)	25	9.73(2)	2.31(1)	70CBa	T
gl	M	0.5 (KCl)	25	9.81(1)	2.45(1)	70FE	T
gl	M	0.1 (NaClO ₄)	25	9.83(3)	2.26(3)	70GP	T
gl	M	0.16 (KNO ₃)	25	9.60		70MB	D
gl	M	0.5 (KCl)	25	9.818	2.440	70SF	T
gl	M	2.0 (NaClO ₄)	25	9.65	2.50	71ALb	T
gl	C	0 (corr)	20	10.035	2.28	71GK	T

TABLE 2.1 (continued)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
			25	9.902	2.28		
			30	9.779	2.28		
			35	9.660	2.28		
gl	C	0.05 (KCl)	20	9.856	2.284	71GK	T
			25	9.723	2.284		
			30	9.596	2.284		
			35	9.482	2.284		
gl	M	0.5 (KNO ₃)	25	9.70(1)	2.38(1)	71KS	T
gl	M	0.5 (KCl)	25	9.82	2.44	71LL	T
gl	M	0.1 (KNO ₃)	25	9.80(3)		71ST	T
gl	C	1.0 (KNO ₃)	25	9.812(2)	2.444(4)	72BPa	R
gl	C	0.05 (KCl)	25	9.73	2.33	72GS	R
gl	C	0.1 (KNO ₃)	25	9.70(1)	2.55(2)	72IN	D
gl	M	0.1 (KNO ₃)	20	9.88		73BS	T
			30	9.70			
			40	9.52			
			50	9.36			
			60	9.22			
gl	C	0.2 (KCl)	25	9.68	2.35	73GS	R
gl	M	0.2 (NaClO ₄)	25		2.43	73SM	T
			35		2.45		
			45		2.45		
gl	M	1.0 (KCl)	20	9.79	2.48	73VB	T
gl	M	0.24 (KCl)	25	9.87		74FL	T
gl	C	0.02 (NaClO ₄)	25	9.77	2.35	74GNa	T
		0.05 (NaClO ₄)	25	9.70	2.34		
		0.1 (NaClO ₄)	25	9.69	2.33		
		0.2 (NaClO ₄)	25	9.67	2.33		
		0.5 (NaClO ₄)	25	9.69	2.36		
		1.0 (NaClO ₄)	25	9.75	2.44		
		1.5 (NaClO ₄)	25	9.77	2.54		
		2.0 (NaClO ₄)	25	9.87	2.62		
gl	C	0.2 (KCl)	25	9.68	2.35	74GNb	R
gl	C?	0.1 (LiClO ₄)	25	9.55(9)	2.40(9)	74KU	D
gl	M	0.1 (KNO ₃)	25	9.80		75HV	T
gl	M	0.5 (KNO ₃)	25	9.75		75HV	T
gl	M	0.1 (KCl)	25	9.86	2.51	77KD	T
gl	C?	0.5 (KNO ₃)	23	9.83	2.44	77NE	D
gl	M	0.1 (NaClO ₄)	31	9.670	2.480	77RR	T
gl	C	1.0 (NaNO ₃)	25	9.746(5)	2.415(22)	78JI	T
gl	M	0.5 (KNO ₃)	25	9.77(1)	2.48(1)	78L	T
gl	C	0.12 (NaCl)	25	9.67(2)	2.35(1)	78RM	R
gl	C	1.0 (NaClO ₄)	25	9.91		79EB	D
gl	M	0.5 (KNO ₃)	30	9.66		79EM	D
gl	C	3.0 (NaClO ₄)	25	10.30(1)	2.79(1)	79MT	D
gl	M	0.1 (NaClO ₄)	30	9.67	2.48	79RR	T
gl	C	0.1 (KNO ₃)	25	9.85(2)	2.26	80OF	T
gl	C	0.1 (NaClO ₄)	25	9.82(1)	2.34(1)	80FS	T
gl	M	0.1 (KNO ₃)	25	9.80	2.33	80SJ	T
gl	?	0.1 ?	30	9.81(2)	2.12(3)	81PU	Rj
gl	M	3.0 (LiClO ₄)	25	9.72(1)		81M	T

TABLE 2.1 (continued)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
gl	C	0.15 (NaClO ₄)	37	9.55(2)	2.26(3)	81NSa	T
gl	M	0.25 (KNO ₃)	30	9.58	2.53	81RK	D
gl	C	0.2 (NaNO ₃)	30	9.61(4)	2.35(1)	81RSb	T
gl	M	1.0 (KNO ₃)	30	9.70		82CG	T
gl	C	3.0 (NaClO ₄)	25	9.72	2.81	82MO	T
gl	C	0.1 (KNO ₃)	25	9.592(3)	2.475(8)	82NM	T
gl	C	0.1 (KNO ₃)	25	9.70(3)	2.43(2)	83AC	T
gl	C	1.0 (KNO ₃)	30	9.70(2)		84CG	T
gl	C	0.15 (NaClO ₄)	37	9.399(1)	2.370(2)	84BPb	T
gl	M	0.15 (NaCl)	20	9.86(2)		85VD	T
gl	C	0.2 (KNO ₃)	25	9.74	2.36	86SV	R
gl	C	0.2 (KNO ₃)	35	9.33	2.27	87PS	T
gl	C	2.25 (NaNO ₃)	25	9.96	2.53	88PB	D

The huge number of data available permits classification of the constants into the appropriate categories. Determinations carried out in solutions of low ionic strength (<0.02 mol dm⁻³) were regarded as doubtful, because of the changes in the activity coefficients during the measurements (23B, 50A, 52P, 54P). The experimental conditions were not completely specified in some publications (40CH, 53TS, 67AM, 74KU, 81PU). These values were regarded as doubtful or rejected and were not incorporated in the evaluation. The protonation constant of the carboxylate group was very high in some cases (23B, 61JW, 67AG, 72IN, 81RK), and accordingly these reports were also omitted from the evaluation, independently on the reliability of the constants obtained for the amino group. The remaining values were mainly determined at 0.0, 0.05-0.5 or 1.0 mol dm⁻³ ionic strength at 25 °C or 37 °C, and were used in a statistical treatment to acquire recommended or tentative values for the protonation of α -alanine at different temperatures and ionic strengths. These values are listed in Table 2.8, together with the protonation constants of the other aliphatic amino acids.

The same evaluation criteria were applied for the protonation constants of the other aliphatic α -amino acids. The literature values for the protonation of valine, 2-aminopentanoic acid, leucine, 2-aminohexanoic acid, leucine and isoleucine are listed in Tables 2.2 to 2.6, respectively.

During the evaluation, it should be considered that the numbers of literature data on valine and leucine and especially on 2-amino-pentanoic and -hexanoic acids and isoleucine are much smaller than those on glycine or α -alanine. Accordingly, average values could be obtained only at 25 °C and in the ionic strength range 0.05 to 0.5 mol dm⁻³. In other cases, tentative values could be given when the data passed the acceptance criteria and were in agreement with the general features of the ionic strength and temperature-dependence of the protonation constants, discussed in details in the previous survey (91KS).

Literature values on the protonation constants of β -alanine are given in Table 2.7. Because of the greater distance between the protonation sites of β -alanine, the basicities of these functional groups are higher than those of the α -amino acids. The protonation constant of the carboxylate group is higher by at least one order of magnitude, which means that the deprotonation of (H_2L^+) occurs in a very accessible pH range (pH \sim 3), and log K_{H_2L} can be determined quite accurately. On the other hand, the deprotonation of the ammonium group takes place above pH 10, which slightly enhances the uncertainty of pH-metric measurements.

There are only a few publications from which the protonation constants are regarded as doubtful, because of the low ionic strength applied (e.g. 50A), or because of the lack of details on the experimental conditions (74DB, 79BJ). Most of the remaining data can be used to obtain recommended or tentative values, which are listed in Table 2.8, together with the protonation constants of the α -amino acids.

TABLE 2.2 Protonation Constants of Valine (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
H	C	→ 0.0	1	10.413	2.320	37ST	T
			12.5	10.064	2.297		
			25	9.719	2.286		
			37.5	9.405	2.292		
			50	9.124	2.310		
gl	M	0.01	25	9.62	2.32	49MM	D
gl	M	0.01	20	9.72	2.20	50A	D
gl	M	< 0.01	20	9.59		52P	D
gl	?	0.02	25	9.81	2.29	54R	D
gl	M	0.15	25	9.61		56LW	D
			30	9.46			
			40	9.15			
gl	M	1.0 (KCl)	20	9.50		59P	D
gl	M	1.0 (NaClO ₄)	20	9.59	2.38	58Pc	T
gl	C	→ 0.0	10	10.04	2.33	60P	T
			15	9.90	2.33		
			25	9.62	2.32		
			30	9.49	2.32		
			35	9.38	2.32		
			40	9.25	2.32		
gl	C	1.0 (KNO ₃)	30	9.44		64RSa	D
gl	C	0.1 (KCl)	20	9.65	2.24	66GI	T
gl	M	0.5 (NaClO ₄)	25	9.62	2.35	67RP	T
gl	C?	0.1 (KNO ₃)	22	9.59	2.20	68ZK	D
gl	C	0.15 (KNO ₃)	37	9.316(4)		69CP	T
gl	M	0.2 (NaClO ₄)	25	9.60(2)	2.32(2)	70CBb	T
gl	M	0.16 (KNO ₃)	25	9.44		70MB	D
gl	C	0.11 (KNO ₃)	25	9.47(2)	2.25(2)	71AA	D
gl	M	0.5 (KNO ₃)	25	9.51(1)	2.31(1)	71KS	T
gl	C	0.1 (KNO ₃)	25	9.50(1)	2.28(3)	72IN	R
gl	C	0.1 (KNO ₃)	25	9.63	2.39	73SA	T
gl	M	0.1(KNO ₃)	25	9.61		75HV	T
gl	M	0.5 (KNO ₃)	25	9.54		75HV	T
gl	C	0.1 (KNO ₃)	25	9.573(1)		77BP	R
gl	M	0.1 (KCl)	25	9.71	2.48	77KD	T
gl	C?	0.5 (KNO ₃)	23	9.62	2.35	77NE	D
gl	C	1.0 (NaNO ₃)	25	9.565(7)	2.316(29)	78JI	T
gl	M	0.5 (KNO ₃)	30	9.48(1)		79EM	T
gl	M	0.5 (NaNO ₃)	?	9.71(1)	2.32(1)	80MJ	Rj
gl	M	0.1 (NaClO ₄)	30	9.49	2.41	80RR	T
gl	M	0.1 (KNO ₃)	25	9.52	2.36	80SJ	T
gl	C	1.0 (NaClO ₄)	25	9.68		81EB	T
gl	M	3.0 (LiClO ₄)	25	9.75		81M	T
gl	C	0.1 (KNO ₃)	25	9.603(2)	2.693(9)	82NM	T
gl	C	0.25 (NaCl)	25	9.50	2.29	83AO	R
gl	C	0.15 (NaClO ₄)	37	9.263(2)	2.392(3)	84BPa	T
gl	M	0.15 (NaCl)	20	9.64(2)		85VD	T
gl	C	0.2 (KNO ₃)	35	9.27	2.25	87PS	T
gl	C	0.1 (KNO ₃)	25	9.51	2.26	88ZZ	R

TABLE 2.3 Protonation Constants of 2-Aminopentanoic acid (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat					
H	C	→0	1	10.508	2.376	37ST	T					
			12.5	10.504	2.340							
			25	9.808	2.318							
			37.5	9.490	2.309							
			50	9.198	2.313							
gl	M	<0.01	20	9.87	2.29	52P	D					
gl	?	0.02	25	9.70	2.29	54R	D					
gl	C	0.05 (KCl)	25	9.68	2.31	72GS	T					
gl	C	0.2 (KCl)	25	9.64	2.34	73GS	T					
gl	M	0.1 (KNO ₃)	20	9.40		73BS	D					
			30	9.26								
			40	9.02								
			50	8.87								
			60	8.60								
			gl	C	0.1 (KNO ₃)			25	9.64(3)	2.290(6)	75IP	T
			gl	M	0.15 (NaCl)			20	9.70(2)		85VD	T

TABLE 2.4 Protonation Constants of Leucine (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
H	M	?	25	9.75	2.26	23B	D
H	C	→ 0.0	1	10.454	2.383	37ST	T
			12.5	10.095	2.348		
			25	9.744	2.328		
			37.5	9.434	2.327		
			50	9.142	2.333		
gl	M	0.01	25	9.60	2.36	49MM	D
pH	C	0.1 (NaCl)	25	9.68		52E	T
gl	M	< 0.01	20	9.92		52P	D
gl	M	1.0 (NaClO ₄)	20	9.62	2.37	58Pc	T
gl	M	0.01	25	9.77	2.36	59DLa	D
gl	M	1.0 (KCl)	20	9.62		59P	T
			25	9.71	2.39		
			25	9.69	2.36		
		L		9.76	2.33		
		D		9.76	2.33		
gl	M	0.2 (NaClO ₄)	25	9.71(1)	2.32(3)	70CBb	T
gl	M	0.16 (KNO ₃)	25	9.54		70MB	D
gl	C	0.15 (KNO ₃)	37	9.36(1)	2.36	71HP	T
gl	M	0.5 (KNO ₃)	25	9.58(1)	2.42(1)	71KS	T
gl	M	0.1 (KCl)	25	9.58	2.34	71SS	D
			35	9.09	1.85		
			45	8.38	1.14		
gl	C	0.1 (KNO ₃)	25	9.67	2.46	73SA	T
gl	C	0.1 (KNO ₃)	25	9.703(1)	2.286(4)	77BP	R

TABLE 2.4 (continued)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
gl	M	0.5 (KNO ₃)	25	9.75(1)	2.42(1)	78L	T
gl	C	0.1 (NaClO ₄)	25	9.66(1)	2.32(1)	80FS	R
gl	C	0.1 (KNO ₃)	25	9.621(2)	2.645(6)	82NM	D
gl	C	0.15 (NaClO ₄)	37	9.266(2)	2.324(2)	84BPb	T
gl	M	0.15 (NaCl)	20	9.73(2)		85VD	T
gl	M	0.2 (KCl)	25	9.77	2.45	86KD	T
gl	C	0.2 (KNO ₃)	35	9.23	2.27	87PS	T
gl	C	0.1 (KNO ₃)	25	9.51	2.35	88ZZ	T

TABLE 2.5 Protonation Constants of 2-Amino-hexanoic acid (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
H	C	→ 0.0	1	10.546	2.394	37ST	T
			12.5	10.190	2.356		
			25	9.834	2.335		
			37.5	9.513	2.324		
			50	9.224	2.328		
gl	M	0.01	20	9.96	2.25	50A	D
gl	M	< 0.01	20	9.92		52P	D
gl	M	0.1	25	9.86	2.39	66MM	D
gl	C	→ 0.0	25	9.76(5)	2.39(2)	69MZ	T
gl	M	0.2 (NaClO ₄)	25	9.82(4)	2.30(1)	70CBb	T
gl	C	0.05 (KCl)	25	9.70	2.30	72GS	T
gl	C	0.1 (KNO ₃)	25	9.671(4)	2.340(9)	75IP	T
gl	M	0.15 (NaCl)	20	9.75(2)		85VD	T

TABLE 2.6 Protonation Constants of Isoleucine (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
H	C	→ 0.0	1	10.460	2.365	37ST	T
			12.5	10.100	2.338		
			25	9.758	2.318		
			37.5	9.439	2.317		
			50	9.157	2.332		
gl	M	< 0.01	20	9.86		52P	D
gl	M	0.5 (KCl)	25	9.70	2.66	66LHa	D
gl	M	0.1 DL	25	9.76	2.38	66MM	D
		L		9.69	2.31		
		D		9.73	2.39		
gl	M	0.2 (NaClO ₄)	25	9.67(1)	2.27(1)	70CBb	T
gl	C	0.15 (KNO ₃)	37	9.36(1)	2.36	71HP	T
gl	C?	3.0 (NaClO ₄)	25	10.15(1)	2.84(1)	75BH	D
gl	C	0.1 (NaNO ₃)	25	9.643(24)	2.276(30)	81IS	R
gl	C	0.1 (KNO ₃)	25	9.652(2)	2.689(9)	82NM	D
gl	C	1.0 (KNO ₃)	30	9.74(1)		84CG	T
gl	M	0.15 (NaCl)	20	9.68(2)		85VD	T

