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CRITICAL SURVEY OF STABILITY CONSTANTS OF COMPLEXES OF GLYCINE†

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

Critical survey of stability constants of complexes of glycine

1. INTRODUCTION

Glycine ($C_2H_5O_2N$, 2-aminoethanoic acid, HL) is the simplest α -amino-carboxylic acid:

$$H_2N - CH_2 - CO_2H$$

which, however, never occurs to an appreciable extent in this form. The zwitterionic form is more favoured energetically both in solution and in the solid state. The fully protonated glycine cation, $[H_2L]^+$, contains two ionizable hydrogen ions, which dissociate stepwise in fully separated processes. Depending on the pH of its solution, glycine can exist in three different forms: the cationic $[H_2L]^+$, the zwitterionic $[HL]^{\pm}$, and the anionic L^- forms. Since the dissociation steps are well separated, the concentration of the neutral form HL is negligible (80H). Besides these monomeric proton complexes, various polymeric associates, e.g. $[HL_2]^-$, H_2L_2 and $[H_3L_2]^+$, can also be formed in concentrated solution (78VV). The main reason for the association of the monomeric species is the formation of hydrogen-bonds between them, whereas in dilute aqueous solution the monomeric species are stabilized through hydrogen-bonds with the water molecules.

Glycine can generally act as a bidentate ligand with most of the metal ions, forming mono, bis and tris complexes having stable 5-membered chelate rings via the amino N and the carboxylate O donors. With some metal ions (e.g. Ag(I), Be(II), Fe(III), In(III), Pb(II), V(IV), Zn(II) and lanthanides), protonated complexes can also be formed via the monodentate coordination of the carboxylate or the amino group. At higher pH, especially when there is not a sufficient excess of ligand, the formation of soluble mixed hydroxo complexes must also be taken into account.

Almost 300 papers have appeared in which the proton and metal complex formation equilibria of this ligand have been described and discussed. Many different procedures, such as electrochemical methods (pH-metry, potentiometry, polarography, conductance and electrophoresis), spectroscopic methods (spectrophotometry, NMR), ion exchange and liquid-liquid distribution, have been employed to determine the stability constants of the complexes formed. The applicability of each method is discussed in detail in the various textbooks (e.g. 61RR, 69B, 90BN), and the problems associated with the use of these methods and with the determination of complex formation constants have been considered to various extents in all parts of this IUPAC series on the critical evaluation of the stability constants of metal complexes in solution (77B, 82A, 82NT, 82SL, 83T, 84P, 84Pa, 87B). Of the above-mentioned methods, however, pH-metry with a glass electrode (or a hydrogen electrode, mainly in the early works) has been applied most extensively. Direct pH method is based on the fact that the pH-metric titration of solutions of a protonated ligand, alone and in the presence of a metal ion, through the stepwise addition of a strong base allows evaluation of the constants for the ligand deprotonation equilibrium and for the proton displacement equilibrium due to the metal ion competition. In the simplest case of a monoprotic acid (HL) where the anion reacts with a metal ion (M^+) to form a 1:1 complex only, these equilibria are as follows:

$$HL = H^+ + L^- \qquad (1)$$

$$HL + M^+ = ML + H^+ \qquad (2)$$

The recommended procedure for testing the potentiometric apparatus and technique for the pH-metric measurement of metal-complex equilibrium constants was described in a recent publication (87BO). A complete statistical analysis of the error distribution of potentiometric data used to standardize the apparatus and that of the equilibrium constants determined by competitive pH-metry has been reported in 82BO and 86BB. The results of these papers can greatly help researchers to assess the reliability of the equilibrium constants and their standard deviations.

In order to overcome problems resulting from the activity effects, most work has been carried out in media with constant ionic strengths attained by the use of different inert salts. The ionic strengths most frequently used were 0.1, 0.2, 0.5, 1.0, 3.0 and 0 mol dm^{-3}. Stability constants at zero ionic strenth were obtained either by extrapolation to infinite dilution of the constants determined at different concentrations of the ionic medium, or by calculating the activity coefficients of the ions via some theoretical (e.g. the Davies equation) or empirical formula and using these values to correct the measured stability constants (see e.g. 80SH).

In potentiometric titrations with a glass electrode the calibration technique will govern the type of constant calculated. Concentration constants can be determined by calibrating the electrode system with solutions of known hydrogen ion concentration (e.g. $HClO_4$ or any other monofunctional strong acid) or by the conversion of pH values using the appropriate hydrogen ion activity coefficient. 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 ^{o}C) mixed constants are obtained, which include both activity (hydrogen ion) and concentration (all other reacting species) terms. The electrode calibration methods, the advantages of the use of concentration constants, and the disadvantages of the use of mixed stability constants have been discussed in various publications (67IM, 82MW, 84P). Here, only the use of the more exact concentration stability constants is emphasized.

Most measurements have been carried out at 25 ^{o}C, although other temperatures, such as 20 ^{o}C, 30 ^{o}C and 37 ^{o}C, or a range of temperatures between 0 ^{o}C and 75 ^{o}C have also been employed.

The enthalpies ($\Delta \underline{H}^{o}$) accompanying protonation and metal complex formation can be determined calorimetrically or from the temperature-dependence of the stability constants by using the van't Hoff relationship:

$$\frac{d(\log \underline{K})}{d\,\underline{T}} = \frac{\Delta \underline{H}^{o}}{2.303\ \underline{RT}^2} \qquad (3)$$

The accuracy of the latter method is generally less than that of the direct calorimetric method, as it needs very accurate stability constants over a sufficiently wide temperature range, which calls for considerable sophistication in the experimental techniques. However, in some cases (e.g. for the protonation processes of glycine) a very good agreement has been found between the values obtained by the two methods.
If the temperature-dependence of the $\Delta \underline{H}^{o}$ values is neglected (i.e. it is assumed that $\Delta \underline{C}_p = 0$), these values may be used to estimate log $\underline{K}$ values at other temperatures by using the van't Hoff relationship:

$$\log \underline{K}_2 = \log \underline{K}_1 + \Delta \underline{H}^{o} (\underline{T}_2 - \underline{T}_1)/2.303\ \underline{R}\underline{T}_1\underline{T}_2 \qquad (4)$$

The wider the temperature range employed, the greater the uncertainty in the calculated values. In some cases, the internal consistency of the recommended and tentative constants has been checked in this way.

1.1. Presentation of equilibrium data

Throughout this evaluation, stability (association) constants are used for both proton and metal complexes.

The proton complex formation constants of glycine are expressed as stepwise protonation constants. For the equilibria

$H^+ + L^- = HL$ (protonation of $-NH_2$ group) and
$H^+ + HL = H_2L^+$ (protonation of $-COO^-$ group)

the constant $\underline{K}_1$ relates to the first of these processes, and $\underline{K}_2$ to the second:

$$\underline{K}_1 = \frac{[HL]}{[H^+][L^-]}, \qquad \underline{K}_2 = \frac{[H_2L^+]}{[H^+][HL]} \qquad (5,6)$$

For the formation equilibrium

$$M^{m+} + n\,L^- = ML_n^{(m-n)+} \qquad (7)$$

the overall stability constants β_1, β_2 ..., β_n, or in some cases the stepwise stability constant K is used and the reaction, which it is concerned, is in bracket. For the formation of protonated, hydroxo or polynuclear species the overall stability constants $\beta(M_pH_qL_r)$ are used:

$$\beta(M_pH_qL_r) = \frac{[M_pH_qL_r]}{[M]^p[H]^q[L]^r} \qquad (8)$$

Negative subscripts values for H refer to complex formation reactions in which a hydrogen ion which does not normally dissociate is eliminated. In the case of the metal complexes of glycine this hydrogen ion originates from a coordinated water molecule.

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

1.2. Data evaluation criteria

The huge number of data published in the literature have been surveyed by considering the following general criteria:

(a) The degree of specification of the essential reaction conditions (the purity of the ligand, temperature, ionic strength, the nature of the supporting electrolyte, etc.).

(b) The correctness of the calibration of the apparatus used (e.g. calibration of the electrode system for potentiometric measurements).

(c) Unambiguous definition of the equilibrium constants reported (i.e. whether concentration or mixed constants were calculated).

(d) Details on the calculation method used (data obtained by either graphical or computational methods of any kind are considered without any prejudice).

(e) The control of the constancy of temperature and ionic strength during titration.

(f) Reliable treatment of the experimental data (e.g. careful consideration of the formation of all possible species: parent and mixed hydroxo complexes of readily hydrolysable metal ions, tris complexes in the case of a large ligand excess, etc.).

(g) Correct selection of auxiliary data from the literature (e.g. the selection of the concentration constants of the proton complexes for the evaluation of polarographic measurements carried out only on metal-ligand systems).

On the basis of these criteria, data were evaluated and grouped in 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 acceptance criteria were then averaged, and depending on the standard deviation (s.d.), the average values were regarded as recommended (s.d. $<$ 0.05 log unit) or tentative (0.05 $<$ s.d. $<$ 0.2 log unit).

The stability constants of the complexes of the various ions are given and surveyed in the following groups: hydrogen ion, group 2A-3B-4B, group 3d, group 4d-5d and group 4f-5f metal ions. For each group, a nearly complete list of all published values is given. The stability constants (in parenthesis the standard deviation of the last digit) are tabulated together with the most important information (method, medium, temperature, type of constant, reference) and with the evaluation category. Because of the relatively low number of data, the enthalpy values are discussed only in two groups: proton complexes and metal complexes.

The methods used are denoted by the following symbols in the Tables:

H	hydrogen electrode (pH-metry)
gl	glass electrode (pH-metry)
M	metal electrode (e.m.f. measurement)
M/Hg	amalgam electrode (e.m.f. measurement)
E	e.m.f. measurement, not specified
red	redox electrode (e.m.f. measurement)
cpot	chronopotentiometry
con	conductivity
pol	polarography
ix	ion-exchange
kin	rate of reaction
sp	spectrophotometry
NMR	nuclear magnetic resonance
sol	solubility
dis	distribution between two phases
elph	electrophoresis
T	temperature-variation
cal	calorimetry
cv	cyclic voltammetry

2. PROTON COMPLEXES OF GLYCINE

2.1. Protonation constants

In aqueous solutions, glycine (HL) exists as a zwitterion, the amino group being protonated ($-NH_3^+$) while the carboxyl group is deprotonated (CO_2^-). The latter group undergoes protonation in acid solution (pH 2-3) and the proton complex $[H_2L]^+$ is formed; the former group loses a proton in basic solution (pH 9-10) to give L^-. The two dissociation processes of the fully protonated cationic form $[H_2L]^+$ are completely separated. The amine deprotonation reaction takes place within a very accessible pH range, and thus the protonation constant can be determined fairly accurately. The carboxyl deprotonation occurs at low pH, where the accuracy of pH measurement is lower; accordingly, the accuracy of the constant too is lower.

Literature protonation constant values are listed in Table 2.1.

The number of determinations is very high and most were carried out under clearly defined conditions. A majority of the authors applied pH-metry and used a glass electrode to measure pH. In a few cases, other methods, such as conductivity (38D) and NMR (73RB, 74RO) measurements, were used. More than half of the published constants are concentration (C) constants and one-fourth are mixed (M); for the remainder there were not enough reported experimental details to permit decision.

TABLE 2.1. Protonation Constants of Glycinate (Literature Values)

Method	Type of constant	Medium mol dm^{-3}	Temp °C	log K_{HL}	log K_{H_2L}	Ref	Category
H	C	?	25	9.75	2.33	23B	D
H	C	→ 0	25	9.78	2.35	34O	R
con	C	→ 0	25	9.67		38D	Rj
H	C?	0.1	25	9.75	2.41	40CH	D
gl	M	0.5 (KNO_3)	20	9.76		45FL	D
H	C	→ 0	5		2.4176	45K	R
			10		2.3980		
			15		2.3795		
			20		2.3640		
			25		2.3508		
			30		2.3404		
			35		2.3318		
			40		2.3252		
			45		2.3212		
			50		2.3194		
			55		2.3194		
gl	M?	0.1 (KNO_3)	25	9.69		46K	D
		1.0 (KNO_3)	25	9.84			
gl	M?	0.01	25	9.78	2.35	49MM	Rj
gl	M	?	24	9.88	2.41	49V	Rj
gl	M	0.01	20	9.86	2.22	50A	Rj
H	C	→ 0	10	10.1928	2.3971	51K	R
			15	10.0439	2.3800		
			20	9.9103	2.3640		
			25	9.7796	2.3503		
			30	9.6517	2.3394		
			35	9.5300	2.3312		
			40	9.4124	2.3266		
			45	9.2988	2.3242		
			50	9.1887	2.3200		
E	C	0.1 (NaCl)	25	9.76	2.38	52E	T
gl	M?	0.1 (KCl)	25	9.60	2.34	52K	D
gl	M	0.02	22	9.73		52P	Rj
gl	M?	0.15(KNO_3)	25.15	9.69		53TS	D
gl	C?	0.1 ($NaClO_4$)	25	9.62	2.43	54BC	D
gl	M	0.1 (KCl)	20	9.85	2.24	54IW	T
gl	M	0.01	25	9.73		54P	Rj
gl	M?	?	20	9.86	2.22	55DK	Rj
H	C	→ 0	25	9.78	2.335	55EM	R
gl	M	0.15	25	9.68		55LM	T
gl	M	0.001	20	9.61	2.35	56CD	Rj
gl	M	0.05	32	9.55	2.25	56DR	D
gl	M	0.15	25	9.68		56LW	D
			30	9.52			
			40	9.21			

