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Thermodynamic parameters for the formation of glycine complexes with magnesium(II), calcium(II), lead(II), manganese(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) at different temperatures and ionic strengths, with particular reference to natural fluid conditions

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Abstract

Protonation constants and Mg^{2+}–, Ca^{2+}–, Pb^{2+}–, Mn^{2+}–, Co^{2+}–, Ni^{2+}–, Cu^{2+}–, Zn^{2+}– and Cd^{2+}–glycine complex formation constants have been determined in different aqueous media at different temperatures. Salt effects are explained by a complex formation model which takes into account the formation of weak species. From the temperature dependence of the formation constants, thermodynamic parameters $\Delta H^{\ominus}$ (and in some cases $\Delta C_p^{\ominus}$) have been obtained. A rigorous analysis of literature data, together with experimental findings, allows recommended formation parameters, in the ranges $0 \leq I_e \leq 1$ mol l^{-1} (I_e is the effective ionic strength) and $5°C \leq T \leq 45°C$, to be obtained. Because the proposed model can be used in any electrolyte mixture in the above I and T ranges, the speciation in seawater, and other natural fluids, can be simulated by appropriate computer programs. The validity of the present approach which takes into account the ionic strength dependence of formation constants, together with the concepts of effective ionic strength and complex formation model, is discussed.

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1. Introduction

Glycine, the simplest amino acid, is the most abundant amino-carboxylic ligand present in natural fluids. It is a widely studied ligand (together with its complexes) in solution [1–5] and the most used model ligand. Recently, Kiss et al. [6] reported a critical survey of stability constants of complexes of glycine based on about 300 literature reports (considering solution studies only). Ni^{2+}–glycine complexes have also been studied [7,8] as a test of potentiometric apparatus and other experimental and calculation techniques for the determination of metal complex formation constants. Nevertheless, some unacceptable discrepancies in the literature formation data, the scarcity of the data on the temperature dependence of the stability constants, and the absence of systematic studies concerning salt effects on thermodynamic formation data, make it necessary to do further studies. Moreover, the uncritical use of the constant-medium method [9–11] (see also Section 4) does not allow weak interactions to be determined, although when considering the species present in multielectrolyte solutions weak complexes may play an important role.

In this paper we reconsider all the information on the complexing ability of glycine with the aim of obtaining both reliable values of the metal complex stability constants and a reliable model for the effect of multielectrolyte media on complex stability. To this end the following studies are reported: (a) protonation of glycine in different salt media; (b) complex formation of glycine with Mg^{2+}, Ca^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}; (c) analysis of literature data; (d) calculation of recommended values from both experimental and literature values; (e) calculation of $\Delta H^{\ominus}$ (and in some cases $\Delta C_p^{\ominus}$); (f) values for weak complex formation, (g) proposal for a general model describing the stability of glycine complexes in multielectrolyte solutions.

2. Experimental

2.1. Chemicals

Glycine (analytical grade from Fluka, Aldrich or C. Erba) was used without further purification. Its purity checked by alkalimetric titrations was greater than 99.8%. Metal chlorides $MgCl_2$, $CaCl_2$, $MnCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ and $CdCl_2$ (Fluka purum p.a.) were standardized by EDTA titrations [12]. Lead(II) perchlorate was prepared by adding $HClO_4$ in small excess to PbO, the Pb^{2+} content was determined by EDTA titration and the excess was determined pH-metrically using the Gran method. Sodium or potassium hydroxide solutions (0.1, 0.5, 1 mol dm^{-3}), prepared by diluting concentrated ampoules, were standardized against potassium biphthalate. Tetraethylammonium iodide (Et_4NI) and tetramethylammonium hydroxide (Me_4NOH) were purified as recommended by Perrin et al. [13]. Hydrochloric acid, nitric acid and perchloric acid solutions were standardized against tris(hydroxymethyl)aminomethane or sodium carbonate. Concentrations of NaOH, KOH or Me_4NOH and strong acids were also checked by cross titrations. NaCl, $NaClO_4$, and Na_2SO_4 (analytical grade from various firms) solutions were prepared by weighing the salts; their concentrations were checked by standard methods. All solutions were prepared with twice distilled water, using grade A glassware.

2.2. Apparatus

Potentiometric measurements were performed using six different types of equipment: (a) a Metrohm E654 potentiometer–Metrohm Dosimat 665 Dispenser (automatic); (b) a Metrom E654 potentiometer–Amel 232 Dispenser (semiautomatic); (c) an Orion 801A potentiometer with an Amel 232 Dispenser (semiautomatic); (d) an Orion 801A–Metrohm Dosimat 665 (manual); (e) a Metrohm E605–Amel 232 Dispenser (manual); (f) a laboratory made system–Amel 232 Dispenser (semiautomatic). The measurement cells (25–50 cm^3) were thermostatted at $T = 25 \pm 0.1°C$. All titrations were carried out by stirring magnetically and by bubbling purified and presaturated N_2 through the solution. The calibration of the electrode couple was achieved by titrating HCl or $HClO_4$ (10 mM) with standard KOH, NaOH or Me_4NOH under the same conditions of temperature and ionic strength as the solution being considered. The reliability of the calibration in the alkaline range was checked by calculating pK_w values.

2.3. Procedure

Each solution investigated was prepared just before measurements in one of two ways: either (a) by mixing in a volumetric flask (100–250 cm^3) a weighted quantity of glycine and a suitable volume of the background salt and metal salt concentrated solutions; or (b) by mixing concentrated solutions of all the components directly in the measurement cell. Calculations performed in trials of these two methods showed no significant differences. The cell solutions were titrated with standard NaOH, KOH or Me_4NOH to 99% neutralization. In most cases, a selected quantity of strong acid (HCl or $HClO_4$) was also added in order to completely protonate the ligand and to calculate the internal E^0 value. Experimental details are reported in Table 1.

2.4. Calculations

The least-squares computer programs ESAB [14] or ESAB2M [15] were used to refine all the parameters of an acid–base titration such as E^0, K_w, junction potential and analytical concentration and to calculate conditional protonation constants. The programs BSTAC [16] and STACO [17] were used for the calculation

Table 1
Experimental details of potentiometric measurements ($T = 5, 10, 15, 20, 25, 30, 35, 40, 45°C$)

System	C_{gly}	C_M	I	No. of titrations (points)	Notes
H^+-gly	2–10	–	0.01–0.09 (NaCl)	90 (2700)	Molar scale
H^+-gly	2–10	–	0.1–0.75 ($NaClO_4$)	72 (2150)	Molar scale
H^+-gly	2–10	–	0.1–0.75 (Et_4NI)	72 (2150)	Molar scale
H^+-gly-SO_4	5–30	Na_2SO_4 10–300	0.05–1 (Na_2SO_4)[a]	40 (1200)	Molar scale
Ca^{2+}-gly	2–10	(Ca^{2+})[b]	0.1–0.75 ($CaCl_2$)	68 (1850)	Molar scale
Mg^{2+}-gly	2–10	(Mg^{2+})[b]	0.1–0.75 ($MgCl_2$)[c]	38 (1000)	Molar scale
Pb^{2+}-gly	2–10	Pb^{2+} 0.5–5	0.1–1 ($NaClO_4$)	54 (1890)	Molar scale
M^{2+}-gly[d]	2–20	M^{2+} 1–10	0.01–0.09 (NaCl)	70 (2000)	Molar scale

[a] $T = 5, 15, 25, 35, 45°C$. [b] Self medium. [c] $T = 10, 25, 40°C$. [d] M^{2+} is Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}.

of formation constants and other titration parameters directly from potentiometric data obtained at different ionic strengths. The first is an implemented version of SUPERQUAD [18], which refined formation constants by minimizing the error squares sum in the e.m.f. readings. STACO is a new computer program which refines formation constants by minimizing the error squares sum in the titrant volume. The distribution of the species was calculated by the computer program ES4EC [16,19–22], which calculated the errors in formation percentages arising from errors in formation constants. ES4EC was also used for simulating titration curves. The dependence on temperature of the formation constants was calculated by the computer programs REGIS [23] and TDA [24]. For the calculation of formation constants of weak complexes from conditional protonation data, the program ES2WC [25] was used. Because Cl^- associates weakly with alkali and alkaline earth cations, we considered in the calculations the effective ionic strength I_e by using the formation constants obtained from preceding work [23]. The estimated standard deviation in calculating I_e, arising from the use of these formation constants is about $0.05I$ (where I is the ionic strength calculated without allowing for the association of alkali and alkaline earth chlorides). In the calculations of metal complex formation constants, the hydrolysis of metal ions was always considered.

3. Results

3.1. Protonation and weak complexes

The protonation of glycine was studied in three steps. (a) At low ionic strength, measurements were performed in NaCl 0.01–0.09 mol kg^{-1} in order to obtain accurate protonation constants which could be extrapolated to zero ionic strength and to obtain reliable thermodynamic parameters $\Delta H^{\ominus}$ and $\Delta C_p^{\ominus}$. Results are reported in Table 2. All the values reported in Table 2 are reproducible and, by

Table 2
Thermodynamic protonation parameters [a] of glycine in aqueous NaCl, $(C_2H_5)_4NI$ and $NaClO_4$ solution at 25°C

Parameter	$I = 0$	$I = 0.01$	$I = 0.04$	$I = 0.09$
$\log K_1^H$	9.7786 ± 0.0011 [b]	9.6929 ± 0.0010 [b]	9.6368 ± 0.008 [b]	9.6070 ± 0.0009 [b]
$\log K_2^H$	2.351 ± 0.001	2.352 ± 0.001	2.352 ± 0.002	2.353 ± 0.001
$\Delta H_1^\ominus$	-44.47 ± 0.08			
$\Delta H_2^\ominus$	-4.2 ± 0.1			
$\Delta C_{p1}^\ominus$	60 ± 7			
$\Delta C_{p2}^\ominus$	151 ± 12			
	$I = 0.1$	$I = 0.25$	$I = 0.5$	$I = 0.75$
$(C_2H_5)_4NI$, molar scale				
$\log K_1^H$	9.543 ± 0.008	9.527 ± 0.012	9.539 ± 0.014	9.547 ± 0.016
$\log K_2^H$	2.376 ± 0.005	2.413 ± 0.008	2.461 ± 0.010	2.496 ± 0.010
	$I = 0.1$	$I = 0.25$	$I = 0.5$	$I = 0.75$
$NaClO_4$, molar scale				
$\log K_1^H$	9.601 ± 0.005	9.575 ± 0.005	8.575 ± 0.005	9.641 ± 0.010
$\log K_2^H$	2.352 ± 0.002	2.364 ± 0.002	2.387 ± 0.004	2.414 ± 0.0
	$I = 0$	$I = 0.1$	$I = 0.5$	$I = 1$
Literature values (see text), molar scale				
$\log K_1^H$	9.767 ± 0.003	9.615 ± 0.003	9.667 ± 0.003	9.707 ± 0.003
$\log K_2^H$	2.347 ± 0.005	2.353 ± 0.005	2.389 ± 0.005	2.447 ± 0.005

[a] $\Delta H^\ominus$ in kJ mol^{-1}, $\Delta C_p^\ominus$ in J K^{-1} mol^{-1}, I in mol kg^{-1}. [b] ± Std. dev.

avoiding systematic errors, accurate. (In this paper we report thermodynamic data at 25°C and various ionic strengths. Complete listings of thermodynamic parameters are reported in Appendix A.). The agreement with the best literature reports [6] on thermodynamic parameters for protonation of glycine is excellent. (b) Measurements in the ionic strength range $0.1 \leq I \leq 0.75$ mol dm^{-3} were performed using tetraethylammonium iodide (Et_4NI) and (c) $NaClO_4$, as background salts. The results are reported in Table 2. Only a few data, in particular at 25°C in $NaClO_4$, are reported in the literature, and in general the accord with the present findings is fairly good. No data were found in Et_4NI aqueous solution, except our previous findings [26] (in accord with present results). The two background salts $NaClO_4$ and Et_4NI were chosen for two reasons. $NaClO_4$ and Et_4NI are considered to be completely dissociated. Sodium does not interact significantly with the amino group and Et_4N^+ does not interact significantly with the carboxylic group, as widely reported in previous works (see Ref. [31] and references cited therein). Therefore it is possible to attribute the differences in protonation constants to the formation of some weak complexes, using the following simple model: (i) Na^+ forms weak complexes with $-COO^-$; (ii) Et_4N^+ forms weak complexes with $-NH_2$; (iii) ClO_4^-

Table 3
Formation constants of H(gly)^0, H_2(gly)$^+$, (gly)H_2X^0 (X is Cl^-, I^-), Na(gly)^0, NaH(gly)$^+$, Et_4N(gly)^0 and (gly)H$(SO_4)^{2-}$ species in aqueous solution; $I = 0.5$ mol dm^{-3}; $T = 25$°C

Species	log β [a]	log β [a]
H(gly)^0	9.62 ± 0.005 [b]	9.65 ± 0.005 [b]
H_2(gly)$^+$	12.01 ± 0.01	12.04 ± 0.01
(gly)H_2X^0	11.5 ± 0.05	11.4 ± 0.05
Na(gly)^0	−0.4 ± 0.05	−0.6 ± 0.05
NaH(gly)$^+$	9.1 ± 0.05	9.1 ± 0.05
Et_4N(gly)^0	−0.4 ± 0.05	–
(gly)H$(SO_4)^{2-}$	10.6 ± 0.05	–

[a] Overall formation constants. [b] From literature protonation constants.

