ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 5, pp. 389–394. © Pleiades Publishing, Ltd., 2009.
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Thermochemical Study of Coordination Equilibria in the Zinc(II)–β-Alanine–Water System in Aqueous Solution

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Received June 18, 2008

Abstract—The heats of formation of β-alanine (HAla) complexes with Zn^{2+} ion at temperatures of 288.15, 298.15, and 308.15 K and ionic strengths of 0.25, 0.50, and 0.75 mol/l (KNO_3) were determined by calorimetry; the heats of dilution of a zinc nitrate solution in supporting electrolyte solutions were found for introduction of appropriate corrections. The standard heats of complexation in the zinc(II)–β-alanine–water system were determined. The standard thermodynamic characteristics of zinc(II) complexation with β-alanine and standard enthalpies of formation of $ZnAla^+$ and $ZnAla_2$ complex species were calculated.

DOI: 10.1134/S1070328409050121

Amino acids serve as monomer units that constitute proteins. Functioning of proteins forms the basis of important vital processes in the organism including metabolism, muscle contraction, nerve conduction, and cell life as a whole. Amino acids can serve as model compounds for more complex biosystems. Since all biochemical processes take place in water, study of the properties of amino acids in aqueous solutions appears most important.

Acid–base interaction and complexation play an important role in many biological systems. Identification of the key features of protolytic equilibria in solutions of amino acids is significant for the understanding of the mechanisms of many biochemical reactions.

In turn, metal ions play an enormous role in a living organism. In combination with amino acids, protein molecules, and peptides, they operate as parts of metalloenzymes that ensure normal course of numerous biochemical reactions, and participate in accumulation and transport of various compounds.

Analysis of published data [1–6] allows one to choose the most probable values for thermodynamic stability constants of Zn^{2+} complexes with β-Ala^- anion at 298.15 K: log $\log\beta_1^0 = 4.05 \pm 0.19$, $\log\beta_2^0 = 7.27 \pm 0.15$. To interpret the results of calorimetric measurements, the chosen thermodynamic stability constants of the complexes were converted to a constant ionic strength using the equation [7]:

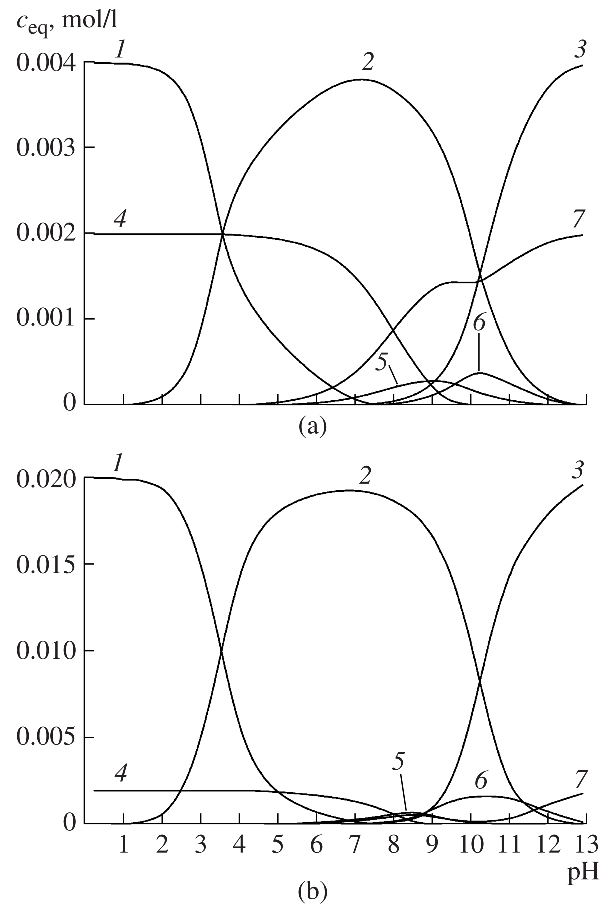
$$\log\beta^c = \log\beta^0 - \Delta Z^2 A\left(\frac{\sqrt{I}}{1 + 1.6\sqrt{I}}\right) + bI, \qquad (1)$$

where β^c and β^0 are concentration and thermodynamic stability constants; ΔZ^2 is the difference between squared charges of the products and the reactants; A is the constant of the limiting Debye law equal to 0.5107 for an aqueous solution at 25°C; b is an empirical coefficient; I is the solution ionic strength.

