ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2015, Vol. 89, No. 9, pp. 1540–1544. © Pleiades Publishing, Ltd., 2015.
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Thermochemical Study of the Processes of Complexation of Cobalt(II) Ions with L-Histidine in Aqueous Solution

G. G. Gorboletova and A. A. Metlin

Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia
e-mail:gorboletova@mail.ru

Received November 21, 2014

Abstract—Thermal effects of the complexation of cobalt(II) ions with L-histidine at 298.15 K and several values of the ionic strength against the background of KNO_3 are determined by means of direct calorimetry. The standard thermodynamic characteristics of the reactions of complexation in the aqueous solution have been calculated.

Keywords: complexation of Co ions with L-histidine, thermochemistry.

DOI: 10.1134/S0036024415090125

INTRODUCTION

Processes that occur in the cobalt(II)–L-histidine system were studied in our laboratory by means of potentiometric titration [1]. It was found that a cobalt(II) ion (Co^{2+}) forms complex particles with the composition of CoL^+, CoL_2, and CoL_3^- with L-histidine (L^-) and their stability constants were estimated as $\log\beta^0(CoL^+) = 7.52 \pm 0.05$, $\log\beta^0(CoL_2) = 13.49 \pm 0.05$, and $\log\beta^0(CoL_3^-) = 15.55 \pm 0.10$. The constants were recalculated for fixed values of the ionic strength using the equation proposed in [2].

Data on the thermodynamic characteristics of the formation of the histidinate complex of cobalt(II) are scarce. The authors of [3] determined the enthalpy of formation of the bis-complex of L-histidine with cobalt(II) via calorimetric titration at a value of the ionic strength of 0.1 (KNO_3) as $\Delta H(CoL_2) = -48.92$ kJ/mol.

The aim of this work was to determine the enthalpies of formation of complexes of cobalt(II) with L-histidine via direct calorimetry at a temperature of 298.15 K, and to study the effect the ionic strength of a solution has on the thermodynamic characteristics of the processes of complexation in the cobalt(II)–L-histidine system.

EXPERIMENTAL

The thermal effects of mixing and dilution were measured in a calorimeter with an isothermal jacket and automatic recording of the curve of the calorimetric experiment [4]. The calorimeter was calibrated by electric current heating. Reagent-grade L-histidine was used in the work. The preparation was not additionally purified. Solutions of L-histidine were prepared by dissolving weighed amounts of the reagent in a freshly prepared distilled water immediately before conducting a calorimetric experiment. The concentration of the $Co(NO_3)_2$ solution was determined complexometrically. KNO_3 recrystallized from the distilled water was used to maintain a specified ionic strength. Reagent-grade KOH was used in our experiments. The experiments were conducted at 298.15 K and at ionic strengths of 0.2, 0.5, and 1.0. The pH values were monitored using a Multitest IPL-11 pH meter. The Student test was used at a probability of 0.95 to calculate the confidence interval of the mean value of ΔH from three replicate experiments.

To choose the conditions for conducting the calorimetric experiments, the equilibrium composition of the solutions was calculated using the RRSU software [5] with allowance for the following reactions:

$$L^- + H^+ \leftrightarrow HL^{\pm}, \tag{1}$$

$$L^- + 2H^+ \leftrightarrow H_2L^+, \tag{2}$$

$$L^- + 3H^+ \leftrightarrow H_3L^{2+}, \tag{3}$$

$$Co^{2+} + L^- \leftrightarrow CoL^+, \tag{4}$$

$$Co^{2+} + 2L^- \leftrightarrow CoL_2, \tag{5}$$

$$Co^{2+} + 3L^- \leftrightarrow CoL_3^-, \tag{6}$$

$$H^+ + OH^- \leftrightarrow H_2O, \tag{7}$$

$$Co^{2+} + HOH \leftrightarrow CoOH^+ + H^+. \tag{8}$$

The thermal effect of the formation of the CoL^+ particle was determined in a pH range of 10.5–6.9 at the ratio of concentrations $c_M^\circ : c_L^\circ = 1 : 1$. A solution