Table 4
Formation constants log β [a] of Mg^{2+}–, Ca^{2+}– and Pb^{2+}–glycine complexes in aqueous solution at $I = 0.5$ mol dm^{-3}, $T = 25$°C

Species	M		
	Mg^{2+}	Ca^{2+}	Pb^{2+}
M(gly)$^+$	1.68 ± 0.03 [b]	1.04 ± 0.03 [b]	4.76 ± 0.04 [b]
MH(gly)$^{2+}$	10.05 ± 0.05	10.07 ± 0.05	11.1 ± 0.1
M(gly)$_2^0$	–	–	7.4 ± 0.1

[a] Overall formation constants. [b] ±Std. dev.

or I^- form weak complexes with $-NH_3^+$; (iv) the dependence on ionic strength is given for the formation of all species by the equation reported in the next section. By taking into account this model it was possible (ES2WC calculations) to show the formation of the weak species Na(gly)^0, NaH(gly)$^+$, Et_4N(gly)^0 and (gly)H_2X^0 (X is ClO_4^- or I^-) and to calculate the relative formation constants, as reported in Table 3. Analogous calculations, performed on apparent protonation constants determined in aqueous $CaCl_2$ media (d), allowed the formation constants of Ca(gly)$^+$ and CaH(gly)$^{2+}$ species to be determined. These constants are reported in Table 4. Further measurements were performed in Na_2SO_4 solutions (e) in order to study the effect of SO_4^{2-} on the protonation of glycine. Calculations performed with ES2WC and BSTAC computer programs showed the formation of (gly)H(SO)$_4^{2-}$ species, whose formation constant is reported in Table 3. In the review of Kiss et al. [6] no work is reported on the complexation of Na^+, Et_4N^+ or monocharged anions with glycine, and values for stability constants of calcium complexes are reported as being doubtful.

3.2. The dependence of the formation constants on ionic strength

The dependence on ionic strength of the formation constants was accounted for by using the Debye–Hückel type equation [26,28–32]

$$\log\beta = \log^{\mathrm{T}}\beta - z^*\sqrt{I}/(2+3\sqrt{I}) + L(I) \tag{1}$$

where

$$L(I) = CI + DI^{3/2} \tag{1a}$$

$$C = c_0p^* + c_1z^*$$

$$D = d_0p^* + d_1z^*$$

$$p^* = \sum(\text{moles})_{\text{reactants}} - \sum(\text{moles})_{\text{products}}$$

$$z^* = \sum(\text{charges})^2_{\text{reactants}} - \sum(\text{charges})^2_{\text{products}}$$

$$c_0 = 0.10 - 0.0026(T-25)$$

$$c_1 = 0.23 - 0.0011(T-25)$$

$$d_0 = 0$$

$$d_1 = -0.10 + 0.0018(T-25) \qquad (T/°\mathrm{C})$$

Numerical values of c_0, c_1, d_1, together with their temperature coefficients, were recalculated from serveral preceding reports on the dependence of protonation on ionic strength and metal complex formation constants of several low molecular weight ligands. In this work, we calculated for each formation constant an empirical parameter C, using the simplified equation

$$\log\beta = \log^{\mathrm{T}}\beta - z^*g(I) + CI \tag{1b}$$

where

$$g(I) = [\sqrt{I}/(2+3\sqrt{I}) + 0.1I^{3/2}]$$

Values of C (reported in the discussion, Table 6) were always quite close to those obtained using the above numerical values for c_0 and c_1.

3.3. *Analysis of the literature data on the protonation constants*

About 110 protonation constant values were selected from the literature and analysed as follows: (a) the effective ionic strength was calculated by using literature data on the association of NaCl, KNO_3, ($NaClO_4$ was considered as being completely dissociated and data for which other salts were used as background salt were excluded); (b) mixed protonation constants were converted to concentration constants as suggested in Ref. [33]; (c) data in molal scale were corrected for molar scale; (d) data at different temperatures and ionic strengths were analysed by the computer programs REGIS and TDA. Smoothed values of $\log K_1^{\mathrm{H}}$ and $\log K_2^{\mathrm{H}}$ are reported in Table 2. Empirical parameters for the dependence on ionic strength, C and D, of Eq (1) are (25°C) $C_1 = 0.84$ and $D_1 = -0.50$ for $\log K_1^{\mathrm{H}}$, and $C_2 = 0.94$ $D_2 = -0.50$ for $\log\beta_2^{\mathrm{H}}$, whilst expected values are $C_1 = 0.56$, $C_2 = 0.66$, $D_1 = -0.20$, $D_2 = -0.20$ as reported above. These differences were explained, as before, by assuming that weak complexes of Na^+ (or K^+) and Cl^- are formed (it was considered that Na^+ and K^+ form species with the same stability. ES2WC calculations gave the effective protonation constants and weak complex formation constants reported in Table 3.

3.4. *Magnesium(II) complexes*

The self-medium method, used in the determination of the formation constants of Ca^{2+}–glycine complexes, was used also in the study of the Mg^{2+}–glycine system. Calculations could not be performed with ES2WC because, before complete deprotonation of glycine, hydrolysis of magnesium(II) occurred. Therefore in this case BSTAC and STACO computer programs were used. Two species $Mg(gly)^+$ and $MgH(gly)^{2+}$, whose formation constants are reported in Table 4, were found. Tentative values of the formation constants reported by Kiss et al. [6] are in good accord with the present values.

3.5. *Lead(II) complexes*

Owing to the formation of fairly strong complexes of Pb^{2+} with chloride, we used $NaClO_4$ as the background salt for the study of Pb^{2+}–glycine complexes. Calculations performed with BSTAC and STACO showed that the species $Pb(gly)^+$, $Pb(gly)_2^0$ and $PbH(gly)^{2+}$ are formed under our experimental conditions. Formation constants are reported in Table 4. Other species ($PbH(gly)_2^+$, $PbH_2(gly)_2^{2+}$ and $Pb(gly)(OH)^0$) have been proposed [6], but in our experimental conditions the above three-species model is sufficient.

3.6. *Copper(II), manganese(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes*

Glycine complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were studied in NaCl at low ionic strength, $I \leq 0.09$ mol kg^{-1} in the temperature range $5°C \leq T \leq 45°C$. In Table 5 we report the formation constants of these complexes

Table 5
Thermodynamic parameter [a] for the formation of Mn^{2+}–, Co^{2+}–, Ni^{2+}–, Cu^{2+}–, Zn^{2+}– and Cd^{2+}–glycine complexes at 25°C and $I = 0$ mol kg^{-1}

Glycine complex	$\log K_1$	$\log \beta_2$	$\log \beta_3$	$\Delta H_1^\ominus$	$\Delta H_2^\ominus$	$\Delta H_1^\ominus$
Mn^{2+}	3.18 ± 0.01 [b]	5.47 ± 0.02 [b]		-1.1 ± 0.2 [b]	-1.0 ± 2 [b]	
Co^{2+}	5.04 ± 0.03	9.16 ± 0.03	11.58 ± 0.04 [b]	-11.2 ± 0.9	-26.9 ± 1.1	-40.5 ± 4 [b]
Ni^{2+}	6.12 ± 0.02	11.10 ± 0.02	14.37 ± 0.05	-18.6 ± 0.8	-39.3 ± 1.0	-61 ± 3
Cu^{2+}	8.50 ± 0.02	15.66 ± 0.04		-25.9 ± 0.8	-54.8 ± 1.4	
Zn^{2+}	5.43 ± 0.02	9.90 ± 0.04	12.29 ± 0.10	-11.4 ± 0.9	-25.3 ± 2.7	-40.2 ± 5
Cd^{2+}	4.69 ± 0.03	8.50 ± 0.06	10.60 ± 0.2	-8.8 ± 1.2	-22.6 ± 1.9	-35.9 ± 4

[a] $\Delta H^\ominus$ in kJ mol^{-1}. [b] ±Std dev.

(calculated by BSTAC and STACO computer programs), together with $\Delta H^{\ominus}$ (and in some case $\Delta C_p^{\ominus}$) values. In our experimental conditions, the species $M(gly)^+$ and $M(gly)_2^0$ are formed for all these cations, for Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} the species $M(gly)_3^-$, was also found. Looking at table 3.4 of Ref. [6], where recommended and tentative values of stability constants of Co^{2+}–, Ni^{2+}–, Cu^{2+}– and Zn^{2+}–glycine complexes are reported, it is possible to affirm that at 25°C the general accord is fairly good. Note that in their critical examination of literature reports Kiss et al. [6] did not consider the effect of background salt, by taking into account the dependence on ionic strength only. This may lead to serious errors when comparing formation constants determined in different media at $I > 0.1$–0.5 mol dm^{-3} (also see Section 4).

3.7. Analysis of literature data for nickel(II), copper(II) and zinc(II) complexes

As already noted, metal–glycine complexes have been widely studied, in particular those of nickel(II), copper(II) and zinc(II). Nevertheless, the discrepancies among different values of thermodynamic formation parameters reported by different authors are quite high. These discrepancies may be due to two causes: (a) different concentration scales, different media, and different calibration methods; and (b) experimental and calculation errors.

Type (a) differences can be accounted for fairly easily, providing the experimental conditions are clearly described by authors. Corrections for different concentration scales can be calculated from densities [14] and in aqueous solution are quite small. Corrections for different calibration methods can be obtained from estimates of activity coefficients, and are fairly small [33]. Corrections for medium effects imply the knowledge of weak complex formation constants of the metal under study and the anion of the background salt. In order to cancel the effect of complex formation between the metal ion and the anion of background salt we can use the equation:

$$\log K' = \log K - \log(1 + K^{MX}[X]) \qquad (2)$$

where K^{MX} is the formation constant of the complex species MX, and [X] is the concentration of the generical anion X. K and K' refer to formation constants correct and apparent, respectively.

Type (b) discrepancies can be corrected only if all experimental conditions and original data are available. It is possible to demonstrate that when considering the proton displacement reactions

$$M^{2+} + H(gly)^0 = M(gly)^+ + H^+ \qquad (3)$$

$$M^{2+} + gly^- + H(gly)^0 = M(gly)_2^0 + H^+ \qquad (4)$$

$$M(gly)^+ + H(gly)^0 = M(gly)_2^0 + H^+ \qquad (5)$$

most of discrepancies disappear. In fact, both differences in calibration (when the pH-metric technique is used) and the medium are cancelled if protonation constants and formation constants are determined separately. Moreover, since internal consistency is always greater than external consistency of experimental data, indirect formation parameters for reactions (3)–(5) are intrinsically affected by a lower error with respect to the classic formation constant. Therefore we calculated the equilibrium constants for reactions (3)–(5) using experimental data on protonation and on metal complex formation (protonation and formation data of the same author were used for each value). Equilibrium constants for reactions (3)–(5) can be expressed by the following equations (at 25°C)

For Ni^{2+}–glycine complexes

$$\log K_{(3)} = -3.67(\pm 0.01) - 2g(I) + 0.51(\pm 0.06)I$$

$$\log K_{(4)} = 1.29(\pm 0.02) - 4g(I) + 1.02(\pm 0.08)I$$

$$\log K_{(5)} = -4.80(\pm 0.01) - 0.15(\pm 0.09)I$$

For Cu^{2+}–glycine complexes

$$\log K_{(3)} = -1.22(\pm 0.02) - 2g(I) + 0.48(\pm 0.04)I$$

$$\log K_{(4)} = 5.84(\pm 0.01) - 4g(I) + 0.99(\pm 0.07)I$$

$$\log K_{(5)} = -2.72(\pm 0.01) + 0.8(\pm 0.06)I$$

For Zn^{2+}–glycine complexes

$$\log K_{(3)} = -4.44(\pm 0.02) - 2g(I) + 0.54(\pm 0.08)I$$

$$\log K_{(4)} = 0.02(\pm 0.04) - 4g(I) + 0.71(\pm 0.14)I$$

$$\log K_{(5)} = -5.38(\pm 0.03) - 0.10(\pm 0.09)I$$

Estimated errors are quite acceptable even if original data, in terms of formation constants, showed much higher discrepancies. Moreover, the empirical parameters C, for the dependence on ionic strength (Eq. 1b), should at 25°C be, according to Eqs. (1)–(1b), 0.46, 1.02 and 0, for reactions (3), (4) and (5), respectively. By making allowance for errors, values of C in the above equations are very close to those expected.

3.8. Protonated complexes

Protonated complexes $MH(gly)^{2+}$ have been studied experimentally only for Ca^{2+}, Mg^{2+} and Pb^{2+}. It is also expected that the other cations studied here will form weak protonated complexes, the stabilities of which can be estimated empirically, as reported elsewhere [35,36] using the equation

$$\log {}^{T}K_{MHL} = a + b \log^{T} K^{H}_{COO^-} \qquad (6)$$

where ${}^{T}K_{MHL}$ is the equilibrium constant (at infinite dilution) for the reaction

$$M^{2+} + H(gly)^{0} = MH(gly)^{2+} \qquad (7)$$

$\log {}^{T}K^{H}_{COO^-}$ is the protonation constant of carboxylic group at infinite dilution, and a and b are empirical parameters which can be estimated from literature data. The values obtained for glycine complexes are $\log {}^{T}K_{MHL} = 1.4, 0.8, 0.7, 1.1, 1.65, 0.75$ for Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+} and Mn^{2+}, respectively.