Currently, there are two publications [5, 8], which present the heats of complex formation between Zn(II) and β-alanine in aqueous solution. In one study [8], the heat of $ZnAla^+$ formation reaction was estimated at I = 0.1 (KCl) in the temperature range of 5–45°C on the basis of potentiometric measurements of the stability constants of $ZnAla^+$: $\Delta H_{\beta1} = –6.1 \pm 0.3$ KJ/mol. In the other study [5], only heat of formation of $ZnAla_2$ was determined by calorimetry. The studies were carried out at 22°C using KNO_3 as the supporting electrolyte. The value $\Delta H_{\beta2}$ = -17.26 KJ/mol was reported [5].

On the basis of critical survey of published data carried out for the IUPAC, the following heats of formation reactions of Zn(II) mono- and di-complexes with β-alanine were reported [1]: $\Delta H_{\beta1} = –7.8 \pm 1.2$ KJ/mol and $\Delta H_{\beta2} = –17.4 \pm 0.5$ KJ/mol. However, no information on the effects of temperature and supporting electrolyte concentration on the thermodynamic characteristics of complexation in the zinc(II)–β-alanine–water system is now available.

The purpose of this study is direct colorimetric determination of the heats of complexation of β-alanine with the Zn^{2+} ion at T = 288.15, 298.15, and 308.15 K and I = 0.25, 0.50, and 0.75 (KNO_3), calculation of the standard thermodynamic characteristics of these reactions and the standard enthalpies of formation of the complex species $ZnAla^+$ and $ZnAla_2$ in an aqueous solution.



(a)

(b)

Fig. 1. Equilibrium diagram in the zinc–β-alanine–water system at 298.15 K and $I = 0.1$ mol/l and (a) M : L = 1 : 2 and (b) 1 : 10 ((*1*) H_2Ala^+, (*2*) $HAla^{\pm}$, (*3*) Ala^- , (*4*) Zn^{2+}, (*5*) $ZnAla^+$, (*6*) $ZnAla_2$, (*7*) $ZnOH^+$).

EXPERIMENTAL

Chromatographically homogeneous reagent grade (Reanal) crystalline β-alanine (99.9% purity) was used as received; KOH was prepared from a reagent grade chemical by a known procedure [9]. The specified ionic strength was maintained using recrystallized reagent grade potassium nitrate [10]. A solution of $Zn(NO_3)_2$ with concentration of 0.8416 mol/kg was prepared from recrystallized analytical grade zinc nitrate whose concentration was determined by complexometry [11].

The following reactions may take place on mixing of Zn^{2+} and β-alanine solutions in a calorimeter:

$$Zn^{2+} + Ala^- \rightleftharpoons ZnAla^+, \quad (2)$$

$$Zn^{2+} + 2Ala^- \rightleftharpoons ZnAla_2, \quad (3)$$

$$H^+ + Ala^- \rightleftharpoons HAla^{\pm}, \quad (4)$$

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+, \quad (5)$$

$$H_2O \rightleftharpoons OH^- + H^+. \quad (6)$$

The equilibrium ionic composition of solutions was determined by the RRSU program [12] taking into account processes (2)–(6). The calculation results were used to construct the equilibrium diagrams in the zinc–β-alanine system in aqueous solution as dependences of equilibrium concentrations of species (c_{eq}) in the solution vs. pH (Fig. 1) at different metal to ligand (M : L) ratios. They were used to choose the optimal conditions of thermochemical experiments.

The key goal of optimization of conditions of the calorimetric determination of the heats of formation reactions of $ZnAla^+$ and $ZnAla_2$ is to distinguish such pH regions and M : L ratios that would ensure the highest yields of the compounds under study and the lowest proportions of other processes.