TABLE 2.7 Protonation Constants of β -Alanine (Literature Values)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
gl	M	0.01	20	10.36	3.60	50A	D
H	C	→ 0.0	0	11.00	3.66	51MF	T
			5	10.83	3.63		
			15	10.53	3.58		
			25	10.23	3.55		
			35	9.96	3.52		
			40	9.84	3.52		
gl	M	0.1 (KCl)	20	10.26	3.52	54IW	T
gl	C	0.1 (KCl)	30	10.55		62CTa	D
gl	C	1.0 (KNO ₃)	30	10.09		64RSa	T
gl	C	0.2 (KCl)	15	10.44	3.68	65SMb	T
			25	10.16	3.66		
			40	9.80	3.65		
gl	M	0.5 (KCl)	25	10.21	3.62	66LHa	T
H	C	→ 0.0	0	11.05	3.65	67BB	T
			15	10.58	3.58		
			25	10.29	3.55		
			35	10.03	3.53		
			45	9.78	3.52		
gl	C	0.5 (KNO ₃)	20	10.39(1)		68AL	T
gl	M	0.5 (KNO ₃)	20	10.17		68TV	T
gl	C	0.1 (NaClO ₄)	25	10.08	3.53	68TK	T
gl	M	0.1 (KCl)	5	11.07		69MG	T
			25	10.33			
			45	9.88			
gl	C	0.1 (KNO ₃)	25	10.15	3.55	69YH	R
gl	M	0.2 (NaClO ₄)	25	10.20(2)	3.51(1)	70CBa	T
gl	M	0.5 (KNO ₃)	0	11.00		70VT	T
			15	10.45			
			40	9.76			
gl	M	0.5 (KNO ₃)	25	10.03(1)	3.68(1)	71KS	T
gl	M	0.5 (KCl)	25	10.21	3.62	71LL	T
gl	C	0.1 (NaClO ₄)	25	10.22(1)	3.56(1)	71SH	T
gl	C	0.1 (KNO ₃)	25	10.15	3.55	71YM	R
gl	C	0.1 (NaClO ₄)	25		3.58	72SM	T
			35		3.60		
			45		3.62		
		0.2 (NaClO ₄)	25		3.57		
			35		3.58		
			45		3.59		
		0.3 (NaClO ₄)	25		3.56		
			35		3.56		
			45		3.57		
		0.4 (NaClO ₄)	25		3.55		
			35		3.55		
			45		3.56		
gl	M	0.1 (KNO ₃)	20	10.22		73BS	T
			30	10.02			
			40	9.87			
			50	9.70			
			60	9.56			

TABLE 2.7 (continued)

Method	Type of constant	Medium mol dm ⁻³	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Cat
H	C	0.1 (KCl)	5	10.764(30)		73RD	T
			25	10.162(30)			
			45	9.610(30)			
gl	C?	0.5 (NaClO ₄)	?	10.12	3.68	74DB	D
NMR	M	0.2-0.3	25	10.25	3.61	74RO	T
gl	C	0.1 (KNO ₃)	25	10.09(2)	3.56(5)	76DO	T
gl	C	1.0 (NaNO ₃)	25	10.155(3)	3.683(10)	78JI	T
gl	C?	3.0 (NaClO ₄)	25	10.71(3)	4.19(3)	79BJ	D
gl	M?	0.1 (NaClO ₄)	30	10.07	3.60	79RR	T
gl	C	3.0 (LiClO ₄)	25	10.65(2)	4.03(3)	80OZ	T
gl	M?	0.1 (NaClO ₄)	30	10.07	3.61	80RR	T
gl	C	0.15 (NaClO ₄)	37	9.91(1)	3.58(1)	81NS	T
gl	M	0.25 (KNO ₃)	30	10.20	3.54	81RK	T
gl	C	0.2 (NaNO ₃)	30	10.16(4)	3.60(1)	81RSb	T
gl	C	1.0 (KCl)	25	10.10	3.66	82ND	T
gl	C	0.5 (NaClO ₄)	25	10.08	3.70	86GG	T
gl	C	1.0 (NaClO ₄)	25		3.77	87BR	T

From Table 2.8, it can be seen that, as a result of the huge number of data available, recommended and tentative values for the protonation constants of α -alanine can be obtained in a wide range of ionic strength (0-1.0 mol dm⁻³). For the other ligands, the equilibrium measurements were carried out at an ionic strength of around 0.1 mol dm⁻³, and much fewer data have been reported, especially for 2-amino-pentanoic and -hexanoic acids and isoleucine. The standard deviations of the protonation constants of the above mentioned ligands might allow the data to be regarded as recommended values. The average values were obtained only from 2 to 3 independent determinations, however, and accordingly the data are rather considered to be tentative values.

The differences between the concentration and mixed protonation constants obtained under the same experimental conditions (0.05-0.2 mol dm⁻³, 25 °C) are in the range of 0.00 to 0.13 log units, which is rather wide, although comparable with the uncertainty of the data. The average difference is 0.06 log units, which is about the same as found for the protonation processes of glycine or other amino acids (91KS, 84Pa).

Concentration protonation constants are reported for all ligands at room temperature (25 °C) and in the ionic strength range of 0.1-0.2 mol dm⁻³, which corresponds well to the physiological conditions (0.16 mol dm⁻³). These values (together with those for glycine (91KS)) are given in Table 2.9.

Table 2.9 again indicates that the most basic functional groups are present in β -alanine, while the protonation constants of the α -amino acids are very close to each other. As a tendency, the increase in length of the aliphatic side chains is accompanied by a slight increase in the basicity of the amino group. The amino acids containing even numbers of carbon atoms also tend to be more basic than the homologues containing odd numbers of carbon atoms. Comparison of the data on valine and 2-aminopentanoic acid or leucine and 2-aminohexanoic acid indicates that the functional groups in the normal analogues are more basic than those in the isomers.

2.2 Protonation enthalpies

The enthalpy changes accompanying the protonation processes of the amino acids are listed in Table 2.10 for all ligands. The data were obtained from both calorimetric and potentiometric measurements at different temperatures.

TABLE 2.8 Recommended(R) or Tentative(T) Values for the Protonation Constants of Aliphatic Amino Acids

Ligand	Temp °C	Medium mol dm ⁻³	Type of constant	log K_{HL}	Cat	log K_{H_2L}	Cat
α -Alanine	25	0.0	C	9.89(2)	R	2.33(4)	R
	25	0.05-0.2	C	9.72(5)	R	2.33(5)	R
	25	0.05-0.2	M	9.78(8)	T	2.40(10)	T
	25	1.0	C	9.81(7)	T	2.43(2)	R
	37	0.05-0.2	C	9.49(7)	T	2.32(5)	T
Valine	25	0.05-0.2	C	9.54(5)	R	2.28(3)	R
	25	0.05-0.2	M	9.60(8)	T	2.38(8)	T
2-Amino-pentanoic acid	25	0.05-0.2	C	9.66(2)	T	2.32(3)	T
Leucine	25	0.05-0.2	C	9.66(3)	R	2.32(3)	R
	25	0.05-0.2	M	9.66(10)	T	2.39(7)	T
2-Amino-hexanoic acid	25	0.05-0.2	C	9.68(2)	T	2.32(2)	T
	25	0.05-0.2	M	9.81(6)	T	2.34(6)	T
Isoleucine	25	0.05-0.2	C	9.65(2)	T	2.28(3)	T
β -Alanine	25	0.0	C	10.26(3)	R	3.55(1)	R
	25	0.1-0.2	C	10.14(5)	R	3.57(5)	R
	25	0.2-0.5	M	10.18(8)	T	3.61(6)	T

TABLE 2.9: Recommended(R) and Tentative(T) Values for the Protonation Constants of Aliphatic Amino Acids. $T = 25\text{ }^\circ\text{C}$; $I = 0.1\text{-}0.2\text{ mol dm}^{-3}$

Amino acid	log K_{HL}	Cat	log K_{H_2L}	Cat
Glycine	9.60(5)	R	2.37(7)	T
α -Alanine	9.72(5)	R	2.33(5)	R
Valine	9.54(5)	R	2.28(3)	R
Leucine	9.66(3)	R	2.32(3)	R
2-Aminopentanoic acid	9.66(2)	T	2.32(3)	T
Isoleucine	9.65(2)	T	2.28(3)	T
2-Aminohexanoic acid	9.68(2)	T	2.32(2)	T
β -Alanine	10.14(5)	R	3.57(5)	R

TABLE 2.10 Enthalpy Changes in the Protonation of Aliphatic Amino Acids (kJ mol^{-1})
 (Literature Values)

Method	Medium mol dm^{-3}	Temp $^{\circ}\text{C}$	$-\Delta H_{\text{COO}^-}^{\circ}$	$-\Delta H_{\text{NH}_2}^{\circ}$	Ref	Cat
<u>α-Alanine</u>						
T	0.0	20	3.820	45.606	33NS	T
		25	3.012	45.229		
		30	2.251	44.936		
		5	1.544	44.685		
		40	0.900	44.476		
		45	0.330	44.267		
T	0.0	1	6.318	45.982	37ST	T
		12.5	5.063	46.539		
		25	3.347	46.191		
		37.5	1.339	45.564		
		50	-1.046	44.267		
cal	0.0	25	2.585	45.341	42S	T
T	0 (corr)	0-40	2.9	44.3	61IW	T
T	0.2 (KCl)	15-40		33.8	65SMb	D
T	0.0	10-40	2.9	43.5	66AN	T
cal	0.0	25		44.98	67A	T
cal	0.0	10	5.23(25)		68CO	T
		25	3.14(21)			
		40	0.96(59)			
cal	0.16 (KNO_3)	25		44.4	70MB	T
T	0 (corr)	20-35		43.15(C)	71GK	D
T	0.05 (KCl)	20-35		43.19(C)	71GK	D
cal	0.2 (KCl)	25	2.72	47.24	73GS	T
cal	1.0 (NaClO_4)	25		49.20	79EB	T
cal	0.1 (KNO_3)	25	3.1(8)	44.98(36)	83AC	T
<u>Valine</u>						
T	0.0	1	3.724	43.388	37ST	T
		12.5	2.259	45.187		
		25	0.335	44.936		
		37.5	-1.925	44.183		
		50	-4.602	42.802		
cal	0.0	25		44.51	67A	T
cal	0.0	25		44.9(2)	69CI	T
cal	0.16 (KNO_3)	25		45.9	70MB	T
cal	0.1	25		44.73	71BP	T
cal	1.0 (NaClO_4)	25		47.46(6)	81EB	T
<u>2-Aminopentanoic acid</u>						
T	0.0	1	5.397	45.355	37ST	T
		12.5	4.058	45.647		
		25	2.301	45.522		
		37.5	0.209	44.769		
		50	-2.259	43.430		

TABLE 2.10 (continued)

Method	Medium mol dm ⁻³	Temp °C	$-\Delta H_{\text{COO}^-}^{\circ}$	$-\Delta H_{\text{NH}_2}^{\circ}$	Ref	Cat
cal	0.0	25		45.39	67A	T
cal	0.0	10	3.48(29)		68CO	T
		25	1.63(17)			
		40	-0.25(17)			
cal	0.2 (KCl)	25	1.67	48.03	73GS	T
<u>Leucine</u>						
T	0.0	1	4.937	45.480	37ST	T
		12.5	3.598	45.773		
		25	1.757	45.606		
		37.5	-0.377	44.894		
		50	-2.929	43.555		
cal	0.16 (KNO ₃)	25		44.9	70MB	T
T	0.1 (KCl)	25-45	108.6	108.6	71SS	Rj
<u>2-Aminohexanoic acid</u>						
T	0.0	1	5.439	45.815	37ST	T
		12.5	4.100	46.150		
		25	2.343	46.233		
		37.5	0.251	45.355		
		50	-2.259	44.099		
cal	0.0	10	3.85(88)		68CO	T
		25	1.80(21)			
		40	-0.29(9)			
<u>Isoleucine</u>						
T	0.0	1	4.519	45.187	37ST	T
		12.5	3.096	45.480		
		25	1.255	45.313		
		37.5	-0.920	44.560		
		50	-3.515	43.221		
cal	0.1 (NaNO ₃)	25		43.2(5)	78IS	T
<u>β-Alanine</u>						
T	0.0	0-40	5.83(C)	47.58(C)	51MF	D
T	0.2 (KCl)	15-40	2.02(C)	44.13(C)	65SMb	D
T	0.0	0-45	4.85(C)	46.93(C)	67BB	D
cal	0.0	25		47.15	67A	T
cal	0.0	25	4.52		67CI	T
cal	0.0	10	6.69(25)		68CO	T
		25	4.35(13)			
		40	2.59(21)			
cal	0.0	25		47.3(2)	69CI	T
T	0.1 (KCl)	5-45		50.58(C)	69MG	D
T	0.5 (KNO ₃)	0-40		49.8	70VT	T
T	0.1 (KCl)	5		46.2(1.2)	73RD	T
		25		49.0(1.2)		
		45		51.2(1.2)		

Calorimetric studies generally provide enthalpy changes of higher accuracy, but careful potentiometric studies at many different temperatures can give data with almost the same accuracy (e.g. 37ST, 61IW, 71GK). As may be seen from Table 2.10, protonation enthalpies of α - and β -alanine were obtained at different ionic strengths and with different methods; in contrast, only relatively few data have been published on the protonation heats of 2-aminopentanoic acid, 2-aminohexanoic acid, leucine and isoleucine. Accordingly, a critical evaluation of the data can be performed for α - and β -alanine and valine, whereas the protonation enthalpies of the other α -amino acids can be regarded only as tentative values if the enthalpy changes of the ligands are similar to those of α -alanine. The average enthalpy changes on the protonation of α - and β -alanine and valine are listed in Table 2.11.

On the basis of Tables 2.10 and 2.11, it can be concluded that protonation of the carboxylate group is accompanied by a very small negative enthalpy change, while protonation of the amino group is strongly exothermic. It can also be seen that an increase of the ionic strength slightly raises the protonation enthalpy of the amino group, but the length of the side chain does not have a significant effect on the protonation enthalpy values. The enthalpy change accompanying the protonation of the amino group of β -alanine, however, is more exothermic than those of the α -amino acids, which is consistent with the higher $\log K_{HL}$ value of the amino group in the β -position.

TABLE 2.11 Tentative Protonation Enthalpies of Some Aliphatic Amino Acids (kJ mol^{-1})

Amino acid	Medium mol dm^{-3}	Temp $^{\circ}\text{C}$	$-\Delta H_{\text{COO}^-}^{\circ}$	$-\Delta H_{\text{NH}_2}^{\circ}$
α -Alanine	0.0	25	3.0(3)	44.5(5)
	0.1-0.2	25	2.9(2)	45.0(1.5)
β -Alanine	0.0	25	5.1(4)	47.3(2)
	0.1-0.2	25		48.4(2)
Valine	0.0	25		44.8(2)
	0.1-0.2	25		45.3(5)

3. METAL COMPLEX FORMATION EQUILIBRIA OF THE ALIPHATIC AMINO ACIDS

The complex formation processes and stability constants of the aliphatic amino acids have been studied with various metal ions. Most of the studies revealed that the aliphatic amino acids form the same type of complexes as those of glycine or α -alanine, and the presence of a side chain does not result in a new type of coordination. This means that all the didentate amino acids form ML , ML_2 and ML_3 parent complexes with metal ions favouring six-coordination. Of course, the stability of these species slightly depends on the nature of the non-coordinating side chains.