Abbreviations used in the table are explained on page 602

TABLE 2.1. (continued)

Method	Type of constant	Medium mol dm^{-3}	Temp ^oC	log $\underline{K}_{HL}$	log $\underline{K}_{H_2L}$	Ref	Category
gl	C	0.09(KCl)	0.35	10.25		57MM	T
			30	9.44			
			48.8	9.00			
H	C	$\rightarrow 0$	5	10.340(2)		58DG	R
			15	10.048(2)			
			25	9.778(2)			
			35	9.528(2)			
			45	9.528(2)			
E	M	1.0 ($NaClO_4$)	20	9.76	2.43	58Pb	T
gl	C	0.01	5	10.26		59DG	Rj
			15	9.97			
			25	9.66			
			35	9.44			
			45	9.21			
			55	8.98			
gl	M	0.3 (K_2SO_4)	25	9.53(3)		61JW	T
gl	C	0.1 (KCl)	30	9.53		62CTb	T
gl	C	0.15($NaClO_4$)	25	9.62	2.44	63MP	T
		1.0 ($NaClO_4$)	25	9.65	2.45		
gl	C	$\rightarrow 0$	20	9.73	2.34	64IC	T
			30	9.65	2.45		
gl	C	0.65(KCl)	10	10.10	2.76	64LS	T
			25	9.70	2.46		
gl	C	1.0 (KNO_3)	30	9.64(2)		64RSa	T
gl	C	1.0 (NH_4ClO_4)	25	9.80	2.50	65BM	D
sp	C	1.0 ($NaClO_4$)	25	9.75	2.45	65MB	T
gl	C	0.2 (KCl)	15	9.92	2.46	65SMb	D
			25	9.68	2.47		
			40	9.34	2.40		
gl	C	$\rightarrow 0$	10	10.20	2.41	66AG	R
			25	9.77	2.39		
			40	9.46	2.33		
gl	?	0.6	25	9.96(5)		67AM	Rj
gl	C	0.1 (KNO_3)	20	9.84	2.52	67GN	T
			25	9.70	2.51		
			30	9.60	2.50		
gl	C	0.1 ($NaClO_4$)	25	9.68(1)	2.33(1)	67SG	T
gl	C	0.5 (KNO_3)	20	9.86(1)		68AL	D
gl	M	1.0 (KCl)	25	9.80	2.34	68L	T
gl	C	0.02	?	9.73		68RK	Rj
gl	C	2.0 ($NaClO_4$)	2	9.64(3)	2.79(2)	68TC	D
			25	9.56(8)	2.76(5)		
			40	9.6(1)	2.72(5)		
gl	M	0.5 (KNO_3)	25	9.61		68TV	T
gl	C	0.15(KNO_3)	37	9.382(14)		69CP	T
gl	C	0.1 (KNO_3)	25	9.61	2.26	69G	T
gl	M?	0.1 (KCl)	5	10.39		69MG	D
			25	9.58			
			45	9.05			

TABLE 2.1. (continued)

Method	Type of constant	Medium mol dm^{-3}	Temp ^{o}C	log K_{HL}	log K_{H_2L}	Ref	Category
gl	M	1.0 (KNO_3)	25	9.83	2.47	69VB	R
gl	C	0.1 (KNO_3)	25	9.63	2.41	69YH	R
gl	M	0.2 ($NaClO_4$)	25	9.60(2)	2.33(3)	70CBa	T
gl	C	0.5 ($LiClO_4$)	25	9.53(1)	2.39(1)	70FR	T
gl	C?	0.1 ($NaClO_4$)	25	9.56	2.39	70L	D
gl	M	1.0 ($NaClO_4$)	25	9.76	2.47	70MM	R
gl	M	0.5 (KNO_3)	0	10.42		70VT	T
			15	9.94			
			40	9.27			
gl	C	0.11(KNO_3)	25	9.54(1)	2.35(2)	71AA	T
gl	C	0.05(KCl)	25	9.61	2.26	71GNa	T
gl	M	0.5 (KNO_3)	25	9.63(1)	2.41(1)	71KS	D
gl	C	0.1 (KNO_3)	25	9.56(1)	2.39(1)	71LN	R
gl	M	0.5 (KCl)	25	9.70	2.48	71LL	T
gl	M	0.1 (KNO_3)	25	9.71(1)		71ST	D
gl	C	0.1 (KNO_3)	25	9.63	2.41	71YM	R
gl	M	1.0 (KNO_3)	25	9.719(1)	2.449(3)	72BPa	T
gl	C	0.05(KCl)	25	9.61	2.33	72GS	T
gl	C	0.1 (KNO_3)	15	9.84(1)		72IV	R
			25	9.55(1)			
			50	8.92(1)			
			70	8.56(1)			
gl	M	0.1 (KNO_3)	25	9.70		72UT	R
gl	C	0.2 (KCl)	25	9.55	2.36	73GS	R
NMR	M	0.4-0.6(KNO_3)	25	9.70	2.38	73RB	T
H	C	0.1 (KCl)	5	10.231(30)		73RD	R
			25	9.655(30)			
			45	9.135(30)			
gl	M	0.2 ($NaClO_4$)	25		2.38	73SM	D
			35		2.40		
			45		2.41		
gl	M	3.0 ($NaClO_4$)	25	10.15	2.75	74CP	T
gl	C?	0.5 ($NaCLO_4$)	?	9.59	2.41	74DB	D
gl	M?	0.24(KCl)	25	9.55		74FL	D
gl	C?	0.1 ($LiClO_4$)	25	9.40(9)	2.40(9)	74KU	D
gl	C	0.1 (KNO_3)	25	9.65	2.34	74MM	R
		0.1 ($NaClO_4$)	25	9.60	2.33		
NMR	M	0.2-0.3	25	9.69	2.34	74RO	T
gl	C?	3.0 ($NaClO_4$)	25	10.12(1)	2.76(1)	75BH	D
gl	C	0.15($NaClO_4$)	37	9.173(3)	2.338(3)	75CM	T
gl	C	3.0 ($NaClO_4$)	25	10.070(7)	2.682(12)	75CM	T
gl	C	0.1 (KNO_3)	25	9.57(2)	2.32(5)	75DO	R
gl	M	0.1 (KNO_3)	25	9.69		75HV	R
gl	M	0.5 (KNO_3)	25	9.69			
gl	C	0.1 (KNO_3)	25	9.582(5)	2.322(7)	75IP	R
gl	C	0.1 ($NaNO_3$)	25	9.647(4)	2.415(5)	75SS	T
H	C	1.0 (KCl)	25	9.67(1)	2.48(1)	76GM	R

TABLE 2.1. (continued)

Method	Type of constant	Medium mol dm^{-3}	Temp ^oC	log K_{HL}	log K_{H_2L}	Ref	Category
gl	?	?	22	9.65		76HS	Rj
gl	C	0.2 (KCl)	25	9.55	2.36	76SG	R
gl	M?	0.2 ($NaClO_4$)	30	9.225	2.250	77MS	D
gl	M	$\rightarrow$ 0	30	9.78	2.25	77PU	D
gl	M	0.1 (KNO_3)	30	9.90(1)	2.25(1)	77PU	D
gl	M?	0.1 ($NaClO_4$)	30	9.60		77RS	D
gl	C?	0.5 (KNO_3)	23	9.70	2.50	78AE	D
gl	C	1.0 ($NaNO_3$)	25	9.642(2)	2.431(9)	78JI	R
gl	M	0.5 (KNO_3)	25	9.72(1)	2.49(1)	78L	T
gl	C	0.12(NaCl)	25	9.52(2)	2.370(4)	78RM	T
gl	M	0.1 (KNO_3)	25	9.620(1)	2.430(2)	78SP	T
gl	C	1.0 (NaCl)	25	9.629	2.407	78BB	R
gl	C	1.0 (NaCl)	25	9.67(4)	2.47(6)	78BB	R
gl	C	1.0 (NaCl)	25	9.654(2)	2.413(3)	78BB	R
gl	C	1.0 (NaCl)	25	9.656(7)	2.420(10)	78BB	R
gl	C	1.0 (NaCl)	25	9.652(12)	2.457(10)	78BB	R
gl	C	1.0 (NaCl)	25	9.659(15)	2.412(22)	78BB	R
gl	C	1.0 ($NaClO_4$)	25	9.77		79EB	D
gl	M?	0.5 (KNO_3)	30	9.56(1)		79EM	D
gl	M?	2.5 (KNO_3)	25	9.78	2.35	79FS	D
gl	C	0.15($NaClO_4$)	25	9.533(6)	2.345(9)	79HJ	T
gl	M?	1.0 ($NaClO_4$)	25	9.76	2.47	79KC	D
gl	C	0.2 (KNO_3)	25	9.60	2.33	79MB	R
gl	C	3.0 ($NaClO_4$)	25	10.21(1)	2.80(1)	79MT	T
gl	M?	0.1 ($NaClO_4$)	30	9.60	2.45	79RR	D
gl	C	0.15(KNO_3)	37	9.39	2.38	79SP	T
gl	C	$\rightarrow$ 0	25	9.78	2.35	79VKb	T
gl	C	3.0 ($LiClO_4$)	25	9.91(2)	2.69(3)	80OZ	T
gl	M	0.1 (KNO_3)	25	9.70	2.33	80SJ	R
gl	C	0.1 (NaCl)	20	9.68	2.16	80SK	D
gl	C	0.15($NaClO_4$)	37	9.239(5)	2.415(7)	81AB	T
gl	C	0.1 ($NaNO_3$)	25	9.647(4)	2.415(5)	81IS	R
gl	?	0.1	30	9.78(1)	2.25(1)	81PU	D
gl	M	0.25(KNO_3)	30	9.66	2.32	81RK	T
gl	C	0.2 ($NaNO_3$)	30	9.53(3)	2.33(1)	81RSb	D
gl	C	1.0 ($NaClO_4$)	25	9.64	2.47	82FN	R
gl	C	3.0 ($LiClO_4$)	25	9.68	2.76	82MO	D
gl	?	0.1 ($NaClO_4$)	50	9.167(9)	2,31	83VS	D
gl	C?	1.0 (KNO_3)	30	9.62(2)		84CG	D
gl	?	0.15(NaCl)	20	9.78(2)		85VD	D
gl	C	1.0 ($NaClO_4$)	25	9.65	2.42	86A	R
gl	C	3.0 ($LiClO_4$)	25	9.94	2.68	86IP	T
gl	M?	0.1 (KNO_3)	35	9.75(2)	2.50(2)	86RRa	D
gl	C	0.7 ($NaClO_4$)	25	9.54		86SGa	T
gl	C	0.2 (KNO_3)	25	9.55	2.36	86SV	R
gl	C	0.2 (KNO_3)	35	9.32	2.28	87PS	T

Determinations carried out in solutions of low ionic strength (< 0.02 mol dm^{-3}) were regarded as doubtful because of changes in activity during measurements (23B, 40CH, 49MM, 50A, 54P, 56CD, 59DG, 68RK). In references 38D, 45FL, 46K, 49V, 52K, 53TS, 54BC, 55DK, 67AM, 69MG, 70L, 71KS, 73SM, 74DB, 74FL, 74KU, 75BH, 76HS, 77PU, 77RS, 78AE, 79FS, 79KC, 79RR, 80SJ, 80SK, 81PU, 83VS, 84CG, 85VD and 86RRa, the experimental information provided was not sufficient, and thus these values were omitted from the evaluation. The values in 77MS and 82MO are significantly lower, while those in 65BM, 65SMb, 68AL, 77PU and 79EB are significantly higher than all others, and accordingly were rejected. The temperature-variation measurements in the range of 2-40 ^{0}C in 68TC result in incorrect enthalpy data, and hence were omitted from the evaluation. The remaining values are satisfactorily close in magnitude (see Figure 1) to allow to giving of recommended or tentative constants together with standard deviations for different experimental circumstances. These values are compiled in Table 2.2.

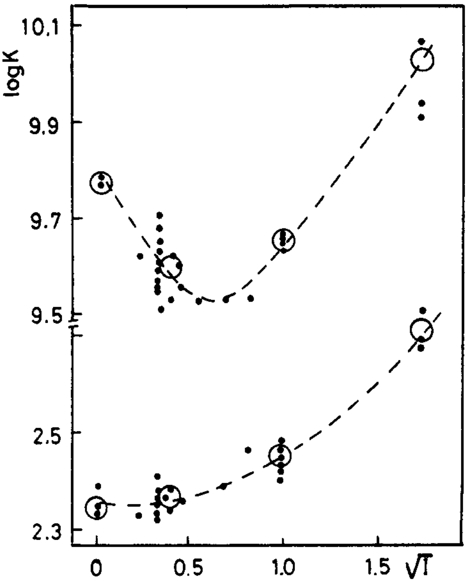

Fig. 1. The ionic strength dependence of the protonation constants of glycine at 25 ^{0}C. The open circles are the recommended values at different ionic strengths (see Table 2.2). The dotted lines are fitted on the accepted protonation constants.