In determination of the heats of mixing ($\Delta_{mix}H$), solutions of amino acids were prepared from a precise weighed portion of β-alanine. Using a calibrated pipette, a calculated amount of a KOH solution was added in order to attain specified pH and the required amount of the supporting electrolyte was added for maintaining the appropriate ionic strength of the solution. The M : L ratio was varied from 1 : 6 to 1 : 10. The choice of metal and ligand concentrations is due to the fact that the presence of excess of the ligand minimizes side formation of metal hydroxo complexes. This is illustrated by the equilibrium diagrams shown in Fig. 1. As shown by calculation of ionic equilibria, for M : L = 1 : 10 and pH 10 the complex $ZnAla_2$ predominates in the solution (more than 99%); for M : L = 1 : 6, 20% $ZnAla^+$ and 80% $ZnAla_2$ are formed.

A precise weighed portion of a solution of $Zn(NO_3)_2$ was placed into a glass tube and the prepared β-alanine solution was placed in a calorimetric cup. In determining the heats of dilution ($\Delta_{dil}H$) of a $Zn(NO_3)_2$ solution, a solution of KNO_3 with a specified ionic strength was used as the calorimetric liquid. The experiments were carried out at $T = 288.15$, 298.15, and 308.15 K and $I = 0.25$, 0.50, and 0.75 (KNO_3). The pH value in the beginning and at the end of the calorimetric experiment was checked by an IPL-311 pH-meter. Equal experimental and calculated pH values (±0.10–0.25 pH units) attested to correct interpretation of the results of calorimetric measurements. The experimental mixing and dilution heats are summarized in Table 1. The error of measured heats of reactions in the system was found as the root-mean-square deviation.

Table 1. Heats of reaction of a β-alanine solution with a $Zn(NO_3)_2$ solution at different ionic strengths ($T = 298.15$ K)

I, mol/l	Weighed portion of $Zn(NO_3)_2$, g	$c^0_{Zn} \times 10^3$, mol/l	$c^0_L \times 10^2$, mol/l	$c^0_H \times 10^2$, mol/l	$-\Delta_{mix}H$, kJ/mol	$-\Delta_{dil}H$, kJ/mol	$-\Delta H$, kJ/mol
0.25	0.1500	5.060	3.005	1.839	16.516	2.201	14.315
	0.1488	5.066	5.005	3.075	26.642		24.441
0.50	0.1502	5.043	3.008	1.956	18.460	2.515	15.945
	0.1468	5.441	5.000	2.719	27.938		25.423
0.75	0.1457	5.164	2.987	1.689	19.316	2.737	16.579
	0.1537	5.136	5.011	2.204	28.337		25.600

RESULTS AND DISCUSSION

The heats of formation reactions of $ZnAla^+$ and $ZnAla_2$ were calculated by solving the set of two equations with two variables:

$$\begin{aligned}&\Delta_{mix}H_1 - \Delta_{dil}H_1\\ &= \alpha_1[ZnAla^+]\Delta_{comp}H(ZnAla^+)\\ &+ \alpha_1[ZnAla_2]\Delta_{comp}H(ZnAla_2)\\ &+ \alpha_1[OH^-]\Delta H_w + \alpha_1[HAla^{\pm}]\Delta_{dis}H,\end{aligned}\tag{7}$$

$$\begin{aligned}&\Delta_{mix}H_2 - \Delta_{dil}H_2\\ &= \alpha_2[ZnAla^+]\Delta_{comp}H(ZnAla^+)\\ &+ \alpha_2[ZnAla_2]\Delta_{comp}H(ZnAla_2)\\ &+ \alpha_2[OH^-]\Delta H_w + \alpha_2[HAla^{\pm}]\Delta_{dis}H,\end{aligned}\tag{8}$$

corresponding to two different M : L ratios (1 : 6 for $\Delta_{mix}H_1$, $\Delta_{dil}H_1$ and 1 : 10 for $\Delta_{mix}H_2$ and $\Delta_{dil}H_2$); $\Delta_{comp}H(ZnAla^+)$, and $\Delta_{comp}H(ZnAla_2)$ are the heats of formation reactions of $ZnAla^+$ and $ZnAla_2$, respectively; $\Delta_{dis}H$ is the heat of dissociation of the amino acid zwitter-ion [13]; H_w is the heat of formation of water from ions [14]; $\alpha_1[ZnAla^+]$, $\alpha_1[ZnAla_2]$, $\alpha_1[HL^{\pm}]$, and $\alpha_1[OH^-]$ characterize the extent to which the formation of $ZnAla^+$, $ZnAla_2$, $HAla^{\pm}$, and water, respectively, proceed.