Table 1. Thermal effects (kJ/mol) of the interaction between the solution of L-histidine (0.012 mol/L) and the solution of $Co(NO_3)_2$ (0.8738 mol/kg of solution)

Ionic strength (KNO_3)	Weighed amount of the solution of $Co(NO_3)_2$, g	$-\Delta_{mix}H$, kJ/mol	Weighed amount of the solution of $Co(NO_3)_2$, g	$-\Delta_{dil}H$, kJ/mol	$-\Delta H = \Delta_{mix}H - \Delta_{dil}H$, kJ/mol
0.2	0.45005	33.88	0.45025	1.60	32.36
	0.44995	33.95	0.45015	1.46	32.43
	0.44995	34.00	0.45010	1.51	32.48
0.5	0.45025	35.11	0.45025	2.83	32.21
	0.45020	34.95	0.45025	2.96	32.05
	0.44995	34.98	0.45015	2.90	32.08
1.0	0.44995	35.79	0.45000	3.77	31.95
	0.45025	35.73	0.45010	3.86	31.89
	0.45000	35.84	0.45015	3.90	32.00

Table 2. Thermal effects (kJ/mol) of the interaction between our solution of L-histidine (0.020 mol/L) and the solution of $Co(NO_3)_2$ (0.8738 mol/kg of solution)

Ionic strength (KNO_3)	Weighed amount of the solution of $Co(NO_3)_2$, g	$-\Delta_{mix}H$, kJ/mol	$-\Delta H = \Delta_{mix}H - \Delta_{dil}H$, kJ/mol
0.2	0.45015	45.86	44.34
	0.44995	45.71	44.19
	0.45020	45.66	44.14
0.5	0.45020	46.91	44.01
	0.45005	47.04	44.14
	0.45015	47.12	44.22
1.0	0.45010	48.14	44.30
	0.45000	48.12	44.28
	0.45025	48.36	44.52

Table 3. Thermal effects (kJ/mol) of the interaction between our solution of L-histidine (0.090 mol/L) and the solution of $Co(NO_3)_2$ (0.8738 mol/kg of solution)

Ionic strength (KNO_3)	Weighed amount of the solution of $Co(NO_3)_2$, g	$-\Delta_{mix}H$, kJ/mol	$-\Delta H = \Delta_{mix}H - \Delta_{dil}H$, kJ/mol
0.2	0.45020	57.38	55.86
	0.45015	57.54	56.02
	0.45025	57.48	55.96
0.5	0.45025	58.65	55.75
	0.45025	58.39	55.49
	0.45015	58.52	55.62
1.0	0.44995	59.56	55.72
	0.44995	59.79	55.95
	0.45000	59.64	55.80

of L-histidine with the concentration of 0.012 mol/L (39.86 mL) was used as the calorimetric fluid. Accurately weighed amounts of a solution of $Co(NO_3)_2$ were introduced into a glass ampoule. The concentration of the solution of $Co(NO_3)_2$ in the calorimetric cell after the ampoule was broken was ~0.01 mol/L. The heats of dilution of the solution of $Co(NO_3)_2$ in the solutions of the background electrolyte KNO_3 were measured as well. The experimental data are presented in Table 1.

In order to determine the thermal effect of the formation of the CoL_2 complex at the ratio of concentrations $c^\circ_M : c^\circ_L \sim 1:2$, an ampoule containing the accurately weighed amount of the solution of $Co(NO_3)_2$ was broken into a solution of L-histidine with a concentration of 0.02 mol/L (ΔpH of 10.0–6.6). The values of the thermal effects of mixing are presented in Table 2.

The thermal effect of the formation of the CoL_3^- particle was determined in a pH range of 9.2–8.7 at the ratio of concentrations $c^\circ_M : c^\circ_L = 1:9$. A solution of L-histidine with a concentration of 0.09 mol/L was used as the calorimetric fluid. The experimental data are presented in Table 3.