TABLE 2.2. Recommended (R) and Tentative (T) Values for the Protonation Constants of Glycinate

Type of constant	Medium mol dm^{-3}	Temp ^{0}C	log K_{HL}	Category	log K_{H_2L}	Category
C	0	25	9.78±0.01	R	2.36±0.02	R
C	0.1-0.2	25	9.60±0.05	R	2.37±0.07	T
M	0.1-0.2	25	9.67±0.04	R	2.36±0.04	T
C	1.0	25	9.65±0.01	R	2.44±0.03	R
M	1.0	25	9.78±0.04	R	2.46±0.06	T
C	3.0	25	10.05±0.13	T	2.71±0.06	T
M	3.0	25	10.15	T	2.75	T
C	0.15	37	9.30±0.10	T	2.38±0.09	T

Abbreviations used in the table are explained on page 602

A detailed study (78BB) was made by seven research laboratories on the proton and nickel(II)-glycine system to recommend a general procedure for testing the apparatus and technique for pH-metric measurements (87BO). Their data together with other acceptable findings (64RSa, 76GM, 78JI, 82FN, 86A) provide recommended concentration constants at 25 ^{0}C and an ionic strength of 1.0 mol dm^{-3}. Similarly, recommended mixed and concentration constants can be given for the protonation of the glycinate anion at 25 ^{0}C at ionic strengths of 0 and 0.1-0.2 mol dm^{-3}. The electrode calibration differences and various uncertainties including whether the reference electrode used was with or without intervening salt bridge (in order to eliminate the "junction potential problem" (67IM)), cause particularly large errors in high ($\log K < 3$) or low ($\log K > 11$) protonation constants. Thus, only tentative mixed constants can be given for the process of protonation of the carboxylate group. For the same reason, care should be taken when numerical factors (74MS) are used to convert mixed constants to concentration constants, since these factors are valid only approximately and take into account only the conversion of hydrogen ion activity to hydrogen ion concentration. The errors originating from the junction potentials, which may not always be calculable (67IM), are not incorporated in these conversion factors.

The values in 75CM, 79MT, 80OZ and 86IP referring to an ionic strength of 3.0 mol dm^{-3}, allow the postulation only of tentative concentration constants. The data reported in 69CP, 75CM, 79SP and 81AB can be compared directly, giving concentration stability constants at 37 °C and at $I = 0.15$ mol dm^{-3}. Although the standard deviations of the averaged values are rather high, so that the constants can be considered only to be tentative, they are in very good agreement with those calculated via the van't Hoff equation by taking into account the recommended enthalphy changes for the dissociation of these groups; these constants are $\log K_1 = 9.29$ and $\log K_2 = 2.33$.

2.2. Protonation enthalpies

The enthalpies accompanying protonation given in Table 2.3 were calculated from calorimetric and potentiometric measurements.

Potentiometric studies generally provide enthalpy values of lower accuracy. However, as the early results (34HE, 34O, 39EW, 41S, 45K, 51K, 58DG) show, careful potentiometric work at many different temperatures can give data with the same accuracy.

Merely the protonation constants at different temperatures, but without the respective enthalpy values, were reported in references 56LW, 64LS, 66AG, 68TC, 69MG and 73SM. We have calculated these data too, but in most cases they were either much lower (66AG, 68TC, 73SM) or much higher (56LW, 69MG) than most of the other literature data, or measurements were carried out at only two different temperatures (64LS). Hence, these calculated values were omitted from the evaluation and are not included in Table 2. The values in 68CW were obtained by the "entropy titration" method. In this method both formation constants and enthalpies of single association reactions are calculated from the same calorimetric measurement. The values reported are reliable, but it must be mentioned that the method, even in its extended form, can be used only under rather restricted conditions.

From the remaining values (34HE, 34O, 39EW, 41S, 45K, 51K, 57MM, 58DG, 62A, 67AG, 68CO, 72IV, 73GS, 73RD, 76SG), it is possible to give recommended values for the enthalpies of protonation of both the carboxylate and the amino groups at 25 °C and $I = 0$ or 0.1-0.2 mol dm^{-3}. The recommended values are:

$$I = 0 \qquad \Delta \underline{H}^{o}_{NH_2} = -44.6(6), \quad \Delta \underline{H}^{o}_{CO_2^-} = -4.4(4) \text{ kJ mol}^{-1}$$

$$I \blacksquare 0.1\text{-}0.2 \qquad \Delta \underline{H}^{o}_{NH_2} = -45.4(1.2), \quad \Delta \underline{H}^{o}_{CO_2^-} = -4.3(2) \text{ kJ mol}^{-1}.$$

TABLE 2.3. Enthalpies for the Protonation of Glycinate (kJ mol^{-1}) (Literature Values)

Method	$\underline{I}$/mol dm^{-3}	T/^{o}C	$-\Delta \underline{H}^{o}_{CO_2^-}$	$-\Delta \underline{H}^{o}_{NH_2}$	Ref	Category
T	0	10	6.99		34HE	T
		25	4.94			
		40	2.64			
T	0	10	6.535		34O	T
		15	6.021			
		20	5.460			
		25	4.849	44.84		
		30	4.184			
		35	3.469			
		40	2.702			
		45	1.879			
T	0	25	4.602	44.350	39EW	R
cal	0	25	3.891	44.460	41S	R
T	$\rightarrow$ 0	25	4.008		45K	R
	0.1 (NaCl)		4.088			
	0.3 (NaCl)		4.205			
	0.725(NaCl)		4.531			
	1.25(NaCl)		5.025			
	2.0 (NaCl)		5.807			
	3.0 (NaCl)		6.841			
T	$\rightarrow$ 0	10-50	3.987	44.141	51K	T
	0.1 (NaCl)			44.974		
	0.3 (NaCl)			45.518		
T	0.09(KCl)	0.35-48.8		42.7	57MM	T
T	$\rightarrow$ 0	5-45		44.22	58DG	D
cal	0	25	4.85		62A	T
T	$\rightarrow$ 0	20-30	5.9	44.3	64IC	D
cal	0.01	25		44.2(3)	66PC	D
cal	$\rightarrow$ 0	25		44.52	67A	R
T	$\rightarrow$ 0	10		48.5(4)	67AG	R
		25		45.0(2)		
		40		42.8(3)		
cal	$\rightarrow$ 0	10	5.90(33)		68CO	R
		25	4.10(21)			
		40	1.97(13)			
cal	0.01	25		44.68(13)	68CW	D
T	0.5 (KNO_3)	0-40		48.7	70VT	D
T	0.1 (KNO_3)	15-70		44.3	72IV	R
T	$\rightarrow$ 0	10		45.40(12)	72IJ	T
		25		43.93(12)		
		40		43.43(12)		
cal	0.2 (KCl)	25	4.39	46.52	73GS	R
T	0.1 (KCl)	5		44.7(1.2)	73RD	R
		25		46.7(1.2)		
		45		47.6(1.2)		
cal	0.2 (KCl)	25	4.4	44.3	76SG	R
cal	1.0 ($NaClO_4$)	25		45.94(7)	79EB	T
cal	$\rightarrow$ 0	25	4.27	45.68	79VKa	T
cal	3.0 ($NaClO_4$)	25	5.5	57.9	86IP	T

Abbreviations used in the table are explained on page 602

3. METAL COMPLEX STABILITY CONSTANTS

Of the metal complexes, those of the 3d transition metal ions (especially Cu(II), Ni(II) and Zn(II)) have been studied in most detail. Ag(I) and Cd(II) are the best studied of the 4d and 5d transition metal ions. Data on complexes of other metal ions are generally limited to only a few studies each. For an estimation of the stability constants of metal ion - glycine complexes that have not yet been measured, reference 85SM gives a procedure based on the known stability constants available in the literature (74MS, 82MS).

The various calibration methods in glass electrode pH-metric works result in inconsistencies not only in the ligand protonation constants, but in the metal complex formation constants too, even if the hydrogen ion is not involved in the stoichiometric composition of the metal complex. The less the overlap between the metal complex formation and the ligand dissociation processes (i.e. the more shifted in favour of the metal ion the competition equilibrium, M + HL = ML + H, between protons and metal ions for coordination with the ligand), the smaller the difference between the calculated concentration (C) and mixed (M) constants. The reason for this is that the equilibrium constant, $\underline{K}_e$, for the competition reaction followed by pH-metry is a product of the acid dissociation constant of the ligand, $\underline{K}_{HL}$, and the metal complex formation constant, $\underline{K}_{ML}$. If the effects of the activity coefficient of the hydrogen ion on the equilibrium constants are approximately the same for the ligand dissociation and the competition equilibria, they compensate each other, which results in the same concentration or mixed stability constants for ML. To demonstrate this, a model calculation was performed with real (calibration for the hydrogen ion concentration) and simulated (with activity coefficient 0.75 for the hydrogen ion) titration curves on the protonation and some metal complex formation processes of glycine. The results are shown in Table 3.1.

TABLE 3.1. Calculation of Mixed (M) or Concentration (C) Stability Constants for the Proton and Some Metal Complexes of Glycinate from pH-metric Data

Constant	Mixed (M)	Concentration (C)	Δ(M - C)
	stability	constant	
$pK_{NH_3^+}$	9.67(1)	9.55(1)	0.12
pK_{COOH}	2.62(2)	2.36(2)	0.26
$\log \underline{K}_{CuA}$	8.09(1)	8.07(1)	0.02
$\log \underline{K}_{CuA_2}$	6.76(1)	6.77(1)	-0.01
$\log \beta_{CuA_2}$	14.85(1)	14.84(1)	0.01
$\log \underline{K}_{NiA}$	5.65(1)	5.65(1)	0.00
$\log \underline{K}_{NiA_2}$	4.76(1)	4.75(1)	0.01
$\log \beta_{NiA_2}$	10.41(1)	10.40(1)	0.01
$\log \underline{K}_{NiA_3}$	3.29(2)	3.39(2)	-0.10
$\log \beta_{NiA_3}$	13.70(2)	13.79(2)	-0.09

Abbreviations used in the table are explained on page 602

It can be seen from the data that there are practically no differences between the respective mixed (M) and concentration (C) constants of the metal complexes. The only exception is log $\underline{K}_{NiL_3}$; in this process, the coordination of a third ligand is relatively weak and overlaps considerably with the dissociation of the free ligand. As the metal ion - ligand interaction is relatively strong inmost metal complexes of glycine, and thus the difference between the mixed and concentration constants is negligible (or is within experimental error), and as a precise description of the electrode system and the means of its calibration is not to be found in many references, no distinction is made in this survey between the concentration (C) and mixed (M) constants for the metal complexes of glycine.

In the references surveyed, the stability constants were calculated from the experimental data via a variety of numerical, graphical or computational methods. For an insight into the problems of data-handling in the various calculation methods, mention may be made of reference 78FM, in which the results of model calculations on the copper(II)-glycine system are reported and discussed.

3.1. Complex formation with group 2A, 3B and 4B metal ions

Relatively few stability constants on the complexes of these metal ions with glycine are available in the literature. The data reported are listed in Table 3.2.

The alkaline earth cations form rather weak complexes and hence it is not easy to obtain accurate stability constants. Most of the published data should be regarded at best as doubtful or tentative. In the case of Be(II), hydrolysis of the metal ion and the formation of mixed hydroxo complexes cannot be neglected, and thus the values in 52P and 60B are rejected. The data in 74DB are considered to be more reliable, though the speciation model is questionable. For Mg(II), only the data reported in reference 87BB seem to be reliable and can be accepted tentatively. For the values in 49MM, 51Mc, 52A, the reason for rejection is the lack of a constant ionic strength, while for those in 86RRa it is the insufficient information on the way in which the experimental data were treated. For Ca(II), Sr(II) and Ba(II), two sets of data are available for evaluation, which were obtained by different methods: solubility measurements (38D, 50DW, 51Ma, 52CM) and ion-exchange study (76TG). The stability constants of the MA complexes show the trend Ca(II) > Sr(II) > Ba(II), as expected on the basis of the ionic model. The numerical values agree fairly well with each other, but the large differences in experimental conditions (ionic strength and temperature) suggest that the agreement is merely accidental.

The stability data reported for the complexes of group 3B cations with glycine are hardly sufficient for an objective evaluation. In the case of Ga(III) the values in 75BH and 85SA cannot be compared because of the large difference in ionic strength, while the data in 68ZK and 85SA are very different in spite of the similar experimental conditions; thus, all these results must be classified as doubtful. In accordance with the opinion of Tuck in the "Critical Survey of Stability Constants of Complexes of Indium" (83T), the values reported in references 76KF, 77KK and 85SA should be regarded as doubtful because the experimental conditions were not specified or display little agreement.