The extent of formation of complex species was calculated from the equations

$$\alpha_1 = [ZnAla^+]_c/c^0_{Zn},\tag{9}$$

$$\alpha_1 = [ZnAla_2]_c/c^0_{Zn},\tag{10}$$

where $[ZnAla^+]_c$, $[ZnAla_2]_c$ are equilibrium concentrations of $[ZnAla^+]$ and $[ZnAla_2]$ at the end of the calorimetric experiment; c^0_{Zn} is the total Zn^{2+} concentration in the solution added to the tube taking into account the dilution to the volume of the calorimetric liquid.

The heats of formation reactions of β-alanine complexes with Zn^{2+} obtained under these conditions are presented in Table 2.

The standard heats of formation reactions of β-alanine complexes of zinc(II) were found by graphical extrapolation of the obtained ΔH values at constant ionic strengths to $I = 0$ by the equation [7]

$$\Delta H - \Delta Z^2\Psi(I) = \Delta H^\circ + b/I,\tag{11}$$

where ΔH is the heat (KJ/mol) of the reaction at the specified ionic strength; ΔH° is the standard change in enthalpy in the process (KJ/mol); ΔZ^2 is the difference between squared charges of the products and the reactants; I is the ionic strength of the solution; $\psi(I)$ is a function of ionic strength calculated theoretically; b is an empirical coefficient.

Figures 2 and 3 show the graphical extrapolation of the heats of formation of zinc(II) complexes with β-alaninate ion by equation (11). The $\Delta_{comp}H$ values fit satisfactorily in straight lines; the y-intercepts correspond to the standard enthalpies of formation of zinc(II) complexes with β-alanine. The optimal positions of the straight lines were found by the least-squares method.

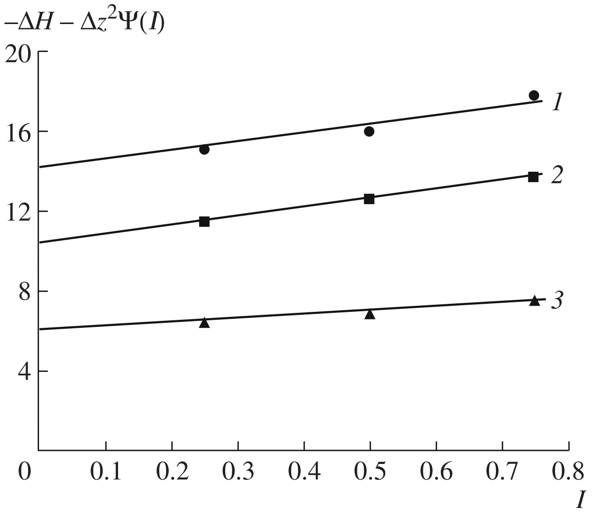


Fig. 2. Graphical determination of the standard enthalpies of formation of $ZnAla^+$ at T = (*1*) 88.15, (*2*) 298.15, (*3*) 308.15 K.