RESULTS AND DISCUSSION

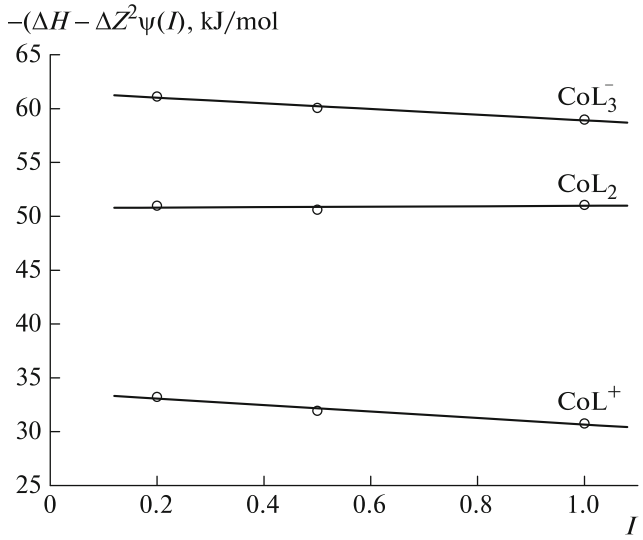
The experimental thermal effect was

$$\Delta_{mix}H - \Delta_{dil}H = \alpha_1\Delta H_{CoL^+} + \alpha_2\Delta H_{CoL_2} + \alpha_3\Delta H_{CoL_3^-} + \sum \alpha_i \Delta_r H_i, \quad (9)$$

Table 4. Standard thermodynamic characteristics of the processes of complexation in the Co^{2+}–L-histidine system

Process	$\log\beta^o$	$-\Delta_r H°$, kJ/mol	$-\Delta_r G°$, kJ/mol	$\Delta_r S°$, J/(mol K)
$I = 0$				
(4)	7.52 ± 0.05	33.68 ± 0.34	42.92 ± 0.29	31.0 ± 0.6
(5)	13.49 ± 0.05	50.77 ± 0.37	77.00 ± 0.29	87.9 ± 0.6
(6)	15.55 ± 0.10	61.54 ± 0.27	88.76 ± 0.57	91.3 ± 1.0
$I = 0.2$				
(4)	6.98 ± 0.05	34.16 ± 0.17	39.84 ± 0.29	19.1 ± 0.5
(5)	12.68 ± 0.05	52.38 ± 0.20	72.38 ± 0.29	67.1 ± 0.5
(6)	14.74 ± 0.10	62.54 ± 0.23	84.14 ± 0.57	72.4 ± 1.1
$I = 0.5$				
(4)	6.88 ± 0.05	33.24 ± 0.20	39.27 ± 0.29	20.2 ± 0.5
(5)	12.52 ± 0.05	52.56 ± 0.27	71.46 ± 0.29	63.4 ± 0.5
(6)	14.55 ± 0.10	62.00 ± 0.22	83.05 ± 0.57	70.6 ± 1.2
$I = 1.0$				
(4)	6.80 ± 0.05	32.28 ± 0.16	38.81 ± 0.29	21.9 ± 0.5
(5)	12.38 ± 0.05	53.35 ± 0.24	70.66 ± 0.29	58.1 ± 0.5
(6)	14.39 ± 0.10	61.59 ± 0.27	82.14 ± 0.57	68.9 ± 1.1

where $\Delta_{mix}H$ are the thermal effects of the interaction between the solutions of $Co(NO_3)_2$ and the solutions of L-histidine with the specified pH value; $\Delta_{dil}H$ is the heat of dilution of $Co(NO_3)_2$ in the solutions of the background electrolyte; α_1, α_2, and α_3 denote the completeness of processes (4), (5), and (6), respectively; and $\sum \alpha_i \Delta_r H_i$ is the contribution from concurrent side processes (1)–(3), (7), and (8) to the measured thermal effect.