In the literature surveyed, the stability constants were determined with various experimental methods, and the data were calculated via a large variety of different numerical, graphical or computational methods. Potentiometry and polarography were the most frequently used and most accurate methods for determination of the stability constants of amino acid complexes. The reproducibility and accuracy of these methods, however, largely depend on the calibration technique applied, and on the other experimental conditions, as discussed in the previous critical reviews (86BB, 87BO, 91KS). The use of an activity or concentration scale for the hydrogen ion is one of the governing factors during potentiometric titrations. As mentioned in Section 2, the mixed constants can cause large uncertainties in the low or high protonation constants. On the other hand, it was demonstrated on the example of

glycine complexes (91KS) that there are practically no differences between the "mixed" and "concentration" constants of the metal complexes, if the metal ion-ligand interaction is relatively strong, as in the case of the simple bidentate amino acids. As it was discussed in the previous review (91KS) this statement is not valid if complex formation and ligand dissociation processes are in the same pH range. Consequently, the type of the constants is not included in the following Tables.

3.1 Stability constants of the metal complexes of α -alanine

The stability constants of the metal ion complexes of α -alanine have been determined by many authors, and therefore the equilibrium data are grouped into four separate Tables; for main group elements (Table 3.1), 3d transition metal ions (Table 3.2), 4d and 5d transition metal ions (Table 3.3) and f-block elements (Table 3.4).

TABLE 3.1 Formation Constants of Complexes of α -Alanine with the Main Group Elements
(Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Be ^{II}	gl	0.005-0.01	21		13.1		52P	Rj
Mg ^{II}	gl	→ 0.0	25	1.96			51Mc	T
	gl	0.15 (NaCl)	20	1.96(8)			85VD	T
Ca ^{II}	sol	→ 0.0	25	1.24			50DW	T
Sr ^{II}	sol	→ 0.0	25	0.73			52CM	T
Ba ^{II}	sol	→ 0.0	25	0.77			51Md	T
In ^{III}	gl	0.2 (NaClO ₄)	25	log K(M + HL) = 2.51			73SM	D
			35			2.57		
			45			2.63		
	gl	0.1 (NaClO ₄)	31	8.40	16.65		76KF	D
	pol	0.2 (NaClO ₄)	30	9.85	15.93		77KK	D
				10.10	15.92			
Tl ^I	gl	0.1 (LiClO ₄)	25	1.48			74KU	T
Pb ^{II}	sol	→ 0.0	25	5.52			41KR _a	D
	gl	→ 0.0	25	5.00	8.24		51Mc	D
	pol	1.0 (KNO ₃)	30	4.18	6.83		64RS _b	D
	gl	0.37 (KNO ₃)	20	4.15	9.39		66SW	D
				log $\beta_{ML_2(OH)} = 9.85$				
	gl, Pb/Hg	3.0 (NaClO ₄)	25	5.17(2)	8.13(5)		79MT	T
				log $\beta_{MHL} = 11.58(4)$				
	gl	1.0 (NaClO ₄)	25	5.43(4)	9.22(12)		82BC	T
				log $\beta_{MHL} = 12.71(4)$				
				log $\beta_{MH_1L} = -3.02(6)$				
	Pb/Hg	0.1 (KNO ₃)	25	5.43(4)	7.00(4)		85DV	T
				log $\beta_{MHL} = 13.20(5)$				
				log $\beta_{MH_1L} = -2.92(5)$				

TABLE 3.2 Formation Constants of Complexes of α -Alanine with 3d Transition Metal Ions (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ti ^{III}	gl	?	?	8.53			70FMb	Rj
V ^{IV} O	gl	?	?	8.75			70FMb	Rj
	gl	? (NaClO ₄)	25	8.34(19)	15.63(19)		70CBa	Rj
	gl	2.25 (NaNO ₃)	25	6.87(2)	12.4(1)		88PB	T
				log β_{MHL} = 11.16(1)				
				log $\beta_{MH_2L_2}$ = 21.4(2)				
				log β_{MHL_2} = 17.6(1)				
				log $\beta_{M_2H_2L_2}$ = 5.8(2)				
				log $\beta_{MH_{-1}L_2}$ = 4.4(2)				
				log $\beta_{M_2H_{-3}L_2}$ = -1.3(2)				
				log β_{MH_2L} = -6.7(2)				
Cr ^{II}	Pt,gl	?	?	6.76			70FMa	Rj
Cr ^{III}	gl	0.5	25	8.6	15.2	20.8	63KM	D
	gl	0.1 (NaClO ₄)	25	8.53	15.97		65MO	D
	sp	0.6 (Mg(ClO ₄) ₂)	25	log $K(M + HL)$ = 3.09			73BF	D
				log $K(M + 2 HL)$ = 5.35				
				log $K(M + 3 HL)$ = 7.15				
				log $K(M + 4 HL)$ = 8.73				
				log $K(M + 5 HL)$ = 10.11				
				log $K(M + 6 HL)$ = 11.45				
Mn ^{II}	CD	0.1 (KCl)	20			25.27	73VB	D
	gl	0.01	25	3.24	6.05		49MM	D
	gl	→ 0.0	25	3.02			51Mc	D
	elph	0.1 (KNO ₃)	20	3.4	5.3		64J	D
	ix	1.0 (NaNO ₃)	20	3.15			69BZ	D
			40	3.07				
			60	2.94				
	gl	0.15 (KNO ₃)	37	2.39(8)	4.29(6)	5.70(17)	69CP	T
	gl	0.05 (KCl)	25	2.45			71GK	T
	gl	0.1 (NaClO ₄)	25	2.67			70GP	T
	gl	0.1 (KNO ₃)	20	3.08	6.08		73BS	D
			30	3.00	5.96			
			40	2.94	5.87			
			50	2.89	5.80			
			60	2.85	5.74			
	gl	0.2 (KNO ₃)	25	2.27(2)	4.17(6)		83KG	D
Fe ^{II}	gl	0.01	25		7.3		50A	D
	gl	1.0 (KCl)	20	3.54			59P	T
Fe ^{III}	red	1.0 (NaClO ₄)	20	10.4			58Pc	D
	pol	1.0 (KCl)	30	10.98			67KM	D
Co ^{II}	gl	0.01	25		8.4		50A	D
	gl	0.01	25		8.78		50MM	D
	sol,gl	→ 0.0	25	4.82	8.48		51Mc	T
	gl	0.15 (KNO ₃)	25.15	4.27	7.72	9.47	53TS	T
	gl	0.1 (KCl)	20	4.32	7.92		63IP	T
	elph	0.1 (KNO ₃)	20	5.0	8.2	10.6	64J	D
	gl	0.2 (KCl)	15	4.41	7.68		65SMb	T
			25	4.36	7.56			
			40	4.25	7.33			
	gl	0.1 (NaClO ₄)	25	4.44			70GP	T
	gl	0 (corr)	20	4.730	8.460		71GK	T

TABLE 3.2 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat	
Ni ^{II}			25	4.718	8.407				
			30	4.669	8.309				
			35	4.667	8.321				
		gl	0.05 (KCl)	20	4.366	7.912		71GK	T
				25	4.354	7.871			
				30	4.305	7.761			
				35	4.303	7.773			
		gl	0.05 (KCl)	25	4.35	7.86		71GNb	T
		gl	0.5 (KNO ₃)	30	4.27(9)	9.30(9)	11.53(8)	79EM	D
		gl	0.2 (KCl)	25	4.24(2)	7.65(3)	9.91(8)	83KG	T
		gl	→ 0.0	25	5.96	10.66		51Mc	T
		gl	0.1 (KCl)	20	5.40	9.90		63IP	T
		elph	0.1 (KNO ₃)	20	6.0	10.3	13.2	64J	D
		gl	1.0 (NaClO ₄)	25	5.40	9.91	13.02	64MPb	T
		gl	0.2 (KCl)	15	5.65	10.22		65SMb	T
				25	5.53	9.98			
				40	5.38	9.66			
		gl	0.5 (KCl)	25	5.31	9.73	12.73	66LHa	T
		gl	0.37 (KNO ₃)	20	5.22	9.91		66SW	T
		gl	→ 0.0	10	5.93	10.80		67AG	T
				25	5.81	10.54			
				40	5.69	10.19			
		ORD	0.5(NaClO ₄)	25	5.40	9.55	12.72	67RP	T
		gl	? (NaClO ₄)	25	5.85(3)	10.34(10)		70CBa	D
		gl	1.0 (NaClO ₄)	25	5.39(1)	9.91(2)	13.05(3)	70MM	R
		gl	0 (corr)	20	5.868	10.554		71GK	T
				25	5.832	10.476			
			30	5.791	10.372				
			35	5.744	10.293				
	gl	0.05 (KCl)	20	5.499	10.011		71GK	T	
			25	5.463	9.930				
			30	5.422	9.829				
			35	5.375	9.751				
	gl	0.05 (KCl)	25	5.46	9.93		71GNb	T	
	gl	0.05 (KCl)	25	5.48	10.01		72GS	T	
	gl	0.2 (NaClO ₄)	20	5.95	10.66		72KP	T	
	gl	1.0 (NaClO ₄)	25	5.39	9.91	13.05	73MS	R	
	gl	0.2 (KCl)	25	5.32	9.74		75SG	T	
	gl	0.2 (KCl)	25	5.35	9.79		77GK	T	
	gl	1.0 (NaClO ₄)	25	5.39	9.92	13.06	79EB	R	
	gl	0.5 (KNO ₃)	30	5.15(1)	9.32(1)	11.76(4)	79EM	D	
	gl	0.2 (KCl)	25	5.32	9.74	12.80	79GK	T	
				log $\beta_{MH_1L_2} = -1.79$					
Cu ^I Cu ^{II}	gl	0.1 (KNO ₃)	25	5.50(4)	10.16(4)	13.45(8)	80OF	D	
	gl	0.2 (NaNO ₃)	30	5.51	9.98		81RSb	T	
	red	0.3 (K ₂ SO ₄)	25		9.6		61JW	D	
	pol	0.1 (KNO ₃)	25		15.01		46K	T	
	sol	→ 0.0	25	8.40	15.76		48K	T	
	gl	0.01	25		15.10		50A	D	

TABLE 3.2 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
	pol	0.1	25		14.82		50LD	D
	gl	→ 0.0	25	8.51	15.37		51Ma	T
	sp,gl	3.0	25	log $K(M + HL) = 0.57$			56Ca	D
				log $K(M + 2 HL) = 3.09$				
				log $K(M + 2 HL \rightleftharpoons MHL_2 + H) = 8.89$				
				7.51	14.03			
	gl	0.375	25	8.07	14.79		56Cb	D
			25	log $K(M + HL) = 0.72$				
	gl	0.0	25	8.45	15.54		56Cb	D
	gl	0.01	25		15.1		56N	D
	gl	0 (corr)	0	8.95	16.28		61IW	T
			10	8.76	15.89			
			20	8.66	15.68			
			30	8.56	15.46			
			40	8.34	15.00			
	red	0.3 (K ₂ SO ₄)	25		15.0	15.05	61JW	T
	gl	0.1 (KCl)	20	8.15	14.93		63IP	T
	eiph	0.1 (KNO ₃)	20	8.5	15.2		64J	D
	gl	0.05 (NaClO ₄)	25	8.21	15.02		64MPa	T
		0.16 (NaClO ₄)	25	8.17	14.98			
		0.36 (NaClO ₄)	25	8.13	15.01			
		0.64 (NaClO ₄)	25	8.15	15.04			
		1.0 (NaClO ₄)	25	8.26	15.16			
		2.0 (NaClO ₄)	25	8.42	15.50			
	gl	0.2 (KCl)	15	8.40	15.26		65SMb	T
			25	8.29	15.01			
			40	8.10	14.61			
	gl	→ 0.0	10	8.70	15.96		66AN	T
			25	8.54	15.52			
			40	8.32	15.08			
	gl	0.1 (KCl)	20	8.22	15.07		66GI	T
	gl	0.37 (KNO ₃)	20	8.17	15.01		66SW	T
	ORD	0.5 (NaClO ₄)	25	8.21	15.00		67RP	T
	CD	0.1 (ClO ₄ ⁻)	25	7.59	14.76		68BV	D
	gl	0.2 (KNO ₃)	?	log $K(ML_2 + L) = 0.76$			68GS	D
	gl	0.15 (KNO ₃)	37	8.046(25)	14.714(43)		69CP	T
	gl	0.2 (NaClO ₄)	25	8.18(4)	15.00(5)		70CBc	T
	gl	0.1 (NaClO ₄)	25	8.25	15.30		70GP	T
	gl	0.16 (KNO ₃)	25	7.84	14.48		70MB	D
	gl	0 (corr)	20	8.603	15.603		71GK	T
			25	8.546	15.484			
			30	8.474	15.304			
			35	8.437	15.232			
	gl	0.05 (KCl)	20	8.231	15.073		71GK	T
			25	8.174	14.953			
			30	8.102	14.773			
			35	8.065	14.701			
	gl	0.05 (KCl)	25	8.17	14.95		71GNb	T
	gl	0.05 (KCl)	25	8.18	14.99		72GS	T
	gl	0.2 (NaClO ₄)	20	8.32	15.41		72KP	T

TABLE 3.2 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat	
Zn ^{II}	gl	0.2 (KCl)	25	8.07	14.79		73GS	T	
	gl	0.24 (KCl)	25	8.69(10)	15.58(12)		74FL	D	
	gl	0.02 (NaClO ₄)	25	8.19	14.91		74GNa	T	
		0.05 (NaClO ₄)	25	8.12	14.82				
		0.1 (NaClO ₄)	25	8.08	14.76				
		0.2 (NaClO ₄)	25	8.04	14.71				
		0.5 (NaClO ₄)	25	8.03	14.74				
		1.0 (NaClO ₄)	25	8.09	14.90				
		1.5 (NaClO ₄)	25	8.16	15.07				
		2.0 (NaClO ₄)	25	8.25	15.25				
		gl	0.2 (KCl)	25	8.04	14.73		74GNb	T
		gl	0.2 (KCl)	25	8.04	14.73		77GK	T
		gl	0.1 (KCl)	25	8.19	15.45		77KD	D
		gl	0.1 (KCl)	25	7.26	15.45		78KZ	Rj
		gl	0.12 (NaCl)	25	8.15(6)			78RM	D
		gl	0.5 (KNO ₃)	30	7.83(7)	14.87(8)		79EM	D
		gl	0.1 (NaClO ₄)	30	8.09(3)	14.81		80AS	T
		gl	0.1 (NaClO ₄)	25	8.33(2)	15.27(2)		80FS	T
		gl	0.15 (NaClO ₄)	37	8.16(2)	15.03(3)		81NS	T
		gl	0.25 (KNO ₃)	30	8.20	14.90		81RK	T
		gl	0.2 (NaNO ₃)	30	8.12	14.83		81RSb	T
		gl	0.1 (KNO ₃)	25	8.17(3)	14.94(5)		83AC	R
		gl	0.15 (NaClO ₄)	37	7.947(4)	14.460(9)		84BPb	T
		Cu/Hg	0.1 (KNO ₃)	25	8.24			86DV	D
		gl	0.2 (KNO ₃)	35	7.94	14.73		87PS	T
		gl	0.01	25	5.16	9.50		49MM	D
		gl	→ 0.0	25	5.21	9.54		51Mc	T
		gl	0.005-0.01	21		9.1		52P	D
		gl	0.01	25	4.9			54P	D
		gl	0.1 (KCl)	20	4.55	8.65		63IP	T
		elph	0.1 (KNO ₃)	20	5.7	9.6	11.9	64J	D
		gl	0.2 (KCl)	15	4.98	9.10		65SMb	T
				25	4.88	8.84			
				40	4.80	8.66			
		gl	0.5 (KCl)	25	4.56	8.52	10.51	66LHa	T
		gl	0.37 (KNO ₃)	20	4.63	9.0		66SW	D
		ORD	0.5 (NaClO ₄)	25	4.67	8.95		67RP	T
		pol	0.5 (KCl)	30		8.85		67SSb	D
		gl	0.15 (KNO ₃)	37	4.57(2)	8.56(2)	10.65(8)	69CP	T
		gl	? (NaClO ₄)	25	5.15(8)	9.26(14)		70CBa	D
		gl	0.5 (KCl)	25	4.57	8.56	10.59	70FE	T
		gl	0.1 (NaClO ₄)	25	4.51			70GP	T
	gl	0.5 (KCl)	25	4.564	8.558	10.578	70SF	T	
	gl	0 (corr)	20	4.997	9.295		71GK	T	
			25	4.952	9.230				
			30	4.931	9.195				
			35	4.910	9.145				
	gl	0.05 (KCl)	20	4.649	8.738		71GK	T	
			25	4.604	8.673				
			30	4.583	8.638				

