Thermodynamic Study on the Interaction between Phenylglycine and Some Transition Metal Ions

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The proton ionization constants (pK_{011} and pK_{012}) of phenylglycine were determined in aqueous solution using Bjerrum's potentiometric technique. The measurements were carried out at three ionic strengths [(μ = 0.05, 0.10, and 0.15) M KNO_3] and three temperatures [(25, 35, and 45) °C]. From the data obtained, the thermodynamic ionization constants (p$K°_{011}$ and p$K°_{012}$) and the isoelectric points (pI_s) for phenylglycine were calculated. The interactions between phenylglycine and some transition metal ions (Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) were studied at the same conditions of the ionic strengths and temperatures in aqueous media by using the same technique. The stoichiometric and thermodynamic stability constants as well as the degree of formation (ñ) for all studied systems were determined and discussed. The standard thermodynamic parameters (Δp$K°$ and Δ log $K°$) and the thermodynamic parameter differences ($\Delta G°$, $\Delta\Delta G°$, $\Delta H°$, $\Delta\Delta H°$, $\Delta S°$, and $\Delta\Delta S°$) were calculated for all possible reactions. Advanced discussions of these functions as well as the factors that may control the ionization and complexation processes from the thermodynamic point of view have been reported.

Introduction

Now, with the start of the 21st century, and because of the importance of amino acids which act as building blocks in protein molecules and hormones and the importance of transition metal ions in vital processes in living organisms, many authors have directed their studies to the reactions between them.[1−8] No data were found in the literature about the dissociation constant of phenylglycine. Accordingly, as an important stage in our laboratory program,[9−12] this study presents the application of a new thermodynamic treatment of the complexation processes between phenylglycine and some transition metal ions (Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}). The reactions were studied at three ionic strengths [(μ = 0.05, 0.10, and 0.15) M KNO_3] and three temperatures [(25, 35, and 45) °C] in aqueous solutions by using the Bjerrum pH titration procedure.[13] Such techniques prerequisite the determination of the ionization constants (pK_{011} and pK_{012}) of pure phenylglycine at the same conditions of the ionic strength and temperature. The isoelectric points (pI_s) for pure phenylglycine as well as the degree formed (ñ) for the complexes were determined. From these data, the stoichiometric stability constants (K), the thermodynamic stability constants ($K°$), and the standard thermodynamic parameters ($\Delta G°$, $\Delta\Delta G°$, $\Delta H°$, $\Delta\Delta H°$, $\Delta S°$, and $\Delta\Delta S°$) were calculated and discussed to determine the factors which control the studied complexation processes from a thermodynamic point of view.

Experimental Section

1. Materials. $MnNO_3\cdot 6H_2O$, 98.5 %, $NiNO_3\cdot 6H_2O$, 99.0 %, $CuNO_3\cdot 3H_2O$, 99.0 %, $ZnNO_3\cdot 6H_2O$, 99.5 %, $CdNO_3\cdot 4H_2O$, 98.7 %, NaOH, 97.0 % and phenylglycine, 98 %, were all purchased from the Riedel-deHäen, Co. All of the solutions were made by weight just before the pH measurement by using conductivity water (very pure bidistilled water, i.e., very low conductance water). Sodium phenylglycine was prepared by the addition of equivalent amounts of NaOH solution and pure phenylglycine. The transition metal nitrates were analyzed by complexometric methods.[14]

2. Procedure. a. Instrumentation. An Orion research ionalyzer pH meter was standardized by using buffers at pH 7, 4, and 10. The pH values were precise to ± 0.01 pH units by using a correction factor according to the following equation:[9,10]

$$\mathrm{pH} = 7.00 + (\mathrm{pH}_{\mathrm{meter}} - 7.00)C_{\mathrm{meter}} \qquad (1)$$

where C_{meter} is the correction factor in the acidic range or in the alkaline range,[9,10] assuming the correction needed in either the acidic or alkaline range is linear.

b. Determination of the Ionization Constants of Phenylglycine. A 100 mL solution containing $8\cdot 10^{-4}$ M phenylglycine and a sufficient amount of 1 M KNO_3 [to adjust the ionic strength[15] to μ = (0.05, 0.10, and 0.15) M] was thermostatted at the desired temperatures [t = (25, 35, and 45) °C]. The solution was then titrated with $2\cdot 10^{-3}$ M HNO_3 to determine pK_{012} (and at another time titrated against $2\cdot 10^{-3}$ M NaOH to determine pK_{011}). The pH was recorded after each addition of titrant.

c. Determination of the Stability Constants. A 100 mL aqueous solution containing $1\cdot 10^{-3}$ M HNO_3 and $1\cdot 10^{-3}$ M $M(NO_3)_2$ (where M = Mn, Ni, Cu, Zn, and Cd) and a sufficient amount of 1 M KNO_3 to adjust the ionic strength [at μ = (0.05, 0.10, and 0.15) M] was thermostatted at the desired temperatures [t = (25, 35, and 45) °C]. The pH was recorded after each addition of 0.05 M sodium phenylglycinate as a ligand.