As concerns the group 4B cations, there are a reasonably large number of reported data on the Pb(II) complexes. However, the experimental conditions are not sufficiently similar, to allow the establishment of recommended values for the complexes formed. Some of the publications do not give detailed experimental conditions (51Mc, 61MM, 64JM, 69HL) or the ionic strength used is not high enough to remain constant throughout the titration (49MM, 52P); these data are therefore excluded from the evaluation. In these papers, hydroxo complex formation was neglected. In the recent studies (75CM, 76CW, 78BS, 79KC, 79MT, 83NR, 84YS, 85DV, 86SGa, 88BB), besides the formation of PbL and

TABLE 3.2. Stability Constants of Complexes of Glycine with 2A, 3B and 4B Metal Ions (Literature Values)

Metal	Method	$\underline{I}$/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Be(II)	gl	0.01	22		13.3		52P	Rj
	sp	?	?	4.95			60B	Rj
	gl	0.5 ($NaClO_4$)	?	log β_{MHL}=10.69 log $\beta_{M_2(HL)_2(OH)}$=18.85 log $\beta_{M_3(HL)(OH)_3}$=1.78 log $\beta_{M_3(HL)_2(OH)_3}$=12.98 log $\beta_{M_3L(OH)_3}$=-4.35			74DB	D
Mg(II)	gl	0.01	25	3.45	6.46		49MM	Rj
	gl	→ 0	25	3.44			51Mc	D
	gl	0.01	20	2	4		52A	Rj
	gl	0.09(KCl)	0.35	2.12			57MM	D
			30	2.23				
	gl	0.5 (KCl)	25	1.34			69HL	D
	gl	0.15(NaCl)	20	2.23(6)			85VD	D
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=2.67			86RRb	Rj
	gl	0.15($NaClO_4$)	37	1.979(19) log β_{MHL}=10.879(42) log $\beta_{MH_{-1}L}$=-8.735 log $\beta_{MH_2L_2}$=21.614(103)			87BB	T
Ca(II)	sol	→ 0	25	1.38			38D	D
	sol	→ 0	25	1.43			50DW	D
	sol	→ 0	25	1.35			52CM	D
	ix	1.0 ($NaNO_3$)	?	1.39			76TG	D
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=2.39			86RRb	Rj
Sr(II)	sol	→ 0	25	0.91			52CM	D
	ix	0.16	25	0.6			52SL	D
	ix	1.0 ($NaNO_3$)	?	1.02			76TG	D
Ba(II)	sol	→ 0	25	0.77			51Ma	D
	ix	1.0 ($NaNO_3$)	?	0.87			76TG	D
Al(III)	elph	0.1 ($NaClO_4$)	35			19.40	84YS	D
Ga(III)	pol	0.1 (KNO_3)	22	9.33(5)			68ZK	D
	gl	3.0 ($NaClO_4$)	25	9.60(4) log $\underline{K}$(M + HL)=2.11(4)			75BH	D
	gl	0.1 ($NaClO_4$)	20	9.71(13)			85SA	D
In(III)	gl	0.2 ($NaClO_4$)	25	log $\underline{K}$(M + HL)=2.39			73SM	D
			35	2.46				

Abbreviations used in the table are explained on page 602

TABLE 3.2. (continued)

Metal	Method	$\underline{I}$/mol dm^{-3}	$T/^{\circ}C$	$\log \beta_{ML}$	$\log \beta_{ML_2}$	$\log \beta_{ML_3}$	Ref	Category
In(III)			45		2.54			
	gl	?	24	8.22	16.24		76KF	D
	pol	0.2 ($NaClO_4$)	30	10.25	16.21		77KK	D
				10.67	16.22			
	gl	0.1 ($NaClO_4$)	20	8.55(14)			85SA	D
Tl(I)	gl	0.1 ($LiClO_4$)	25	1.51			74KU	D
Sn(II)	gl	0.7 ($NaClO_4$)	20	8.93			74W	D
Pb(II)	sol	→ 0	25	5.17			41KRa	D
	gl	0.01	25	5.53	9.98		49MM	Rj
	gl	→ 0	25	5.47	8.86		51Mc	D
	gl	0.01	22		9.3		52P	Rj
	gl	0.1 (KNO_3)	25		7.7		61MM	D
	pol	0.1 (KNO_3)	25		7.4			
	elph	0.1 (KNO_3)	20		7.5		64JM	D
	pol	1.0 (KNO_3)	30	5.11	7.08		64RSb	D
	gl	0.5 (KNO_3)	25	4.36	7.62		69HL	D
	gl	3.0 ($NaClO_4$)	25	5.600(34)			75CM	T
				$\log \beta_{MHL}$=11.396(127)				
				$\log \beta_{MH_{-1}L}$=-2.142(35)				
	gl	3.0 ($NaClO_4$)	10	5.893(34)			76CW	T
				$\log \beta_{MHL}$=12.212(79)				
				$\log \beta_{MH_{-1}L}$=-2.071(38)				
			25	5.752(45)				
				$\log \beta_{MHL}$=11.880(108)				
				$\log \beta_{MH_{-1}L}$=-1.886(50)				
			40	5.675(27)				
				$\log \beta_{MHL}$=11.772(47)				
				$\log \beta_{MH_{-1}L}$=-1.781(26)				
	gl,Pb/Hg	1.0 ($NaClO_4$)	25	4.78(5)	7.66(5)		78BS	T
				$\log \beta_{MHL}$=10.75(10)				
				$\log \beta_{MH_2L_2}$=21.15(15)				
				$\log \beta_{MHL_2}$=14.7(2)				
	gl	1.0 ($NaClO_4$)	25	5.46(5)	9.32(6)		79KC	T
				$\log \beta_{MHL}$=12.60(10)				
				$\log \beta_{MH_{-1}L}$=-2.77(5)				
	gl,Pb/Hg	3.0 ($NaClO_4$)	25	5.28(2)	8.32(5)		79MT	T
				$\log \beta_{MHL}$=11.41(4)				
	NMR	0.4 ($NaNO_3$)	25	$\log \underline{K}$(M + HL)=1.48(8)			83NR	T
		95/5 H_2O/D_2O		$\log \underline{K}$(M + 2HL)=2.08(10)				
	elph	0.1 ($NaClO_4$)	35	5.86	8.38		84YS	T
Pb(II)	Pb/Hg	0.1 (KNO_3)	25	5.63(12)	8.10(6)		85DV	T
				$\log \beta_{MHL}$=13.33(10)				
				$\log \beta_{MH_{-1}L}$=-2.85(10)				
	gl	0.7 ($NaClO_4$)	25	4.91	8.01		86SGa	T
	gl,Pb/Hg	3.0 ($NaClO_4$)	25	5.01	8.00(1)		88BB	T
				$\log \beta_{MHL}$=11.28(1)				
				$\log \beta_{MH_2L_2}$=21.85(2)				
				$\log \beta_{MH_3L_3}$=32.22(2)				

PbL_2, the protonated complexes, PbHL, $Pb(HL)_2$, $PbHL_2$ and $Pb(HL)_3$ and a mixed hydroxo complex PbL(OH) were assumed. The formation of protonated complexes was confirmed by ^{207}Pb n.m.r. study too (83NR). Mainly two techniques were used to determine the stability constants: pH-metry with a glass electrode (75CM, 76CW, 79KC) and combined potentiometry using a glass electrode and a lead amalgam electrode (78BS, 79MT, 85DV, 88BB). The stability constants in 88BB were calculated by regarding HL as the complex-forming species. For easier comparison, these values have been recalculated with the recommended value $pK_{NH_3^+}$ = 10.05. It is rather interesting that the studies based on glass electrode measurements report notably higher values (~ 0.5-0.8 log units) for all complexes. The explanation of these differences necessitates further investigations; accordingly, only tentative values can be given at this time. The difficulties inherent in obtaining accurate stability data on the Pb(II)-glycine system are well illustrated by the results reported by the same research group in 1975 (75CM) and in 1976 (76CW). The titration data obtained under the same experimental conditions, but evaluated with different computer programs (PSEUDOPLOT and MINIQUAD), resulted in rather different values for the same constant.

3.2. Complex formation with group 3d transition metal ions

Literature values on the formation constants of complexes with the group 3d transition metal ions are given in Table 3.3.

In general, simple mono, bis and in some cases tris complexes are formed with the divalent cations of this group, though the presence of minor amount of protonated complexes at low pH and of mixed hydroxo complexes at high pH has also been assumed for some metal ions (73TG, 75CM, 79SP, 82FN). Ions such as Ti(III), V(IV), Cr(II), Fe(II) and Co(II) are easily oxidized by air, especially in basic solution. The rigorous exclusion of air during measurements is therefore mandatory if satisfactory stability constants are to be obtained.

No reliable stability constants are available for the glycine complexes of Ti(III). The lack of essential experimental information (due to the facile oxidation of the metal ion) means that the only value in 70FMb should be regarded as very doubtful.

The values reported for V(IV)-glycine in 70CBa and 70FMb must be rejected because they are much higher (2-3 orders of magnitude) than those in 73TG and 82FN, which were obtained from very precise spectrophotometric and/or pH-metric measurements. In the former cases, the oxidation of the metal ion presumably led to erroneous results. The stability constants in 73TG were determined at a high ligand excess (between 1:10 and 1:50) to avoid metal ion hydrolysis. The stabilities of the monodentate and bidentate mono and bis microspecies, together with a protonated 1:1 complex, were determined by combined pH-spectrophotometric measurements. In reference 82FN a wider range of metal ion:ligand ratio (between 1:1 and 1:100) was applied to determine the stability of the mixed hydroxo complexes too. The agreement between the results in these two papers is satisfactory, if the differences in ionic strength is taken into account. The constants in both references can be accepted tentatively.

TABLE 3.3. Stability Constants of Complexes of Glycine with 3d Transition Metal Ions (Literature Values)

Metal	Method	$\underline{I}$/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Ti(III)	gl	?	?	8.52			70FMb	D
V(III)	sp	?	?	9.08			70PK	D
V(IV)	gl	? ($NaClO_4$)	25	8.24(5)	15.66(5)		70CBa	Rj
	E	?	?	9.10			70FMb	Rj
	gl,sp	2.0 ($NaClO_4$)	25	log K(M + HL)=0.46			73TG	T
				log K(M + (L))=6.04				
				log K(M + L)=5.78				
				log K(M + 2(L))=10.77				
				where, L monodentate, (L) chelate				
V(IV)	gl	1.0 ($NaClO_4$)	25	6.51(3)	11.82(5)		82FN	T
				log β_{MHL}=10.81(3)				
				log $\beta_{MH_{-1}L}$=1.3(3)				
				log $\beta_{MH_{-2}L}$=-6.3(3)				
				log β_{MHL2}=16.63(4)				
				log $\beta_{MH_{-1}L2}$=4.10(6)				
				log $\beta_{M_2H_{-2}L_2}$=5.1(4)				
Cr(II)	gl	0.1 ($NaClO_4$)	25	7.72(5)	15.26(5)		70FK	Rj
	Pt,gl	?	?	9.05			70FMa	Rj
	gl	1.0 (KCl)	25	4.21(2)	7.27(3)		83MD	T
Cr(III)	gl	0.5	25	8.4	14.8	20.5	63KM	D
	gl	0.1 ($NaClO_4$)	25	8.62	16.27		65MD	T
	sp	0.6($Mg(ClO_4)_2$)	25	log $\underline{K}$(M + HL)=3.05			73BF	D
				log $\underline{K}$(M + 2HL)2=5.44				
				log $\underline{K}$(M + 3HL)3=7.49				
				log $\underline{K}$(M + 4HL)4=9.29				
				log $\underline{K}$(M + 5HL)5=10.98				
				log $\underline{K}$(M + 6HL)6=12.57				
	gl	0.1 ($NaClO_4$)	50	8.70(11)	16.33(6)	23.07(25)	83VS	D
				log β_{MHL}=11.14(13)				
				log $\beta_{M_2L_2(OH)_2}$=27.57(14)				
	sp	0.45($NaClO_4$)	44.8	7.60			84AB	T
	elph	0.1 ($NaClO_4$)	35	8.07	14.32	19.23	84YS	T
Mn(II)	gl	0.01	25	3.66	6.63		49MM	D
	gl	→ 0	25	3.44			51Mc	T
	gl	0.1 (KCl)	25	2.85			52K	T
	gl	0.01	20	3.2	5.5		53A	D
	H	→ 0	0	3.199(9)			64BD	T
			15	3.179(9)				
			25	3.167(6)				
			35	3.161(6)				
			45	3.161(6)				
	elph	0.1 (KNO_3)	20	3.9	5.6		64J	Rj
	elph	0.1 (KNO_3)	20	4.1	5.7		64JM	Rj
	gl	0.65 (KCl)	10	2.66	4.71	6.0	64LS	T
			25	2.60	4.58	5.7		
	gl	0.5 (KCl)	25	2.65	4.7		68LB	T
	gl	0.1 (KNO_3)	25	3.0			69G	T

Abbreviations used in the table are explained on page 602

TABLE 3.3. (continued)

Metal	Method	I/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Mn(II)	gl	0.5 (KCl)	25	2.56	4.27	4.87	69HL	D
	gl	0.15(KNO_3)	37	2.711(32)	4.755(60)	5.52(30)	69CP	T
	gl	→ 0	10	3.23(3)			72IJ	T
			25	3.21(2)				
			40	3.15(2)				
	gl	0.1 (KNO_3)	25	2.83	4.83		74MM	T
		0.1 ($NaClO_4$)	25	2.94				
	elph	0.5 (KNO_3)	15	4.03	5.92	6.99	75CB	Rj
	gl	0.15(NaCl)	20	3.00(6)			85VD	D
	gl	0.1 (KNO_3)	35	log K(M + HL)=3.41			86RRb	Rj
Fe(II)	gl	0.01	20	4.3	7.8		53A	Rj
	gl	1.0 (KCl)	20	3.83			59P	T
	elph	0.1 (KNO_3)	20	5.1			64JM	Rj
	gl	0.1 (KNO_3)	25	4.13	7.65		69G	T
	gl	→ 0	10	4.36(3)			72IJ	T
			25	4.31(2)				
			40	4.28(2)				
	gl	1.0 (KCl)	25	3.73(1)	6.65(1)	8.87(1)	87M	T
Fe(III)	red,sp	1.0 ($NaClO_4$)	20	10.0			58Pc	D
	red,gl	1.0 ($NaClO_4$)	25	8			86A	D
				log β_{MHL}=11.41(7)				
				log $\beta_{M_2L(OH)_2}$=6.8(1)				
Co(II)	gl	0.5 (KNO_3)	20	4.61	8.36	11.92	45FL	D
	gl	0.01	25	4.95	8.94		49MM	D
	gl	0.01	20	5.1	8.9		50A	D
	gl	→ 0	25	5.23	9.25		51Mc	T
	gl	0.01	22		8.8		52P	D
	gl	0.15(KNO_3)	25.15	4.65	8.43	10.71	53TS	T
		→ 0		5.08	9.10	11.49		
	H	→ 0	25	5.02	9.01		55EM	T
	gl	0.15	26	4.65	8.43	10.76	55GO	T
	H	→ 0	0	5.276(10)	9.51(2)		64BD	T
			15	5.143(6)	9.21(2)			
			25	5.072(8)	9.04(2)			
			35	5.009(5)	8.91(2)			
			45	4.953(5)	9.77(2)			
	elph	0.1 (KNO_3)	20	5.5	9.0	11.3	64J	Rj
	elph	0.1 (KNO_3)	20	5.7	9.2	11.4	64JM	Rj
	gl	0.2 (KCl)	15	4.76	9.32		65SMb	T
			40	4.64	7.98			
	gl	0.1 (KNO_3)	25	4.75	8.63	11.03	69G	T
	gl	0.5 (KCl)	25	4.51	8.16	10.45	69HL	T
	gl	0.05(KCl)	25	4.66	8.64		71GNa	T
	gl	0.1 ($NaClO_4$)	25	4.63(1)	8.50		71GS	T
	gl	0.05(KCl)	25	4.70	8.58		72GS	T
	gl	→ 0	10	5.16(1)	9.23(1)	11.90(6)	72IJ	T
			25	5.07(1)	9.09(1)	11.63(4)		
			40	4.98(1)	8.89(1)	11.34(5)		