4. Discussion

4.1. Recommended values of formation constants

On the basis of experimental and literature data reported in the previous section, we have been able to obtain formation constants for several proton– and metal–glycinate species, together with their dependence on ionic strength, at different temperatures. These constants can be "recommended", from the following considerations.

(i) Experimental values obtained in this work are quite accurate: the use of different equipment and different procedures avoids systematic errors.

(ii) All calibrations were made in terms of H^+ concentrations and therefore errors in estimating activity coefficients are eliminated.

(iii) The accurate analysis of literature data has allowed reliable formation constants to be obtained: these are in very good accord with present experimental values.

(iv) $\Delta H^{\ominus}$ values obtained from the dependence on temperature are in very good agreement with literature values obtained from direct calorimetric measurements.

(v) The dependence on ionic strength of formation constants fits expected trend, as reported for several other metal–low-molecular-ligand complexes.

Recommended formation constants reported in Table 6 are to be considered as independent of medium, because in deriving them all possible interactions occurring in solution, including the background salt, were taken into account (for $K > 0.2$ $dm^3\ mol^{-1}$).

4.2. Effective and apparent formation constants

In the determination of formation constants, some assumptions and simplifications are generally made. When using the well known "constant-medium" method, it is assumed that, (a) activity coefficients are constant in that medium and, (b) formation constants obtained are strictly valid in that medium only. Assumption (b) may be valid for the comparison of a series of complexes having the same homogeneous characteristics, such as carboxylic ligands (with the same complexing tendency towards the cation of background electrolyte) and transition metals (having the same complexing tendency towards the anion of background electrolyte). If formation constants have to be used in the speciation of multicomponent systems, much attention must be paid in selecting coherent thermodynamic data. The matter has been discussed by several authors; quite interesting are the papers of Dickson et al. [10] and Anderegg [11]. Our model for taking into account weak interactions and ionic strength dependence of formation constants has been discussed in some previous papers [26–32]. In this paper we have tried to give

Table 6

Recommended values (±estimated standard deviations) of proton and metal–glycine complex formation constants at different temperatures together with the parameters C (Eq. (1b)) for the dependence of ionic strength; all formation constants are given at $I = 0.5$ mol dm^{-3} in the molar scale

T/°C	log β	C	log β	C	log β	C
	$H(gly)^0$		$MgH(gly)^{2+}$		$Mn(gly)_2^0$	
5	10.218 ± 0.004	0.580 ± 0.009	10.60 ± 0.07	0.82 ± 0.18	5.06 ± 0.10	1.57 ± 0.15
15	9.911 ± 0.002	0.576 ± 0.006	10.31 ± 0.04	0.73 ± 0.15	5.06 ± 0.10	1.57 ± 0.15
25	9.653 ± 0.002	0.571 ± 0.005	10.05 ± 0.04	0.64 ± 0.09	5.05 ± 0.09	1.58 ± 0.12
35	9.384 ± 0.002	0.566 ± 0.006	9.83 ± 0.05	0.54 ± 0.14	5.04 ± 0.09	1.59 ± 0.15
45	9.157 ± 0.004	0.562 ± 0.010	9.64 ± 0.07	0.46 ± 0.18	5.02 ± 0.11	1.59 ± 0.15
	$H_2(gly)^+$		$Ca(gly)^+$		$Co(Gly)^+$	
5	12.703 ± 0.005	0.714 ± 0.012	0.93 ± 0.06	0.46 ± 0.14	5.02 ± 0.06	1.06 ± 0.10
15	12.334 ± 0.003	0.694 ± 0.008	0.98 ± 0.04	0.61 ± 0.11	4.92 ± 0.04	1.03 ± 0.07
25	12.027 ± 0.003	0.674 ± 0.007	1.04 ± 0.03	0.77 ± 0.10	4.83 ± 0.04	1.00 ± 0.05
35	11.749 ± 0.003	0.654 ± 0.008	1.10 ± 0.04	0.92 ± 0.12	4.76 ± 0.05	0.97 ± 0.07
45	11.505 ± 0.005	0.634 ± 0.012	1.16 ± 0.06	1.0 ± 0.2	4.70 ± 0.06	0.94 ± 0.10
	$(gly)H_2X^0$		$CaH(gly)^{2+}$		$Co(Gly)_2^0$	
5	11.8 ± 0.2	1.2 ± 0.1	10.43 ± 0.04	0.61 ± 0.06	9.06 ± 0.10	1.51 ± 0.10
15	11.6 ± 0.1	1.2 ± 0.1	10.22 ± 0.03	0.66 ± 0.05	8.86 ± 0.08	1.52 ± 0.10
25	11.4 ± 0.1	1.2 ± 0.1	10.06 ± 0.02	0.72 ± 0.05	8.69 ± 0.06	1.52 ± 0.08
35	11.3 ± 0.1	1.2 ± 0.1	9.93 ± 0.03	0.79 ± 0.05	8.53 ± 0.06	1.52 ± 0.10
45	11.2 ± 0.2	1.2 ± 0.1	9.83 ± 0.04	0.83 ± 0.06	8.40 ± 0.11	1.53 ± 0.11
	$Na(gly)^0$		$Pb(gly)^+$		$Ni(gly)^+$	
5	−0.40 ± 0.07	0.29 ± 0.16	5.00 ± 0.12	1.06 ± 0.11	6.05 ± 0.01	1.08 ± 0.02
15	−0.45 ± 0.05	0.41 ± 0.11	4.89 ± 0.11	1.05 ± 0.09	5.92 ± 0.01	1.06 ± 0.01
25	−0.50 ± 0.04	0.52 ± 0.09	4.76 ± 0.07	1.05 ± 0.08	5.80 ± 0.01	1.05 ± 0.01
35	−0.55 ± 0.06	0.64 ± 0.11	4.61 ± 0.09	1.05 ± 0.10	5.71 ± 0.01	1.03 ± 0.01
45	−0.58 ± 0.10	0.75 ± 0.17	4.45 ± 0.10	1.04 ± 0.10	5.63 ± 0.01	1.02 ± 0.02
	$NaH(gly)^+$		$Pb(gly)_2^0$		$Ni(gly)_2^0$	
5	9.54 ± 0.10	0.53 ± 0.14	7.6 ± 0.2	1.6 ± 0.2	11.21 ± 0.02	1.70 ± 0.03
15	9.30 ± 0.05	0.58 ± 0.10	7.5 ± 0.2	1.6 ± 0.2	10.89 ± 0.02	1.62 ± 0.02
25	9.07 ± 0.06	0.63 ± 0.08	7.4 ± 0.1	1.6 ± 0.2	10.61 ± 0.01	1.54 ± 0.02
35	8.88 ± 0.06	0.69 ± 0.12	7.3 ± 0.2	1.6 ± 0.2	10.35 ± 0.02	1.47 ± 0.02
45	8.70 ± 0.11	0.74 ± 0.15	7.2 ± 0.2	1.6 ± 0.2	10.12 ± 0.02	1.39 ± 0.03
	$(gly)H(SO_4)^{2-}$		$PbH(gly)^{2+}$		$Cu(gly)^+$	
5	11.0 ± 0.2	0.82 ± 0.1	11.5 ± 0.2	0.8 ± 0.1	8.63 ± 0.01	1.12 ± 0.02
15	10.8 ± 0.1	0.82 ± 0.1	11.3 ± 0.1	0.7 ± 0.1	8.43 ± 0.01	1.09 ± 0.02
25	10.6 ± 0.1	0.82 ± 0.1	11.1 ± 0.1	0.7 ± 0.1	8.23 ± 0.01	1.06 ± 0.01
35	10.45 ± 0.1	0.78 ± 0.1	10.9 ± 0.1	0.7 ± 0.1	8.06 ± 0.01	1.03 ± 0.02
45	10.3 ± 0.2	0.82 ± 0.1	10.8 ± 0.1	0.6 ± 0.1	7.91 ± 0.01	1.00 ± 0.02

Table 6 (continued)

T/°C	log β	C	log β	C	log β	C
	$Mg(gly)^+$		$Mn(gly)^+$		$Cu(gly)_2^0$	
5	1.43 ± 0.05	1.08 ± 0.11	3.01 ± 0.04	1.02 ± 0.09	16.01 ± 0.02	1.71 ± 0.04
15	1.55 ± 0.03	1.04 ± 0.07	3.00 ± 0.03	1.02 ± 0.08	15.55 ± 0.01	1.62 ± 0.03
25	1.68 ± 0.03	1.00 ± 0.06	2.99 ± 0.03	1.02 ± 0.07	15.15 ± 0.01	1.53 ± 0.02
35	1.81 ± 0.03	0.97 ± 0.07	2.99 ± 0.03	1.02 ± 0.08	14.80 ± 0.01	1.44 ± 0.02
45	1.95 ± 0.05	0.93 ± 0.11	2.99 ± 0.04	1.02 ± 0.09	14.50 ± 0.02	1.35 ± 0.03
	$Zn(gly)^+$		$Zn(gly)_2^0$		$Cd(gly)^+$	
5	5.26 ± 0.03	1.09 ± 0.04	9.67 ± 0.04	1.38 ± 0.05	4.48 ± 0.06	0.91 ± 0.10
15	5.16 ± 0.02	1.07 ± 0.04	9.42 ± 0.03	1.29 ± 0.05	4.41 ± 0.04	0.94 ± 0.07
25	5.08 ± 0.02	1.06 ± 0.03	9.21 ± 0.02	1.19 ± 0.04	4.34 ± 0.03	0.97 ± 0.06
35	5.02 ± 0.02	1.04 ± 0.04	9.00 ± 0.03	1.10 ± 0.04	4.28 ± 0.04	1.00 ± 0.06
45	4.98 ± 0.03	1.03 ± 0.04	8.82 ± 0.04	1.01 ± 0.06	4.22 ± 0.05	1.03 ± 0.09
	$Cd(gly)_2^0$					
5	8.36 ± 0.08	1.58 ± 0.10				
15	8.20 ± 0.05	1.59 ± 0.08				
25	8.05 ± 0.05	1.60 ± 0.06				
35	7.92 ± 0.05	1.61 ± 0.06				
45	7.81 ± 0.07	1.62 ± 0.09				

thermodynamic data for the formation of proton– and metal–glycine complexes in an unambiguous way. In particular we must stress the fact that Table 6 reports formation constant values independent of medium.

4.3. *Comparison with literature findings*

In Table 7 we report our values for stability constants of glycine complexes with Pb^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}, compared with mean values calculated by Smith and Martell [4,5] and recommended values reported by Kiss et al. [6]. Also in Table 7, some $\Delta H^{\ominus}$ literature values are compared with present findings. As affirmed in Section 3, the general accord is good at 25°C. Unfortunately, reported literature values are not corrected for the effect of background salt, and therefore comparisons at $I > 0.5$ mol dm^{-3} cannot be made. Few thermodynamic parameters are reported at $T \neq 25$°C and comparisons are useless.