3. Calculations. i. Calculations of the Ionization Constants of Phenylglycine. The Bjerrum's pH titration procedure assumes the presence of the reacting species H_2L^+ (the dipro-

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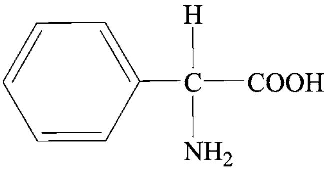
tonated phenylglycine), HL (the monoprotonated phenylglycine), and L^- (the phenylglycine anion) according to the following equilibria:[11,16]

$$H_2L^+ \overset{K_{011}}{\rightleftharpoons} HL + H^+ \qquad K_{011} = ([HL][H^+])/[H_2L^+] \tag{2}$$

$$HL \overset{K_{012}}{\rightleftharpoons} L^- + H^+ \qquad K_{012} = ([L^-][H^+])/[HL] \tag{3}$$

where HL (the phenylglycine itself) for the ligand under study is represented by the following structure:



phenylglycine

The values of the ionization constants (K_{011} and K_{012}) of phenylglycine were calculated from the following equations:[11,16]

$$\mathrm{p}K_{011} = -\log[H^+] + \log \frac{[NO_3^-] + [OH^-] - [H^+]}{L_{\mathrm{tot}} - [NO_3^-] - [OH^-] + [H^+]} \tag{4}$$

$$\mathrm{p}K_{012} = -\log[H^+] + \log \frac{L_{\mathrm{tot}} - \{[H^+] + [Na^+] - [OH^-]\}}{[H^+] + [Na^+] - [OH^-]} \tag{5}$$

where L_{tot} is the total phenylglycine concentration. The H^+ concentration is calculated from pH (where pH = $-\log a_{H^+}$ and $a_{H^+} = \gamma_+[H^+]$). The activity coefficient (γ_+) was calculated using the Davies equation. The $[OH^-]$ is calculated from the water dissociation constant K_w and pH (where $\mathrm{p}K_w$ = pH + pOH, then $\log[OH^-] = \mathrm{pH} - \log \gamma_\pm - \mathrm{p}K_W$). The mean activity coefficient ($\gamma_\pm$) was also calculated using the Davies equation, and the needed values of $\mathrm{p}K_w$ were selected on the basis of temperature (13.9965 at 25 °C, 13.6801 at 35 °C, and 13.3960 at 45 °C).[17] The $[NO_3^-]$ and $[Na^+]$ are from the amount of titrand.

ii. Calculation of the Stability Constants. In most previous studies of the complexation processes between amino acids and different metal cations, the authors considered that the complexation processes were carried out by only one of the reacting species (H_2L^+, HL, or L^-). In the present study only HL and L^- were considered as ligating species where the electrostatic repulsion between H_2L^+ and M^{2+} is expected to be strong. The determined ionization constants K_{011} and K_{012} (from eqs 4 and 5) of pure phenylglycine were used to calculate the concentrations of H_2L^+, HL, and L^- which are present in the reaction medium. The most probable reactions between the phenylglycine and the studied metal cations were carried out according to the following suggestions.

A. Reaction Scheme I. The deprotonated phenylglycine anion L^- could act as an interacting ligating species as follows:

$$M^{2+} + L^- \overset{K_{110}}{\rightleftharpoons} ML^+ \qquad K_{110} = \frac{[ML^+]}{[M^{2+}][L^-]} \tag{6}$$

$$M^{2+} + 2L^- \overset{K_{111}}{\rightleftharpoons} ML_2 \qquad K_{111} = \frac{[ML_2]}{[M^{2+}][L^-]^2} \tag{7}$$

where K_{110} and K_{111} are the overall stability constants of the complexes formed from the suggested reaction I. Then, the L^- concentration can be obtained by combining eqs 2 and 3[9] as follows.