Table 2. Thermodynamic characteristics of Zn^{2+} complexation with β-alanine at different ionic strengths and temperatures

Process	I, mol/l	$\log \beta_n$		$-\Delta_{comp}G$, kJ/mol		$-\Delta_{comp}H$, kJ/mol		$\Delta_{comp}S$, J/(mol K)	
288.15 K									
$Zn^{2+} + Ala^- \rightleftarrows ZnAla^+$	0.00	3.90	0.08	21.52	0.44	14.11	0.24	25.7	1.6
	0.25	3.87	0.08	21.35	0.44	15.93	0.24	18.8	1.2
	0.50	3.75	0.08	20.69	0.44	17.02	0.19	12.7	1.6
	0.75	3.68	0.08	20.30	0.44	18.78	0.20	5.3	1.7
$Zn^{2+} + 2Ala^- \rightleftarrows ZnAla_2$	0.00	7.20	0.09	39.72	0.50	21.17	0.23	64.4	1.8
	0.25	7.17	0.09	39.56	0.50	22.88	0.16	57.9	1.8
	0.50	7.14	0.09	39.39	0.50	25.07	0.23	49.7	1.8
	0.75	7.11	0.09	39.22	0.50	25.97	0.19	46.0	1.9
298.15 K									
$Zn^{2+} + Ala^- \rightleftarrows ZnAla^+$	0.00	4.05	0.09	23.11	0.44	10.31	0.24	42.9	1.9
	0.25	3.87	0.09	22.08	0.44	12.46	0.24	32.2	1.7
	0.50	3.75	0.09	21.40	0.44	13.84	0.19	25.4	1.9
	0.75	3.52	0.09	20.08	0.44	15.02	0.26	17.0	1.9
$Zn^{2+} + 2Ala^- \rightleftarrows ZnAla_2$	0.00	7.27	0.11	41.50	0.50	17.02	0.23	82.1	1.8
	0.25	7.15	0.11	40.82	0.50	19.98	0.16	69.9	1.8
	0.50	7.10	0.11	40.53	0.50	21.37	0.23	64.3	1.8
	0.75	7.06	0.11	40.30	0.50	22.96	0.29	58.2	1.9
308.15 K									
$Zn^{2+} + Ala^- \rightleftarrows ZnAla^+$	0.00	3.79	0.08	22.36	0.44	6.18	0.24	52.5	1.6
	0.25	3.69	0.08	21.77	0.44	7.59	0.24	46.0	1.2
	0.50	3.61	0.08	21.30	0.44	8.35	0.19	42.0	1.6
	0.75	3.58	0.08	21.12	0.44	9.08	0.23	39.1	1.7
$Zn^{2+} + 2Ala^- \rightleftarrows ZnAla_2$	0.00	7.02	0.09	41.42	0.50	13.78	0.23	89.7	1.8
	0.25	6.97	0.09	41.12	0.50	15.97	0.16	81.6	1.8
	0.50	6.93	0.09	40.89	0.50	17.02	0.23	77.5	1.8
	0.75	6.89	0.09	40.65	0.50	17.89	0.19	73.9	1.9

The heats of formation processes of the β-alanine complexes with Zn^{2+} ion are exothermic at any ionic strength (Figs. 2, 3). An increase in the supporting electrolyte concentration increases the exothermicity for all of the complexation reactions. Such trends for the thermodynamic characteristics of complexation under the action of variable ionic strength have been noted previously in the study of formation reactions of "life metals" with various bioligands, in particular, in the Cu^{2+}-β-alanine and Ni^{2+}–β-alanine systems. As temperature increases, the heats of complexation decrease in magnitude. The enthalpies of formation reactions of $ZnAla^+$ and $ZnAla_2$ complexes at 288.15, 298.15, and 308.15 K over a broad range of supporting electrolyte concentrations and in a standard solution are reported here for the first time (Table 2).

It is expedient to compare the resulting heats of formation processes of $ZnAla^+$ and $ZnAla_2$ with published data [1, 5, 8] at the same concentrations and temperatures. To this end, we estimated the enthaplies of the formation process of these complexes at $I = 0.1$ (taking into account $\Delta Z^2\psi(I)$) and 298.15 K using the extrapolation plot (Fig. 2). This gave the following values: $\Delta H_{\beta_1} = -10.71 \pm 0.95$ KJ/mol and $\Delta H_{\beta_2} = -17.49 \pm 0.85$ KJ/mol, which coincide to within the determination error with the values reported previously [1]. This confirms the validity of our experimental data.