4.4. *Speciation of natural fluids containing glycine*

The thermodynamic parameters reported here can be correctly used for the speciation of glycine in natural fluids containing all cations and anions taken into account in this investigation. In particular, all major components of seawater have

Table 7
Literature comparisons

Metal ion	I/(mol dm^{-3})	Smith and Martell [a]		Kiss et al. [b]		This work	
		log K_1	log β_2	log K_1	log β_2	log K_1	log β_2
Pb^{2+}	0	5.47	8.86	–	–	5.06	–
	0.5	–	–	–	–	4.76	7.4
Mn^{2+}	0	3.19	–	–	–	3.18	5.47
	0.5	2.65	4.7	–	–	2.99	5.05
Co^{2+}	0	5.07	9.04	5.10	9.10	5.04	9.16
	0.5	4.57	8.28	–	–	4.83	8.69
Ni^{2+}	0	6.18	11.13	6.16	11.11	6.12	11.10
	0.5	5.64	10.50	5.64	10.35	5.80	10.61
Cu^{2+}	0	8.56	15.64	8.52	15.75	8.50	15.66
	0.5	8.14	14.97	8.11	14.80	8.23	15.15
Zn^{2+}	0	5.38	9.81	5.45	9.91	5.43	9.90
	0.5	4.88	9.06	4.86	9.07	5.08	9.21
Cd^{2+}	0	4.7	8.4	4.69	8.40	4.69	8.50
	0.5	–	–	4.3	7.7	4.34	8.05

$\Delta H^{\ominus}$ (overall formation reaction, in kJ mol^{-1})

Species	I/(mol dm^{-3})	Recommended values of Kiss et al. [b]	Our values
$H(gly)^0$	0	-44.6 ± 0.6	-44.47 ± 0.08
	0.1–0.2	-45.4 ± 1.2	
$H_2(gly)^+$	0	-49.0 ± 0.7	-48.7 ± 0.1
	0.1–0.2	-49.7 ± 1.2	
$Ni(gly)^+$	0–1	-19.3 ± 1.6	-18.6 ± 0.8 ($I = 0$)
$Ni(gly)_2^0$	0–1	-39.6 ± 1.3	-38.3 ± 1.0 ($I = 0$
$Ni(gly)_3^-$	0–1	-61.8 ± 1.1	-61 ± 3 ($I = 0$)
$Cu(gly)^+$	0–1	-25.6 ± 1.4	-25.9 ± 0.8 ($I = 0$)
$Cu(gly)_2^0$	0–1	-54.3 ± 1.7	-54.8 ± 1.4 ($I = 0$)

[a] Refs. [4,5]. [b] Ref. [6].

been considered, and therefore the speciation of glycine in this medium with the addition, as trace component, of a cation such as Pb^{2+}, . . . , Cd^{2+}, may be made. Two simulations were performed in order to account for the speciation of glycine in seawater. The first one relates to the speciation of glycine in synthetic seawater [37] at 35‰, when other components are absent. In Table 8 the distribution of the species versus pH is reported. As one can see, glycine is distributed among various species, and though generally weak species of amino acids are neglected in the literature, these account for percentages which are not negligible. For example, at seawater of pH approximately 8, Na^+ species represent about 9% of total glycine, and by also taking into account Mg^{2+} and Ca^{2+} species, the total percentage of

Table 8
Distribution of glycinate species in synthetic seawater[a] (percentages calculated with respect to total glycine) at 25°C; $C_{gly} = 1$ mmol dm^{-3}

pH	HL	H_2L	NaL	NaHL	LH_2Cl	MgL	MgHL	CaL	CaHL	$LHSO_4$
3	64	16	0	7	2	0	5	0	1	5
4	76	2	0	9	0	0	6	0	1	5
5	78	0	0	9	0	0	6	0	1	6
6	78	0	0	9	0	0	6	0	1	6
7	78	0	0	9	0	0	6	0	1	6
8	74	0	0	9	0	2	6	0	1	5
9	53	0	2	6	0	17	4	1	1	4

[a] Composition (in mol dm^{-3}) of synthetic seawater (35‰): Na^+, 0.4797; K^+, 0.011; Mg^{2+}, 0.0548; Ca^{2+}, 0.0111; Cl^-, 0.5648; SO_4^{2-}, 0.0288. In the calculations, interactions between components of this medium were also considered. Effective ionic strength, $I_e = 0.56$ mol dm^{-3}. See also Ref. [37]. L is glycine.

glycine complexes reaches about 23%. Also Cl^- and SO_4^{2-} species cannot be neglected in the speciation model. Note that in most literature reports only ML species have been reported, whilst in the pH range of interest for natural fluids (blood, pH 7.3; seawater, pH 8.2; etc.) protonated species are more important. The second simulation relates to the speciation of glycine in synthetic seawater (35‰ salinity) in the presence of Cu^{2+}. In Table 9 we report some formation percentages. In this system also chloride, sulphate and hydrolytic species of Cu^{2+} must be taken

Table 9
Percentages of copper(II) species in synthetic seawater[a], in the presence of glycine, at 25°C

pH	$(CuCl)^+$ + $(CuSO_4)^0$	Hydrolytic species	CuL^+	CuL_2^0	$CuHL^{2+}$
C_{Cu} 1, C_{gly} 2 mmol dm^{-3}					
3	43	0	3	0	2
4	33	0	23	1	1
5	12	0	60	11	0
6	2	0	49	46	0
7	0	0	22	78	0
8	0	0	8	92	0
9	0	0	3	97	0
C_{Cu} 0.1, C_{gly} 0.1 mmol dm^{-3}					
3	44	0	0	0	0
4	43	0	2	0	0
5	38	0	13	0	0
6	23	0	45	3	0
7	10	3	60	13	0
8	3	23	46	23	0
9	0	44	16	40	0

[a] See footnote to Table 8.

into account [5,38] (the mean values $\log {}^{T}K^{CuCl} = 0.3$ and $\log {}^{T}K^{CuSO_4} = 2.3$ were calculated from various literature findings). As one can see, inorganic complexes (Note that this simulation example refers to a synthetic seawater containing only the anions Cl^- and SO_4^{2-}, whilst in real situations CO_3^{2-} and their complexes with Cu^{2+} must be taken into account.) and hydrolytic species can be neglected at $pH > 6$ for analytical concentrations above 1 mmol dm^{-3} and $C_{gly}/C_{Cu} > 1$, whilst they play an important role for lower concentrations and $C_{gly}/C_{Cu} < 1$. Furthermore, part of the glycine is complexed by the components of synthetic seawater. These two examples show that the complete speciation of a multicomponent system must take into account, in order to be rigorous, the effect of medium, by considering all possible interactions.

4.5. Ionic strength and medium dependence of formation constants

We have considered the effect of ionic strength and of medium on the protonation constants and on metal complex formation constants by using Eqs. (1)–(1b), and by taking into account weak interactions in solutions under study. Other methods, which in general neglect weak interactions, can be adopted. These are based on the original "specific interaction" approach of Guggenheim [39] or the specific interaction models of Bromley [40] and Pitzer [41]. We performed some calculations using different semiempirical equations (including those of Bromley and Pitzer): the fit obtained was always satisfactory, providing the same number of parameters was refined. In a parallel study we are comparing different approaches when considering the function $\log \beta = f(I, \text{medium})$.

Acknowledgements

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Appendix A: Supplementary Data

Table A1
Thermodynamic protonation parameter [a] of glycine in aqueous NaCl solution (molal scale)

T/°C	I			
	0.01	0.04	0.09	0
	$\log K_1^H$			
5	10.2611 ± 0.0015 [b]	10.2064 ± 0.0013 [b]	10.1787 ± 0.0015 [b]	10.3464 ± 0.0017 [b]
10	10.1101 ± 0.0012	10.0551 ± 0.0010	10.0268 ± 0.0012	10.1955 ± 0.0013
15	9.9653 ± 0.0011	9.9099 ± 0.0008	9.8811 ± 0.0010	10.0508 ± 0.0012
20	9.8263 ± 0.0010	9.7706 ± 0.0008	9.7413 ± 0.0010	9.9119 ± 0.0011
25	9.6929 ± 0.0010	9.6368 ± 0.0008	9.6070 ± 0.0009	9.7786 ± 0.0011
30	9.5647 ± 0.0010	9.5083 ± 0.0008	9.4780 ± 0.0009	9.6506 ± 0.0011

Table A1 (continued)

T/°C	I			
	0.01	0.04	0.09	0
35	9.4415 ± 0.0011	9.3848 ± 0.0008	9.3539 ± 0.0009	9.5275 ± 0.0012
40	9.3231 ± 0.0011	9.2661 ± 0.0008	9.2346 ± 0.0009	9.4091 ± 0.0012
45	9.2091 ± 0.0012	9.1518 ± 0.0009	9.1198 ± 0.0010	9.2953 ± 0.0014
	$\log K_2^{\mathrm{H}}$			
5	2.423 ± 0.002 [b]	2.424 ± 0.002 [b]	2.424 ± 0.002 [b]	2.423 ± 0.002 [b]
10	2.401 ± 0.002	2.401 ± 0.002	2.402 ± 0.002	2.400 ± 0.002
15	2.381 ± 0.001	2.382 ± 0.001	2.383 ± 0.002	2.381 ± 0.002
20	2.365 ± 0.001	2.365 ± 0.001	2.366 ± 0.002	2.365 ± 0.001
25	2.351 ± 0.001	2.352 ± 0.001	2.353 ± 0.002	2.351 ± 0.001
30	2.340 ± 0.001	2.341 ± 0.001	2.342 ± 0.002	2.340 ± 0.001
35	2.332 ± 0.001	2.333 ± 0.001	2.334 ± 0.001	2.332 ± 0.002
40	2.326 ± 0.002	2.326 ± 0.001	2.327 ± 0.001	2.326 ± 0.002
45	2.322 ± 0.002	2.322 ± 0.001	2.324 ± 0.002	2.322 ± 0.002

T/°C	$\Delta H_1^\ominus$ [c]	$\Delta H_2^\ominus$ [c]	
5	−45.66 ± 0.18 [b]	−7.2 ± 0.3 [b]	
10	−45.36 ± 0.15	−6.4 ± 0.2	
15	−45.06 ± 0.12	−5.7 ± 0.2	
20	−44.76 ± 0.10	−4.9 ± 0.1	
25	−44.47 ± 0.08	−4.2 ± 0.1	
30	−44.17 ± 0.08	−3.4 ± 0.1	
35	−43.87 ± 0.10	−2.7 ± 0.2	
40	−43.58 ± 0.13	−1.9 ± 0.2	
45	−43.28 ± 0.16	−1.1 ± 0.3	
25	$\Delta C_{p_1}^\ominus = 60 \pm 7$ [b]	$\Delta C_{p_2}^\ominus = 151 \pm 12$ [b]	($I = 0$ mol kg^{-1})

[a] $\Delta H^\ominus$ in kJ mol^{-1}, $\Delta C_p^\ominus$ in J K^{-1} mol^{-1}; I in mol kg^{-1}. [b] ±Std. dev. [c] $I = 0$ mol kg^{-1}.

Table A2
Protonation constants of glycine in aqueous tetraethylammonium iodide solutions (molar scale)

T/°C	0.1 [a]	0.25	0.5	0.75
	$\log K_1^{\mathrm{H}}$			
5	10.104 ± 0.009 [b]	10.075 ± 0.016 [b]	10.064 ± 0.027 [b]	10.051 ± 0.042 [b]
10	9.954 ± 0.008	9.928 ± 0.014	9.924 ± 0.023	9.916 ± 0.035
15	9.811 ± 0.008	9.787 ± 0.013	9.789 ± 0.020	9.787 ± 0.028
20	9.674 ± 0.008	9.655 ± 0.012	9.661 ± 0.016	9.664 ± 0.022
25	9.543 ± 0.008	9.527 ± 0.012	9.539 ± 0.014	9.547 ± 0.016
30	9.417 ± 0.008	9.404 ± 0.012	9.421 ± 0.014	9.435 ± 0.013
35	9.296 ± 0.008	9.287 ± 0.012	9.309 ± 0.015	9.329 ± 0.013
40	9.181 ± 0.008	9.174 ± 0.013	9.202 ± 0.017	9.227 ± 0.017
45	9.069 ± 0.009	9.066 ± 0.015	9.100 ± 0.021	9.130 ± 0.024

Table A2 (continued)

T/°C	0.1 [a]	0.25	0.5	0.75
	$\log K_2^H$			
5	2.453 ± 0.006 [b]	2.493 ± 0.010 [b]	2.547 ± 0.014 [b]	2.588 ± 0.018 [b]
10	2.429 ± 0.006	2.469 ± 0.009	2.521 ± 0.012	2.560 ± 0.016
15	2.408 ± 0.005	2.447 ± 0.009	2.498 ± 0.011	2.536 ± 0.013
20	2.391 ± 0.005	2.429 ± 0.008	2.478 ± 0.010	2.514 ± 0.011
25	2.376 ± 0.005	2.413 ± 0.008	2.461 ± 0.010	2.496 ± 0.010
30	2.364 ± 0.005	2.400 ± 0.008	2.446 ± 0.009	2.480 ± 0.009
35	2.354 ± 0.005	2.389 ± 0.008	2.434 ± 0.010	2.467 ± 0.009
40	2.347 ± 0.005	2.381 ± 0.009	2.425 ± 0.010	2.456 ± 0.010
45	2.342 ± 0.006	2.375 ± 0.009	2.418 ± 0.011	2.447 ± 0.012

[a] I in mol dm^{-3}. [b] ±Std. dev.

Table A3
Protonation constants of glycine in aqueous $NaClO_4$ solutions (molar scale)

T/°C	I			
	0.1 [a]	0.25	0.5	0.75
	$\log K_1^H$			
5	10.169 ± 0.006 [b]	10.133 ± 0.008 [b]	10.117 ± 0.012 [b]	10.105 ± 0.017 [b]
10	10.018 ± 0.005	9.984 ± 0.007	9.979 ± 0.010	9.980 ± 0.014
15	9.873 ± 0.005	9.842 ± 0.006	9.846 ± 0.009	9.862 ± 0.012
20	9.734 ± 0.005	9.706 ± 0.005	9.719 ± 0.008	9.749 ± 0.011
25	9.601 ± 0.005	9.575 ± 0.005	9.598 ± 0.008	9.641 ± 0.010
30	9.473 ± 0.005	9.450 ± 0.005	9.481 ± 0.008	9.539 ± 0.011
35	9.349 ± 0.005	9.329 ± 0.006	9.370 ± 0.009	9.442 ± 0.013
40	9.231 ± 0.005	9.213 ± 0.006	9.264 ± 0.011	9.349 ± 0.015
45	9.117 ± 0.005	9.102 ± 0.007	9.162 ± 0.013	9.261 ± 0.018
	$\log K_2^H$			
5	2.424 ± 0.003 [b]	2.436 ± 0.002 [b]	2.459 ± 0.005 [b]	2.486 ± 0.007 [b]
10	2.402 ± 0.003	2.413 ± 0.002	2.436 ± 0.004	2.463 ± 0.006
15	2.382 ± 0.002	2.393 ± 0.002	2.416 ± 0.004	2.443 ± 0.005
20	2.366 ± 0.002	2.377 ± 0.002	2.400 ± 0.004	2.427 ± 0.005
25	2.352 ± 0.002	2.364 ± 0.002	2.387 ± 0.004	2.414 ± 0.005
30	2.342 ± 0.002	2.353 ± 0.002	2.377 ± 0.004	2.404 ± 0.005
35	2.333 ± 0.002	2.345 ± 0.002	2.369 ± 0.004	2.397 ± 0.005
40	2.327 ± 0.003	2.340 ± 0.002	2.364 ± 0.004	2.393 ± 0.006
45	2.323 ± 0.003	2.336 ± 0.002	2.362 ± 0.004	2.392 ± 0.007

[a] I in mol dm^{-3}. [b] ±Std. dev.