TABLE 3.3. (continued)

Metal	Method	$\underline{I}$/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Co(II)	sp	0.666($NaClO_4$)	17.5	4.31	7.67		74KN	D
	elph	0.5 (KNO_3)	15	4.99	8.57	11.00	75CB	D
	gl	0.1 (KNO_3)	25	4.72(1)	8.76(1)		75IP	T
	gl	0.5 (KNO_3)	30	4.77	8.99(12)	12.4(24)	79EM	D
	gl	0.2 (KCl)	25	4.56	8.30		83HS	T
	elph	0.1 ($NaClO_4$)	35	4.60	10.01		84YS	D
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=2.26			86RRb	Rj
Ni(II)	gl	0.5 (KNO_3)	20	5.77	10.57	14.18	45FL	D
	gl	0.01	25	6.12	11.15		49MM	D
	gl	0.01	20	6.1	11.0		50A	D
	gl	→ 0	25	6.18	11.14		51Mc	R
	gl	0.01	22		11.0		52P	D
	gl	0.1 ($NaClO_4$)	25	5.86	10.64		54BC	T
	gl	0.15	25	5.97	10.92		56LW	T
			30	5.88	10.74			
			40	5.72	10.42			
	H	→ 0	0	6.465(3)	11.751(10)		64BD	R
			15	6.286(3)	11.362(8)			
			25	6.179(3)	11.130(5)			
			35	6.083(4)	10.919(7)			
			45	6.000(9)	10.75(2)			
	elph	0.1 (KNO_3)	20	6.4	10.8	13.8	64J	Rj
	elph	0.1 (KNO_3)	20	6.5	11.4	14.7	64JM	Rj
	gl	0.65(KCl)	10	5.73	10.80	14.4	64LS	T
			25	5.66	10.51	14.0		
	gl	1.0 ($NaClO_4$)	25	5.69	10.50	13.95	64MPb	T
	gl	0.2 (KCl)	15	6.04	11.02		65SMb	T
			25	5.94	10.78			
			40	5.78	10.49			
	gl	0.5 (KCl)	25	5.65	10.51	13.95	66LHa	T
	gl	→ 0	10	6.36	11.65		67AG	T
			25	6.18	11.25			
			40	6.09	11.01			
	gl	0.1 (KNO_3)	20	5.80	10.70		67GN	T
			25	5.73	10.56			
			30	5.70	10.47			
	gl	0.5 (KCl)	25	5.63	10.48	14.0	68LB	T
	gl	1.0 (KNO_3)	25		10.55	14.06	68FV	T
	gl	0.1 (KNO_3)	25	5.73	10.56	14.00	69G	T
	gl	? ($NaClO_4$)	25	5.86(6)	10.84(10)		70CBa	Rj
	gl	0.5 ($LiClO_4$)	25	5.60(1)	10.34(2)	13.78(3)	70FR	T
	gl	1.0 ($NaClO_4$)	25	5.69(1)	10.50(2)	13.94(2)	70MM	T
	gl	0.05(KCl)	25	5.77	10.65		71GNa	T
	gl	0.1 ($NaClO_4$)	25	5.83	10.74	14.04	71GS	T
	gl	0.1 (KNO_3)	25	5.79	10.57	14.68	71LN	T
	gl	→ 0	10	6.28(1)	11.42(2)	14.93(3)	72IJ	R
			25	6.13(1)	11.05(2)	14.23(3)		
			40	6.00(1)	10.76(2)	13.76(3)		

TABLE 3.3. (continued)

Metal	Method	I/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Ni(II)	gl	0.05(KCl)	25	5.80	10.65		72GS	T
	gl	0.1 (KNO$_3$)	25	5.94	10.79	14.00	72UT	T
	gl	1.0 (NaClO$_4$)	25	5.69	10.50	13.94	73MS	T
	gl	0.1 (KNO$_3$)	25	5.83	10.53	13.83	74MM	T
		0.1 (NaClO$_4$)	25	5.96	10.72	14.01		
	elph	0.5 (KNO$_3$)	25	5.69	10.06	13.44	75CB	D
	gl	0.1 (KNO$_3$)	25	5.75(2)	10.65(1)		75IP	T
	gl	0.2 (KCl)	25	5.65	10.40	A	75SG	T
	gl	0.1 (KNO$_3$)	25	5.74(2)	10.55(3)	13.95(3)	76DO	T
	gl	0.1 (NaClO$_4$)	30	5.69	10.09		77RS	Rj
				log β_{MHL}=11.35				
				log $\beta_{MH_2L_2}$=24.04				
				log β_{MHL_2}=17.33				
	gl	1.0 (NaCl)	25	5.80	10.588	14.308	78BB	T
	gl	1.0 (NaCl)	25	5.53(3)	10.26(4)	13.59(5)	78BB	T
	gl	1.0 (NaCl)	25	5.625(5)	10.356(7)	13.75(1)	78BB	R
	gl	1.0 (NaCl)	25	5.625(10)	10.398(22)	13.911(45)	78BB	R
	gl	1.0 (NaCl)	25	5.600(15)	10.325(25)	13.65(4)	78BB	R
	gl	1.0 (NaCl)	25	5.625(17)	10.381(20)	13.805(75)	78BB	R
	gl	1.0 (NaClO$_4$)	25	5.69	10.51	13.95	79EB	T
	gl	0.5 (KNO$_3$)	30	5.55(1)	10.17(1)	13.41(2)	79EM	D
	gl	2.5 (KNO$_3$)	25	5.33			79FS	D
	gl	0.2 (KCl)	25	5.65	10.40		79SG	T
	gl	0.2 (NaNO$_3$)	30	5.83	10.64		81RSb	D
	elph	0.1 (NaClO$_4$)	35	6.56	10.39		84YS	Rj
	gl	3.0 (NaClO$_4$)	25	5.74	10.70	14.44	86IP	T
	gl	0.1 (KNO$_3$)	35	log K(M + HL)=2.59			86RRb	Rj
	gl	→ 0	15	6.05(3)	10.99(3)	14.52(9)	86VK	R
			25	6.15(3)	11.12(3)	14.63(10)		
			35	6.25(3)	11.27(3)	14.76(10)		
Cu(I)	red	0.3 (K$_2$SO$_4$)	25		10.0		61JW	D
Cu(II)	Cu	0.03	20		16.4		34FR	D
	gl	0.5 (KNO$_3$)	20	8.22	15.17		45FL	D
				log K(ML$_2$ + L)=1				
	pol	0.1 (KNO$_3$)	25		15.13		46K	T
		1.0 (KNO$_3$)	20		15.28	16.25		
	sol	→ 0	25	8.29	15.90		48K	T
	pol	0.05(KH$_2$PO$_4$)			15.1		49LO	Rj
	gl	0.01	25	8.51	15.42		49MM	D
	gl,sol	→ 0	25	8.62	15.59		51Ma	T
	E,pol	0.06(KH$_2$PO$_4$)	25		15.1		52LD	Rj
	gl	0.1 (NaClO$_4$)	25	8.38	15.25		54BC	T
	gl	0.1 (KCl)	20	8.12	15.03		54IW	T
	gl,Cu	?	20	8.5	15.5		55DK	D
	gl	0.001	20	8.60	15.54		56CD	D
	pol	0.001	20		15.20			
	gl	0.05	32	8.13	14.98		56DR	D
	ix	?	22	8.1	15.0		57WF	T

TABLE 3.3. (continued)

Metal	Method	$\underline{I}$/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Cu(II)	gl	0.09(KCl)	0.35	8.61	15.95		57MM	T
			30	8.04	14.43			
			48.8	7.73	14.22			
	gl	0.01($NaClO_4$)	20	8.34	15.39		60AS	D
		0.0001	20	8.60	15.73			
	sp,gl	0.1 (KNO_3)	25	8.15	15.08		61DR	T
	gl	0.1 (KNO_3)	25	8.07	14.97		61MM	T
	red	0.3 (K_2SO_4)	25		15.2	15.67	61JW	T
	pol	0.25	25		14.6		63GT	D
	gl	0.15($NaClO_4$)	25	8.18	15.02		63MP	T
		1.0 ($NaClO_4$)	25	8.33	15.20			R
	gl	$\rightarrow$ 0	20	8.59	15.83		64IC	T
			30	8.47	15.51			
	elph	0.1 (KNO_3)	20	8.6	15.8	15.95	64J	Rj
	elph	0.1 (KNO_3)	20	7.8	15.9		64JM	Rj
	gl	0.05($NaClO_4$)	25	8.23	15.04		64MPa	R
		0.16($NaClO_4$)		8.17	15.01			
		0.36($NaClO_4$)		8.15	15.04			
		0.64($NaClO_4$)		8.18	15.11			
		1.0 ($NaClO_4$)		8.30	15.20			
		2.0 ($NaClO_4$)		8.47	15.56			
	gl	1.0 (NH_4ClO_4)	25	8.29	15.30		65BM	T
	sp	1.0 ($NaClO_4$)	25	8.33	15.20		65MB	T
	gl	0.2 (KCl)	15	8.54	15.54		65SMb	D
			25	8.46	15.29			
			40	8.25	14.89			
	gl	$\rightarrow$ 0	10	8.85(3)	16.21(3)		66AG	T
			25	8.58(3)	15.67(3)			
			40	8.42(3)	15.27(3)			
	gl	0.5 (KCl)	25	8.11	14.43		66LHa	T
	gl	0.1 (KNO_3)	20	8.313	15.363		67GN	T
			25	8.23	15.19			
			30	8.17	15.06			
	gl	0.1 ($NaClO_4$)	25	8.22(5)	15.14(5)		67SG	T
	gl	0.5 (KCl)	25	8.12	14.87	15.3	68LB	T
	gl	0.2 (KNO_3)	?	log $\underline{K}$(ML_2 + L)=1.34			68GS	D
	gl	0.15(KNO_3)	37	8.056(25)	14.784(47)		69CP	T
	gl	0.1 (KNO_3)	25	8.23	15.19		69G	T
	sp	0.5 ($NaClO_4$)	25	8.16(1)	15.07(2)		69PP	T
	gl	0.1 (KNO_3)	25	8.20			69YH	T
	gl	0.2 ($NaClO_4$)	25	8.79(4)	16.13(7)		70CBc	Rj
	gl	0.5 ($LiClO_4$)	25	8.05(2)	14.84(2)		70FR	T
	gl	0.1 ($NaClO_4$)	25	8.27(1)	15.19		70GS	T
	gl	0.1 ($NaClO_4$)	25	8.22	15.02		70L	D
	gl	0.05(KCl)	25	8.18	15.05		71GNa	T
	gl	0.1 (KNO_3)	25	8.20	15.10		71YM	T
	gl	0.05(KCl)	25	8.22	15.11		72GS	T

TABLE 3.3. (continued)