TABLE 3.2 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
			35	4.562	8.588			
	gl	0.05 (KCl)	25	4.60	8.67		71GNb	T
	gl	1.0 (KNO ₃)	25	4.545(3)	8.536(6)	10.650(25)	72BPb	T
	gl	0.2 (KCl)	25	4.56	8.51		79GK	T
				log $\beta_{MH_1L} = -3.6$ log $\beta_{MH_1L_2} = -0.15$				
	gl	0.1 (NaClO ₄)	25	4.62(4)	8.85	12.16	80FS	D
	gl	0.2 (NaNO ₃)	30	4.81	8.83		81RSb	T
	gl	0.1 (KNO ₃)	25	4.65(5)	8.78(8)		83AC	T
	Zn/Hg	0.1 (KNO ₃)	25	5.01(6)	9.57(6)	11.37(4)	85DV	D
				log $\beta_{MHL} = 13.11(6)$ log $\beta_{MH_1L} = -3.51(5)$				

TABLE 3.3 Formation Constants of Complexes of α -Alanine with 4d and 5d Transition Metal Ions (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag ^I	sol	→ 0.0	25	4.86			41KRa	D
	gl,sol	→ 0.0	25	3.64	7.18		51Mb	D
	Ag	0.6	25	3.60(5)	7.06(2)		67AM	T
	gl	0.2 (NaClO ₄)	30	3.85(2)	7.51(3)		75JB	T
	gl,Ag	0.1 (KNO ₃)	25	4.23	7.02		79MS	Rj
				log $\beta_{MH_2L} = 14.49$ log $\beta_{MHL} = 10.75$ log $\beta_{MH_1L} = -6.16$ log $\beta_{MH_3L_2} = 27.89$ log $\beta_{MH_2L_2} = 25.04$ log $\beta_{MHL_2} = 16.09$				
	gl	0.1 ?	30	3.85	6.60		81PU	D
	Ag	0.1 (KNO ₃)	25	4.30(10)			81SB	Rj
				log $\beta_{MHL} = 12.40(20)$ log $\beta_{MH_2L} = 14.90(20)$				
Au ^{III}	gl	? (Cl ⁻)	25	6.92	9.96		74FAb	D
Cd ^{II}	gl	0.005-0.01	21		7.6		52P	D
	gl	?	25	4.2			54P	D
	pol	1.0	30			9.15	62RS	D
	pol	2.0 (KNO ₃)	25	5.13	7.82	9.16	62SC	D
	elph	0.1 (KNO ₃)	20	5.9	9.4	11.8	64J	D
	pol	1.0 (KNO ₃)	30		7.56	9.15	64RSa	T

TABLE 3.3 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
$\log \beta_{M(OH)L_2} = 8.42$								
	gl	0.37 (KNO ₃)	20	4.02	7.40		66SW	T
	ORD	0.5 (NaClO ₄)	25	3.96	7.57		67RP	T
	gl	1.0 (KNO ₃)	25	3.802(3)	7.100(7)	9.089(12)	72BPa	T
	gl	0.1 (KNO ₃)	25	4.0	7.4		75HV	T
	Cd	0.1 (KNO ₃)	25	4.4	7.2		75HV	T
				4.1	7.3			
	gl	0.2 (NaClO ₄)	30	4.27(3)	7.73(3)		75JB	T
	gl	0.1 (KNO ₃)	30	4.16	7.46		78MS	T
	pol	0.5 (KNO ₃)	23	4.50	7.15	8.94	78AE	T
	pol	0.3 (KNO ₃)	30	4.40	7.40	9.50	81AP	T
	gl	3.0 (LiClO ₄)	25	3.99(1)	7.28(1)		81M	T
	pol	1.0 (KNO ₃)	30	4.24	7.54	9.54	82CG	T
	gl	3.0 (NaClO ₄)	25	3.69	6.93		82MO	T
	gl	0.7 (NaClO ₄)	20	3.902(2)	7.27(6)		84GS	T
	pol	0.7 (NaClO ₄)	20	3.75(5)	7.20(4)		84GS	T
	gl	0.7 (NaClO ₄)	25	3.875(7)	7.28(1)		85GS	T
	gl	0.2 (KNO ₃)	25	3.96	7.37	9.98	86SV	T
Hg ^{II}	gl	0.01	21		18.4		52P	D
	gl	0.005	21		18.8		53P	D
	pol	0.6 (KNO ₃)	25		18.25(3)		66TA	D
CH ₃ Hg ^I	gl	1.0 (NaNO ₃)	25	7.516(52)	9.450(227)		78JI	D
Os ^{IV}	gl	? (Cl ⁻)	25		6.97		74FAc	D
Pd ^{II}	gl	?	27		18.17		73FA	Rj
	gl	0.5 (KNO ₃)	20	9.98(2)	18.33(4)		74KH	D
Rh ^{III}	gl	? (Cl ⁻)	27	7.19	10.28		74FAa	D
Zr ^{IV}	sp	0.1	?	log $K(M + HL) = 4.1(1)$			76KV	D

TABLE 3.4 Formation Constants of Complexes of α -Alanine with the f-block Elements (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Sc ^{III}	gl	0.1 (KNO ₃)	25	7.7(2)			67EM	D
Y ^{III}	gl	0.1 (KNO ₃)	25	5.0(3)			67EM	D
Ce ^{III}	gl	0.2 (NaClO ₄)	25	6.03			86LS	Rj
Dy ^{III}	gl	0.1 (KNO ₃)	25	4.7(1)			67EM	D
Er ^{III}	gl	0.1 (KNO ₃)	25	4.7(1)			67EM	D
Eu ^{III}	gl	0.1 (KNO ₃)	25	4.7(1)			67EM	D
	dis	2.0 (NaClO ₄)	25	log $K(M + HL) = 0.74(2)$			71Alb	D
Ho ^{III}	gl	0.1 (KNO ₃)	25	4.6(1)			67EM	D
La ^{III}	gl	0.1 (KNO ₃)	25	4.5(1)			67EM	D
	gl	0.2 (NaClO ₄)	25	5.82			86LS	Rj

TABLE 3.4 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Lu ^{III}	gl	0.1 (KNO ₃)	25	4.8(1)			67EM	D
Nd ^{III}	gl	0.1 (KNO ₃)	25	4.8(2)			67EM	D
	sp	?	?	5.5			70EM	Rj
Pr ^{III}	gl	0.2 (KCl)	22	log $K(M + HL) = 0.64$			73SY	D
	NMR	0.2 (KCl)	22	log $K(M + HL) = 0.81$				
	gl	0.2 (NaClO ₄)	25	6.52			86LS	Rj
	gl	0.1 (KNO ₃)	25	4.7(2)			67EM	D
Sm ^{III}	gl	0.2 (NaClO ₄)	25	6.36			86LS	Rj
	gl	0.1 (KNO ₃)	25	4.7(1)			67EM	D
Tb ^{III}	gl	0.2 (NaClO ₄)	25	6.68			86LS	Rj
	gl	0.1 (KNO ₃)	25	4.7(2)			67EM	D
Tm ^{III}	gl	0.1 (KNO ₃)	25	4.7(1)			67EM	D
Yb ^{III}	gl	0.1 (KNO ₃)	25	4.9(1)			67EM	D
Am ^{III}	dis	2.0 (NaClO ₄)	25	log $K(M + HL) = 0.78(1)$			71ALa	D
Pu ^{III}	ix	1.0 (NaCl)	18	p $K(ML) = 3.40(3)$			73RK	D
U ^{VI} O ₂	gl	?	?	9.00			70FMb	Rj
	pot	0.5	25	7.0(1)			73SK	D
	sp	0.5	25	7.0(1)				
	gl	0.1 (NaClO ₄)	31	8.55			77RR	D
	pol	0.1 (NaClO ₄)	30	log $K(M + 2HL) = 2.15$			79RR	T
	pol	0.5 (NaClO ₄)	26	2.04(2)	2.08(4)		80DD	T
				log $K(M + 4L) = 3.85(2)$				
	gl	0.1 (NaClO ₄)	30	2.03			80RR	T
U ^{IV}	gl	0.1 (KNO ₃)	25	7.33(2)	14.97(4)		82NM	T
	sp	0.5 (Cl ⁻)	20	10.43(5)			74SK	D
	pol	0.1 (NaClO ₄)	?	10.0			75FN	D
	pol	?	22	10.3	13.4		76NF	D
				log $K(M + 4L) = 18.8$				
Th ^{IV}	gl	0.5 (KNO ₃)	25	8.84(4)			71KS	T
	ix	0.5 (KNO ₃)	20	8.80(6)			80S	T
	gl	0.1 (KNO ₃)	25	7.18(8)	14.51(3)		83NM	T

The main group elements generally form rather weak complexes with amino acids, and it is not easy to obtain accurate stability constants. The applicability of pH-metry is generally limited, because of the very small changes in pH during the titrations or because of the various hydrolytic processes. Accordingly, most of the data published should be regarded as doubtful or tentative at best.

In the case of the beryllium(II) complexes, the hydrolysis of the metal ion can not be neglected, and thus the value in 52P is rejected. The stability constants of the other alkaline earth metal ions are very low; they follow the stability sequence $Mg^{II} > Ca^{II} > Sr^{II} \approx Ba^{II}$. The indium(III) and lead(II) complexes of α -alanine have been studied by several authors, but the data available are hardly sufficient for an objective evaluation, and they are mainly regarded as doubtful. The more recent studies (79MT, 82BC, 85DV) on the α -alanine complexes of lead(II) establish the existence of protonated and hydroxo complexes, which were not taken into account in the previous studies. However, the differences in the speciation and in the values of the stability constants are significant in the recent studies, too. Thus, recommended values can not be given for the complexation with lead(II).

It can be seen from Table 3.2 that the complexation of α -alanine has been the most frequently studied with the 3d transition metal ions. The formation of simple mono, bis and tris complexes is

characteristic for all divalent cations, though a minor amount of protonated complexes at low pH, or of mixed hydroxo complexes at high pH, has also been assumed in some cases (56Ca, 73BF, 79GK, 85DV, 88PB). Various transition metal ions (such as Ti^{III} , V^{IV} , Cr^{II} , Mn^{II} and Fe^{II}) are readily oxidized in the presence of trace amounts of oxygen. Thus, it is rather difficult to obtain reliable stability constants for the complexes of these metal ions, and most of the data reported are regarded as doubtful or even rejected if the experimental conditions are not well specified (70FMa, 70FMb, 70CBa). Accordingly, reliable stability constants are not available on the complexation of Ti^{III} and Cr^{II} with α -alanine. Stability constants for the V^{IV} - α -alanine interaction have been reported by several authors, but only the results from 88PB can be accepted, where the formation of various protonated and mixed hydroxo complexes was taken into account.

The determination of stability constants for the trivalent chromium and iron complexes is extremely difficult. In the case of chromium(III), the very slow formation kinetics makes it necessary to apply sophisticated experimental techniques, while the consideration of hydrolytic processes is crucial for the complexation of iron(III). As a consequence of the low number of data reported, the values are to be taken as doubtful.

The amino acid complexes of the divalent cations of $3d^5$ - $3d^{10}$ transition metals have been most thoroughly studied. Among them, manganese(II) and iron(II) form rather weak complexes with nitrogen donors, and the metal ions are readily oxidized in basic solution, which makes stability constant determination inaccurate. However, the relatively large number of data available for manganese(II) permits a critical evaluation of the reported values. Because of the low stability of the manganese(II) complexes, the complex formation processes overlap with those of metal ion hydrolysis. Thus, reliable values can be obtained easily only for the mono complexes ($\log \beta_{\text{ML}}$), while the ratio of the successive stability constants largely depends on the adequate experimental conditions and on the calculation method. $\log(K_1/K_2)$ is very small or even negative in some cases, and therefore these data are regarded as doubtful, although the stability constants of the mono complexes are in good agreement with the results of other studies (49MM, 73BS, 83KG). On the other hand, the values obtained with electrophoretic or ion-exchange techniques for the mono complexes are much larger than those resulting from potentiometric studies and they are again considered to be doubtful (64J, 69BZ). Average values of $\log \beta_{\text{ML}}$ can be calculated from the data obtained in pH-metric studies performed in the ionic strength range around 0.2 mol dm^{-3} ; such values appear in Table 3.5, together with the recommended or tentative stability constants for the α -alanine complexes of the other 3d transition metal ions.

TABLE 3.5 Recommended (R) and Tentative (T) Values for the Stability Constants of α -Alanine Complexes with Transition Metal Ions

Metal	Temp °C	Medium mol dm^{-3}	$\log \beta_{\text{ML}}$	Cat	$\log \beta_{\text{ML}_2}$	Cat	$\log \beta_{\text{ML}_3}$	Cat
Mn^{II}	25	0.05-0.2	2.60(15)	T				
Co^{II}	25	0.0	4.77(5)	T	8.44(4)	T		
	25	0.05-0.5	4.33(5)	T	7.73(10)	T		
Ni^{II}	25	0.0	5.87(6)	T	10.56(7)	T		
	25	0.05-0.5	5.41(8)	T	9.89(10)	T	12.99(15)	T
	25	1.0	5.40(1)	R	9.92(1)	R	13.04(2)	R
Cu^{II}	25	0.0	8.50(5)	R	15.53(8)	T		
	25	0.05-0.5	8.14(10)	T	14.96(10)	T		
	25	1.0	8.17(7)	T	14.98(10)	T		
	37	0.15	8.05(8)	T	14.58(20)	T		

TABLE 3.5 (continued)

Metal	Temp °C	Medium mol dm ⁻³	log β_{ML}	Cat	log β_{ML_2}	Cat	log β_{ML_3}	Cat
Zn ^{II}	25	0.05-0.5	4.63(8)	T	8.66(10)	T		
Cd ^{II}	25	0.1-0.2	4.12(15)	T	7.32(10)	T		
	25	0.5-1.0	3.88(8)	T	7.38(10)	T		

pH-metry is an excellent technique for determination of the stability constants of the cobalt(II), nickel(II), copper(II) and zinc(II) complexes of amino acids. This is supported by the huge number of independent investigations, which permits classification of the equilibrium constants for these complexes, as recommended or tentative.

Cobalt(II) complexes of amino acids are readily oxidized in basic solution, but this can be avoided with an inert atmosphere. The stability constant values were considered as doubtful if the ionic strength during the determination was too low (50A, 50MM) or the constants obtained were much higher than those from other measurements (64J, 79EM). The remaining data were mainly determined in careful potentiometric studies and were used for critical evaluation. Tentative values for the mono and bis complexes of cobalt(II) with α -alanine are given in Table 3.5.

Stability constants for the nickel(II) complexes of amino acids can readily be obtained with various methods, but especially with pH-metry. There are only a few data which are considered to be doubtful, because the experimental conditions were not well specified (70CBa), or the reported values significantly exceed the data reported from other determinations (64J, 79EM). The accuracy of the pH measurements reported in 79EM is rather low (0.03 pH units), and therefore these values were also omitted from the evaluation. Tentative values of the stability constants for the nickel(II)- α -alanine system are listed in Table 3.5, at three different ionic strengths. The values obtained from independent determinations at an ionic strength of 1.0 mol dm⁻³ are in very good agreement, and they are given as recommended values. At the same time, it should be considered that most of the authors determined stability constants only for mono and bis complexes. Equilibrium data on the tris complexes can be obtained only at a high ligand excess, which renders the log β_{ML_3} values slightly less accurate.

Most stability constant determinations are available for the interaction with the copper(II) ion. In agreement with the Irving-Williams series, of the 3d transition metal ions copper(II) forms the most stable complexes with amino acids. Because of the distorted octahedral geometry of the copper(II) complexes, mono and bis complexes are readily formed, but the formation of tris complexes requires the presence of a very large ligand excess. Accordingly, reliable equilibrium values can not be obtained for the ML₃ complexes by pH-metry.