Table A4
Effective formation constants of $H(gly)^0$, $H_2(gly)^+$, $(gly)H_2X^0$ (X is Cl^-, I^-), $Na(gly)^0$, $NaH(gly)^+$, $Ca(gly)^+$, $CaH(gly)^{2+}$, $Et_4N(gly)^0$ and $(gly)H(SO_4)^{2-}$ in aqueous solution

T/°C	I/(mol dm^{-3})	log β [a,b]								
		HL	H_2L	LH_2X	NaL	NaHL	CaL	CaHL	Et_4NL	$LH(SO_4)$
5	0.10	10.16	12.59	11.9	0.0	9.7	1.12	10.29	−0.1	10.9
10	0.10	10.00	12.41	11.7	−0.1	9.5	1.12	10.20	−0.2	–
15	0.10	9.85	12.24	11.6	−0.2	9.3	1.12	10.12	−0.3	10.7
20	0.10	9.71	12.08	11.5	−0.4	9.2	1.12	10.05	−0.3	–
25	0.10	9.58	11.93	11.4	−0.5	9.0	1.12	9.99	−0.4	10.55
30	0.10	9.46	11.79	11.2	−0.6	8.9	1.12	9.93	−0.5	–
35	0.10	9.34	11.67	11.2	−0.7	8.7	1.12	9.88	−0.5	10.4
40	0.10	9.23	11.55	11.1	−0.8	8.6	1.12	9.84	−0.6	–
45	0.10	9.13	11.45	11.0	−1.0	8.5	1.12	9.81	−0.7	10.3
5	0.25	10.17	12.62	11.9	0.0	9.7	1.01	10.32	−0.1	–
10	0.25	10.01	12.44	11.8	−0.1	9.5	1.02	10.23	−0.2	–
15	0.25	9.86	12.26	11.6	−0.2	9.4	1.03	10.15	−0.3	–
20	0.25	9.71	12.10	11.5	−0.4	9.2	1.04	10.07	−0.3	–
25	0.25	9.58	11.94	11.4	−0.5	9.0	1.05	10.00	−0.4	–
30	0.25	9.45	11.80	11.3	−0.6	8.9	1.07	9.94	−0.5	–
35	0.25	9.33	11.67	11.1	−0.7	8.7	1.08	9.88	−0.6	–
40	0.25	9.22	11.55	11.1	−0.8	8.6	1.09	9.84	−0.6	–
45	0.25	9.12	11.44	11.0	−1.0	8.5	1.10	9.80	−0.7	–
5	0.50	10.22	12.72	12.1	0.1	9.8	0.92	10.42	−0.1	11.0
10	0.50	10.06	12.52	11.9	−0.1	9.6	0.95	10.32	−0.2	–
15	0.50	9.90	12.34	11.7	−0.2	9.4	0.98	10.23	−0.2	10.8
20	0.50	9.76	12.17	11.6	−0.3	9.3	1.01	10.14	−0.3	–
25	0.50	9.62	12.01	11.5	−0.4	9.1	1.04	10.07	−0.4	10.6
30	0.50	9.49	11.86	11.3	−0.6	8.9	1.07	10.00	−0.4	–
35	0.50	9.37	11.72	11.2	−0.7	8.8	1.10	9.94	−0.5	10.45
40	0.50	9.25	11.60	11.1	−0.8	8.7	1.13	9.89	−0.6	–
45	0.50	9.14	11.48	11.0	−0.9	8.5	1.16	9.84	−0.7	10.3
5	0.75	10.28	12.82	12.2	0.1	9.9	0.85	10.52	0.0	11.1
10	0.75	10.12	12.62	12.0	0.0	9.7	0.90	10.41	−0.1	–
15	0.75	9.96	12.43	11.9	−0.1	9.5	0.95	10.31	−0.2	10.9
20	0.75	9.81	12.25	11.7	−0.3	9.4	1.00	10.22	−0.2	–
25	0.75	9.67	12.09	11.6	−0.4	9.2	1.05	10.14	−0.3	10.7
30	0.75	9.54	11.93	11.5	−0.5	9.0	1.09	10.07	−0.4	–
35	0.75	9.42	11.79	11.4	−0.6	8.9	1.14	10.01	−0.5	10.5
40	0.75	9.30	11.66	11.2	−0.8	8.7	1.19	9.95	−0.5	–
45	0.75	9.19	11.54	11.1	−0.9	8.6	1.24	9.90	−0.6	10.4
Std dev. [c]		0.005	0.01	0.05	0.05	0.05	0.03	0.05	0.05	0.05
		0.03	0.03	0.2	0.2	0.2	0.15	0.2	0.2	0.2

[a] Overall formation constants. [b] L is glycine. [c] Estimated standard deviation: first row, minimum; second row, maximum.

Table A5
Smoothed literature values of glycine protonation constants (molar scale) corrected for the association of ionic medium

T/°C	I [a]	$\log K_1^H$	$\log K_2^H$	I [a]	$\log K_1^H$	$\log K_2^H$
0	0	10.472 [b]	2.443 [c]	0.5	10.403	2.486
5	0	10.318	2.417	0.5	10.243	2.460
10	0	10.170	2.395	0.5	10.090	2.437
15	0	10.030	2.376	0.5	9.943	2.418
20	0	9.896	2.360	0.5	9.802	2.402
35	0	9.767	2.347	0.5	9.667	2.389
30	0	9.644	2.336	0.5	9.538	2.378
35	0	9.527	2.328	0.5	9.414	2.369
40	0	9.414	2.322	0.5	9.295	2.363
45	0	9.306	2.318	0.5	9.181	2.360
50	0	9.202	2.316	0.5	9.071	2.358
0	0.1	10.332	2.449	1	10.425	2.545
5	0.1	10.176	2.424	1	10.268	2.519
10	0.1	10.026	2.401	1	10.118	2.496
15	0.1	9.883	2.382	1	9.975	2.477
20	0.1	9.746	2.366	1	9.838	2.461
25	0.1	9.615	2.353	1	9.707	2.447
30	0.1	9.489	2.342	1	9.581	2.436
35	0.1	9.369	2.334	1	9.460	2.427
40	0.1	9.254	2.328	1	9.345	2.421
45	0.1	9.143	2.324	1	9.234	2.417
50	0.1	9.037	2.322	1	9.128	2.415

[a] I in mol dm^{-3}. [b] ±0.003-0.01 (std. dev.). [c] ±0.005-0.015 (std. dev.).

Table A6
Formation constants (effective) of $H(gly)^0$, $H_2(gly)^+$, $(gly)H_2X^0$ (X is Cl^-, I^-), $Na(gly)^0$, and $NaH(gly)^+$ in aqueous solution (from the analysis of literature data)

T/°C	I/(mol dm^{-3})	$\log \beta$ [a,b]				
		HL	H_2L	LH_2X	NaL	NaHL
5	0.1	10.18	12.61	11.5	−0.8	9.3
10	0.1	10.03	12.44	11.4	−0.7	9.2
15	0.1	9.89	12.27	11.4	−0.7	9.1
20	0.1	9.75	12.12	11.3	−0.6	9.0
25	0.1	9.62	11.97	11.3	−0.6	9.0
30	0.1	9.49	11.83	11.3	−0.5	8.9
35	0.1	9.37	11.70	11.2	−0.5	8.9
40	0.1	9.25	11.58	11.2	−0.4	8.8
45	0.1	9.14	11.47	11.1	−0.3	8.8

Table A6 (continued)

T/°C	I/(mol dm^{-3})	log β [a,b]				
		HL	H_2L	LH_2X	NaL	NaHL
5	0.25	10.19	12.63	11.5	−0.8	9.3
10	0.25	10.03	12.46	11.4	−0.7	9.2
15	0.25	9.89	12.29	11.4	−0.7	9.1
20	0.25	9.75	12.13	11.3	−0.6	9.1
25	0.25	9.61	11.98	11.3	−0.6	9.0
30	0.25	9.48	11.84	11.2	−0.5	8.9
35	0.25	9.36	11.70	11.2	−0.5	8.9
40	0.25	9.24	11.58	11.2	−0.4	8.8
45	0.25	9.12	11.46	11.1	−0.4	8.8
5	0.5	10.23	12.71	11.6	−0.7	9.4
10	0.5	10.08	12.53	11.6	−0.7	9.3
15	0.5	9.93	12.36	11.5	−0.6	9.2
20	0.5	9.78	12.20	11.5	−0.6	9.1
25	0.5	9.65	12.04	11.4	−0.6	9.1
30	0.5	9.52	11.90	11.3	−0.5	9.0
35	0.5	9.39	11.76	11.3	−0.4	8.9
40	0.5	9.27	11.63	11.2	−0.4	8.9
45	0.5	9.15	11.51	11.2	−0.3	8.8
5	0.75	10.27	12.78	11.7	−0.7	9.4
10	0.75	10.12	12.60	11.7	−0.6	9.4
15	0.75	9.97	12.43	11.6	−0.6	9.3
20	0.75	9.83	12.27	11.6	−0.6	9.2
25	0.75	9.69	12.11	11.5	−0.5	9.1
30	0.75	9.56	11.97	11.5	−0.5	9.1
35	0.75	9.44	11.83	11.4	−0.4	9.0
40	0.75	9.32	11.70	11.4	−0.3	8.9
45	0.75	9.21	11.58	11.3	−0.3	8.9
5	1.0	10.30	12.84	11.8	−0.7	9.5
10	1.0	10.15	12.66	11.8	−0.6	9.4
15	1.0	10.01	12.50	11.7	−0.6	9.3
20	1.0	9.87	12.34	11.7	−0.5	9.3
25	1.0	9.74	12.19	11.6	−0.5	9.2
30	1.0	9.61	12.04	11.6	−0.4	9.1
35	1.0	9.49	11.91	11.5	−0.3	9.1
40	1.0	9.38	11.78	11.5	−0.3	9.0
45	1.0	9.27	11.66	11.4	−0.2	9.0
Std dev. [c]		0.005	0.01	0.05	0.05	0.05
		0.03	0.03	0.2	0.2	0.2

[a] Overall formation constants. [b] L is glycine. [c] Estimated standard deviation: first row, minimum; second row, maximum.

Table A7
Formation constants of Mg^{2+}–glycine complexes in aqueous solution (molar scale)

T/°C	I/(mol dm^{-3})	log β [a,b]	
		MgL^+	$MgHL^{2+}$
10	0.1	1.44	10.33
25	0.1	1.66	9.98
40	0.1	1.88	9.70
10	0.25	1.42	10.36
25	0.25	1.63	9.99
40	0.25	1.84	9.70
10	0.5	1.49	10.45
25	0.5	1.68	10.05
40	0.5	1.88	9.73
10	0.75	1.57	10.55
25	0.75	1.75	10.12
40	0.75	1.93	9.77
Std. dev. [c]		0.03	0.05
		0.05	0.1

[a] Overall formation constants. [b] L is glycine. [c] Estimated standard deviation: first row, minimum; second row, maximum.

Table A8
Thermodynamic parameters for the formation of Pb^{2+}–glycine complexes (molar scale), in $NaClO_4$ aqueous solution

T/°C	I/(mol dm^{-3})	log β [a,b]		
		PbL^+	PbL_2^0	$PbHL^{2+}$
5	0.1	4.96	7.6	11.5
10	0.1	4.91	7.5	11.4
15	0.1	4.85	7.4	11.3
20	0.1	4.79	7.4	11.2
25	0.1	4.72	7.3	11.1
30	0.1	4.65	7.3	11.1
35	0.1	4.58	7.2	11.0
40	0.1	4.50	7.2	10.9
45	0.1	4.42	7.1	10.9
5	0.5	5.00	7.6	11.5
10	0.5	4.94	7.6	11.4
15	0.5	4.89	7.5	11.3
20	0.5	4.82	7.4	11.2
25	0.5	4.76	7.4	11.1
30	0.5	4.68	7.3	11.0
35	0.5	4.61	7.3	10.9
40	0.5	4.53	7.2	10.9
45	0.5	4.45	7.2	10.8

Table A8 (continued)

T/°C	I/(mol dm^{-3})	PbL^+	PbL_2^0	$PbHL^{2+}$
5	1.0	5.15	7.9	11.4
10	1.0	5.10	7.8	11.3
15	1.0	5.04	7.7	11.2
20	1.0	4.98	7.7	11.1
25	1.0	4.91	7.6	11.0
30	1.0	4.84	7.6	10.9
35	1.0	4.76	7.5	10.8
40	1.0	4.68	7.5	10.7
45	1.0	4.59	7.4	10.7
Std dev. [c]		0.04	0.1	0.1
		0.09	0.2	0.2

[a] Overall formation constants. [b] L is glycine. [c] Estimated standard deviation: first row, minimum; second row, maximum.