Metal	Method	$\underline{I}$/mol dm^{-3}	T/^oC	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Cu(II)	gl	→ 0	10	8.85(2)	16.37(2)		72IJ	T
			25	8.57(2)	15.83(2)			
			40	8.33(2)	15.33(2)			
	gl	0.2 (KCl)	25	8.07	14.84		73GS	T
	Cu	0.1 (KNO_3)	25	8.07	14.92		73HR	T
	gl	0.24(KCl)	25	8.48(10)	14.97(13)		74FL	Rj
	elph	0.5 (KNO_3)	15	7.94	14.73		75CB	D
	gl	0.1 (KNO_3)	25	8.21(1)	15.09(1)		75IP	T
	Cu	0.1 (KNO_3)	25		15.28		75NW	T
	gl	0.1 ($NaNO_3$)	25	8.130(4)	14.970(7)		75SS	T
	gl	0.1 (KNO_3)	25	8.14(1)	14.96(3)		77DO	T
	gl	0.1 ($NaNO_3$)	25	8.07	14.88		78FM	T
	gl	0.12(NaCl)	25	8.18(4)			78RM	D
	gl	0.5 (KNO_3)	30	7.72(10)	14.61(12)		79EM	D
	gl	2.5 (KNO_3)	25	8.38			79FS	D
	gl	0.2 (KNO_3)	25	8.16	14.98		79MB	T
	gl	0.15(KNO_3)	37	7.98	14.65	11.2	79SP	T
	gl	0.1 ($NaClO_4$)	30	8.07(2)	14.86(3)		80AS	T
	gl	0.1 ($NaNO_3$)	25	8.132(8)	14.966(13)		81IS	T
	gl	0.2 ($NaNO_3$)	30	8.19	15.04		81RSb	D
	elph	0.1 ($NaClO_4$)	35	8.02	14.62		84SY	D
	Cu/Hg	0.1 (KNO_3)	25	8.23			86DV	D
	gl	0.2 (KNO_3)	35	8.00	14.86		87PS	T
Zn(II)	gl	0.5 (KNO_3)	20	4.80	8.94	11.5	45FL	D
	gl	0.01	25	5.33	8.72		49MM	D
	gl	0.01	20	5.2	9.3		50A	D
	gl	→ 0	25	5.52	9.96		51Mc	T
	gl	0.01	22		9.2		52P	D
	gl	0.1 (KCl)	20	5.16	9.50		54IW	T
	gl	0.15(KNO_3)	25	5.42	9.94		55LM	D
	gl	0.1 (KNO_3)	25	5.03	9.30		61MM	T
	elph	0.1 (KNO_3)	20	5.9	10.1	13.2	64J	Rj
	gl	0.65(KCl)	10	4.96	9.24	11.9	64LS	T
			25	4.88	9.01	11.0		
	gl	0.2 (KCl)	15	5.27	9.58		65SMa	D
			25	5.19	9.41			
			40	5.07	9.14			
	gl	0.5 (KCl)	25	4.88	9.01	11.02	66LHa	T
	Zn/Hg	3.0 ($NaClO_4$)	20	3.70	7.74	12.17	67K	Rj
	gl	0.5 (KCl)	25	4.88	9.11	11.56	68LB	R
	gl	0.15(KNO_3)	37	4.898(20)	9.007(22)	11.314(34)	69CP	R
	gl	0.1 (KNO_3)	25	4.96	9.20	11.74	69G	D
	gl	? ($NaClO_4$)	25	5.24(8)	9.65(8)		70CBa	Rj
	gl	0.5 (KCl)	25	4.85	9.14	11.81	70FE	T
	gl	0.5 ($LiClO_4$)	25	4.81(1)	9.00(1)	11.51(1)	70FR	R

TABLE 3.3. (continued)

Metal	Method	I/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Zn(II)	gl	0.05(KCl)	25	5.06	9.44		71GNa	T
	gl	0.1 (NaClO$_4$)	25	4.96(7)	9.19		71GS	T
	gl	0.5 (KCl)	25	4.88	9.11	11.56	71LL	R
	gl	1.0 (KNO$_3$)	25	4.892(3)	9.066(6)	11.507(15)	72BPb	T
	gl	→ 0	10	5.50	10.07	12.70	72IJ	T
			25	5.38	9.81	12.33		
			40	5.29	9.58	11.98		
	NMR	0.5 (NaCl)	31.6	5.92	10.05		73H	D
	H	0.1 (KCl)	5	5.156(70)			73RD	T
			25	5.052(70)				
			45	4.951(70)				
	gl	0.1 (KNO$_3$)	25	5.08	9.14	11.53	74MM	T
		0.1 (NaClO$_4$)	25	5.19	9.33	12.06		
	gl	3.0 (NaClO$_4$)	25	4.909(21)	8.997(43)	11.306(35)	75CM	T
				log β_{MHL}=9.297(239)				
				log $\beta_{MH_{-1}L}$=-2.706(384)				
	gl	0.1 (KNO$_3$)	25	4.96(2)	9.19(3)	11.65(3)	75DO	T
	elph	0.5 (KNO$_3$)	15	5.28	9.36	12.02	75CB	D
	gl	0.1 (KNO$_3$)	25	4.93(1)	9.26(1)		75IP	T
	gl	0.2 (KCl)	25	4.84	9.02		78SK	T
	gl	0.15(KNO$_3$)	37	4.88	8.95	11.27	79SP	R
				log $\beta_{MH_{-1}L}$=-3.76				
	gl	0.15(NaClO$_4$)	37	4.832(5)	8.92(1)	10.76(13)	81AB	T
				log β_{MHL}=10.07(8)				
				log $\beta_{MH_{-1}L}$=-4.23(56)				
				log $\beta_{MH_{-1}A_2}$=-0.59(5)				
	gl	0.2 (KNO$_3$)	30	5.02	9.22		81RSb	D
	elph	0.1 (NaClO$_4$)	35	4.60	10.01		84SY	D
	Zn/Hg	0.1 (KNO$_3$)	25	5.09(3)	9.78(3)	11.85(9)	85DV	T
	gl	0.1 (KNO$_3$)	35	log K(M + HL)=3.04			86RRb	Rj

Only one work (83MD) was published reliable data on the Cr(II)-glycine system; the other two (70FK and 70FMa) listed in Table 2.3 were rejected, although a source of serious error is not apparent from the publications. The authors found that Cr(II) formed more stable complexes with glycine than did Cu(II), which is evidently unrealistic. The complex formation equilibrium between Cr(III) and glycine is extremly slow, and thus accurate stability constants can be obtained only by means of very precise and sometimes sophisticated experimental techniques. With regard to the differences in experimental conditions (temperature and ionic strength), the values in 65MB, 84AB and 84YS, obtained by different methods (pH-metry, spectrophotometry and electrophoresis) exhibit satisfactory agreement and can therefore be regarded as tentative data. In 73BF, only the formation of carboxylate coordinated, protonated complexes is assumed in the acidic pH range. As a consequence of the lack of sufficient experimental details, the data are to be taken as doubtful.

For Mn(II), most of the reported data (51Mc, 52K, 64BD, 64LS, 68LB, 69CP, 69G, 72IJ, 74MM) seem to be reliable. Due to the rather weak complexation between Mn(II) and glycine, accurate constants can be obtained only on the mono complexes. The values in 64J, 64JM and 75CB determined from paper electrophoretic measurements are significantly larger than most of the other data, and thus were omitted from the evaluation. In some cases the non-ensurance of a constant ionic strength (49MM, 53A) or the insufficient experimental details (69HL, 85VD, 86RRb) allow classification of the data only as doubtful. The mean values calculated from the reliable data at 25 ^{0}C and I = 0 and 0.1 mol dm^{-3} may be accepted tentatively; they are listed in Table 3.4.

Similarly to Mn(II), Fe(II) forms relatively weak complexes with simple amino acids. The difficulty in determination (the metal ion competition is too weak for accurate pH-metric determination) and the air-sensitivity of the metal ion have the result that only few reliable data are available (59P, 69G, 72IJ, 87M). Further, because of the large variations in the experimental conditions, recommended data cannot be given. The data relating to the mono complex of Fe(III) in references 58Pc and 86A are rather high and differs from each other by two orders of magnitude, thus must be classified as doubtful values; further investigations are needed prior to any recommendation.

The constants obtained from pH-metric determinations at low ionic strength ($\leq$ 0.02 mol dm^{-3}) in the Co(II)-glycine system are to be regarded as doubtful values (49MM, 50A, 52P). Those reported in references 64J, 64JM, 79EM and 84YS are significantly larger than all others and were consequently rejected. The remaining values, however, are satisfactorily close in magnitude to provide tentative stability constants. The mean values calculated from these determinations are given in Table 3.4.

TABLE 3.4. Recommended (R) and Tentative (T) Values for the Stability Constants of Glycinato Complexes with 3d Transition Metal Ions

Metal	I/mol dm^{-3}	T/^{0}C	log β_{ML}	Category	log β_{ML_2}	Category	log β_{ML_3}	Category
Co(II)	0	25	5.10±0.09	T	9.10±0.10	T		
	0.1-0.2	25	4.66±0.07	T	8.51±0.16	T	10.83±0.17	T
Ni(II)	0	25	6.16±0.02	R	11.11±0.04	R	14.43±0.23	T
	0.1-0.2	25	5.80±0.10	T	10.62±0.12	T	13.97±0.12	T
	0.5	25	5.64±0.04	R	10.35±0.21	T	13.79±0.25	T
	1.0	25	5.66±0.08	T	10.44±0.11	T	13.89±0.21	T
Cu(II)	0	25	8.52±0.15	T	15.75±0.14	T		
	0.1-0.2	25	8.20±0.10	T	15.07±0.13	T		
	0.5	25	8.11±0.05	R	14.80±0.26	T		
	1.0	25	8.31±0.02	R	15.23±0.05	R		
Zn(II)	0	25	5.45±0.10	T	9.91±0.07	T	12.33	T
	0.1-0.2	25	5.03±0.10	T	9.23±0.11	T	11.77±0.20	T
	0.15	37	4.87±0.04	R	8.96±0.05	R	11.25±0.08	T
	0.5	25	4.86±0.03	R	9.07±0.05	R	11.49±0.29	T

Abbreviations used in the table are explained on page 602

Due to the biological importance and the fairly strong complex formation, the complexation equilibria of glycine with Ni(II), Cu(II) and Zn(II) are the most widely studied. As a well-defined equilibrium system, the nickel(II)-glycine has been recommended for testing of the potentiometric apparatus and technique for the determination of metal complex equilibrium constants (87BO).
The early values in 34FR, 49MM, 50A, 56CD, 60AS) are imprecise because the ionic background was low and varied excessively during titration. In references 49LO and 52LD, a dihydrogenphosphate/hydrogenphosphate buffer in 0.05-0.06 mol dm^{-3} concentration was used as a background electrolyte, but this cannot be regarded as an inert salt as concerns the copper(II) ion. References 55DK, 56DR, 63GT, 67K, 68GS, 70CBa, 70L, 77RS, 79FS, 81RSb, 84SY, 86DV and 86RRb do not contain sufficient experimental details to permit an objective evaluation. The constants reported in 55LM, 64J, 64JM, 65SMa, 70CBa, 70CBc, 81RSb and 84YS are abnormally high (cf. cobalt(II)) and hence were rejected. The stepwise constants in references 67K, 73H and 74FL show an unacceptable order. The accuracy of the pH measurements reported in 79EM is rather low ($\pm$0.03 pH unit), and as a result the constants determined from this measurement are regarded as doubtful. The values in 78RM for the Cu(II)-glycine complexes seem to be reliable, although the paper also presents stability constants for the copper(II)-D-penicillamine system, where, an irreversible redox reaction takes place between the reactants.

The remaining data pass the acceptance criteria and there are sufficient reports under identical experimental conditions to allow the presentation of recommended and tentative data for these metal ions in different ionic backgrounds. The mean values calculated from these determinations are listed in Table 3.4. For illustration the accepted stability constants for the nickel(II) and copper(II)-glycine systems as functions of the ionic strength are depicted in Figures 2 and 3.

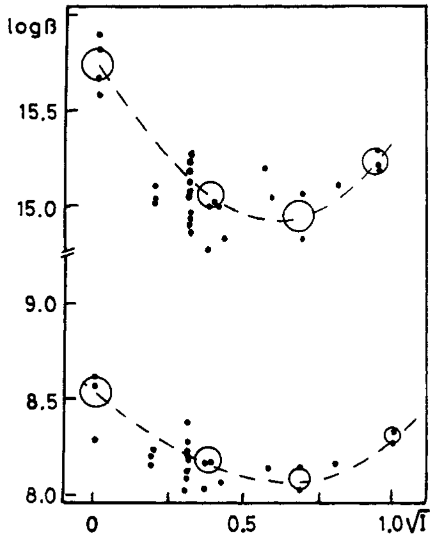

Fig. 2. The ionic strength dependence of the stability constants of copper(II)-glycine complexes CuA and CuA_2 at 25 °C.

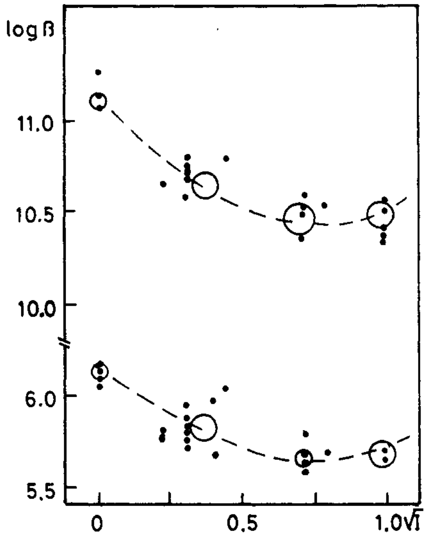

Fig. 3. The ionic strength dependence of the stability constants of nickel(II)-glycine complexes NiA and NiA_2 at 25 °C.

3.3. Complex formation with group 4d and 5d transition metal ions

The literature data on the group 4d and 5d transition metal complexes of glycine are listed in Table 3.5.