Some results from the early studies are regarded as doubtful, because of the low ionic strength used (50A, 56N), or because the experimental conditions are not satisfactorily clarified (50LD, 56Ca, 56Cb, 68GS). The ratio of the stepwise stability constants is very small in some cases, and the values are regarded as doubtful (68BV, 77KD, 79EM) or rejected if log(K_1/K_2) is negative (78KZ). The remaining data passed the acceptance criteria and there is a sufficient number of independent reports relating to identical experimental conditions to yield recommended or tentative values, which are compiled in Table 3.5.

The zinc(II) ion also forms mono, bis and tris complexes with the aliphatic amino acids, but complex formation here generally overlaps metal ion hydrolysis, which results in some uncertainty in the equilibrium constants of the species ML₂ and ML₃. The reports were again regarded as doubtful if a low ionic strength was applied during the measurements, or if the experimental conditions were not well specified in the publications (49MM, 52P, 54P, 70CBa). The remaining values were mainly obtained by potentiometric methods in the ionic strength range around 0.2 mol dm⁻³. In Table 3.5, the stability constants are treated together in the ionic strength range 0.05 to 0.5 mol dm⁻³. This is only an approximation, based upon the ionic strength-dependence of the metal ion glycine complexes discussed in the previous paper (91KS). It was found that the stability constant varies via a minimum curve as a

function of the ionic strength, and the minimum is situated at around 0.2 mol dm^{-3} . It should be noted, however, that for the exact evaluation of a system the values for the given medium should be used.

The silver(I) and cadmium(II) complexes are the best studied of those of the 4d-5d transition elements, and only a few independent determinations are available for the other metal ions. The single values reported for the α -alanine complexes of Zr^{IV} , Rh^{III} , Os^{IV} and Au^{III} can be used only as informatory data; these values are regarded as doubtful, because the experimental conditions are generally not satisfactorily specified (74FAa, 74FAB, 74FAC, 76KV). The $\log \beta_{\text{ML}_2}$ values reported for the mercury(II) complexes of α -alanine are in good agreement, but they are considered to be doubtful, because the species distribution is not discussed in these publications. Palladium(II) forms complexes of very high stability, and thus pH-metry is not an appropriate method of obtaining reliable equilibrium data. The values reported in 73FA are rejected, because the stable chloro complexes were not taken into account, while 74KH is regarded as doubtful, because pH-metry was applied for the determination.

There are several publications dealing with the stability constants of the silver(I) complexes of α -alanine. Some of the results (41KRa, 51Mb, 81PU) are regarded as doubtful, because of the low ionic strength applied, or because the experimental conditions are not satisfactorily clarified. The results from 79MS and 81SB are rejected because the formation of AgH_2L is impossible with a bidentate ligand. The remaining data were obtained at different temperatures and at different ionic strengths, and thus average values can not be calculated.

The cadmium(II) complexes of the various amino acids can be conveniently studied by polarographic, pH-metric or other potentiometric methods. Most of the published data are in close agreement, except those in 64J and 62SC, in which higher values were reported than in the other cases. The data determined at very low ionic strengths were also considered to be doubtful, but the remaining values passed the acceptance criteria and were used to obtain the tentative values listed in Table 3.5.

Stability constants for the f-block elements (including Sc^{III} and Y^{III}) are listed in Table 3.4. It is well known from many other studies that the rare earth elements form rather weak complexes with nitrogen donors, and accordingly the hydroxo complex formation should be taken into account because it significantly influences the stability constant determinations with these metal ions. For the lanthanides, two sets of data are available (67EM and 86LS). The values reported in 86LS are generally very high, due to exclusion of the hydrolytic processes, and these values are rejected. All the other constants are regarded as doubtful and can be used only as informatory data, because the coordination mode of the ligand is questionable.

$\text{U}^{\text{VI}}\text{O}_2$, U^{IV} and Th^{IV} complexes of α -alanine have also been studied by several authors. The values reported in 70FMb, 73SK, 74SF, 75FN and 76FN are considered to be doubtful, because the experimental conditions are not well specified, and the values of the stability constants are rather high. The remaining data can be accepted tentatively, although different values and different types of coordination are supposed in some cases (e.g. 80DD, 80RR, 82NM).

Table 3.5 contains the recommended and tentative stability constants of the complexes of α -alanine with several transition metal ions. It can be seen that, in spite of the numerous investigations recommended values can be offered in only a few cases. This does not mean that the stability constant determinations were not careful and accurate enough, but the various laboratories used different experimental (calibration) techniques, different ionic strengths and different temperatures. Thus, it is advisable for the reader to use tentative stability constants obtained under well-identified experimental conditions and given in the respective Tables.

3.2 Stability constants of the metal complexes of valine

Valine occurs frequently in polypeptides, and therefore its metal complexes have been thoroughly studied. The literature data for the complexes of 3d transition elements are given in Table 3.6, and those for the complexes of the other metal ions in Table 3.7.

The formation processes of valine complexes are very similar to those of other aliphatic amino acids; mono, bis and tris complexes are formed with most of the metal ions. As concerns the 3d transition elements, only a few publications are available on complexation with Ti^{III} , $\text{V}^{\text{IV}}\text{O}$, Cr^{II} and Cr^{III} . The experimental conditions are not specified in these reports and the data are rejected (70FMa,

TABLE 3.6 Formation Constants of Complexes of Valine with 3d Transition Metal Ions
(Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat	
Ti ^{III}	gl	?	?	8.12			70FMb	Rj	
V ^{IV} O	gl	?(NaClO ₄)	25	8.52(6)	15.84(7)		70CBb	Rj	
	gl	?	?	8.65			70FMb	Rj	
Cr ^{II}	Pt,gl	?	?	8.68			70FMa	Rj	
Cr ^{III}	gl	0.5	25	8.3	14.7	20.1	63KM	D	
Mn ^{II}	gl	0.01	25	2.84	5.56		49MM	D	
	gl	0.15 (KNO ₃)	37	2.337(85)	3.97(27)	5.19(42)	69CP	T	
Fe ^{II}	gl	0.01	20		6.8		50A	D	
	gl	1.0 (KCl)	20	3.39			59P	T	
Fe ^{III}	red	1.0 (NaClO ₄)	20	9.6			58Pc	D	
Co ^{II}	gl	< 0.01	25	4.57	9.24		49MM	D	
	gl	0.01	20		8.60		50A	D	
	gl	0.02	25	4.70	8.40		54R	T	
	gl	0.5 (KNO ₃)	30	4.32(6)	8.77	11.62(6)	79EM	T	
	elph	0.1 (NaClO ₄)	35	4.60	8.01		84SY	D	
	Ni ^{II}	gl	0.15	25	5.37	9.53		56LW	T
				30	5.27	9.34			
				40	5.11	9.02			
		gl	?	18	5.53	9.88	12.71	56PC	D
		gl	→ 0.0	25	5.45	9.72	12.20	57P	T
gl		?	10	5.62	10.10	12.76	60P	D	
			15	5.54	9.94	12.55			
			25	5.45	9.72	12.20			
			30	5.37	9.53	11.96			
			35	5.34	9.46	11.84			
Cu ^{II}			40	5.31	9.39	11.71			
	sp,gl	0.1 (KNO ₃)	25	5.17	9.12		61DR	T	
	pol	0.5 (NaClO ₄)	25	5.26	9.42	11.95	67RP	T	
	gl	?(NaClO ₄)	25	5.48(4)	9.90(7)		70CBb	D	
	gl	0.2 (NaClO ₄)	20	5.45	10.72		72KP	T	
	gl	1.0 (NaClO ₄)	25	5.26	9.58	12.39	73MS	T	
	gl	0.5 (KNO ₃)	30	5.07(2)	9.04(2)	10.94(17)	79EM	T	
	gl	1.0 (NaClO ₄)	25	5.26	9.59	12.40	81EB	T	
	gl	0.1 (NaClO ₄)	35	5.40	9.70		86SR	T	
	gl	0.01	25	7.92	14.44		49MM	D	
	gl	0.01	20		15.1		50A	D	
	gl	0.02	25	8.32	15.42		54R	T	
	pol	0.15	25		14.76		56LW	T	
			30		14.51				
			35		14.28				
	sp	?	25	7.93	13.50		57MS	D	
	sp	0.72	25	8.03			57MS	D	
	sp,gl	0.1 (KNO ₃)	25	7.81	14.50		61DR	T	
gl	0.1 (KCl)	20	8.19	15.18		66GI	T		
ORD	0.5	25	7.98	14.71		67RP	T		
sp	0.5 (NaClO ₄)	25	8.06(1)	14.78(3)		68PP	T		
gl	0.15 (KNO ₃)	37	8.017(33)	14.726(44)		69CP	T		
gl	0.16 (KNO ₃)	25	7.80	14.50		70MB	T		
gl	0.1 (KNO ₃)	25	8.11(1)	14.79(1)		72IN	T		

TABLE 3.6 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Zn ^{II}	gl	0.2 (NaClO ₄)	20	8.32	14.89		72KP	T
	gl	0.1 (KNO ₃)	25	8.049(5)	14.913(7)		77BP	T
	gl	0.1 (KCl)	25	8.18	15.44		77KD	D
	gl	0.1 (KCl)	25	7.26	15.44		78KZ	Rj
	gl	0.5 (KNO ₃)	30	7.68(3)	14.39(4)		79EM	T
	gl	0.1 (NaClO ₄)	30	8.05(2)	14.91(2)		80AS	T
	gl	0.5 (NaNO ₃)	?	8.14(1)	14.99(1)		80MJ	D
				log $\beta_{MH_1L} = 0.43(4)$				
	pol	1.0 (KNO ₃)	30	8.00	14.90		80SG	T
	gl	0.25 (NaCl)	25	7.98	14.70(L)		83AO	T
				7.98	14.69(DL)			
	gl	0.25 (NaCl)	25	7.980	14.699		84AO	T
	gl	0.15 (NaClO ₄)	37	7.93(5)	14.59(1)		84BPa	T
				log $\beta_{MHL} = 10.28(4)$				
				log $\beta_{MHL_2} = 18.38(6)$				
	elph	0.1 (NaClO ₄)	35	8.02	14.62		84SY	D
	Cu/Hg	0.1 (KNO ₃)	25	7.62			86DV	D
	gl	0.2 (KNO ₃)	35	8.08	14.68		87PS	T
	gl	0.1 (KNO ₃)	25	8.11	14.96		88ZZ	T
	gl	0.01	25	5.00	9.10		49MM	D
	gl	< 0.01	20		8.2		52P	D
	Cd/Hg	4.0	25	4.60	9.06		58Pa	T
	Cd/Hg	4.0	25	4.67	8.97		58PQ	T
	sp,gl	0.1 (KNO ₃)	25	4.46	8.38		61DR	T
	ORD	0.5	25	4.40	8.17		67RP	T
	gl	0.15 (KNO ₃)	37	4.442(8)	8.235(7)	10.622(80)	69CP	T
	gl	? (NaClO ₄)	25	5.04(5)	9.18(5)		70CBb	D
	elph	0.1 (NaClO ₄)	35	4.40	7.81		84SY	D
Zn/Hg	0.1 (KNO ₃)	25	4.50(10)	8.16(3)		85DV	T	

70FMb, 70CBb). Thus, reliable stability constants are not available for the 3d¹-3d⁴ transition metal ion-valine interactions.

It is surprising that the Mn^{II}, Fe^{II}, Fe^{III} and even Co^{II} complexes of valine have likewise scarcely been studied. Some of the results were obtained at very low ionic strength (49MM, 50A, 54R) and these data are regarded as doubtful, as are the values obtained for Fe^{III} (58Pc), where the hydrolytic processes were not taken into account. The data from the other reports are taken as tentative values, but further equilibrium studies are necessary on the valine complexes of these metal ions.

Stability constants for the nickel(II), copper(II) and zinc(II) complexes of valine have been reported for different experimental conditions. As for α -alanine, the data are regarded as doubtful if the experimental conditions are not completely specified (57MS, 80MJ, 56PC, 60Pd, 70CBb), or a very low ionic strength was applied (49MM, 50A, 52P). Log (K_1/K_2) is very small (77KD) or even negative (78KZ) in some cases, and these reports have also been omitted from the evaluation. The other reports passed the acceptance criteria, and have been used to give tentative stability constants for the Ni^{II}, Cu^{II} and Zn^{II} complexes of valine, which are listed in Table 3.8.

Stability constants of the valine complexes of other metal ions are collected in Table 3.7. It can be seen from this Table that in most cases only individual determinations are available, and hence the data are to be regarded as informative. As was discussed for the complexes of α -alanine, some values

TABLE 3.7 Formation Constants of Complexes of Valine with Other Metal Ions
(Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag ^I	gl	0.5 (KNO ₃)	20	3.29(5)	7.31(5)		74KH	T
Au ^{III}	gl	? (Cl ⁻)	25	6.80	9.85		74FAb	D
Be ^{II}	gl	< 0.01	20		12.4		52P	Rj
	gl	0.1 (NaClO ₄)	35	6.70	12.02		86SR	Rj
Cd ^{II}	gl	< 0.01	20		6.7		52P	D
	Cd/Hg	4.0	25	3.80	7.13		58PQ	T
	pol	1.0	30			8.60	62RS	D
	pol	1.0 (KNO ₃)	30		6.66	8.48	64RSa	T
				log $K(M + 2L + OH) = 8.35$				
	ORD	0.5	25	3.46	6.46		67RP	T
	gl	0.1 (KNO ₃)	25	3.7	6.9		75HV	D
	Cd	0.1 (KNO ₃)	25	4.2	6.8		75HV	D
				3.7	7.0			
	pol	0.5 (KNO ₃)	23	3.88	6.48	8.14	78AE	T
	gl	3.0 (LiClO ₄)	25	4.04(1)	7.39(1)		81M	T
	pol	1.0 (KNO ₃)	30	3.95	6.81	8.90	82CG	T
	gl	0.7 (NaClO ₄)	20	3.706(2)	6.81(2)		84GS	T
	pol	0.7 (NaClO ₄)	20	3.67(3)	6.99(2)		84GS	T
	gl	0.7 (NaClO ₄)	25	3.68(3)	7.00(5)		85GS	T
CH ₃ Hg ^I	gl	1.0 (NaNO ₃)	25	7.268(56)	9.157(259)		78JI	D
	NMR	0.4	25	7.41			74RO	D
				log $K(M + HL) = 2.7$				
In ^{III}	gl	0.1 (NaClO ₄)	24	8.28	15.80		76KF	D
Mg ^{II}	gl	0.15 (NaCl)	20	1.56(8)			85VD	T
Os ^{IV}	gl	? (Cl ⁻)	28		7.77		74FAc	D
Pb ^{II}	pol	1.0 (KNO ₃)	30	4.02	5.89		64RSb	D
				log $K(M + 2L + OH) = 9.41$				
	gl	0.1 (NaClO ₄)	35	5.10	8.40		86SR	T
Pd ^{II}	gl	?	27		17.54		73FA	D
	gl	0.5 (KNO ₃)	20	9.62(2)	17.76(4)		74KH	T
Rh ^{III}	gl	? (Cl ⁻)	27	7.14	9.80		74FAa	D
Ce ^{III}	gl	0.2 (NaClO ₄)	25	6.05			86LS	Rj
Er ^{III}	gl	0.03 ?	25	4.20(8)			81PBa	D
Ho ^{III}	gl	0.03 ?	25	4.05			81PBa	D
La ^{III}	gl	0.2 (NaClO ₄)	25	5.94			86LS	Rj
Lu ^{III}	gl	0.03 ?	25	4.30(8)			81PBa	D
Nd ^{III}	gl	0.1 ?	25	3.71(2)			81PBb	D
	sp	0.1 ?	25	3.7			81PBb	D
	gl	0.2 (NaClO ₄)	25	6.52			86LS	Rj
Pr ^{III}	gl	0.2 (NaClO ₄)	25	6.28			86LS	Rj
Sm ^{III}	gl	0.2 (NaClO ₄)	25	6.58			86LS	Rj
Yb ^{III}	gl	0.03 ?	25	4.29(8)			81PBa	D
U ^{VI} O ₂	gl	?	?	8.59			70FMb	Rj
	gl	0.1 (NaClO ₄)	31	7.97			77RR	D
	gl	0.1 (NaClO ₄)	30	2.01			80RR	T
	gl	0.1 (KNO ₃)	25	7.10(1)	14.72(2)		82NM	D
	elph	0.1 (NaClO ₄)	35	8.02	14.53		84SY	D
U ^{IV}	pol	?	22	9.9	13.3	19.6	76NF	D
	sp	0.5 (Cl ⁻)	20	10.25(5)			74SK	D
Th ^{IV}	gl	0.5 (KNO ₃)	25	8.58(5)			71KS	T
	ix	0.5 (KNO ₃)	20	8.60(10)			80S	T
	gl	0.1 (KNO ₃)	25	8.30(1)	14.23(4)		83NM	T

TABLE 3.8 Tentative Values for the Stability Constants of Valine Complexes

Metal	Temp °C	Medium mol dm ⁻³	log β_{ML}	log β_{ML_2}
Ni ^{II}	25	0.1-0.5	5.27(5)	9.36(15)
Cu ^{II}	25	0.1-0.5	7.98(8)	14.76(12)
Zn ^{II}	25	0.1-0.5	4.46(6)	8.24(8)

are rejected or taken as doubtful, because hydrolytic processes were not taken into account (52P, 86SR, 86LS), or the experimental conditions are not well specified (70FMb). With regard to the similarities between the complex formation processes of α -alanine and valine, some values for the complexation with Ag^I, Cd^{II}, Mg^{II}, Pb^{II}, Pd^{II}, U^{VI}O₂ and Th^{IV} can be considered to be tentative, while the others are doubtful, because a reliable comparison of the data is not possible. The cadmium(II) complexes of valine have been quite widely studied, but a critical evaluation of the data is hardly possible, because almost all determinations relate to different temperatures or different ionic strengths.