Table A9
Thermodynamic parameters[a] for the formation of Mn^{2+}–glycine complexes (molal scale) in NaCl aqueous solution

T/°C	I				
	0.01 [a]	0.04	0.09	0	
	log K_1				$\Delta H_1^\ominus$ [b]
5	3.02 ± 0.01 [c]	2.88 ± 0.01 [c]	2.78 ± 0.02 [c]	3.20 ± 0.01 [c]	−2.0 ± 0.5 [b]
10	3.01 ± 0.01	2.88 ± 0.01	2.78 ± 0.02	3.19 ± 0.01	−1.8 ± 0.4
15	3.01 ± 0.01	2.87 ± 0.01	2.78 ± 0.01	3.18 ± 0.01	−1.5 ± 0.3
20	3.00 ± 0.01	2.87 ± 0.01	2.77 ± 0.01	3.18 ± 0.01	−1.3 ± 0.3
25	3.00 ± 0.01	2.87 ± 0.01	2.77 ± 0.01	3.18 ± 0.01	−1.1 ± 0.2
30	3.00 ± 0.01	2.87 ± 0.01	2.77 ± 0.01	3.17 ± 0.01	−0.8 ± 0.3
35	3.00 ± 0.01	2.86 ± 0.01	2.77 ± 0.01	3.17 ± 0.01	−0.6 ± 0.3
40	3.00 ± 0.01	2.86 ± 0.01	2.77 ± 0.02	3.17 ± 0.01	−0.3 ± 0.4
45	2.99 ± 0.01	2.86 ± 0.01	2.77 ± 0.02	3.17 ± 0.01	−0.1 ± 0.5
	log β_2				$-\Delta H_2^\ominus$ [b]
5	5.23 ± 0.05 [c]	5.03 ± 0.05 [c]	4.88 ± 0.05 [c]	5.50 ± 0.05 [c]	−3.0 ± 2 [c]
10	5.22 ± 0.04	5.02 ± 0.04	4.87 ± 0.04	5.49 ± 0.04	−2.5 ± 2
15	5.22 ± 0.03	5.01 ± 0.03	4.86 ± 0.03	5.48 ± 0.03	−2.0 ± 2
20	5.21 ± 0.03	5.01 ± 0.02	4.86 ± 0.02	5.48 ± 0.03	−1.5 ± 2
25	5.21 ± 0.02	5.00 ± 0.02	4.85 ± 0.02	5.47 ± 0.02	−1.0 ± 2
30	5.20 ± 0.02	5.00 ± 0.02	4.85 ± 0.01	5.47 ± 0.02	−0.5 ± 2
35	5.20 ∓ 0.02	5.00 ± 0.02	4.85 ± 0.01	5.47 ± 0.02	−0.0 ± 2
40	5.20 ± 0.02	5.00 ± 0.02	4.85 ± 0.02	5.47 ± 0.02	0.4 ± 2
45	5.21 ± 0.03	5.00 ± 0.03	4.85 ± 0.02	5.47 ± 0.03	0.9 ± 2

[a] I in mol kg^{-1}. [b] $\Delta H^\ominus$ in kJ mol^{-1} at $I = 0$ mol kg^{-1}. [c] ±Std. dev.

Table A10
Thermodynamic parameter[a] for the formation of Co^{2+}–glycine complexes (molal scale) in NaCl aqueous solution

T/°C	I/(mol kg^{-1})	log K_1	log β_2	log β_3
5	0	5.20 ± 0.03 [b]	9.51 ± 0.04 [b]	12.13 ± 0.04 [b]
10	0	5.15 ± 0.03	9.42 ± 0.03	11.97 ± 0.04
15	0	5.11 ± 0.03	9.32 ± 0.03	11.83 ± 0.04
20	0	5.07 ± 0.03	9.24 ± 0.03	11.70 ± 0.04
25	0	5.04 ± 0.03	9.16 ± 0.03	11.58 ± 0.04
30	0	5.01 ± 0.03	9.08 ± 0.03	11.46 ± 0.04
35	0	4.98 ± 0.03	9.01 ± 0.03	11.36 ± 0.04
40	0	4.95 ± 0.03	8.94 ± 0.03	11.26 ± 0.04
45	0	4.93 ± 0.03	8.88 ± 0.04	11.16 ± 0.04
5	0.01	5.02 ± 0.03	9.25 ± 0.04	11.86 ± 0.04
10	0.01	4.98 ± 0.03	9.15 ± 0.03	11.70 ± 0.04
15	0.01	4.94 ± 0.03	9.06 ± 0.03	11.56 ± 0.04
20	0.01	4.90 ± 0.03	8.97 ± 0.03	11.43 ± 0.04
25	0.01	4.87 ± 0.03	8.89 ± 0.03	11.31 ± 0.04
30	0.01	4.83 ± 0.03	8.81 ± 0.03	11.19 ± 0.04
35	0.01	4.80 ± 0.03	8.74 ± 0.03	11.09 ± 0.04
40	0.01	4.78 ± 0.03	8.67 ± 0.03	10.99 ± 0.04
45	0.01	4.75 ± 0.03	8.61 ± 0.03	10.89 ± 0.04
5	0.04	4.90 ± 0.03	9.04 ± 0.03	11.64 ± 0.03
10	0.04	4.85 ± 0.03	8.94 ± 0.03	11.48 ± 0.03
15	0.04	4.81 ± 0.03	8.85 ± 0.03	11.34 ± 0.03
20	0.04	4.77 ± 0.03	8.76 ± 0.03	11.21 ± 0.03
25	0.04	4.74 ± 0.03	8.68 ± 0.03	11.09 ± 0.03
30	0.04	4.70 ± 0.03	8.60 ± 0.03	10.97 ± 0.03
35	0.04	4.67 ± 0.03	8.53 ± 0.03	10.87 ± 0.03
40	0.04	4.64 ± 0.03	8.46 ± 0.03	10.77 ± 0.03
45	0.04	4.62 ± 0.03	8.40 ± 0.03	10.67 ± 0.03
5	0.09	4.81 ± 0.03	8.89 ± 0.03	11.46 ± 0.04
10	0.09	4.76 ± 0.03	8.79 ± 0.03	11.31 ± 0.04
15	0.09	4.72 ± 0.03	8.69 ± 0.03	11.16 ± 0.04
20	0.09	4.68 ± 0.02	8.60 ± 0.03	11.03 ± 0.04
25	0.09	4.64 ± 0.02	8.52 ± 0.03	10.91 ± 0.04
30	0.09	4.61 ± 0.02	8.44 ± 0.03	10.79 ± 0.04
35	0.09	4.57 ± 0.03	8.37 ± 0.03	10.69 ± 0.04
40	0.09	4.54 ± 0.03	8.30 ± 0.03	10.59 ± 0.04
45	0.09	4.52 ± 0.03	8.23 ± 0.03	10.49 ± 0.04

T/°C	$\Delta H_1^{\ominus}$ [c]	$\Delta H_2^{\ominus}$ [c]	$\Delta H_3^{\ominus}$ [c]	T/°C	$\Delta H_1^{\ominus}$ [c]	$\Delta H_2^{\ominus}$ [c]	$\Delta H_3^{\ominus}$ [c]
5	−13.6 ± 1.8 [b]	−30.1 ± 2.3 [b]	−46.5 ± 4 [b]	30	−10.7 ± 1.0	−26.1 ± 1.3	−39.0 ± 4
10	−13.0 ± 1.4	−29.3 ± 1.9	−45.0 ± 4	35	−10.1 ± 2	−25.3 ± 1.5	−37.5 ± 4
15	−12.4 ± 1.2	−28.5 ± 1.5	−43.5 ± 4	40	−9.5 ± 1.5	−24.4 ± 1.9	−36.0 ± 4
20	−11.8 ± 1.0	−27.7 ± 1.3	−42.0 ± 4	45	−8.9 ± 1.8	−23.6 ± 2.3	−34.5 ± 4
25	−11.2 ± 0.9	−26.9 ± 1.1	−40.5 ± 4				

[a] $\Delta H^{\ominus}$ in kJ mol^{-1}. [b] ±Std. dev. [c] $I = 0$ mol kg^{-1}.

Table A11
Thermodynamic parameters[a] for the formation of Ni^{2+}–glycine complexes (molal scale) in NaCl aqueous solution

T/°C	I			
	0.01[b]	0.04	0.09	0
	log K_1			
5	6.22 ± 0.02[c]	6.12 ± 0.02[c]	6.09 ± 0.02[c]	6.38 ± 0.02[c]
10	6.14 ± 0.02	6.05 ± 0.01	6.01 ± 0.01	6.31 ± 0.02
15	6.08 ± 0.02	5.98 ± 0.01	5.94 ± 0.01	6.24 ± 0.02
20	6.01 ± 0.02	5.92 ± 0.01	5.88 ± 0.01	6.18 ± 0.02
25	5.96 ± 0.02	5.86 ± 0.01	5.82 ± 0.01	6.12 ± 0.02
30	5.90 ± 0.02	5.81 ± 0.01	5.77 ± 0.01	6.07 ± 0.02
35	5.86 ± 0.02	5.76 ± 0.01	5.72 ± 0.01	6.02 ± 0.02
40	5.81 ± 0.02	5.71 ± 0.01	5.67 ± 0.01	5.98 ± 0.02
45	5.77 ± 0.02	5.67 ± 0.02	5.63 ± 0.02	5.94 ± 0.02
	log β_2			
5	11.38 ± 0.02[c]	11.23 ± 0.02[c]	11.17 ± 0.02[c]	11.63 ± 0.03[c]
10	11.23 ± 0.02	11.09 ± 0.02	11.02 ± 0.02	11.48 ± 0.02
15	11.10 ± 0.02	10.95 ± 0.02	10.89 ± 0.01	11.34 ± 0.02
20	10.97 ± 0.02	10.82 ± 0.02	10.76 ± 0.01	11.22 ± 0.02
25	10.85 ± 0.02	10.70 ± 0.02	10.64 ± 0.01	11.10 ± 0.02
30	10.74 ± 0.02	10.59 ± 0.02	10.54 ± 0.01	10.98 ± 0.02
35	10.64 ± 0.02	10.49 ± 0.02	10.43 ± 0.01	10.88 ± 0.02
40	10.54 ± 0.02	10.40 ± 0.02	10.34 ± 0.02	10.78 ± 0.02
45	10.45 ± 0.02	10.31 ± 0.02	10.25 ± 0.02	10.70 ± 0.02
	log β_3			
5	14.92 ± 0.07[c]	14.74 ± 0.06[c]	14.61 ± 0.06[c]	15.18 ± 0.07[c]
10	14.70 ± 0.06	14.51 ± 0.06	14.39 ± 0.05	14.96 ± 0.06
15	14.49 ± 0.06	14.30 ± 0.05	14.18 ± 0.05	14.75 ± 0.06
20	14.29 ± 0.05	14.11 ± 0.05	13.99 ± 0.05	14.55 ± 0.05
25	14.11 ± 0.05	13.92 ± 0.05	13.80 ± 0.04	14.37 ± 0.05
30	13.94 ± 0.05	13.75 ± 0.05	13.63 ± 0.05	14.20 ± 0.05
35	13.78 ± 0.05	13.59 ± 0.05	13.47 ± 0.05	14.04 ± 0.06
40	13.63 ± 0.06	13.44 ± 0.06	13.32 ± 0.05	13.88 ± 0.06
45	13.48 ± 0.06	13.30 ± 0.06	13.17 ± 0.06	13.74 ± 0.06

T/°C	$\Delta H_1^{\ominus}$	$\Delta H_2^{\ominus}$	$\Delta H_3^{\ominus}$ [d]
5	−22.3 ± 1.7[c]	−45.3 ± 2.0[c]	−68 ± 6[c]
10	−21.4 ± 1.4	−43.8 ± 1.7	−66 ± 5
15	−20.5 ± 1.1	−42.3 ± 1.3	−64 ± 4
20	−19.5 ± 0.9	−40.8 ± 1.1	−62 ± 4
25	−18.6 ± 0.8	−39.3 ± 1.0	−61 ± 3
30	−17.7 ± 0.9	−37.8 ± 1.1	−59 ± 5
35	−16.8 ± 1.1	−36.3 ± 1.3	−57 ± 5
40	−15.9 ± 1.4	−34.8 ± 1.7	−55 ± 5
45	−15.0 ± 1.7	−33.3 ± 2.1	−53 ± 6
25	$\Delta C_{p_1}^{\ominus} = 183 \pm 75$ [c,d]	$\Delta C_{p_2}^{\ominus} = 301 \pm 91$ [c,d]	$\Delta C_{p_3}^{\ominus} = 380 \pm 120$ [c,d]

[a] $\Delta H^{\ominus}$ in kJ mol^{-1}; $\Delta C_p^{\ominus}$ in kJ mol^{-1}. [b] I in mol kg^{-1}. [c] ±Std. dev. [d] $I = 0$ mol kg^{-1}.