$[H^+]_{\mathrm{bound}} = [H^+]_{HNO_3} + [H^+]_{\text{from dissociation of water}} - [H^+]_{\mathrm{free}}$, which can expressed as follows: $[H^+]_{\mathrm{bound}} = [HNO3] + [OH^-] - [H^+]$, from which $[H^+]_{\mathrm{bound}}$ can be calculated. $[H^+]_{\mathrm{bound}}$ can be expressed in another form as follows: $[H^+]_{\mathrm{bound}} = 2[H_2L^+] + [HL]$, where there are two hydrogen ions bound in $[H_2L^+]$ and one in [HL]. From eq 2, $[HL] = K_{011}\,[H_2L^+]/[H^+]$; then by substitution of [HL], $[H^+]_{\mathrm{bound}} = 2[H_2L^+] + K_{011}\,[H_2L^+]/[H^+]$, and then $[H^+]_{\mathrm{bound}} = [H_2L^+]\{(2[H^+] + K_{011})/[H^+]\}$, from which $[H_2L^+]$ can be calculated by knowing K_{011} (from eq 4) and the pH and $[H^+]_{\mathrm{bound}}$ calculated above. From the calculated $[H_2L^+]$, the value of [HL] can be calculated from eq 2 by knowing K_{011} (from eq 4) and the pH. Also from the calculated values of $[H_2L^+]$ and [HL], the value of $[L^-]$ can be calculated from the combination of eqs 2 and 3 as follows: $[L^-] = K_{011}K_{012}[H_2L^+]/[H^+]^2$, by knowing the value of K_{012} from eq 5.

B. Reaction Scheme II. The phenylglycine itself, HL (i.e., the monoprotic amino acid), could act as a ligating species with proton release according to the following equilibra:

$$M^{2+} + HL \overset{K_{000}}{\rightleftharpoons} ML^+ + H^+ \qquad K_{000} = \frac{[ML^+][H^+]}{[M^{2+}][HL]} \tag{8}$$

$$M^{2+} + 2HL \overset{K_{001}}{\rightleftharpoons} ML_2 + 2H^+ \qquad K_{001} = \frac{[ML_2][H^+]^2}{[M^{2+}][HL]^2} \tag{9}$$

where K_{000} and K_{001} are the overall stability constants of the complexes formed from the suggested reaction II. Then, [HL] was calculated from eq 2 as described above in the reaction scheme I.

The overall stability constants, K, can be calculated from the well-known equation:[9,12,13]

$$\frac{\tilde{n}}{(1-\tilde{n})[L]} = \sum_{i=1}^{j} \frac{(i-\tilde{n})}{(1-\tilde{n})} K_i [L]^{i-1} \tag{10}$$

where j is the maximum number of ligands which can be bound with the metal ion while i is a numerical number whose value depends on the nature of the formed complex, that is, the number of ligands which are suggested to be bound with the metal ion ($i = 1$ for a 1:1 and $i = 2$ for a 2:1 (L:M) stoichiometric complex). [L] is the free ligand concentration. ñ is the average number of ligands bound per metal ion concentration which can be expressed as follows:[9,12,18]

$$\tilde{n} = \frac{\text{bound ligand}}{\text{total metal ion concentration}} = \frac{L_{\mathrm{bound}}}{C_M} = \frac{L_{\mathrm{total}} - L_{\mathrm{free}}}{C_M} \tag{11}$$

where the free ligand concentration L_{free} was calculated by: $L_{\mathrm{free}} = [H_2L^+] + [HL] + [L^-]$ where $[H_2L^+]$, [HL], and $[L^-]$ were calculated as described above in reaction scheme I. The total ligand concentration L_{total} was calculated by applying the dilution law after each addition of the ligand during the titration process.

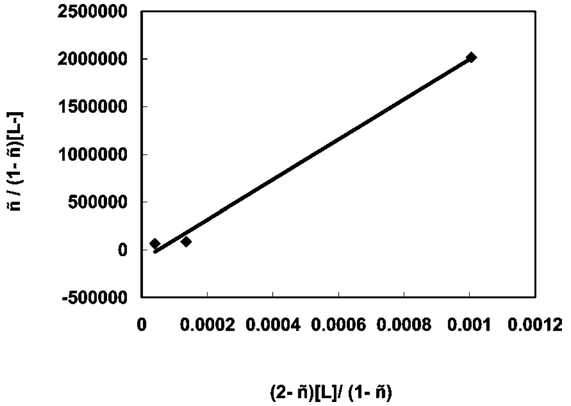


Figure 1. (2 − ñ)[L]/(1 − ñ) vs ñ/(1 − ñ)[L] for phenylglycine at 25 °C and $\mu = 0.05$.

The bound ligand concentration L_{bound} was then calculated: $L_{bound} = L_{total} - L_{free}$. More details of the calculations of ñ and [L] values have been previously described.[18,19] The observed values of ñ are in the range $0.0 < ñ \leq 1.12$. This indicates the formation of a 1:1 stoichiometric complex.