3.3 Stability constants of the metal complexes of leucine

Literature data on the metal ion complexes of leucine are listed in Tables 3.9 and 3.10, for 3d transition elements and for other metal ions, respectively.

The complex forming ability of leucine is very similar to those of α -alanine or valine, and the literature data have been evaluated in the same way. As concerns the 3d transition metal ions, reliable data are not available for the complexation with Ti^{III}, V^{III}, V^{IV}O and Cr^{II}, because hydrolysis was not taken into account, or the experimental conditions are not specified (70FMa, 70FMb, 70CBb, 86KD). Two sets of data have been reported for the Cr^{III} complexes of leucine, which differ significantly in speciation. The presence of mono, bis and tris complexes was suggested in 63KM and 86SGb, while only carboxylate-coordinated species were presumed in another study (73BF).

The Mn^{II}, Fe^{II}, Fe^{III} and Co^{II} complexes of leucine have scarcely been studied. The data obtained at low ionic strength were previously proposed as doubtful, but we now suggest that they be taken as tentative values (49MM, 59DLa), because there are no more reliable studies available. The results obtained electrophoretically are generally higher than the other values, and they are classified as doubtful. The stability constants reported for the iron(III) complexes are also regarded as doubtful, because of the occurrence of hydrolytic processes.

TABLE 3.9 Formation Constants of Complexes of Leucine with 3d Transition Metal Ions (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ti ^{III}	gl	?	?	8.55			70FMb	Rj
V ^{III}	gl	0.2 (KCl)	25	8.96(4)	16.26(4)		86KD	Rj
V ^{IV} O	gl	? (NaClO ₄)	25	8.55(7)	15.89(8)		70CBb	Rj
	gl	?	?	9.08			70FMa	Rj
Cr ^{II}	Pt,gl	?	?	8.40			70FMa	Rj
Cr ^{III}	gl	0.5	25	8.8	15.6	21.5	63KM	D
	sp	0.6 (Mg(ClO ₄) ₂)	25	log K(M + HL) = 3.16 log K(M + 2HL) = 5.45 log K(M + 3HL) = 7.38 log K(M + 4HL) = 9.07 log K(M + 5HL) = 10.38 log K(M + 6HL) = 11.64			73BF	D
	elph	0.1 (NaClO ₄)	35	7.92	14.01	21.70	86SGb	D

TABLE 3.9 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat	
Mn ^{II}	gl	0.01	25	2.78	5.45		49MM	T	
	gl	0.1	25	2.15			52K	D	
	elph	0.1 (KNO ₃)	20	3.9	5.7		64J	D	
	gl	0.1 (KCl)	25	2.83			71SS	T	
				35	2.76				
			45	2.73					
Fe ^{II}	gl	1.0 (KCl)	20	3.42			59P	T	
Fe ^{III}	red	1.0 (NaClO ₄)	20	9.9			58Pc	D	
	red	0.1 (KNO ₃)	25	7.59			86DV	D	
Co ^{II}	gl	0.01	25	4.55	8.26		49MM	T	
	gl	0.01	25	4.53	8.16		59DLa	T	
Ni ^{II}	elph	0.1 (KNO ₃)	20	5.2	8.4	10.7	64J	D	
	gl	0.01	25	5.66	10.21		59DLa	T	
Cu ^{II}	elph	0.1 (KNO ₃)	20	6.3	10.3	12.8	64J	D	
	gl	0.1 (DL)	25	5.71	10.26	14.97	66MM	D	
		(L)		5.53	9.46	14.38			
		(D)		5.68	10.02	14.27			
	gl	? (NaClO ₄)	25	5.50(7)	10.08(9)		70CBb	D	
	gl	0.2 (NaClO ₄)	20	5.45	10.70		72KP	D	
	elph	0.1 (NaClO ₄)	35	5.50	9.90		85SR	D	
	gl	0.01	25	7.89	14.44		49MM	T	
	Cu	0.1	25	8.11	15.84		57Ba	D	
	pol	0.4	25	7.78			58B	D	
pol	1.5	25	7.77						
E	3.0	25	7.55	15.00		57Bb	D		
sp	3.0	25		14.97		57Bb	D		
-	→ 0.0	25		8.51(6)	16.51(5)		58B	D	
gl	0.01	25		8.36	15.35		59DLb	T	
elph	0.1 (KNO ₃)	20		8.6	15.6		64J	D	
gl	0.16 (KNO ₃)	25		7.90	14.60		70MB	T	
gl	0.15 (KNO ₃)	37		8.04(4)	14.69(5)		71HP	T	
				log K(M + HL) = 2.13(4)					
				log K(M + HL + L) = 5.81(16)					
	gl	0.2 (NaClO ₄)	20	8.71	14.87		72KP	T	
	gl	0.1 (KNO ₃)	25	8.276(1)	15.174(1)		77BP	R	
	gl	0.1 (NaClO ₄)	25	8.32(1)	15.34(3)		80FS	T	
	gl	0.15 (NaClO ₄)	37	7.902(4)	14.533(6)		84BPb	T	
				log $\beta_{MH_1L_2}$ = 2.32(9)					
Zn ^{II}	gl	0.2 (KNO ₃)	35	8.04	14.77		87PS	T	
	gl	0.1 (KNO ₃)	25	8.19	15.10		88ZZ	T	
	gl	0.01	25	4.92	8.93		49MM	T	
	gl	0.1	20		9.1		52P	D	
	gl	0.01	25	4.89	9.19		59DLa	T	
	elph	0.1 (KNO ₃)	20	5.8	10.0	13.3	64J	D	
	gl	? (NaClO ₄)	25	5.11(5)	9.27(6)		70CBb	D	
	gl	0.15 (KNO ₃)	37	4.51(2)	8.56(1)		71HP	T	
					log β_{MH_1L} = -4.25(10)				
					log K(M + HL + L) = 5.81(16)				
	gl	0.1 (NaClO ₄)	25	4.56(2)	8.74(2)	11.86(15)	80FS	T	

TABLE 3.10 Formation Constants of Complexes of Leucine with Other Metal Ions (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag ^I	gl	0.5 (KNO ₃)	20	3.41(6)	7.44(6)		74KH	T
	gl	0.2 (NaClO ₄)	30	3.74(4)	7.20(4)		75JB	T
Al ^{III}	elph	0.1 (NaClO ₄)	35	8.50	15.20	18.90	86SGb	Rj
Au ^{III}	gl	? (Cl ⁻)	25	7.14	10.18		74FAb	D
Be ^{II}	elph	0.1 (NaClO ₄)	35	7.00	13.30		85SR	Rj
Cd ^{II}	gl	< 0.01	20		7.8		52P	D
	gl	0.01	25	4.04	7.53		59DLa	T
	elph	0.1 (KNO ₃)	20	5.8	9.4	11.8	64J	D
	gl	0.2 (NaClO ₄)	30	3.92(6)	7.48(6)		75JB	T
	pol	1.0 (NaClO ₄)	30	5.00	7.30		79PG	D
	pol	0.1 (NaClO ₄)	25	7.48(6)	10.91(2)		86RQ	D
	gl	0.01	20		17.5		52P	D
Hg ^{II}	gl	0.1 (NaClO ₄)	24	7.76	15.41 (DL)		76KF	D
In ^{III}	gl	0.1 (NaClO ₄)	24	8.26	15.74 (L)		76KF	D
Mg ^{II}	gl	0.15 (NaCl)	20	1.89(8)			85VD	T
Os ^{IV}	gl	? (Cl ⁻)	28		5.82		74FAc	D
Pb ^{II}	elph	0.1 (NaClO ₄)	35	5.20	8.70		85SR	D
Pd ^{II}	gl	?	27		18.22		73FA	D
	gl	0.5 (KNO ₃)	20	9.71(2)	18.15(2)		74KH	T
Pd ^{IIen}	gl	0.5 (KNO ₃)	25	11.41(1)			78L	T
Rh ^{III}	gl	? (Cl ⁻)	27	7.13	10.10		74FAa	Rj
Ce ^{III}	gl	0.2 (NaClO ₄)	25	4.59			86LS	Rj
La ^{III}	gl	0.2 (NaClO ₄)	25	4.31			86LS	Rj
Nd ^{III}	gl	0.2 (NaClO ₄)	25	4.92			86LS	Rj
Pr ^{III}	gl	0.2 (NaClO ₄)	25	4.72			86LS	Rj
Sm ^{III}	gl	0.2 (NaClO ₄)	25	5.09			86LS	Rj
Th ^{IV}	gl	0.5 (KNO ₃)	25	8.70(5)			71KS	T
	gl	0.1 (KNO ₃)	25	8.25(5)	14.14(9)		83NM	T
	elph	0.1 (NaClO ₄)	35	8.80			86SGb	D
U ^{IV}	pol	?	22	7.0	10.5		76NF	D
				log $K(M + 4L) = 15.6$				
U ^{VI} O ₂	gl	?	?	8.61			70FMb	Rj
	gl	0.1 (KCl)	25	6.83	12.49		71SS	T
			35	6.58	11.83			
			45	6.17	11.23			
	gl	0.1 (KNO ₃)	25	7.13	14.36		82NM	D

Several publications deal with the stability constants of the nickel(II), copper(II) and zinc(II) complexes of leucine, but even in this case the results raise some unsolved questions. This is probably due to the low solubility of the bis complexes, which makes the determination of log β_{ML_2} and log β_{ML_3} difficult.

For the nickel(II) complexes of leucine, the earliest determination seems to be the most reliable (59DLa). The details of the experimental procedure are not given in 70CBb, the log(K_1/K_2) ratio is very small in 72KP, while a very significant stereoselectivity was reported to occur in 66MM, and therefore these values are taken as doubtful.

The copper(II)-leucine interaction has been studied by many authors, but the unreliable ratio of the stepwise stability constants, or undefined experimental conditions, led to doubtful results in some cases (57Ba, 57Bb, 58B). The other pH-metric data passed the acceptance criteria and were used to obtain recommended or tentative values. The average values are listed in Table 3.17, together with the stability constants of the copper(II) complexes of the other aliphatic amino acids.

When the problems discussed above are taken into account, the data of three reports on the zinc(II)-leucine interaction can be accepted as tentative (49MM, 71HP, 80FS), but these values relate to different ionic strengths and different temperatures.

It can be seen from Table 3.10 that the number of stability constant determinations concerning the leucine complexes of the other transition and non-transition elements is even lower than in the case of valine. On the other hand, the results mainly originate from the same publications, and therefore we do not repeat the evaluation categories for the reported data.

Leucine is the only amino acid in this compilation for which the stability constants of the Al^{III} complexes have been published (86SGb). The hydrolysis of the metal ion was not taken into account, however, and therefore the constants are rejected.

The complexes of cadmium(II) are the best studied as concerns the metal ions listed in Table 3.10. However, only the data resulting from pH-metric investigations can be regarded as tentative, because the other methods provided values for the stability constants, which are too large, especially for the mono complex.

3.4 Stability constants of the metal complexes of 2-amino-pentanoic and -hexanoic acids and isoleucine

The metal complexes of 2-amino-pentanoic and -hexanoic acids and isoleucine have been much less studied than those of the other aliphatic amino acids. Consequently, the literature data reported on the metal complexes of a given ligand are listed in common Tables, i.e. in Tables 3.11, 3.12 and 3.13.

TABLE 3.11 Formation Constants of Complexes of 2-Aminopentanoic Acid with Metal Ions
(Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag ^I	Ag,gl	0.1 (KNO ₃)	25	3.08(2)	6.27(2)		75IP	T
Be ^{II}	gl	< 0.01	19		12.6		52P	Rj
Cd ^{II}	gl	< 0.01	19		6.6		52P	D
	gl	0.02	25	4.29	7.49		54R	D
	gl	0.1 (KNO ₃)	25	3.73(1)	7.03(1)		75IP	T
	pol	1.0 (NaClO ₄)	30	4.69	6.30		79PG	D
Co ^{II}	gl	0.02	25	4.80	8.38		54R	D
	gl	0.05 (KCl)	25	4.29	7.81		72GS	T
	gl	0.1 (KNO ₃)	25	4.15(1)	7.62(1)		75IP	T
Cu ^{II}	gl	0.02	25	8.6	15.78		54R	D
	gl	0.05 (KCl)	25	8.17	15.04		72GS	T
	gl	0.2 (KCl)	25	8.07	14.82		73GS	T
	gl	0.1 (KNO ₃)	25	8.12(1)	14.94(1)		75IP	T
	gl	0.1 (NaClO ₄)	30	8.05(4)	14.85(4)		80AS	T
Hg ^{II}	gl	< 0.01	20		17.6		52P	D
	gl	< 0.01	19		17.7		53P	D
Mg ^{II}	gl	0.15 (NaCl)	20	1.56			85VD	T
Mn ^{II}	gl	0.1 (KNO ₃)	20	3.30	5.19		73BS	T
			30	3.25	5.15			
			40	3.19	5.12			
			50	3.11	5.09			
			60	3.03	5.06			
			20	2.90			85VD	T
Ni ^{II}	gl	0.02	25	5.68	10.10		54R	D
			25	5.42	9.87		72GS	T
			25	5.27(2)	9.65(2)		75IP	T
			25	5.28	9.62		75SG	T
Zn ^{II}	gl	< 0.01	19		8.1		52P	D
			25	5.09	9.19		54R	D
			25	4.42(2)	8.52(3)		75IP	T

It can be seen from Table 3.11 that, for 2-aminopentanoic acid, the stability constants were mainly determined for the interactions with transition elements. The Be^{II} and Mg^{II} complexes are the exceptions, but in the case of Be^{II} the values are rejected, because the hydrolytic processes were not taken into account (52P). The values obtained at low ionic strength were regarded as doubtful (52P, 53P, 54R).