Extensive possibilities are provided by using the approach based on the Gerney views [15] for interpretation of thermodynamic characteristics of complexation reactions. The change in the standard Gibbs

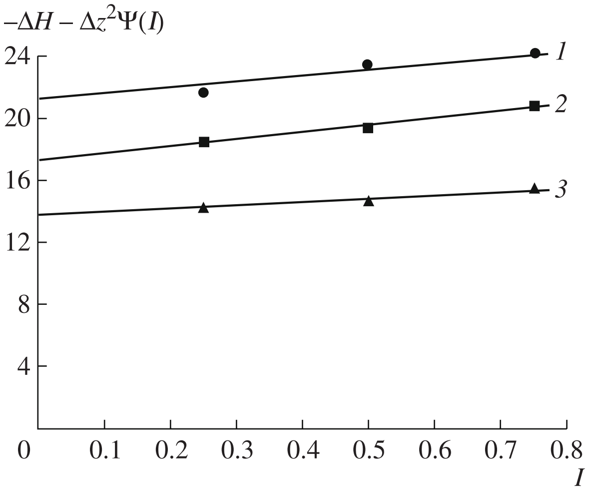


Fig. 3. Graphical determination of the standard enthalpies of formation of $ZnAla_2$ at T = (*1*) 288.15, (*2*) 298.15, (*3*) 308.15 K.

energy in this process is expressed according to the Gerney scheme as follows:

$$\Delta_r G^0 = \Delta_r G^0_{\text{dep}} + \Delta_r G^0_{\text{indep}} + \Delta_r G^0_{\text{cr}} = -RT\log\beta^0, \quad (12)$$

where β^0 is the thermodynamic stability constant of the complex ML_n; $\Delta_r G^0_{\text{dep}}$ and $\Delta_r G^0_{\text{indep}}$ are temperature-dependent and temperature-independent contributions; $\Delta_r G^0_{\text{cr}}$ is the critical (packing) term.

In addition, the enthaply change upon complexation can be represented as the sum of temperature-dependent ($\Delta_r H_{\text{dep}}$) and temperature-independent ($\Delta_r H_{\text{indep}}$) terms:

$$\Delta_r H = \Delta_r H_{\text{dep}} + \Delta_r H_{\text{indep}}. \quad (13)$$

Table 3 presents temperature-dependent and temperature-independent contributions of the thermodynamic characteristics calculated using the Gerney scheme [15] for formation reactions of zinc(II) β-alaninate complexes. When considering the complexation of Zn^{2+} with β-alanine, note that in the overall ligand addition processes, the temperature-dependent enthalpy and entropy contributions regularly increase with increase in the number of ligands. For stepwise addition of ligands, similar $\Delta_{\text{comp}} G^0_{\text{dep}}$ (~16.0 values are observed. Besides, in stepwise ligand addition processes, the temperature-independent enthalpy and Gibbs energy contributions decrease successively in magnitude as the number of ligands increases.

The heats of complexation reactions of Zn^{2+} with β-alanine that we determined, the $\Delta_f H^0$ value (Zn^{2+}, soln, H_2O, stand.state, 298.15 K) equal to –153.56 ± 0.34 KJ/mol [16], and the standard heat of formation of the deprotonated β-alanine anion equal to –255.00 ± 0.54 KJ/mol [17] can be used to calculate the standard enthalpies of formation of complexes of the studied amino acids with Zn^{2+} ions (determined for the first time):

$$\Delta_f H^0\,(\text{ZnAla}_n^{2-n},\ \text{soln, H}_2\text{O, stand.state, hyp.undiss.,}$$
$$298.15\text{ K}) = \Delta_f H^0(\text{Zn}^{2+},\ \text{soln, H}_2\text{O, 298.15 K}) + n\Delta_f H^0\,(\text{Ala}^-,\ \text{soln, H}_2\text{O, 298.15 K}) + \Delta H^0_{\beta n}(298.15\text{ K}), \quad (14)$$

Table 3. Temperature-dependent (dep) and temperature-independent (indep) contributions to thermodynamic characteristics of the formation processes of Zn(II) β-alaninate complexes