Applying eq 10 on the suggested reaction I, when $i = 1$ for the formed 1:1 stoichiometric complex (ML), eq 10 will be transformed to the following equation:

$$\frac{ñ}{(1 - ñ)[L]} = K_{110}$$

When $i = 2$ for the formed 2:1 stoichiometric complex (ML_2), eq 10 will be transformed to the following equation:

$$\frac{ñ}{(1 - ñ)[L]} = K_{111}\frac{(2 - ñ)}{(1 - ñ)}[L]$$

then the overall equation for the reaction scheme I can be formulated as follows:

$$\frac{ñ}{(1 - ñ)[L]} = K_{110} + K_{111}\frac{(2 - ñ)}{(1 - ñ)}[L] \tag{12}$$

A plot of ñ/(1 − ñ)[L^-] against (2 − ñ)[L]/(1 − ñ) (Figure 1) gives a linear relationship with an intercept equal to K_{110} and a slope equal to K_{111}. Similarly, K_{000} and K_{001} for the suggested reaction II can be calculated from the intercept and slope obtained from a plot of ñ[H^+]/(1 − ñ)[HL] versus (2 − ñ)[HL]/(1 − ñ)[H^+] according to the following equation:

$$\frac{ñ[H^+]}{(1 - ñ)[HL]} = K_{000} + K_{001}\frac{(2 - ñ)[HL]}{(1 - ñ)[H^+]} \tag{13}$$

The thermodynamic stability constant $K°$ at each temperature and ionic strength was calculated by applying the following equation from Davies:

$$\log K = \log K° - \frac{0.509Z_+Z_-\sqrt{\mu}}{(1 + 1.5\sqrt{\mu})} - 0.3\mu \tag{14}$$

The standard free energy $\Delta G°$ can be calculated from the equation:

$$\Delta G° = -RT \ln K° \tag{15}$$

The standard enthalpy change, $\Delta H°$, and the standard entropy change, $\Delta S°$, were calculated using a temperature dependence method[9−12] where the slope of a ($\Delta G° - T$) plot is equal to ($-\Delta S°$) and the intercept is equal to $\Delta H°$. All our calculations in this work were computer-programmed (Turbo Basic, tb program).

Results and Discussion

The thermodynamic ionization constants (p$K°_{011}$ and p$K°_{012}$) were calculated, applying the Davies equation, and the isoelectric point values (pI_s) of phenylglycine, which are the mean value of p$K°_{011}$ and p$K°_{012}${(p$K°_{011}$ + p$K°_{012}$)/2}, were then calculated. The ionization constant values (pK_{011} and pK_{012}), the thermodynamic ionization constants (p$K°_{011}$ and p$K°_{012}$), and the isoelectric point values (pI_s) of phenylglycine are reported in Table 1. It is obvious that there is an ionic strength dependence of the ionization constant values (pK_{011} and pK_{012}) at each temperature. In general, it was found that pK_{011} < pK_{012} and p$K°_{011}$ < p$K°_{012}$. This means that the first ionization process of phenylglycine is stronger than the second ionization process. The isoelectric point of phenylglycine (pI_s) at infinite dilution can be determined by applying the following equation:[11,16]

$$\mathrm{p}I_s = \frac{\mathrm{p}K°_{011} + \mathrm{p}K°_{012}}{2} \tag{16}$$

The obtained isoelectric point values (pI_s) lie in a reasonable pH range (6.74 to 6.87). In this pH range, the phenylglycine does not bear net charge and hence does not move in an electrical field [i.e., the phenylglycine structure is isoionic (or zwitterionic)].[11,16] It was found that the isoelectric point decreased as the temperature increased similarly to the p$K°_{011}$ and p$K°_{012}$ values.

Table 2 represents the standard thermodynamics parameters for the two ionization processes of phenylglycine. Both $\Delta G°_{011}$ and $\Delta G°_{012}$ have positive values, while $\Delta S°_{011}$ and $\Delta S°_{012}$ have negative values. This indicates that the forward reaction in the two suggested equilibria, 2 and 3, are nonspontaneous, so the reverse direction in these equilibria can be described as spontaneous reactions. Although the two ionization processes of phenylglycine have an endothermic nature as a result of the positive $\Delta H°_{011}$ and $\Delta H°_{012}$ values, we can conclude that the first ionization step (of the carboxylic group) is highly spontaneous compared to the second ionization step (of the amino group). This is due to the lower $\Delta G°_{011}$ values and the higher $\Delta S°_{011}$ values as compared to $\Delta G°_{012}$ and $\Delta S°_{012}$. To obtain a better understanding of the factors that control the ionization processes, we considered the following eqs:[16]