Table A12
Thermodynamic parameters[a] for the formation of Cu^{2+}–glycine complexes (molal scale) in NaCl aqueous solution

T/°C	I			
	0.01[b]	0.04	0.09	0
	log K_1			
5	8.68 ± 0.03[c]	8.58 ± 0.03[c]	8.54 ± 0.02[c]	8.84 ± 0.04[c]
10	8.58 ± 0.03	8.49 ± 0.02	8.45 ± 0.02	8.75 ± 0.03
15	8.49 ± 0.03	8.40 ± 0.02	8.36 ± 0.02	8.66 ± 0.03
20	8.41 ± 0.03	8.31 ± 0.02	8.27 ± 0.02	8.57 ± 0.03
25	8.33 ± 0.03	8.23 ± 0.02	8.20 ± 0.02	8.50 ± 0.03
30	8.26 ± 0.03	8.16 ± 0.02	8.12 ± 0.02	8.42 ± 0.03
35	8.19 ± 0.03	8.09 ± 0.02	8.05 ± 0.02	8.35 ± 0.03
40	8.12 ± 0.03	8.03 ± 0.02	7.99 ± 0.02	8.29 ± 0.03
45	8.06 ± 0.03	7.97 ± 0.03	7.93 ± 0.02	8.23 ± 0.03
	log β_2			
5	16.11 ± 0.04[c]	15.93 ± 0.03[c]	15.82 ± 0.03[c]	16.37 ± 0.04[c]
10	15.92 ± 0.04	15.74 ± 0.03	15.63 ± 0.03	16.18 ± 0.04
15	15.74 ± 0.03	15.56 ± 0.03	15.45 ± 0.02	16.00 ± 0.04
20	15.57 ± 0.03	15.39 ± 0.03	15.27 ± 0.02	15.82 ± 0.04
25	15.40 ± 0.03	15.22 ± 0.03	15.11 ± 0.02	15.66 ± 0.04
30	15.24 ± 0.03	15.06 ± 0.03	14.95 ± 0.02	15.50 ± 0.04
35	15.09 ± 0.03	14.92 ± 0.03	14.80 ± 0.02	15.35 ± 0.04
40	14.95 ± 0.04	14.77 ± 0.03	14.66 ± 0.02	15.21 ± 0.04
45	14.82 ± 0.04	14.64 ± 0.03	14.53 ± 0.03	15.07 ± 0.04

T/°C	$\Delta H_1^\ominus$ [d]	$\Delta H_2^\ominus$ [d]	T/°C	$\Delta H_1^\ominus$ [d]	$\Delta H_2^\ominus$ [d]
5	−29.0 ± 1.7	−58.3 ± 3.1	30	−25.2 ± 0.9	−53.9 ± 1.6
10	−28.0 ± 1.4	−57.5 ± 2.5	35	−24.4 ± 1.1	−53.0 ± 2.0
15	−27.5 ± 1.1	−56.6 ± 2.0	40	−23.6 ± 1.4	−52.1 ± 2.6
20	−26.7 ± 0.9	−55.7 ± 1.6	45	−22.8 ± 1.7	−51.2 ± 3.2
25	−25.9 ± 0.8	−54.8 ± 1.4			
25	$\Delta C_{p1}^\ominus$ = 154 ± 74[c,d] $\Delta C_{p1}^\ominus$ = 180 ± 100[c,d]				

[a] $\Delta H^\ominus$ in kJ mol^{-1}; $\Delta C_p^\ominus$ in kJ mol^{-1}. [b] I in mol kg^{-1}. [c] ±Std. dev. [d] $I = 0$ mol kg^{-1}.

Table A13
Thermodynamic parameters[a] for the formation of Zn^{2+}–glycine complexes (molal scale) in NaCl aqueous solution

T/°C	I			
	0.01[b]	0.04	0.09	0
5	5.42 ± 0.02[c]	5.28 ± 0.02[c]	5.17 ± 0.02[c]	5.59 ± 0.02[c]
10	5.35 ± 0.02	5.23 ± 0.02	5.13 ± 0.02	5.55 ± 0.02
15	5.35 ± 0.02	5.19 ± 0.02	5.09 ± 0.01	5.51 ± 0.02
20	5.29 ± 0.02	5.16 ± 0.01	5.05 ± 0.01	5.47 ± 0.02
25	5.26 ± 0.02	5.12 ± 0.01	5.02 ± 0.01	5.43 ± 0.02

Table A13 (continued)

T/°C	I			
	0.01 [b]	0.04	0.09	0
30	5.23 ± 0.02	5.09 ± 0.01	4.99 ± 0.01	5.40 ± 0.02
35	5.20 ± 0.02	5.06 ± 0.01	4.96 ± 0.01	5.37 ± 0.02
40	5.17 ± 0.02	5.04 ± 0.02	4.93 ± 0.02	5.35 ± 0.02
45	5.15 ± 0.02	5.01 ± 0.02	4.91 ± 0.02	5.32 ± 0.02
	log β_2			
5	9.98 ± 0.06 [c]	9.77 ± 0.05 [c]	9.62 ± 0.05 [c]	10.25 ± 0.06 [c]
10	9.89 ± 0.05	9.68 ± 0.05	9.52 ± 0.04	10.15 ± 0.05
15	9.80 ± 0.04	9.59 ± 0.04	9.44 ± 0.04	10.06 ± 0.04
20	9.72 ± 0.04	9.51 ± 0.04	9.36 ± 0.03	9.98 ± 0.04
25	9.64 ± 0.04	9.43 ± 0.04	9.28 ± 0.03	9.90 ± 0.04
30	9.57 ± 0.04	9.36 ± 0.04	9.21 ± 0.03	8.83 ± 0.04
35	9.50 ± 0.04	9.30 ± 0.04	9.15 ± 0.04	9.76 ± 0.04
40	9.44 ± 0.05	9.24 ± 0.04	9.08 ± 0.04	9.70 ± 0.05
45	9.38 ± 0.05	9.18 ± 0.05	9.03 ± 0.05	9.64 ± 0.06
	log β_3			
5	12.58 ± 0.11 [c]	12.39 ± 0.10 [c]	12.25 ± 0.11 [c]	12.85 ± 0.11 [c]
10	12.43 ± 0.10	12.23 ± 0.10	12.08 ± 0.10	12.69 ± 0.10
15	12.28 ± 0.10	12.08 ± 0.10	11.93 ± 0.09	12.55 ± 0.10
20	12.15 ± 0.10	11.94 ± 0.09	11.79 ± 0.08	12.41 ± 0.10
25	12.02 ± 0.10	11.82 ± 0.09	11.66 ± 0.08	12.29 ± 0.10
30	11.91 ± 0.10	11.70 ± 0.09	11.53 ± 0.08	12.18 ± 0.10
35	11.81 ± 0.10	11.59 ± 0.09	11.42 ± 0.08	12.07 ± 0.10
40	11.71 ± 0.10	11.49 ± 0.09	11.31 ± 0.08	11.98 ± 0.10
45	11.62 ± 0.10	11.40 ± 0.09	11.21 ± 0.09	11.89 ± 0.10

T/°C	$\Delta H_1^{\ominus}$ [d]	$\Delta H_2^{\ominus}$ [d]	$\Delta H_1^{\ominus}$ [d]	T/°C	$\Delta H_1^{\ominus}$ [d]	$\Delta H_2^{\ominus}$ [d]	$\Delta H_1^{\ominus}$ [d]
5	−13.8 ± 1.8 [b]	−28.9 ± 5.7 [b]	−47.8 ± 5 [b]	30	−10.7 ± 1.0	−24.4 ± 3.0	−38.3 ± 5
10	−13.2 ± 1.5	−28.0 ± 4.6	−45.9 ± 5	35	−10.1 ± 1.2	−23.5 ± 3.7	−36.4 ± 5
15	−12.6 ± 1.2	−27.1 ± 3.7	−44.0 ± 5	40	−9.5 ± 1.5	−22.6 ± 4.6	−34.5 ± 5
20	−12.0 ± 1.0	−26.2 ± 1.0	−42.1 ± 5	45	−8.9 ± 1.8	−21.7 ± 5.6	−32.6 ± 5
25	−11.4 ± 0.9	−25.3 ± 2.7	−40.2 ± 5				

[a] $\Delta H^{\ominus}$ in kJ mol^{-1}. [b] I in mol kg^{-1}. [c] ±Std. dev. [d] $I = 0$ mol kg^{-1}.

Table A14
Thermodynamic parameters[a] for the formation of Cd^{2+}–glycine complexes (molal scale) in NaCl aqueous solution

T/°C	I			
	0.01 [b]	0.04	0.09	0
	log K_1			
5	4.63 ± 0.04 [c]	4.49 ± 0.04 [c]	4.39 ± 0.06 [c]	4.80 ± 0.04 [c]
10	4.60 ± 0.03	4.46 ± 0.04	4.37 ± 0.05	4.77 ± 0.03
15	4.57 ± 0.03	4.44 ± 0.03	4.35 ± 0.04	4.74 ± 0.03

Table A14 (continued)

T/°C	I			
	0.01 [b]	0.04	0.09	0
20	4.54 ± 0.03	4.41 ± 0.03	4.33 ± 0.03	4.71 ± 0.03
25	4.51 ± 0.03	4.39 ± 0.03	4.31 ± 0.02	4.96 ± 0.03
30	4.49 ± 0.03	4.37 ± 0.03	4.29 ± 0.02	4.66 ± 0.03
35	4.47 ± 0.03	4.35 ± 0.03	4.27 ± 0.03	4.64 ± 0.03
40	4.44 ± 0.03	4.33 ± 0.03	4.26 ± 0.04	4.61 ± 0.03
45	4.42 ± 0.03	4.31 ± 0.03	4.24 ± 0.05	4.59 ± 0.03
	log β_2			
5	8.50 ± 0.07 [c]	8.17 ± 0.09 [c]	7.80 ± 0.13 [c]	8.80 ± 0.07 [c]
10	8.42 ± 0.07	8.12 ± 0.08	7.81 ± 0.11	8.72 ± 0.07
15	8.36 ± 0.06	8.09 ± 0.07	7.82 ± 0.08	8.64 ± 0.06
20	8.29 ± 0.06	8.05 ± 0.06	7.84 ± 0.06	8.57 ± 0.06
25	8.24 ± 0.06	8.03 ± 0.06	7.86 ± 0.05	8.50 ± 0.06
30	8.18 ± 0.06	8.00 ± 0.06	7.89 ± 0.05	8.44 ± 0.06
35	8.13 ± 0.06	7.98 ± 0.06	7.92 ± 0.06	8.38 ± 0.06
40	8.08 ± 0.06	7.97 ± 0.06	7.95 ± 0.08	8.32 ± 0.07
45	8.04 ± 0.06	7.95 ± 0.07	7.99 ± 0.11	8.27 ± 0.07
	log β_3			
5	10.82 ± 0.2 [c]	10.63 ± 0.02 [c]	10.51 ± 0.2 [c]	11.98 ± 0.2 [c]
10	10.69 ± 0.2	10.50 ± 0.2	10.38 ± 0.1	10.95 ± 0.2
15	10.57 ± 0.2	10.38 ± 0.2	10.26 ± 0.1	10.82 ± 0.2
20	10.45 ± 0.2	10.26 ± 0.2	10.14 ± 0.1	10.71 ± 0.2
25	10.34 ± 0.2	10.16 ± 0.2	10.03 ± 0.1	10.60 ± 0.2
30	10.24 ± 0.2	10.05 ± 0.2	9.93 ± 0.1	10.50 ± 0.2
35	10.14 ± 0.2	9.96 ± 0.2	9.84 ± 0.1	10.40 ± 0.2
40	10.05 ± 0.2	9.87 ± 0.2	9.74 ± 0.1	10.31 ± 0.2
45	9.97 ± 0.2	9.78 ± 0.2	9.66 ± 0.1	10.23 ± 0.2

T/°C	$\Delta H_1^\ominus$ [d]	$\Delta H_2^\ominus$ [d]	$\Delta H_3^\ominus$ [d]
5	−9.5 ± 2.4 [b]	−25.2 ± 3.6 [b]	−39.9 ± 4 [b]
10	−9.3 ± 2.0	−24.5 ± 3.0	−38.9 ± 4
15	−9.1 ± 1.6	−23.9 ± 2.4	−37.9 ± 4
20	−8.9 ± 1.4	−23.2 ± 2.0	−36.9 ± 4
25	−8.8 ± 1.2	−22.6 ± 1.9	−35.9 ± 4
30	−8.6 ± 1.4	−21.9 ± 2.0	−34.9 ± 4
35	−8.4 ± 1.6	−21.3 ± 2.4	−33.9 ± 4
40	−8.2 ± 2.0	−20.6 ± 3.0	−32.9 ± 4
45	−8.0 ± 2.4	−20.0 ± 3.6	−31.9 ± 4

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[a] $\Delta H^\ominus$ in kJ mol^{-1}. [b] I in mol kg^{-1}. [c] ±Std. dev. [d] $I = 0$ mol kg^{-1}.