TABLE 3.12 Formation Constants of Complexes of 2-Aminohexanoic Acid with Metal Ions
(Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag^{I}	Ag	0.6	25	3.48(7)	6.76(5)		67AM	T
	gl	0.1 (KNO_3)	25	3.21(5)	6.71(3)		75IP	T
Be^{II}	gl	< 0.01	20		12.8		52P	Rj
		< 0.01	18		12.8			
Cd^{II}	gl	0.01	20		8.7		50A	D
	gl	< 0.01	20		6.9		52P	D
	gl	< 0.01	18		7.3		53P	D
	gl	?	25	4.12(4)	7.70(4)		69MZ	T
	gl	0.1 (KNO_3)	25	3.86(1)	7.33(1)		75IP	T
	pol	0.1 (NaClO_4)	20	3.92	7.60		84SD	T
				30	4.27	7.90		
Co^{II}	gl	0.01	20		9.4		50A	D
	gl	0.1 (KNO_3)	25	4.26(1)	7.79(1)		75IP	T
Cu^{II}	gl	0.01	20		15.5		50A	D
	pol	0.1 (KH_2PO_4)	25		15.2		54LD	D
	E	0.08	25	8.46			58B	D
	E	→ 0.0	25	8.71				
Fe^{II}	gl	0.1 (KNO_3)	25	8.18(1)	14.88(1)		75IP	T
	gl	0.01	20		8.6		50A	D
Hg^{II}	gl	< 0.01	20		17.8		52P	D
	gl	< 0.01	18		17.8		53P	D
Mg^{II}	gl	0.01	20		4		50A	Rj
	gl	0.15 (NaCl)	20	1.90(8)			85VD	T
Mn^{II}	gl	0.01	20		5		50A	D
Ni^{II}	gl	0.01	20		11.1		50A	D
	gl	0.1	25	5.51	9.67	13.86	66MM	D
	gl	?	25	5.59(4)	9.67(5)	12.61(5)	69MZ	D
	gl	? (NaClO_4)	25	5.65(3)	10.34(6)		70CBb	D
	gl	0.05 (KCl)	25	5.43	9.88		72GS	T
	gl	0.1 (KNO_3)	25	5.40(2)	10.01(1)		75IP	T
	gl	0.2 (KCl)	25	5.27	9.61		75SG	T
	pol	0.1 (NaClO_4)	20	4.02	7.21		84SD	T
			30	4.11	7.51			
Th^{IV}	gl	0.1 (NaClO_4)	20	log β_{ML_2}	log β_{ML_3}	log β_{ML_4}	83SD	Rj
			30	8.52	16.72	21.71		
			40	8.57	16.80	22.29		
			40	8.62	16.89	24.88		
$\text{U}^{\text{VI}}\text{O}_2$	gl	0.1 (NaClO_4)	20	7.81	14.73		83SD	D
			30	7.72	14.44			
			40	7.61	14.23			
			40	7.61	14.23			
Zn^{II}	gl	? (NaClO_4)	25	8.60(6)	16.09(7)		70CBb	D
	gl	0.01	20		10.4		50A	D
	gl	0.01	20		8.5		52P	D
	gl	0.01	18		8.7		53P	D
	gl	? (NaClO_4)	25	5.27(5)			70CBb	D
	gl	0.1 (KNO_3)	25	4.59(2)	8.93(3)		75IP	T

Most of the other data stem from the investigations of two research groups (72GS, 73GS, 75SG and 75IP) and the reported values are closely correlated; they are therefore evaluated as tentative. On the basis of three publications, average values can be established for the copper(II) complexes, and they are included in Table 3.17.

From Table 3.12, it can be seen that stability constants have been reported for the interaction of 2-aminohexanoic acid with a reasonable number of metal ions. This is somewhat surprising if one takes into account the low solubilities of the ligand and its metal complexes. On the other hand, it means that the accuracy of the data is limited and tentative values can be given only for certain metal ions.

The values obtained for the complexes of Be^{II} (52P), Th^{IV} (83SD) and Mg^{II} (from 50A) are rejected because of the effect of hydrolysis, which was not considered. The values obtained at very low ionic strengths, or from measurements under undefined experimental conditions are regarded as doubtful (50A, 52P, 53P, 66MM, 70CBb). Thus, tentative values can be given for the most common transition metal ions, i.e. Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} , Ag^{I} and for Pb^{II} and Mg^{II} .

The solubilities of the copper(II) complexes of 2-aminohexanoic acid are extremely low as compared to those of the complexes with other aliphatic amino acids. There is only one acceptable publication which reports stability constants for this interaction in aqueous solution (75IP). These data are included in Table 3.17, for comparison.

The stability constants for the complexes of isoleucine were mainly determined by the same authors, as was the case for leucine or 2-aminohexanoic acid. Accordingly, the acceptance criteria are very similar to those applied for the other aliphatic amino acids. This means that tentative values can again be given for the common 3d transition metal ions, i.e. for Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} and for Ag^{I} , Cd^{II} , Mg^{II} , Pd^{II} and Th^{IV} . However, it should be considered that the differences in temperature and in ionic strength make it difficult to compare the individual determinations, even for the divalent 3d transition metal ions. When the values are compared with the data on other aliphatic amino acids, the constants published in references 58B, 81IS, 71HP and 66LHa give the best agreement.

TABLE 3.13 Formation Constants of Complexes of Isoleucine with Metal Ions
(Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag^{I}	gl	0.5 (KNO ₃)	20	3.19(5)	7.26(5)		74KH	T
	gl	0.2 (NaClO ₄)	30	3.63(2)	7.17(6)		75JB	T
Be^{II}	gl	< 0.01	20		12.6		52P	Rj
Cd^{II}	gl	< 0.01	20		6.6		52P	D
	pol	1.0	25		6.9	8.8	65VZ	D
	gl	0.2 (NaClO ₄)	30	3.94(5)	7.31(5)		75JB	T
	gl	0.7 (NaClO ₄)	25	3.635(2)	6.80(5)		85GS	T
	pol	0.7 (NaClO ₄)	25	3.43	6.70		85GS	T
	gl	0.1 (NaNO ₃)	25	4.59(3)	8.93(4)		81IS	T
Co^{II}	E	0.16	25	8.27	15.32		58B	D
		0.19	25	8.34	15.49			
		→ 0.0	25	8.69(8)	16.04(7)		58B	T
	pol	1.1	25	8.4	15.4		65VZ	T
		0.15 (KNO ₃)	37	7.95(1)	14.68(1)		71HP	T
		1.0 (KNO ₃)	30	log $\beta_{\text{MH}_1\text{L}} = 0.32(6)$				
Ga^{III}	gl	0.1 (NaNO ₃)	25	8.30	15.30		80SG	T
	gl	3.0 (NaClO ₄)	25	8.50(6)	15.79(8)		81IS	T
	gl		25	9.60(4)			75BH	D
				log $K(\text{M} + \text{HL}) = 2.04(4)$				
Hg^{II}	gl	< 0.01	20		17.6		52P	D
Mg^{II}	gl	0.15 (NaCl)	20	1.85(8)			85VD	T
Ni^{II}	gl	0.1 DL	25	5.28	9.56	12.40	66MM	D
		L	25	5.52	9.83	12.58		
		D	25	5.48	9.69	13.03		

TABLE 3.13 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Os ^{IV}	gl	0.5 (KCl)	25	5.22	9.45		66LHa	T
	gl	? (NaClO ₄)	25	5.51(6)	9.96(10)		70CBb	D
	gl	? (Cl ⁻)	28		5.72		74FAc	Rj
Pd ^{II}	gl	0.5 (KNO ₃)	20	9.94(3)	18.17(5)		74KH	T
Rh ^{III}	gl	? (Cl ⁻)	27	7.16	9.92		74FAa	Rj
Th ^{IV}	gl	0.1 (KNO ₃)	25	8.26(1)	14.22(2)		83NM	T
V ^{IV} O	gl	? (NaClO ₄)	25	8.57(6)	15.95(10)		70CBb	Rj
	gl	0.1 (KNO ₃)	25	7.02(3)	14.66(8)		82NM	D
Zn ^{II}	gl	< 0.01	20		8.2		52P	D
	pol	1.0	25		11.2		65VZ	D
	gl	0.5 (KCl)	25	4.49	8.49	10.9	66LHa	T
	gl	? (NaClO ₄)	25	5.11(5)	9.21(6)		70CBb	T
	gl	0.15 (KNO ₃)	37	4.40(4)	8.08(6)		71HP	T
				log $K(M + HL + L) = 5.89(36)$				

3.5 Stability constants of the metal complexes of β -alanine

The coordination of both the amino and carboxylate groups of β -alanine results in the formation of a 6-membered chelate ring, the stability of which is lower than that of the 5-membered chelate rings. At the same time, the log K_{HL} of the amino group is higher in β -alanine and the complex formation processes occur at higher pH values than those for α -alanine. Thus, in the case of β -alanine the stability constant determinations are less accurate than those for α -alanine, due to the competition with hydrolysis.

In spite of these experimental complications, there are many publications on the equilibrium relations of the complexes of β -alanine; the literature values for the 3d transition elements are listed in Table 3.14, and those for the other metal ions in Table 3.15.

TABLE 3.14 Formation Constants of Complexes of β -Alanine with 3d Transition Metal Ions (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ti ^{III}	gl	?	?	9.72			70FMb	Rj
V ^{IV} O	gl	? (NaClO ₄)	25	8.34			70CBa	Rj
	gl	?	?	9.77			70FMb	Rj
Cr ^{II}	gl	0.1 (NaClO ₄)	25	7.53(5)			70FK	D
	Pt,gl	?	?	9.89			70FMa	Rj
	gl	1.0 (KCl)	25	3.89(5)			83MD	T
Cr ^{III}	gl	0.1 (NaClO ₄)	25	9.69			68TK	D
Mn ^{II}	ix	1.0 (NaNO ₃)	20	2.54			69BZ	T
			40	2.41				
			60	2.28				
	gl	0.1 (KNO ₃)	20	2.13			73BS	T
			30	2.06				

TABLE 3.14 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
			40	2.01				
			50	1.97				
			60	1.94				
Fe ^{II}	gl	0.01	20		4		50A	D
	gl	1.0 (KCl)	25	2.53(1)			87M	T
Co ^{II}	gl	0.01	20		7		50A	D
	gl	0.2 (KCl)	15	3.69	6.28		65SMb	T
			25	3.58	6.14			
			40	3.53	5.98			
	ix	0.2 (KCl)	40	3.56			65SMa	T
	H	→ 0.0	0	4.47(1)			67BB	T
			15	4.31(1)				
			25	4.21(1)				
			35	4.13(1)				
			45	4.06(1)				
Ni ^{II}	gl	0.1 (KCl)	20	4.63	8.03		54IW	T
	gl	0.2 (KCl)	15	4.80	8.34		65SMb	T
			25	4.71	8.12			
			40	4.65	7.89			
	gl	0.5 (KCl)	25	4.46	7.84	9.55	66LHa	T
	H	→ 0.0	0	5.22(1)			67BB	T
			15	5.08(1)				
			25	4.99(1)				
			35	4.92(1)				
			45	4.86(1)				
	gl	? (NaClO ₄)	25	5.28			70CBa	D
	gl	0.1 (KNO ₃)	25	4.50(2)	7.78(4)	9.7(1)	76DO	T
	gl	0.2 (NaNO ₃)	30	4.64	7.97		81RSa	T
	gl	0.5 (NaClO ₄)	25	4.54	7.66		86GG	T
				log $\beta_{MH_1L} = -4.70$				
				log $\beta_{MH_1L_2} = -2.31$				
Cu ^{II}	gl	0.01	20		12.9		50A	D
	gl	0.1 (KCl)	20	7.13	12.60		54IW	T
	pol	0.1 (KH ₂ PO ₄)	25		12.89		54LD	T
	sp	3.0	25	6.55	12.60		56Ca	D
				log $K(M + HL) = 1.20$				
				log $K(M + 2HL) = 2.31$				
				log $K(M + HL + L) = 7.66$				
	gl	0.375	25	7.34	12.82		56Cb	D
				log $K(M + HL) = 1.71$				
				log $K(M + HL + L) = 7.96$				
	gl	→ 0.0	25	7.68	13.52		56Cb	D
	gl	0.2 (KCl)	15	7.16	12.75		65SMb	T
			25	7.10	12.50			
			40	6.93	12.15			
	gl	0.1 (KNO ₃)	25	6.99			69YH	T
	gl	0.2 (NaClO ₄)	25	7.69(6)	13.88(10)		70CBc	D
	gl	0.1 (KNO ₃)	25	6.99	12.54		71YM	T
	gl	0.1 (NaClO ₄)	30	7.10(1)	12.50(2)		80AS	T

TABLE 3.14 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
	gl	0.15 (NaClO ₄)	37	7.12(2)	12.86(6)		81NS	T
	gl	0.25 (KNO ₃)	30	7.10	12.69		81RK	T
	gl	0.2 (NaNO ₃)	30	7.04	12.58		81RSa	T
	gl	1.0 (KCl)	25	6.65	11.85	12.33	82ND	T
	gl	0.5 (NaClO ₄)	25	log $\beta_{ML(OH)} = 13.07$ 6.90	12.31		86GG	T
				log $\beta_{MH_1L} = -0.52$ log $\beta_{MH_1L_2} = 1.88$				
Zn ^{II}	gl	0.1 (KCl)	20	4			54IW	D
	gl	0.2 (KCl)	15	4.10			65SMb	T
			40	3.82				
	pol	0.5 (KCl)	30	4.2	7.0		67SSb	D
	gl	? (NaClO ₄)	25	5.15			70CBa	D
	gl	0.5 (KCl)	25	3.90	7.20	10.40	71LL	T
	H	0.1 (KCl)	5	4.274(70)			73RD	T
			25	4.205(70)				
			45	4.130(70)				
	Zn/Hg	3.0 (NaClO ₄)	25	4.30(10)	8.00(10)		79BJ	T
				log $\beta_{MHL} = 11.36(5)$ log $\beta_{MH_2L_2} = 22.60(10)$ log $\beta_{MHL_2} = 15.60(15)$				

TABLE 3.15 Formation Constants of Complexes of β -Alanine with the Other Metal Ions (Literature Values)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
Ag ^I	Ag	0.6	25	3.76(3)	7.21(4)		67AM	T
	gl	0.5 (KNO ₃)	20	3.44(5)	7.25(3)		68AL	T
	Ag	0.5 (KNO ₃)	20		7.32			T
	gl	0.5 (KNO ₃)	25	3.33	7.12		68TV	T
	gl	1.0 (KNO ₃)	0	3.72	7.90		70VT	T
			15	3.47	7.41			
			40	3.19	6.69			
	gl	0.2 (NaClO ₄)	30	4.17(3)			75JB	D
	gl	3.0 (LiClO ₄)	25	3.58(3)	7.46(3)		80OZ	T
				log $\beta_{MHL} = 10.88(15)$ log $\beta_{MH_1L} = -6.12(8)$				
Au ^{III}	gl	? (Cl ⁻)	25	6.85	10.46		74FAB	D
Be ^{II}	-	-	?	3.07			60B	Rj
	gl	0.5 (NaClO ₄)	?	log $\beta_{MHL} = 10.58$			74DB	D

TABLE 3.15 (continued)

Metal	Method	Medium mol dm ⁻³	Temp °C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Cat
U ^{IV}	gl	0.1 (NaClO ₄)	30	2.44			80RR	T
	gl	1.0 (NaClO ₄)	25	1.93(3)	3.44(4)	4.82(5)	87BR	T
Th ^{IV}	sp	0.5 (Cl ⁻)	20	11.18(4)			74SK	D
	gl	0.5 (KNO ₃)	25	9.76(2)			71KS	T
	ix	0.5 (KNO ₃)	20	9.80(5)			80S	T

As discussed for the α -amino acids, the stability constants reported on the complexation with Ti^{III}, Cr^{II} and V^{IV}O are rejected because of the experimental difficulties (70FMA, 70FMB, 70CBA). Another pH-metric study (83MD) gives a much lower constant for the Cr^{II}- β -alanine interaction, but which fits in well with the stability order of divalent transition metal ions, and this can be regarded as a tentative value. The situation is the same for the iron(II) complexes, where a reliable stability constant for the mono complex has recently been published (87M). As a result of the low values of the stability constants of the manganese(II) complexes, metal ion hydrolysis overlaps complex formation, and equilibrium data can be determined only for the mono complexes.

There are several reports on the β -alanine complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Some of them have been considered to be doubtful, because of the low ionic strength applied, or the experimental conditions were not defined (50A, 56Ca, 56Cb), while in 70CBA and 70CBc the equilibrium values were much higher than in other reports. The remaining data passed the acceptance criteria and were used in the critical evaluation to provide recommended or tentative values on the copper(II), nickel(II) and zinc(II) complexes of β -alanine. These data, together with the values for the Ag^I and Cd^{II} complexes, are listed in Table 3.16.