$$\Delta \mathrm{p}K°_H = \mathrm{p}K°_{011} - \mathrm{p}K°_{012} \tag{17}$$

$$\Delta\Delta G°_H = \Delta G°_{011} - \Delta G°_{012} \tag{18}$$

$$\Delta\Delta H°_H = \Delta H°_{011} - \Delta H°_{012} \tag{19}$$

$$\Delta\Delta S°_H = \Delta S°_{011} - \Delta S°_{012} \tag{20}$$

The values of Δp$K°$ and the standard thermodynamic parameter differences ($\Delta\Delta G°_H$, $\Delta\Delta H°_H$, and $\Delta\Delta S°_H$) were calculated and are reported in Table 3. Inspecting the data of Δp$K°_H$, we can conclude that the carboxylic groups are several thousand times more acidic than the NH_3^+ group where $\Delta K°_H$ is $1.48 \cdot 10^5$, $1.35 \cdot 10^5$, and $1.66 \cdot 10^5$ at 0.05 μ and (25, 35, and 45) °C, respectively.

The negative $\Delta\Delta H°_H$ value indicates that the carboxylic group ionization has a more exothermic nature than the amino group ionization, where the proton ionization of −COOH group has less enthalpy [about (5 to 10) kJ·mol^{-1}] than that of the NH_3^+ group. The high negative $\Delta\Delta G°_H$ values indicate more spontaneity of the ionization of the −COOH group than the ionization of the $-NH_3^+$ group. This spontaneity can be supported by the high positive $\Delta\Delta S°_H$ values which reflect the high randomness in the case of the first ionization of phenylglycine as a result of the mutual repulsion between the positively

Table 1. Ionization Constant Values and the Isoelectric Points of Pure Phenylglycine

μ		0.10			0.10			0.10	
t(°C)	0.05	pK_{011} (p$K°_{011}$)	0.15	0.05	pK_{012} (p$K°_{012}$)	0.15	0.05	pI_s	0.15
25	4.21	4.11	4.05	9.38	9.29	9.23			
	(4.11)	(3.97)	(3.88)	(9.28)	(9.15)	(9.06)	6.75	6.56	6.47
35	4.15	4.03	3.94	9.28	9.22	9.17			
	(4.05)	(3.89)	(3.77)	(9.18)	(9.08)	(9.00)	6.62	6.49	6.39
45	4.05	3.94	3.86	9.27	9.21	9.15			
	(3.95)	(3.80)	(3.69)	(9.17)	(9.07)	(8.98)	6.56	6.44	6.34

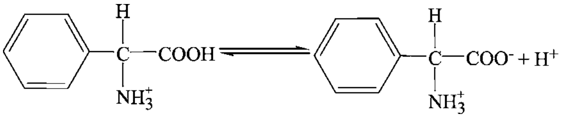
Table 2. Standard Thermodynamic Parameters for Ionization Processes of Pure Phenylglycine

t °C	μ	$\Delta G°_{011}$ kJ·mol^{-1}	$\Delta H°_{011}$ kJ·mol^{-1}	$-\Delta S°_{011}$ kJ·(deg·mol)$^{-1}$	$\Delta G°_{012}$ kJ·mol^{-1}	$\Delta H°_{012}$ kJ·mol^{-1}	$-\Delta S°_{012}$ kJ·(deg·mol)$^{-1}$
25	0.05	23.43	14.53	0.030	52.89	9.74	0.144
	0.10	22.63	15.49	0.024	52.16	7.25	0.151
	0.15	22.12	17.18	0.017	51.64	7.20	0.149
35	0.05	23.86			54.08		
	0.10	22.92			53.49		
	0.15	22.21			53.02		
45	0.05	24.03			55.78		
	0.10	23.11			55.17		
	0.15	22.45			54.62		

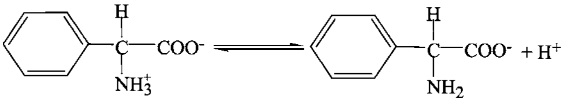
Table 3. Differences of the Standard Thermodynamic Parameters for the Ionization Processes of Pure Phenylglycine

t °C	μ	$-\Delta$p$K°_H$	$-\Delta\Delta G°_H$ kJ·mol^{-1}	$\Delta\Delta H°_H$ kJ·mol^{-1}	$\Delta\Delta S°_H$ J·(deg·mol)$^{-1}$
25	0.05	5.17	29.46	4.79	0.114
	0.10	5.18	29.53	8.24	0.127
	0.15	5.18	29.52	9.98	0.132
35	0.05	5.13	30.22		
	0.10	5.19	30.57		
	0.15	5.23	30.81		
45	0.05	5.22	31.75		
	0.10	5.27	32.06		
	0.15	5.29	32.17		

charged hydrogen ion and the $-NH_3^+$ group according to the following equation:[11,16]