As concerns these metal ions, enough data to suggest at least tentative stability constants are available only for Ag(I) and Cd(II). The single values for Zr(IV), Rh(III), Hf(IV), Os(IV) and Au(III) may be regarded merely as informatory data. For Pd(II) the values in 49MM and 73FA, although they are in

TABLE 3.5. Stability Constants of Complexes of Glycine with 4d and 5d Transition Metal Ions (Literature Values)

Metal	Method	I/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Zr(IV)	sp	0.1	?	log K(M + HL)=4.01(9)			76KV	D
Rh(III)	gl	? (Cl-)	27	7.34	10.37		74FAa	D
Pd(II)	gl	0.01	25	9.12	17.55		49MM	Rj
	gl	?	27		17.58		73FA	Rj
	gl	0.5 (KNO_3)	20	10.38(10)	19.29(10)		74KH	D
	sp	1.0 ($NaClO_4$)	20	15.25	27.50		76AM	T
Ag(I)	sol	$\to$ 0	25	4.28			41KRa	D
	gl	0.5 (KNO_3)	20	3.7	7.0		45FL	D
	Ag	0.1	19	3.59	7.24		47DP	D
	gl,sol	$\to$ 0	25	3.51	6.89		51Mb	D
	gl	0.02	22	3.7			52P	D
	gl	0.01	25	3.43	6.86		59DG	D
	gl	0.01	5-55	ML -7686.3/T+57.454-0.094725T ML_2 1506.7/T-0.763-0.002879T			59DG	D
	Ag	$\to$ 0	20	4.00	7.29(2)		62A	T
	sol	$\to$ 0	20		7.26(1)		62A	T
	Ag	0.6	25	3.54(3)	6.82(3)		67AM	T
	gl	0.5 (KNO_3)	20	3.22(3)	6.75(1)		68AL	T
	Ag	0.5 (KNO_3)	20		6.85(2)		68AL	T
	gl	0.5 (KNO_3)	25	3.15	6.53		68TV	T
	gl	0.5 (KNO_3)	0	3.44	7.43		70VT	T
			15	3.24	6.96			
			40	3.03	6.18			
	Ag,gl	0.1 (KNO_3)	25	3.01(1)	6.22(3)		75IP	T
				log K(M + HL)=1.40(5)				
	gl	0.2 ($NaClO_4$)	30	3.54(5)	6.97(5)		75JB	T
	Ag	$\to$ 0	30	3.98	6.80		77PU	T
		0.1 (KNO_3)	30	3.74(7)	6.57(1)			
	Ag,gl	0.1 (KNO_3)	25	2.83(1)	6.27(1)		78SP	T
	gl	3.0 ($LiClO_4$)	25	3.28(2)	6.96(3)		80OZ	T
				log β_{MHL}=9.99(20)				
				log $\beta_{MH_{-1}L}$=-6.48(15)				
	gl	0.1	30	3.98	6.80		81PU	T
Cd(II)	gl	0.5 (KNO_3)	20	3.88	7.06	8.98	45FL	D
	gl	0.01	25	4.74	8.60		49MM	Rj
	gl	0.01	20	4.5	8.10		50A	D
	gl	0.01	22		7.9		52P	D
	gl	$\to$ 0	25	4.80	8.83		55EM	T
	pol	0.15	25			9.94	56LW	T

Abbreviations used in the table are explained on page 602

TABLE 3.5. (continued)

Metal	Method	I/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Cd(II)	gl	0.1 (KNO$_3$)	25	4.27	7.73		61MM	T
	pol			4.65	8.01			
	pol	1.0	30			9.80	62RS	D
	pol	2.0 (KNO$_3$)	25	5.68(10)	8.45(10)	11.0(1)	62SC	D
	elph	0.1 (KNO$_3$)	20	6.0	9.9	12.5	64J	Rj
	elph	0.1 (KNO$_3$)	20	6.1	10.0	12.8	64JM	Rj
	pol	1.0 (KNO$_3$)	30		8.08	9.78	64RSa	T
				log $\beta_{ML_2(OH)}$=9.27				
	gl	0.5 (KNO$_3$)	25	4.18	7.50	9.76	69HL	T
	gl	0.1 (KCl)	5	4.37(3)	7.86(10)		69MG	T
			25	3.95(10)	7.17			
			45	3.86(5)	6.78			
	Cd/Hg	2.0 (NaNO$_3$)	25	5.08	8.88		71FD	T
	gl	1.0 (KNO$_3$)	25	4.135(3)	7.603(6)	9.738(10)	72BPa	T
	gl	→ 0	10	4.73(2)	8.49(2)	11.02(5)	72IJ	T
			25	4.69(1)	8.40(1)	10.68(5)		
			40	4.60(2)	8.20(2)	10.20(5)		
	gl	0.1 (KNO$_3$)	25	4.26(1)	8.08(2)		75IP	T
	gl	0.2 (NaClO$_4$)	30	4.24(5)	7.93(6)		75JB	T
	gl	0.1 (KNO$_3$)	25	4.5	8.0		75HV	D
	Cd	0.1 (KNO$_3$)	25	4.4	8.0		75HV	D
				4.5	8.0			
	Cd/Hg	2.5 (KNO$_3$)	20	4.29			77SF	T
	pol	0.5 (KNO$_3$)	23	4.44	7.34	9.08	78AE	T
	gl	2.5 (KNO$_3$)	25	4.29			79FS	T
	pol	0.1 (NaClO$_4$)	25	3.78	6.0	8.81	79GB	T
	pol	0.2 (NaClO$_4$)	35	4.26	7.85	10.07	79JK	T
	gl	0.2 (NaClO$_4$)	25	3.98	7.42		79NL	D
	cpot	0.2 (NaClO$_4$)	25	3.90	7.74		79NL	D
	pol	0.3 (KNO$_3$)	30	4.31	7.92	10.06	81AA	T
	gl	3.0 (LiClO$_4$)	25	4.28(1)	7.80(1)		81M	T
	gl	3.0 (NaClO$_4$)	25	4.01	7.49		82MO	T
	pol	1.0 (KNO$_3$)	30	4.30	7.70	9.80	84CG	T
	pol	1.0 (KNO$_3$)	25	4.54	8.04	9.74	84MR	T
	gl	0.2 (KNO$_3$)	25	4.26	7.83	10.51	86SV	T
	gl	0.1 (KNO$_3$)	25	4.24(1)	7.85(1)		90BD	T
	cv	0.1 (KNO$_3$)	25		7.74(5)	9.25(6)	90BD	T
Hf(IV)	kin	?	25	log K(M + HL)=1.47(7)			71KP	D
Os(IV)	gl	? (Cl-)	28		5.04		74FAc	D
Au(III)	gl	? (Cl-)	25	7.05	10.57		74FAb	D
Hg(II)	gl	0.5 (KNO$_3$)	20	10.3	19.2		45FL	D
	gl	0.01	22		18.2		52P	D
Hg(II)	gl	→ 0	25	log K($HgCl_2+L^-=HgClL+Cl^-$)=3.42(1)			66PC	D
				log K($HgClL+L^-=HgL_2+Cl^-$)=2.61(2)				
	pol	0.6 (KNO$_3$)	25		18.36(4)		66TA	D
MeHg(I)	NMR	0.2-0.3	25	7.88			74RO	D
	gl,NMR	?	22	6.07			76HS	D
	gl	1.0 (NaNO$_3$)	25	7.518(50)	9.468(225)		78JI	D
PhHg(I)	gl	?	22	7.13			76HS	D

good agreement, are rejected as the rather strong chloro complex formation was not taken into account. The data obtained by pH-metry (74KH) are regarded as doubtful since this method cannot give reliable constants due to the very high complex stabilities and thus the very weak proton competition. The stability constants in 76AM obtained by spectrophotometric method are much greater than in the proceeding cases (49MM, 73FA) since they refer to equilibria involving aquo ions. These values seems to be reliable and can be accepted tentatively.

For Ag(I), most of the published data (51Mb, 59DG, 62A, 67AM, 68AL, 70VT, 75IP, 75JB,77PU, 78SP, 80OZ) seem to be reliable, and only a few have been omitted from the evaluation because of the lack of a constant ionic strength (41KRa, 47DP, 52P). The remaining data are sufficient for tentative stability constants relating to t = 20-30 ^{o}C and I = 0.1-0.6 mol dm^{-3} to be given (see Table 3.6). (At I = 0 mol dm^{-3} the values are 0.2-0.4 log units higher.) It is worthwhile to mention that the stability constants obtained by means of a combined pH-potentiometric method with a silver/silver chloride - glass electrode system are 0.4-0.5 log units lower than those measured pH-metrically (cf. Pb(II) complexes).

Cd(II) forms octahedral complexes with glycinate and can coordinate up to three ligand molecules. Hence formation of the complex CdL_3 also has to be taken into account in the event of a large enough excess of ligand. Papers which did not consider this (75HV, 77SF, 79FS) have been omitted from the evaluation. The ability of Cd(II) to form chloro complexes is rather strong (76MS), and the formation of mixed chloro complexes cannot be negligible; hence the values obtained in chloride containing media in 49MM and 69MG have been rejected. In some cases, the insufficiency of the reported experimental details (62RS, 79NL) or the lack of a constant ionic strength (50A, 52P) was the reason for omission from the assessment. The values obtained from the electrophoretic mobility curve of the complexes in 64J and 64JM are 1-2 log units higher than the other data. Similarly, the results reported in 71FD are again significantly higher than can be accepted. Evaluation of the remaining values (obtained mostly by pH-metry or polarography) yields the tentative stability constants given in Table 3.6.

TABLE 3.6. Tentative (T) Values for the Stability Constants of Glycinato Complexes with 4d and 5d Transition Metal Ions

Metal	I/mol dm^{-3}	T/^{o}C	log β_{ML}	Category	log β_{ML_2}	Category	log β_{ML_3}	Category
Ag(I)	0	20-30	3.8 $\pm$0.3	T	7.1 $\pm$0.3	T		
	0.1-0.6	25-30	3.45$\pm$0.24	T	6.80$\pm$0.20	T		
Cd(II)	0	25	4.69	T	8.40	T	10.68	T
	0.1-0.5	25-30	4.28$\pm$0.18	T	7.72$\pm$0.25	T	9.93$\pm$0.34	T
	1.0-3.0	25-30	4.26$\pm$0.18	T	7.75$\pm$0.08	T	9.73$\pm$0.24	T

pH-Metry, polarography and NMR have been applied to obtain the formation constants of the mercury(II), methylmercury(I) and phenylmercury(I) complexes. However, the relative scarcity of the data and the very different experimental conditions allow their classification only as informatory data. The values in 66PC for the ligand replacement reactions of glycine with $HgCl_2$(aq) could be compared with other reported values (45FL, 52P, 66TA) if log β values for the Hg^{2+} - Cl^- system were taken into account. Unfortunately, values valid for the given experimental conditions (25 °C and $\underline{I}$ = 0 mol dm^{-3}) are not available (76MS).

3.4. Complex formation with group 4f and 5f metal ions

The stability constants of the f-block elements, and of Sc(III) and Y(III), which are also considered here, are listed in Table 3.7.

The stability constants reported for Sc(III) in references 80SK and 85SA seem to be dependable and can be accepted tentatively; the single datum on Y(III), however, is merely of informatory value (77MS).

TABLE 3.7. Stability Constants of Complexes of Glycine with 4f and 5f Transition Metal Ions (Literature Values)

Metal	Method	$\underline{I}$/mol dm^{-3}	T/°C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
Sc(III)	gl	0.2 ($NaClO_4$)	30	7.749			77MS	D
	gl	0.1 (NaCl)	20	6.95			80SK	T
	gl,Hg	0.1 ($NaClO_4$)	20	7.13(10)			85SA	T
Y(III)	gl	0.2 ($NaClO_4$)	30	5.055			77MS	D
<u>Lanthanides</u>								
La(III)	gl	0.1 (KCl)	30	3.23	6.15		62CTb	T
	gl	0.2 ($NaClO_4$)	30	3.850			77MS	T
	gl	0.1 (NaCl)	20	3.56			80SK	T
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.23			86RRa	Rj
	gl	0.2 ($NaClO_4$)	25	5.32			86LS	Rj
Ce(III)	gl	0.1 (KCl)	30	3.40	6.40		62CTb	T
	dis	2.0 ($NaClO_4$)	0	log $\underline{K}$(M + HL)=0.34(9)			68TC	T
			25	0.53(5)				
			40	0.70(5)				
			55	0.76(4)				
Ce(III)	gl	0.2 ($NaClO_4$)	30	4.455			77MS	T
	gl	0.2 ($NaClO_4$)	25	5.38			86LS	Rj
Ce(IV)	pol	2.0 ($NaClO_4$)	20	log $\underline{K}$($M+H_2L=ML+2H$)=0.95			64T	D
				log $\underline{K}$($ML+H_2L=ML_2+2H$)=-0.46				
				log $\underline{K}$($ML_2+H_2L=ML_3+2H$)=-0.92				
				log $\underline{K}$($ML_3+H_2L=ML_4+2H$)=1.19(?)				
Pr(III)	gl	0.1 (KCl)	30	3.64	6.96		62CTb	T
	gl	0.2 ($NaClO_4$)	30	4.500			77MS	T
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.53			86RRa	Rj
	gl	0.2 ($NaClO_4$)	25	5.55			86LS	Rj
Nd(III)	gl	0.1 (KCl)	30	3.71	7.01		62CTb	T
	E	0.02	?	log $\underline{K}$(MOH + L)=9.46(8)			68KR	D
	E	0.02	?	3.67(6)			68RK	D
	sp	0.1	?	4.74			69SM	D
	gl	0.2 ($NaClO_4$)	30	4.615			77MS	T

Abbreviations used in the table are explained on page 602

TABLE 3.7. (continued)