TABLE 3.16 Tentative Values for the Stability Constants of Metal Complexes of β -Alanine

Metal	Temp °C	Medium mol dm ⁻³	log β_{ML}	log β_{ML_2}	log β_{ML_3}
Ni ^{II}	25	0.1-0.5	4.55(8)	7.85(10)	9.62(7)
Cu ^{II}	25	0.1-0.5	6.99(7)	12.45(10)	-
Zn ^{II}	25	0.1-0.5	4.14(15)	-	-

It can be seen from Table 3.16 that average values can not be given for the bis complexes of zinc(II), because metal ion hydrolysis significantly overlaps complex formation.

Table 3.15 reveals that in the case of β -alanine the stability constant determinations cover almost the whole periodic system. Many of these reports have already been discussed in connection with the metal ion complexes of α -amino acids, and here we merely summarize the most important criteria. There are publications where metal ion hydrolysis was not considered, or the experimental procedure and conditions are not clearly demonstrated, and these reports are rejected (e.g. 60B for Be^{II}, 86LS for lanthanides and 70FMB for U^{VI}O₂), or regarded as doubtful (e.g. 70FAB for Au^{III}, 74DB for Be^{II}, 74RO for CH₃Hg^I, 76KF for In^{III}, 74FAC for Os^{IV}, 74FAA for Rh^{III} and 76KV for Zr^{IV}).

As concerns the silver complexes of β -alanine, most of the reported values are in good agreement, except for 75JB, where the stability of the mono complex is higher than in the other cases. For the cadmium(II) complexes of β -alanine, the stability constants were determined at different ionic strength, and different temperatures. Therefore, direct comparison of the data is rather difficult, but the values obtained from pH-metric and polarographic studies are in reasonable agreement, which makes the reported values acceptable.

A critical evaluation of the stability constants of the other 4d-5d transition metal ions and f-block elements is rather difficult, because only independent determinations are available in general. Among them, the values reported for Hg^{II} (86GG), Pd^{II} (74KH) and the lanthanides (62CTb) are closely related

to the equilibrium data of other amino acids, and they are regarded as tentative values. As concerns the actinide elements, the very large constants of the mono complexes reported in 73SK, 74SK and 73RS are probably due to hydrolytic processes, while the other values, around 2-3 log units, can be considered to be tentative.

For easy survey of the complex forming abilities of the aliphatic amino acids, the stability constants of the various copper(II) complexes are listed in Table 3.17.

The data on glycine are taken from the previous critical review (91KS), while average values are given for α - and β -alanine, valine, leucine and 2-aminopentanoic acid. In the cases of 2-aminohexanoic acid and isoleucine, only individual determinations are available. On the basis of Table 3.17, it can be stated that for the α -amino acids the standard deviations of the stability constants are almost the same as the differences caused by the presence of the various non-coordinating side chains. On the other hand, the presence of the normal aliphatic side chains may slightly decrease the overall stability of the metal ion complexes (see $\log K_{HL} - \log \beta_{ML}$) and increases the ratio of the stepwise constants ($\log(K_1/K_2)$). The formation of six-membered chelate rings (complexes of β -alanine) is accompanied by a significant increase in the ratio of the stepwise stability constants and by decreases in the overall stability constants.

3.6 Enthalpy values of metal complex formation

The enthalpy changes associated with the formation of α -alanine complexes have been determined for various metal ions, and the reported literature values are listed in Table 3.18. For the other aliphatic amino acids considerably fewer data are available; the data for all α -amino acids are included in Table 3.19, and those for β -alanine in Table 3.20.

The enthalpy values were calculated from the results of potentiometric studies via the temperature-dependence of the stability constants, or were obtained directly from calorimetric measurements. At least in principle, the direct calorimetric method provides the more accurate data, but there are many sources of error in both methods.

Application of the van't Hoff equation requires the constancy of enthalpy in the temperature range used, and the availability of very accurate and reproducible stability constants over a sufficiently wide temperature range. This means that fairly accurate enthalpy values can be obtained only if the stability constants were determined properly at many different temperatures, but not in a very wide temperature range. Accordingly, the calculated enthalpies can only be accepted if the stability constants (in the previous Tables) were regarded at least as tentative values.

During a calorimetric measurement, there are again many possibilities for experimental error. Thus, the metal ion complex formation processes are accompanied by deprotonation of the ligand and by the formation of water, which makes it necessary to apply appropriate auxiliary data. On the other hand, the evaluation of the calorimetric experimental data also requires the availability of accurate equilibrium constants.

Table 3.18 reveals that most of the enthalpy values on the complexation with α -alanine are available for the 3d transition metal ions. There is an individual publication on the In^{III} complexes, but these data were obtained from temperature-dependence of the equilibrium constants, which were considered to be doubtful in Table 3.1, and thus the enthalpy values are classified as doubtful (73SM). The same evaluation category should be applied for the values reported on the Mn^{II} complexes of α -alanine, where the ratio of the stability constants is false (73BS).

In the cases of the cobalt(II), nickel(II), copper(II) and zinc(II) complexes of α -alanine, enthalpy values obtained from both potentiometric and calorimetric methods are available. The differences between the literature data reported for the complexation with cobalt(II) are rather high, and the calorimetrically determined values from 71GNb are regarded as doubtful, because the enthalpy changes are much lower in this case than in the other reports. The remaining publications can be used to calculate the averages of the tentative values, and these are given in Table 3.21.

There are many reports on the enthalpy values of the copper(II)- α -alanine complexes and the agreement between the various methods and authors is quite reasonable. All the literature data can be considered to be tentative, and they have been used to establish an average value for ionic strength of around 0.1 mol dm^{-3} .

TABLE 3.17 Recommended and Tentative Values for the Stability Constants of the Copper(II) Complexes of Aliphatic Amino Acids. $T = 25\text{ }^{\circ}\text{C}$; $I = 0.1\text{-}0.5\text{ mol dm}^{-3}$

Amino acid	$\log \beta_{ML}$	Cat	$\log \beta_{ML_2}$	Cat	$\log(K_1/K_2)$	$\log K_{HL} - \log \beta_{ML}$
Glycine	8.20(10)	T	15.07(13)	T	1.33	1.40
α -Alanine	8.14(10)	T	14.96(10)	T	1.32	1.58
2-Amino-pentanoic acid	8.12(5)	R	14.93(10)	T	1.31	1.54
2-Amino-hexanoic acid	8.18	75IP*	14.88	75IP*	1.48	1.50
Valine	7.98(8)	T	14.76(12)	T	1.20	1.56
Leucine	8.26(6)	T	15.20(7)	T	1.32	1.40
Isoleucine	8.27	58B*	15.32	58B*	1.22	1.38
β -Alanine	6.99(7)	T	12.45(10)	T	1.53	3.15

* No other determinations are available

TABLE 3.18 Enthalpy Changes in the Formation of Metal Complexes of α -Alanine (kJ mol^{-1}) (Literature Values)

Metal	Method	Medium mol dm^{-3}	Temp $^{\circ}\text{C}$	$-\Delta H_{ML}^{\circ}$	$-\Delta H_{ML_2}^{\circ}$	$-\Delta H_{ML_3}^{\circ}$	Ref	Cat
Co ^{II}	T	0.2	15-40	10.9	23.8		65SMb	T
	cal	0.1 (KNO ₃)	21.8		24.7		67SSa	T
	T	0.05 (KCl)	20-35	8.4(2.0)	18.0(2.0)		71GK	T
Cu ^{II}	cal	0.05 (KCl)	25	5.4	15.1		71GNb	D
	T	0.0	0-40	23.4	49.4		61IW	T
	T	0.2	15-40	20.5	44.8		65SMb	T
	cal	0.0	10	22.51	45.39		66AN	T
			25	18.87	40.79			
			40	16.69	40.33			
	cal	0.1 (KNO ₃)	22.3		49.78		67SSa	T
	cal	0.16 (KNO ₃)	25	23.5	48.6		70MB	T
	T	0.05 (KCl)	20-35	19.7(2.8)	44.7(2.8)		71GK	T
	cal	0.05 (KCl)	27	20.5	43.5		71GNb	T
	cal	0.0	25		51.5		71BP	T
	cal	0.1 (KNO ₃)	25	23.4	49.1		72IN	T
	cal	0.1 (NaClO ₄)	25	26.4	48.9		72IN	T
	cal	0.2 (KCl)	25	20.67	50.20		73GS	T
	cal	0.1 (KNO ₃)	25	22.9(3)	50.2(8)		83AC	T
In ^{III}	T	0.2 (NaClO ₄)	25-45	-14.6			73SM	D
Mn ^{II}	T	0.1 (KNO ₃)	20-60	10.5	25.9		73BS	D
Ni ^{II}	cal	0.1 (KNO ₃)	25	14.0	30.6	41.5	62SG	T
	T	0.2	15-40	18.4	38.5		65SMb	T
	cal	0.0	10	14.2	33.5		67AG	T
			25	13.8	30.1			
			40	15.1	25.9			
	T	0.05 (KCl)	20-35	14.2(8)	30.5(1.2)		71GK	T
	cal	0.05 (KCl)	25	15.1	31.0		71GNb	T
	cal	0.2 (KCl)	25	16.8	36.3		75SG	T
	cal	1.0 (NaClO ₄)	25	16.82(4)	37.32(21)	56.61(58)	79EB	T
	Zn ^{II}	T	0.2	15-40	12.5	30.5		65SMb
T	0.05 (KCl)	25-40	9.6(1.2)	16.7(1.2)		71GK	T	
cal	0.05 (KCl)	27	6.3	18.0		71GNb	T	
cal	0.1 (KNO ₃)	25	7.5(6)	17.6(8)		83AC	T	

The different values reported for the nickel(II) and zinc(II) complexes of α -alanine are also closely correlated, with the exception of 65SMb for zinc(II)- α -alanine, and the average values are included in Table 3.21.

The literature data on the enthalpy changes accompanying the formation of the metal complexes of other aliphatic amino acids are listed in Table 3.19. It can be seen that only individual determinations are available in most cases; therefore, evaluation of the data can be made via comparison with the literature data on glycine or α -alanine complexes, or on the basis of the experimental procedure and on the accuracy of the equilibrium data used for the calculations.

TABLE 3.19 Enthalpy Changes in the Formation of Metal Complexes of α -Amino Acids (kJ mol^{-1}) (Literature Values)

Metal	Method	Medium mol dm^{-3}	Temp $^{\circ}\text{C}$	$-\Delta H_{\text{ML}}^{\circ}$	$-\Delta H_{\text{ML}_2}^{\circ}$	$-\Delta H_{\text{ML}_3}^{\circ}$	Ref	Cat
Valine								
Cu^{II}	T	0.15	25-35		85.8		56LW	D
	cal	0.16 (KNO_3)	25	22.8	47.3		70MB	T
Ni^{II}	T	-	10-40	18.11	40.8	59.6	60P	T
	cal	1.0 (NaClO_4)	25	16.53(8)	36.34(21)	54.46(82)	81EB	T
Er^{III}	cal	0.03 ?	25	14.4(4)			81PBa	D
Ho^{III}	cal	0.03 ?	25	15.4(4)			81PBa	D
Lu^{III}	cal	0.03 ?	25	13.6(4)			81PBa	D
Nd^{III}	cal	0.03 ?	25	13.4(4)			81PBb	D
Yb^{III}	cal	0.03 ?	25	14.5(4)			81PBa	D
2-Aminopentanoic Acid								
Cu^{II}	cal	0.2 (KCl)	25	21.40	50.16		73GS	T
Mn^{II}	T	0.1 (KNO_3)	20-60	13.0	19.2		73BS	T
Ni^{II}	cal	0.2 (KCl)	25	17.9	35.6		75SG	T
Leucine								
Cu^{II}	cal	0.16 (KNO_3)	25	23.2	47.9		70MB	T
Mn^{II}	T	0.1 (KCl)	25-45	9.1			71SS	T
$\text{U}^{\text{VI}}\text{O}_2$	T	0.1 (KCl)	25-45	59.8	114.2		71SS	D
2-Aminohexanoic Acid								
Cd^{II}	T	0.1 (NaClO_4)	20-30	24.8	21.2		84SD	D
Co^{II}	cal	0.05 (KCl)	25		24.7		72GS	T
Ni^{II}	cal	0.05 (KCl)	25		31.4		72GS	T
	cal	0.2 (KCl)	25	16.7	32.7		75SG	T
Pb^{II}	T	0.1 (NaClO_4)	20-30	6.40	17.95		84SD	D
Th^{IV}	T	0.1 (NaClO_4)	20-40			43.4	83SD	D
$\text{U}^{\text{VI}}\text{O}_2$	T	0.1 (NaClO_4)	20-40	$\Delta H(\text{M} + 4\text{L}) = -102.4$			83SD	Rj
Isoleucine								
Co^{II}	cal	0.1 (NaNO_3)	25	18.5	22.0		78IS	D
Cu^{II}	cal	0.1 (NaNO_3)	25	26.2	44.5		78IS	D
Alloisoleucine								
Co^{II}	cal	0.1 (NaNO_3)	25	12.6	16.8		78IS	D
Cu^{II}	cal	0.1 (NaNO_3)	25	24.0	42.0		78IS	D

TABLE 3.20 Enthalpy Changes in the Formation of Metal Complexes of β -Alanine (kJ mol^{-1}) (Literature Values)

Metal	Method	Medium mol dm^{-3}	Temp $^{\circ}\text{C}$	$-\Delta H_{\text{ML}}^{\circ}$	$-\Delta H_{\text{ML}_2}^{\circ}$	$-\Delta H_{\text{ML}_3}^{\circ}$	Ref	Cat
Ag^{I}	cal	0.5 (KNO_3)	25	22.6	52.0		70VT	T
	T	0.5 (KNO_3)	0-40	21.9	50.0		70VT	T
Co^{II}	T	0.2	15-40	10.9	20.5		65SMb	T
	cal	0.0	25	13.9			67BB	T
Cu^{II}	T	0.2	15-40	25.1	41.8		65SMb	T
	cal	0.1 (KNO_3)	22		45.6		67SSb	T
Mn^{II}	T	0.1 (KNO_3)	20-60	8.8			73BS	T
Ni^{II}	T	0.2	15-40	16.7	37.6		65SMb	T
	cal	0.0	25	15.9			67BB	T
In^{III}	cal	0.1 (KNO_3)	21.7		25.5		67SSb	T
	T	0.0	25-45		-33.5(6.2)		72SM	D
	T	0.01 (NaClO_4)	25-45		-30.5(6.2)		72SM	D
Zn^{II}	T	0.2 (NaClO_4)	25-45	-12.5			73SM	D
	cal	0.1 (KNO_3)	21.4		17.2		67SSb	T
	T	0.1 (KCl)	5 25 45	4.9(3.0) 6.1(3.0) 7.6(3.0)			73RD	T

TABLE 3.21 Enthalpy Changes of the α -Alanine Complexes of Various Transition Metal Ions (kJ mol^{-1})
 $T = 25^{\circ}\text{C}$; $I = 0.1\text{-}0.5 \text{ mol dm}^{-3}$

Metal ion	$-\Delta H_{\text{ML}}^{\circ}$	Cat	$-\Delta H_{\text{ML}_2}^{\circ}$	Cat
Co^{II}	9.7(1.2)	T	22.2(2.0)	T
Ni^{II}	15.6(1.5)	T	33.5(3.0)	T
Cu^{II}	22.2(2.0)	T	47.8(2.5)	T
Zn^{II}	7.8(1.2)	T	17.4(0.5)	T

Very high enthalpy values were reported in some cases (56LW, 81PBa, 81PBb, 71SS and 83SD), while the ratio of the stepwise enthalpy changes (84SD, 78IS) does not correspond to the regular trend observed in the other reports; accordingly, these publications have been regarded as doubtful. The other literature values can be accepted, but in the absence of a reliable comparison they should be considered only as informatory data.

Literature values on the enthalpy changes of the metal complexes of β -alanine are listed in Table 3.20. Most of the publications relate to the transition metal complexes, and they can be considered as tentative values, because the agreement between the calorimetric and potentiometric data is satisfactory. There is no possibility for a reliable comparison in the case of the indium(III) complexes, and the endothermic enthalpy changes should be considered to be doubtful.

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