Process	T, K	A*	$-\Delta_{\text{comp}} G^0_{\text{dep}}$	$-\Delta_{\text{comp}} G^0_{\text{inder}} = -\Delta_{\text{comp}} H^0_{\text{inder}}$	$\Delta_{\text{comp}} H^0_{\text{dep}}$	$\Delta_{\text{comp}} S^0_{\text{dep}}$
			kJ/mol			J/(mol K)
$Zn^{2+} + Ala^- \rightleftarrows ZnAla^+$	288.15	3513	13.02	18.12	4.03	59.2
	298.15	4333	16.80	16.26	5.97	76.4
	308.15	4661	18.91	13.74	7.58	86.0
$Zn^{2+} + 2Ala^- \rightleftarrows ZnAla_2$	288.15	7798	28.90	30.07	8.95	131.3
	298.15	8456	32.79	28.62	11.65	149.0
	308.15	8492	34.46	27.54	13.81	156.6

* A is the empirical coefficient depending on the properties of particular system and solvent.

Table 4. Standard thermodynamic characteristics of complexation of 3*d* metal ions with β-alanine at 298.15 K

Metal cation	Process	$-\Delta_{\text{comp}}H_{\beta n}$, KJ/mol	$-\Delta_{\text{comp}}G$, KJ/mol	$\Delta_{\text{comp}}S$, J/mol K
Co^{2+}	$M^{2+} + L^- \rightleftharpoons ML^+$	13.89 ± 0.11	23.52 ± 0.46	32.3 ± 1.6
	$M^{2+} + 2L^- \rightleftharpoons ML_2$	19.58 ± 0.07	40.75 ± 0.51	68.9 ± 1.7
Ni^{2+}	$M^{2+} + L^- \rightleftharpoons ML^+$	13.38 ± 0.79	28.88 ± 0.51	52.1 ± 1.7
	$M^{2+} + 2L^- \rightleftharpoons ML_2$	20.75 ± 1.35	48.57 ± 0.57	93.3 ± 2.7
	$M^{2+} + 3L^- \rightleftharpoons ML_3^-$	34.40 ± 1.91	58.67 ± 1.71	81.4 ± 2.6
Cu^{2+}	$M^{2+} + L^- \rightleftharpoons ML^+$	23.72 ± 0.11	42.85 ± 0.46	57.9 ± 1.6
	$M^{2+} + 2L^- \rightleftharpoons ML_2$	44.28 ± 0.07	76.36 ± 0.51	97.5 ± 1.7
Zn^{2+}	$M^{2+} + L^- \rightleftharpoons ML^+$	10.31 ± 0.24	23.11 ± 0.44	42.9 ± 1.6
	$M^{2+} + 2L^- \rightleftharpoons ML_2$	17.02 ± 0.23	41.50 ± 0.50	82.1 ± 1.8

where $H^0_{\beta_n}$ (298.15 K) are standard heats of Zn^{2+} complexation with β-alanine; *n* is the coordination number.

By substituting numerical values into equation (14), we get the following results:

$$\Delta_f H^0(\text{ZnAla}^+, \text{soln}, \text{H}_2\text{O}, \text{stand.state}, \text{hyp.undiss.}, 298.15\ \text{K}) = -418.87 \pm 0.88\ \text{kJ/mol};$$

$$\Delta_f H^0(\text{ZnAla}_2, \text{soln}, \text{H}_2\text{O}, \text{stand.state}, \text{hyp.undiss.}, 298.15\ \text{K}) = -680.58 \pm 0.88\ \text{kJ/mol}.$$

The complexing capacity of transition metals towards bioligands is often characterized using the Irving–Williams series: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. From the standpoint of crystal field theory, the Irving–Williams series is the sequence of complex stabilization by crystal field. However, the position of zinc in this series is variable.

The heats of formation processes of β-alanine complexes with transition 3*d*-metals (determined by direct calorimetric method) and, hence, the strengths of ligand binding to the metal ion increase for 1 : 1 and 1 : 2 complexes in the series $Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$ (Table 4). Note that the Irving–Williams series is valid for the β-alanine ligand.

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