(21)

The reduced spontaneity of the ionization of the $-NH_3^+$ group can be attributed to the strong attraction between the negatively charged phenylglycine anion and the positive proton. This gives a stronger backward reaction as follows:[11,16]


(22)

Such an equilibrium indicates that the formation of the neutral phenylglycine molecule leads to excess order in the ionization of the NH_3^+ group. This conclusion is supported by the high negative $\Delta S°_{012}$ (see Table 2).

The importance of the ñ values stems from its backbone position in all calculations of the stoichiometric stability constants as well as an indication about the type of the formed complexes. Because of the richness of the collected ñ data in this article, a chosen simple example is summarized in Table 4. Inspecting the data, we observed that, at a low pH (3.90 < pH < 7.62 for Ni^{2+} complexes), H_2L^+ has a relatively high concentration in the solution without any complexation, or only weak interactions can take place. This was explored from very low calculated ñ values (less than 0.5). This can be considered as another reason to exclude H_2L^+ as a ligating species as well as the electrostatic repulsion with M^{2+} ions. In this case, all of the present reacting species in the solution are free. This is clear from the expression of the ñ function in eq 10. At high pH values (7.62 < pH < 8.55 for Ni^{2+} complexes as an example), the concentration of HL is high and seems to be constant, while the concentration of L^- increases (i.e., proportional to the addition of ligand and consequently proportional to the pH reading), and the H_2L^+ concentration decreases. In this pH range, we note that 0.5 < ñ < 1.12, which indicates that the 1:1 complex was formed. Therefore, we can say that the most probable reactions were carried out according to the previously suggested reactions I or II. Since complex formation is observed in neutral to slightly basic solutions, hydrolysis commences, and insoluble precipitates are formed. The titration was stopped as soon as any turbidity or precipitate appeared as in the case of Mn^{2+} with phenylglycine (maximum ñ = 0.065) where a brown precipitate appeared early before reaching the neutralization region of complexation. At a high pH, there is no chance for

Table 4. Summary of Some ñ Data for the Complexation of Ni^{2+} with Phenylglycine at 25 °C and $\mu = 0.05$

pH	ñ	$[H_2L^+]$	[HL]	$[L^-]$
3.90	0.00	$3.49 \cdot 10^{-4}$	$1.39 \cdot 10^{-4}$	$3.77 \cdot 10^{-10}$
7.62	0.48	$4.65 \cdot 10^{-7}$	$9.70 \cdot 10^{-4}$	$1.39 \cdot 10^{-5}$
7.95	0.72	$2.17 \cdot 10^{-7}$	$9.67 \cdot 10^{-4}$	$2.95 \cdot 10^{-5}$
8.30	0.93	$9.65 \cdot 10^{-8}$	$9.64 \cdot 10^{-4}$	$6.58 \cdot 10^{-5}$
8.55	1.12	$5.41 \cdot 10^{-9}$	$9.61 \cdot 10^{-4}$	$1.17 \cdot 10^{-4}$

Table 5. Stability Constants of M^{2+}−Phenylglycine Complexes

		log K_{110}			log K_{000}		
metal ion	μ	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Ni^{2+}	0.05	5.08	4.90	4.92	−4.25	−4.48	−4.36
	0.10	5.05	4.73	4.85	−4.16	−4.56	−4.36
	0.15	5.00	4.58	4.77	−4.12	−4.64	−4.38
Cu^{2+}	0.05	8.72	8.50	8.25	−0.66	−0.78	−1.01
	0.10	8.15	8.20	8.10	−1.14	−4.01	−1.11
	0.15	7.69	7.66	7.66	−1.53	−1.49	−4.26
Zn^{2+}	0.05	5.28	4.96	4.49	−4.10	−4.32	−4.78
	0.10	4.86	3.81	3.80	−4.44	−5.86	−5.41
	0.15	4.83	3.33	3.23	−4.39	−5.72	−5.92
Cd^{2+}	0.05	4.63	4.61	3.26	−4.75	−4.67	−6.01
	0.10	5.29	3.39	3.23	−4.02	−5.82	−5.98
	0.15	5.25	3.37	3.23	−3.97	−5.78	−6.93