Table A15
Equilibrium constants for the reactions (literature data)

(a) $Ni^{2+} + H(gly)^0 = Ni(gly)^+ + H^+$

(b) $Ni^{2+} + gly^- + H(gly)^0 = Ni(gly)_2^0 + H^+$

(c) $Ni(gly)^+ + H(gly)^0 = Ni(gly)_2^0 + H^+$

T/°C	I/(mol dm^{-3})	Reaction		
		(a)	(b)	(c)
5	0.0	−4.03 ± 0.04 [a]	1.24 ± 0.09 [a]	−5.02 ± 0.05 [a]
10	0.0	−3.93 ± 0.03	1.25 ± 0.07	−4.96 ± 0.04
15	0.0	−3.84 ± 0.02	1.26 ± 0.05	−4.90 ± 0.03
20	0.0	−3.76 ± 0.01	1.27 ± 0.03	−4.85 ± 0.02
25	0.0	−3.67 ± 0.01	1.29 ± 0.02	−4.80 ± 0.01
30	0.0	−3.59 ± 0.01	1.30 ± 0.03	−4.74 ± 0.01
35	0.0	−3.51 ± 0.02	1.32 ± 0.04	−4.69 ± 0.02
40	0.0	−3.43 ± 0.02	1.33 ± 0.06	−4.65 ± 0.03
45	0.0	−3.35 ± 0.03	1.35 ± 0.07	−4.60 ± 0.04
5	0.1	−4.19 ± 0.04	0.91 ± 0.09	−5.04 ± 0.05
10	0.1	−4.10 ± 0.03	0.92 ± 0.07	−4.98 ± 0.03
15	0.1	−4.01 ± 0.02	0.93 ± 0.05	−4.92 ± 0.02
20	0.1	−3.93 ± 0.01	0.94 ± 0.03	−4.86 ± 0.02
25	0.1	−3.84 ± 0.01	0.95 ± 0.02	−4.81 ± 0.01
30	0.1	−3.76 ± 0.01	0.96 ± 0.03	−4.76 ± 0.01
35	0.1	−3.68 ± 0.02	0.97 ± 0.04	−4.71 ± 0.02
40	0.1	−3.60 ± 0.02	0.98 ± 0.06	−4.66 ± 0.03
45	0.1	−3.52 ± 0.03	0.99 ± 0.07	−4.61 ± 0.03
5	0.5	−4.17 ± 0.04	0.99 ± 0.09	−5.10 ± 0.04
10	0.5	−4.08 ± 0.03	0.98 ± 0.07	−5.04 ± 0.03
15	0.5	−4.00 ± 0.02	0.97 ± 0.05	−4.98 ± 0.02
20	0.5	−3.92 ± 0.01	0.97 ± 0.03	−4.92 ± 0.02
25	0.5	−3.84 ± 0.01	0.96 ± 0.02	−4.87 ± 0.01
30	0.5	−3.76 ± 0.01	0.95 ± 0.03	−4.82 ± 0.02
35	0.5	−3.68 ± 0.02	0.95 ± 0.04	−4.77 ± 0.02
40	0.5	−3.61 ± 0.02	0.95 ± 0.06	−4.72 ± 0.03
45	0.5	−3.53 ± 0.03	0.94 ± 0.07	−4.67 ± 0.04
5	1.0	−4.09 ± 0.04	1.20 ± 0.09	−5.17 ± 0.05
10	1.0	−4.00 ± 0.03	1.17 ± 0.07	−5.11 ± 0.05
15	1.0	−3.92 ± 0.02	1.14 ± 0.05	−5.06 ± 0.04
20	1.0	−3.85 ± 0.01	1.11 ± 0.03	−5.00 ± 0.04
25	1.0	−3.77 ± 0.01	1.09 ± 0.02	−4.95 ± 0.04
30	1.0	−3.70 ± 0.01	1.06 ± 0.03	−4.89 ± 0.04
35	1.0	−3.63 ± 0.02	1.04 ± 0.04	−4.84 ± 0.05
40	1.0	−3.56 ± 0.02	1.01 ± 0.06	−4.80 ± 0.05
45	1.0	−3.49 ± 0.03	0.99 ± 0.07	−4.75 ± 0.06
25	C = 0.51 ± 0.06 [b]	C = 1.02 ± 0.08 [b]	C = 0.15 ± 0.09 [b]	

[a] ±Std. dev. [b] C is a parameter of Eq. (1b).

Table A16
Equilibrium constants for the reactions (literature data)

(a) $Cu^{2+} + H(gly)^0 = Cu(gly)^+ + H^+$

(b) $Cu^{2+} + gly^- + H(gly)^0 = Cu(gly)_2^0 + H^+$

(c) $Cu(gly)^+ + H(gly)^0 = Cu(gly)_2^0 + H^+$

T/°C	I/(mol dm^{-3})	Reaction		
		(a)	(b)	(c)
5	0.0	−1.40 ± 0.04 [a]	6.06 ± 0.06 [a]	−2.86 ± 0.04 [a]
10	0.0	−1.35 ± 0.02	5.99 ± 0.04	−2.83 ± 0.03
15	0.0	−1.31 ± 0.02	5.93 ± 0.02	−2.79 ± 0.02
20	0.0	−1.27 ± 0.02	5.88 ± 0.02	−2.76 ± 0.01
25	0.0	−1.22 ± 0.02	5.84 ± 0.01	−2.72 ± 0.01
30	0.0	−1.18 ± 0.02	5.80 ± 0.01	−2.68 ± 0.01
35	0.0	−1.14 ± 0.02	5.78 ± 0.02	−2.63 ± 0.02
40	0.0	−1.10 ± 0.03	5.76 ± 0.03	−2.59 ± 0.02
45	0.0	−1.06 ± 0.04	5.75 ± 0.05	−2.54 ± 0.03
5	0.1	−1.57 ± 0.04	5.73 ± 0.06	−2.87 ± 0.04
10	0.1	−1.52 ± 0.02	5.66 ± 0.04	−2.84 ± 0.03
15	0.1	−1.48 ± 0.02	5.59 ± 0.02	−2.80 ± 0.02
20	0.1	−1.44 ± 0.01	5.54 ± 0.02	−2.77 ± 0.01
25	0.1	−1.40 ± 0.01	5.49 ± 0.01	−2.73 ± 0.01
30	0.1	−1.35 ± 0.01	5.46 ± 0.01	−2.68 ± 0.01
35	0.1	−1.31 ± 0.02	5.43 ± 0.02	−2.64 ± 0.02
40	0.1	−1.27 ± 0.03	5.41 ± 0.03	−2.60 ± 0.02
45	0.1	−1.23 ± 0.04	5.40 ± 0.05	−2.55 ± 0.03
5	0.5	−1.55 ± 0.04	5.81 ± 0.06	−2.90 ± 0.04
10	0.5	−1.51 ± 0.03	5.72 ± 0.04	−2.87 ± 0.03
15	0.5	−1.48 ± 0.02	5.63 ± 0.02	−2.83 ± 0.02
20	0.5	−1.44 ± 0.02	5.56 ± 0.02	−2.80 ± 0.02
25	0.5	−1.40 ± 0.02	5.50 ± 0.01	−2.76 ± 0.01
30	0.5	−1.36 ± 0.02	5.45 ± 0.01	−2.72 ± 0.01
35	0.5	−1.33 ± 0.02	5.41 ± 0.02	−2.67 ± 0.02
40	0.5	−1.29 ± 0.03	5.37 ± 0.03	−2.63 ± 0.03
45	0.5	−1.25 ± 0.05	5.34 ± 0.05	−2.58 ± 0.04
5	1.0	−1.48 ± 0.05	6.01 ± 0.06	−2.94 ± 0.05
10	1.0	−1.45 ± 0.04	5.90 ± 0.04	−2.91 ± 0.04
15	1.0	−1.41 ± 0.04	5.80 ± 0.02	−2.87 ± 0.03
20	1.0	−1.38 ± 0.04	5.71 ± 0.02	−2.84 ± 0.03
25	1.0	−1.35 ± 0.03	5.63 ± 0.01	−2.80 ± 0.03
30	1.0	−1.32 ± 0.03	5.55 ± 0.01	−2.75 ± 0.03
35	1.0	−1.28 ± 0.04	5.49 ± 0.02	−2.71 ± 0.03
40	1.0	−1.25 ± 0.04	5.43 ± 0.03	−2.67 ± 0.04
45	1.0	−1.22 ± 0.06	5.38 ± 0.05	−2.62 ± 0.04
25		$C = 0.48 \pm 0.04$ [b]	$C = 0.99 \pm 0.07$ [b]	$C = 0.08 \pm 0.06$ [b]

[a] ± Std. dev. [b] C is a parameter of Eq. (1b).

Table A17
Equilibrium constants for the reactions (literature data)

(a) $Zn^{2+} + H(gly)^0 = Zn(gly)^+ + H^+$

(b) $Zn^{2+} + gly^- + H(gly)^0 = Zn(gly)_2^0 + H^+$

(c) $Zn(gly)^+ + H(gly)^0 = Zn(gly)_2^0 + H^+$

T/°C	I/(mol dm^{-3})	Reaction		
		(a)	(b)	(c)
5	0.0	−4.84 ± 0.08 [a]	−0.16 ± 0.08 [a]	−5.74 ± 0.06 [a]
10	0.0	−4.74 ± 0.05	−0.12 ± 0.07	−5.64 ± 0.05
15	0.0	−4.64 ± 0.03	−0.07 ± 0.05	−5.55 ± 0.04
20	0.0	−4.54 ± 0.02	−0.03 ± 0.04	−5.47 ± 0.03
25	0.0	−4.44 ± 0.02	0.02 ± 0.04	−5.38 ± 0.03
30	0.0	−4.34 ± 0.02	0.06 ± 0.03	−5.30 ± 0.03
35	0.0	−4.24 ± 0.02	0.10 ± 0.04	−5.22 ± 0.03
40	0.0	−4.14 ± 0.03	0.15 ± 0.05	−5.14 ± 0.04
45	0.0	−4.04 ± 0.05	0.19 ± 0.06	−5.07 ± 0.05
5	0.1	−5.01 ± 0.08	−0.52 ± 0.08	−5.75 ± 0.06
10	0.1	−4.91 ± 0.05	−0.48 ± 0.07	−5.65 ± 0.05
15	0.1	−4.80 ± 0.03	−0.43 ± 0.05	−5.56 ± 0.04
20	0.1	−4.70 ± 0.02	−0.39 ± 0.04	−5.48 ± 0.03
25	0.1	−4.60 ± 0.02	−0.35 ± 0.03	−5.39 ± 0.02
30	0.1	−4.50 ± 0.02	−0.31 ± 0.03	−5.31 ± 0.02
35	0.1	−4.40 ± 0.02	−0.28 ± 0.03	−5.23 ± 0.03
40	0.1	−4.31 ± 0.03	−0.24 ± 0.04	−5.15 ± 0.04
45	0.1	−4.21 ± 0.05	−0.20 ± 0.05	−5.08 ± 0.05
5	0.5	−4.97 ± 0.08	−0.56 ± 0.10	−5.79 ± 0.07
10	0.5	−4.87 ± 0.05	−0.53 ± 0.08	−5.70 ± 0.06
15	0.5	−4.77 ± 0.03	−0.50 ± 0.07	−5.61 ± 0.05
20	0.5	−4.68 ± 0.02	−0.48 ± 0.06	−5.52 ± 0.04
25	0.5	−4.58 ± 0.02	−0.46 ± 0.06	−5.43 ± 0.04
30	0.5	−4.48 ± 0.02	−0.43 ± 0.06	−5.35 ± 0.04
35	0.5	−4.39 ± 0.02	−0.41 ± 0.06	−5.27 ± 0.04
40	0.5	−4.29 ± 0.03	−0.39 ± 0.06	−5.20 ± 0.05
45	0.5	−4.20 ± 0.05	−0.37 ± 0.07	−5.12 ± 0.06
5	1.0	−4.86 ± 0.08	−0.50 ± 0.15	−5.84 ± 0.10
10	1.0	−4.77 ± 0.05	−0.49 ± 0.14	−5.75 ± 0.09
15	1.0	−4.68 ± 0.03	−0.48 ± 0.14	−5.66 ± 0.08
20	1.0	−4.59 ± 0.02	−0.48 ± 0.13	−5.57 ± 0.08
25	1.0	−4.50 ± 0.02	−0.47 ± 0.13	−5.49 ± 0.08
30	1.0	−4.41 ± 0.02	−0.47 ± 0.13	−5.40 ± 0.08
35	1.0	−4.32 ± 0.02	−0.47 ± 0.13	−5.32 ± 0.08
40	1.0	−4.23 ± 0.03	−0.47 ± 0.13	−5.25 ± 0.09
45	1.0	−4.14 ± 0.05	−0.47 ± 0.13	−5.17 ± 0.09
25		$C = 0.54 \pm 0.08$ [b]	$C = 0.71 \pm 0.14$ [b]	$C = 0.10 \pm 0.09$ [b]

[a] ±Std. dev. [b] C is a parameter of Eq. (1b).

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