Metal	Method	I/mol dm^{-3}	T/^{o}C	log β_{ML}	log β_{ML_2}	log β_{ML_3}	Ref	Category
	gl	0.15($NaClO_4$)	25	3.26(9)			79HJ	T
				log $\beta_{MH_{-1}L}$=-4.96(9)				
	gl	0.1	25	4.00(2)			81PBb	D
	sp	0.1	25	3.8			81PBb	D
	pol	1.0 (KCl)	32	4.00			81PC	T
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.71			86RRa	Rj
	gl	0.2 ($NaClO_4$)	25	5.68			86LS	Rj
Pm(III)	dis	2.0 ($NaClO_4$)	0	log $\underline{K}$(M + HL)=0.45(5)			68TC	T
			11	0.52(8)				
			25	0.67(3)				
			40	0.79(3)				
Sm(III)	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.82			86RRa	Rj
	gl	0.2 ($NaClO_4$)	25	5.84			86LS	Rj
Eu(III)	dis	2.0 ($NaClO_4$)	0	log $\underline{K}$(M + HL)=0.61(3)			68TC	T
			25	0.70(3)				
			40	0.78(3)				
			55	0.90(2)				
Gd(III)	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.72			86RRa	Rj
Dy(III)	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.86			86RRa	Rj
Ho(III)	gl	0.03	25	4.44(8)			81PBa	D
Er(III)	gl	0.03	25	4.45(8)			81PBa	D
	gl	0.1 (KNO_3)	35	log $\underline{K}$(M + HL)=3.93			86RRa	Rj
Yb(III)	gl	0.03	25	4.51(8)			81PBa	D
Lu(III)	gl	0.03	25	4.51(8)			81PBa	D
<u>Actinides</u>								
Th(IV)	gl	0.5 (KNO_3)	25	8.91(5)			71KS	T
Th(IV)	ix	0.5 (KNO_3)	20	8.90(10)			80S	T
	gl,Th/Hg	0.1 ($NaClO_4$)	20	9.68(14)			85SA	D
U(VI)	gl	0.1 (KCl)		7.53	14.68		62CTa	T
	gl	?	?	8.62			70FMb	D
	gl	0.5	25	7.15			73SK	D
	sp	0.5	25	7.34				
	pol	0.1 ($NaClO_4$)	30	log $\underline{K}$(M + 2HL)=2.14			79RR	T
	pol	0.5 ($NaClO_4$)	26	log $\underline{K}$(M + HL)=1.34(4)			80DD	T
				log $\underline{K}$(M + 2HL)=2.72(4)				
	elph	0.1 ($NaClO_4$)	35	8.02	14.53		84SY	Rj
U(IV)	sp	0.5 (Cl-)	20	10.50(6)			74SK	D
	pol	?	22	10.03	11.3		76NF	D
				log $\underline{K}$(M + 4L)=17.9				
Pu(III)	ix	1.0 (KCl)	18	log $\underline{K}$(M + HL = ML + H)=-3.21(4)			73RK	T
Am(III)	dis	2.0 ($NaClO_4$)	0	log $\underline{K}$(M + HL)=0.48(5)			68TC	T
			11	0.57(2)				
			25	0.69(2)				
			40	0.78(2)				
Cm(III)	dis	2.0 ($NaClO_4$)	0	log $\underline{K}$(M + HL)=0.62(5)			68TC	T
			11	0.66(6)				
			25	0.80(2)				
			40	0.95(2)				

The lanthanide cations form 1:1 and 1:2 complexes with amino acids. The bonding mode of the ligand is questionable, monodentate carboxylato coordination has been suggested e.g. from liquid-liquid distribution measurements in 68TC, whereas other authors (79HJ, 86LS) assume the involvement of the amino nitrogen too in the coordination. Among others, three sets of data have been reported on the complexes of the group 4f cations. Stability constants of the binary and ternary complexes formed in various Ln(III)-glycine-ligand $\underline{B}$ systems have been reported in 86RRa. The formation of protonated complexes has been assumed in the Ln(III)-glycine systems, however no sufficient details are given for the binary systems. Furthermore the stability constants reported are about two-three orders of magnitude higher than those obtained for the Ln(III)-carboxylato complexes. Thus, these values have not been included in the evaluation. Another set of data (86LS) has likewise been rejected, because these values are considerably higher (by 1.5-2.0 log units) than any others. In a few cases (68KR, 68RK, 69SM, 81PBa, 81PBb), the data are probably reliable, but insufficient experimental data are given to allow assessment. The remaining determinations (62CTb, 77MS, 79HJ, 80SK, 81PC) may be accepted tentatively, but they cover a wide range of experimental conditions.

Of the actinides, only for Th(IV) and U(VI) are sufficient data available to allow an objective evaluation. The values in 70FMb, 74SK, 76NF and 85SA must be regarded as doubtful, because of the inadequacy of the reported experimental details. The remaining data (62CTa, 71KS, 73RK, 80S) can be accepted tentatively. Stability constants for complexes involving monodentate carboxylato coordination have been obtained by polarography (79RR, 80DD) and liquid-liquid distribution (68TC), and may also be regarded as tentative data.

3.5. Enthalpies accompanying metal complex formation

The enthalphies accompanying the formation of metal-glycine complexes have been calculated from potentiometric studies at different temperatures and from calorimetric measurements. Literature data reported on Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Pb(II), In(III), and some of the lanthanides and actinides are given in Table 3.8.

The agreement of the values obtained by the two methods is generally poor. The main reasons for the low accuracy of the potentiometrically determined enthalpies are the facts that the precision of the pH measurement was in many cases low ($> \pm 0.01$ unit) (57MM, 64SMa, 64SMb, 65SMa, 65SMb, 73SM), that only two different temperatures were used (64LS), or that the ΔH values are not temperature-independent. In references 66AG, 67AG, 72IJ and 86VK, $\Delta \underline{H}^0$ values were measured calorimetrically at three different temperatures and a considerable variation was detected with temperature (0.5-1.5 kJ mol^{-1} per 10 degrees). Hence, $\Delta \underline{H}^0$ values obtained from temperature-variation measurements are considered doubtful values or in some cases are rejected (57MM, 64LS, 73RD).

TABLE 3.8. Enthalpies for the Formation of Metal Complexes of Glycinate ($kJ\ mol^{-1}$)(Literature Values)

Metal	Method	I/mol dm^{-3}	T/°C	$-\Delta H^o_{ML}$	$-\Delta H^o_{ML_2}$	$-\Delta H^o_{ML_3}$	Ref	Category
Ag(I)	T	0.01	5	-6.90			59DG	D
			15	3.39				
			25	13.97	33.67			
			35	24.97				
			45	36.27				
			55	48.1				
	cal	0.5 (KNO_3)	20	19.2	48.1		70VT	T
	T	0	0-40	15.9	52.0			
Co(II)	T	0	25	11.8(5)	40.6(8)		64BD	T
	T	0.2	15		23.4		64SMb	D
	T	0.2	15-40	8.4	34.8		65SMa	D
	T	0	25	10.37	21.04		67BB	D
	cal	0.1 (KNO_3)	20		27.6		67SSa	T
	cal	0.05(KCl)	25	12.5	31.0		71GNa	T
	cal	0	10	12.6(2)	29.3(2)	44.5(2)	72IJ	T
			25	12.0(3)	26.8(3)	41.1(3)		
			40	9.0(2)	23.3(2)	35.9(3)		
Cu(II)	T	0.09(KCl)	30	29.3			57MM	D
	cal	0	25	25.1	51.9		64IC	T
	T	0.2	15		44.8		64SMa	D
	T	0.2	15-40	20.1	48.5		65SMb	D
	cal	0	10	30.45	59.40		66AG	R
			25	26.02	55.14			
			40	24.05	54.72			
	cal	0	25	28.28	57.10		67BB	D
	cal	0.1 (KNO_3)	20.5		53.5		67SSa	T
	cal	0.05(KCl)	25	28.4	54.4		71GNa	T
	cal	0.1 ($NaClO_4$)	25	25.1	52.7		72IN	R
	cal	0	10	26.1(3)	56.2(4)		72IJ	R
			25	24.4(3)	53.4(4)			
			40	22.9(4)	50.5(4)			
	cal	0.01($HClO_4$)	24.1		56.9		72ST	T
	cal	0.2 (KCl)	25	24.56	56.47		73GS	T
	cal	0.2 (KCl)	25	25.6	53.9		76SG	R
Cd(II)	cal	0	10	9.5(2)	25.1(2)	37.0(5)	72IJ	T
			25	8.9(2)	22.5(2)	35.9(3)		
			40	8.2(2)	20.5(2)	34.7(7)		
Fe(II)	cal	0	10	15.5(9)			72IJ	T
			25	15.3(6)				
			40	14.9(7)				
In(III)	T	0.2 ($NaClO_4$)	25-45	-12.55			73SM	D
Mn(II)	T	0.09(KCl)	30	20.9(12.5)			57MM	Rj
	T	0	25	1.2(3)			64BD	T
	T	0.65(KCl)	10,25	5.9	13.8		64LS	Rj
	cal	0	10	1.7(1)			72IJ	T
			25	1.3(4)				
			40	0.2(5)				

Abbreviations used in the table are explained on page 602

TABLE 3.8. (continued)

Metal	Method	I/mol dm^{-3}	T/^{o}C	$-\Delta H^{o}_{ML}$	$-\Delta H^{o}_{ML_2}$	$-\Delta H^{o}_{ML_3}$	Ref	Category
Ni(II)	T	0	25	17.1(1)	36.7(1.2)		64BD	T
	T	0.65(KCl)	10,25	7.9	31.4		64LS	Rj
	T	0.2	15		36.8		64SMb	D
	T	0.2	15-40	18.0	36.4		65SMb	D
	cal	0	10	21.8	46.0		67AG	T
			25	20.5	40.2			
			40	18.0	37.6			
	cal	0.05(KCl)	25	15.1	35.1		71GNa	D
	cal	0.1 (KNO_3)	25	20.9	39.3		71LN	R
	cal	0	10	19.4(4)	41.6(4)	65.2(4)	72IJ	R
			25	18.3(3)	39.1(3)	62.3(3)		
			40	15.8(4)	35.0(4)	58.0(4)		
	cal	0.01	24.1		36.4(8)		72ST	D
	cal	0.2 (KCl)	25	21.1	42.0		75SG	T
	cal	1.0 ($NaClO_4$)	25	17.24(14)	37.82(21)	60.46(54)	79EB	T
	cal	0.2 (KCl)	25	19.0	39.0		79SG	R
	cal	3.0 ($NaClO_4$)	25	27.3	59.5	95.0	86IP	D
	cal	0	15	18.80(28)	42.08(45)	64.76(40)	86VK	R
			25	17.74(26)	39.98(41)	62.50(39)		
			35	15.85(29)	38.76(49)	61.18(43)		
Pb(II)	T	3.0 ($NaClO_4$)	25	12.4			76CW	T
				(MHL)=25.1(4)				
				(MH-1L)=-16.5(3)				
Zn(II)	T	0.65(KCl)	10,25	8.8	24.7		64LS	D
	T	0.2	15-40	13.8	30.5		65SMb	D
	cal	0	25	14.18			67BB	D
	cal	0.1 (KNO_3)	20		26.4		67SSa	T
	cal	0.05(KCl)	25	8.4	21.8		71GNa	T
	cal	0	10	13.2(3)	28.8(3)	43.6(3)	72IJ	T
			25	11.5(3)	24.5(3)	39.4(3)		
			40	9.3(3)	21.4(3)	36.6(3)		
	T	0.1 (KCl)	5	7.8(2.9)			73RD	D
			25	8.7(2.9)				
			45	9.5(2.9)				
Ce(III)	T	2.0($NaClO_4$)	0-55	-13.8(1.6)			68TC	D
		pH=3.64						
Eu(III)	T	2.0($NaClO_4$)	0-55	-9.6(1.6)			68TC	D
		pH=3.64						
Er(III)	cal	0.03	25	11.2(4)			81PBa	D
Ho(III)	cal	0.03	25	11.3(4)			81PBa	D
Lu(III)	cal	0.03	25	10.6(4)			81PBa	D
Nd(III)	cal	0.03	25	5.7(4)			81PBa	D
Pm(III)	T	2.0($NaClO_4$)	0-55	-14.6(1.6)			68TC	D
		pH=3.64						
Yb(III)	cal	0.03	25	10.5(4)			81PBa	D
Am(III)	T	2.0($NaClO_4$)	0-55	-12.1(1.6)			68TC	D
		pH=3.64						
Cm(III)	T	2.0($NaClO_4$)	0-55	-13.8(2.6)			68TC	D

TABLE 3.9. Recommended (R) Enthalpies for the Formation of Metal Complexes of Glycinate (in kJ mol^{-1})

Metal	Method	$\underline{I}$/mol dm^{-3}	T/^oC	$-\Delta \underline{H}^o_{ML}$	$-\Delta \underline{H}^o_{ML_2}$	$-\Delta \underline{H}^o_{ML_3}$
Ni(II)	cal	0-1.0	25	19.3 ± 1.6	39.6 ± 1.3	61.8 ± 1.1
Cu(II)	cal	0-0.2	25	25.6 ± 1.4	54.3 ± 1.7	

There are two sets of values for the f-block elements, but these differ in sign. In reference 68TC, the $\Delta \underline{H}^o$ values were obtained from the temperature-dependence of stability constants determined from liquid-liquid distribution measurements at low pH, while in references 81PBa and 81PBb provide data originating from direct calorimetric measurements; however, the experimental details are not sufficient to permit a realistic assessment, which must be preceded by further investigations. The $\Delta \underline{H}^o$ values in 86IP are considerably higher than any other data reported on the Ni(II)-glycine system, and accordingly are omitted from the evaluation. The remaining calorimetric data may be utilized to propose recommended values only for the enthalpies of formation of the Ni(II) and Cu(II) complexes at 25 ^oC and $\underline{I}$=0-1.0 mol dm^{-3}. These values are given in Table 3.9.

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