Table 6. Thermodynamic Stability Constants of M^{2+}−Phenylglycine Complexes

		$\log K°_{110}$			$-\log K°_{000}$		
metal ion	μ	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Ni^{2+}	0.05	5.27	5.09	5.11	4.06	4.29	4.17
	0.10	5.29	4.98	5.09	3.91	4.31	4.11
	0.15	5.29	4.87	5.06	3.83	4.35	4.09
Cu^{2+}	0.05	8.91	8.69	8.44	0.47	0.59	0.82
	0.10	8.39	8.45	8.35	0.89	0.76	0.86
	0.15	7.98	7.95	7.95	1.24	1.19	0.96
Zn^{2+}	0.05	5.47	5.15	4.68	3.91	4.13	4.59
	0.10	5.11	4.06	4.05	4.19	5.61	5.16
	0.15	5.12	3.62	3.52	4.09	5.43	5.63
Cd^{2+}	0.05	4.82	4.79	3.45	4.56	4.48	5.82
	0.10	5.54	3.64	3.48	3.77	5.57	5.73
	0.15	5.54	3.66	3.52	3.68	5.49	5.63

Table 7

a. Standard Thermodynamic Parameters of M^{2+}−Phenylglycine Complexes

		$\Delta G°$ (kJ·mol^{-1})					
		Reaction I ($-\Delta G°$)			Reaction II ($+\Delta G°$)		
metal ion	μ	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Ni^{2+}	0.05	30.07	30.02	31.12	23.17	25.30	25.39
	0.10	30.19	29.37	30.99	22.31	25.42	25.03
	0.15	30.19	28.72	30.81	21.85	25.65	24.90
Cu^{2+}	0.05	50.84	51.25	51.39	02.68	03.48	04.99
	0.10	47.87	49.83	50.84	05.08	04.48	05.24
	0.15	45.53	46.88	48.41	07.08	07.02	05.85
Zn^{2+}	0.05	31.21	30.37	28.49	22.31	24.36	27.95
	0.10	29.16	23.94	24.66	23.91	33.09	31.42
	0.15	29.22	21.35	21.43	23.34	32.02	34.28
Cd^{2+}	0.05	27.50	28.25	21.01	26.02	26.42	35.44
	0.10	31.61	21.47	21.19	21.51	32.85	34.89
	0.15	31.61	21.59	21.43	20.99	32.38	34.28

b. Standard Thermodynamic Parameters of M^{2+}−Phenylglycine Complexes

		Reaction I		Reaction II	
		$-\Delta H°$	$\Delta S°$	$-\Delta H°$	$-\Delta S°$
metal ion	μ	kJ·mol^{-1}	J·(K·mol)$^{-1}$	kJ·mol^{-1}	J·(deg·mol)$^{-1}$
Ni^{2+}	0.05	14.23	0.05	09.57	0.11
	0.10	17.86	0.04	17.63	0.14
	0.15	20.36	0.03	22.84	0.15
Cu^{2+}	0.05	42.69	0.03	31.86	0.12
	0.10	03.78	0.15	02.47	0.01
	0.15	02.59	0.14	25.59	0.06
Zn^{2+}	0.05	71.91	−0.14	61.98	0.28
	0.10	95.22	−0.23	86.18	0.37
	0.15	143.9	−0.39	138.6	0.55
Cd^{2+}	0.05	125.5	−0.33	115.8	0.47
	0.10	185.2	−0.52	176.3	0.67
	0.15	181.6	−0.51	175.5	0.66

Table 9. Ionic Radii of Studied Metal Ions

metal ion	radius (Å)	Z/r
Ni^{2+}	0.72	2.78
Cu^{2+}	0.69	2.90
Zn^{2+}	0.74	2.70
Cd^{2+}	0.97	2.06

complexes to be formed as a result of the precipitation of hydroxide species. Therefore, we conclude that the Bjerrum's method is not valid in the determination of the stability constant of the formed complex between Mn^{2+} and phenylglycine.

Inspecting the stoichiometric and thermodynamic stability constants which are tabulated in Tables 5 and 6, we can observe that $\log K_{110} >>> \log K_{000}$. The high decrease in the stability constants obtained from reaction II is attributed to the contribution of the second phenylglycine ionization constant in this reaction according to the following equation:[9,12]

$$\beta_1 = K_{110}K_{012}\,(\text{phenylglycine}) \tag{23}$$

As a new thermodynamic point of view for the complexation processes between the phenylglycine and the transition metal ions is under study, we suggested earlier the following equations to get an idea about the difference between the two suggested reactions:

$$\Delta \log K_1^{\circ} = \log K_{110}^{\circ}(\text{reaction I}) - \log K_{000}^{\circ}(\text{reaction II}) \tag{24}$$

$$\Delta\Delta G° = \Delta G°(\text{reaction I}) - \Delta G°(\text{reaction II}) \tag{25}$$

$$\Delta\Delta H° = \Delta H°(\text{reaction I}) - \Delta H°(\text{reaction II}) \tag{26}$$

$$\Delta\Delta S° = \Delta S°(\text{reaction I}) - \Delta S°(\text{reaction II}) \tag{27}$$

Tables 7 and 8 illustrate the standard thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ (as well as the differences of the thermodynamic parameters $\Delta \log K°$, $\Delta\Delta G°$, $\Delta\Delta H°$, and $\Delta\Delta S°$) for all possible complexation processes. The high negative $\Delta G°$ values of reaction I indicate that these complexation processes are spontaneous, while the complexation processes for reaction II are nonspontaneous as reflected from their positive $\Delta G°$ values. The differences of the thermodynamic parameters $\Delta \log K°$, $\Delta\Delta G°$, $\Delta\Delta H°$, and $\Delta\Delta S°$ indicate that the most predominant reaction is that suggested in reaction I.

Although L^- has a lower concentration than HL (Table 4), we can interpret the high spontaneity of reaction I due to the electrostatic attraction of the two oppositely charged reactants according to the following eq 28. This interpretation can be supported by the high $\Delta \log K°$ values.

$$M^{2+} + L^- \overset{K_{110}}{\rightleftharpoons} ML^+ \tag{28}$$

Inspecting the $\Delta S°$ values, we found that $\Delta S°$ values were negative (with the exception of some cases such as the

Table 8. Difference of Thermodynamic Parameters for M^{2+}−Phenylglycine Complexes

		$\Delta \log K°$			$-\Delta\Delta G°$ (kJ·mol^{-1})			$-\Delta\Delta H°$	$+\Delta\Delta S°$
metal ion	μ	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	kJ·mol^{-1}	J·(deg·mol)$^{-1}$
Ni^{2+}	0.05	1.21	0.80	0.94	53.24	55.32	56.51	23.80	0.16
	0.10	1.38	0.67	0.98	52.50	54.79	56.02	35.49	0.18
	0.15	1.46	0.52	0.97	52.04	54.37	55.71	43.20	0.18
Cu^{2+}	0.05	8.44	8.10	7.62	53.52	54.73	56.38	74.55	0.15
	0.10	7.50	7.69	7.49	52.95	54.31	56.08	26.24	0.16
	0.15	6.74	6.76	6.99	52.61	53.90	54.26	28.18	0.08
Zn^{2+}	0.05	1.56	1.02	0.09	53.52	54.73	56.44	133.9	0.14
	0.10	0.92	−1.55	−1.11	53.07	57.03	56.08	181.2	0.15
	0.15	1.03	−1.81	−2.11	52.56	53.37	55.71	282.5	0.16
Cd^{2+}	0.05	0.26	−0.31	−2.37	53.52	54.67	56.45	241.3	0.14
	0.10	1.77	−1.93	−2.25	53.12	54.32	56.08	361.5	0.15
	0.15	1.86	−1.83	−2.11	52.60	53.97	55.71	357.1	0.15

complexation of Ni^{2+} and Cu^{2+} with L^- which have positive $\Delta S°$ values). The high positive $\Delta\Delta S°$ values indicate that the standard entropy changes for reaction I were higher than those for reaction II (with the exception of the complexation of Cu^{2+} in reaction II which can be considered as an entropy-favored reaction). This reflects more spontaneity of reaction I which can be characterized by its negative $\Delta H°$ values (i.e., exothermic nature). Therefore, the high negative $\Delta G°$ values for reaction I are attributed to the higher contribution of the $\Delta H°$ term. This indicates that these complexation processes are enthalpy-favored processes. This conclusion was supported by the negative $\Delta\Delta H°$ and positive $\Delta\Delta S°$.

Inspecting the $\Delta G°$ values, we note that the spontaneity and stability of the complex formations were increased in the following order: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+}$. This is in good agreement with the Irving-Williams order.[20] According to Davies, a simple relation exists between the stability of the formed complexes and the radius, r, of the unhydrated ion and its valence, Z, as shown in Table 9. Therefore, the lower stability of the Cd^{2+} complex than the other studied transition metal complexes is attributed to the high value of its radius in comparison with the other studied metal ions.[21,22] It can be concluded that Cu^{2+} complexes are more stable than the other metal ion complexes as a result of the larger ratio of (valency/radius) and the Jahn−Teller effect.[23]

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