Determination of the standard thermal effects of the formation of our CoL^+, CoL_2, and CoL_3^- complexes at 298.15 K.

The conditions of the calorimetric experiments were selected such that the contribution from the side processes was minimal. The data on the ionization constants of water against the background of KNO_3 were taken from [6], the enthalpies and constants of the reactions of acid–base interaction in the solutions of L-histidine required for the calculation were taken from [7], the thermodynamic parameters of the dissociation of water were taken from [8], and the equilibrium constant of the reaction (8) was taken from [9]. The contribution from the thermal effect of process (8) tended to zero.

When determining the enthalpy of formation of the complexes of cobalt(II) with L-histidine, the reaction of the formation of the complex of the 1 : 2 composition occurred along with equilibrium (4). The percentage of the formation of the CoL^+ complex varied from 40 to 65%, depending on the concentration of the amino acid and the pH of the solution, while that of CoL_2 varied from 30 to 60%. Under the concentration conditions for determining the enthalpy of formation of CoL_3^-, the fraction of the metal bound into the complex was 40%. The thermal effects of the formation of CoL^+, CoL_2, and CoL_3^- were calculated using the

HEAT universal software [10] by minimizing criterion function F with respect to the desired parameters:

$$F = \sum_{i=1}^{N} \omega_i \left(\Delta H_i^{\exp} - \Delta H_i^{\text{calc}}\right)^2, \qquad (10)$$

where ΔH_i^{calc} is the calculated thermal effect at the specified values of the overall concentrations $c^0_{M^{2+}}, c^0_{L^-}$ and current logβ and $\Delta_r H$, N is the number of experiments, and ω_i are the weight factors. The calculated enthalpies of the processes of formation of the CoL^+, CoL_2, and CoL_3^- particles are presented in Table 4.

The thermal effects at fixed values of the ionic strength were extrapolated to zero ionic strength according to the equation [11]

$$\Delta H - \Delta z^2 \Psi(I) = \Delta H^0 + bI, \qquad (11)$$

where ΔH and ΔH^0 are the change in the enthalpy at the final value of the ionic strength and at $I = 0$, $\Psi(I)$ is the theoretically calculated function of the ionic strength.

The figure presents the results from the graphic processing of the thermal effects of the formation of the complexes of cobalt(II) with L-histidine according to Eq. (11). As can be seen, the dots fall satisfactorily onto straight lines that yield y-intercepts equal to the thermal effect of the formation of the complexes of cobalt(II) with L-histidine at zero ionic strength. The optimum position of the straight lines in the diagram was found via the least squares method.

The calculated values of the thermodynamic characteristics of complexation in the cobalt (II)–L-histidine system are presented in Table 4. The enthalpy of formation of the CoL_2 particle that we determined differed somewhat from the one obtained in [3]. The authors of [3] apparently did not consider the process of the formation of the *tris*-complex. The values presented in Table 4 do not conflict with the results from structural studies of cobalt histidinates. The authors of [12] established that in CoL^+ и CoL_2 complexes, the ligand is tridentate coordinated due to the introduction of the carboxylic group, imidazole ring, and amino group into the coordination. It was noted in [13] that the CoL^+ complex contains water molecules, while water is completely displaced from the internal coordination sphere of the complex during the formation of CoL_2. The octahedral structure of the *bis*-complex of L-histidine with cobalt(II) with the *trans*-configuration of the imidazole groups was established in [14].

The substantial change in enthalpy with the formation of the CoL^+ particle (Table 4) that exceeds $\Delta_r H$ of the formation of nickel(II) histidinate with the composition of 1 : 1 in the modulus stands out [15]. We may assume that the third donor group in the CoL^+ complex (apparently the carboxyl group) participates in coordination with the cobalt(II) ion in the axial position via the water molecule. The low value of the change in entropy $\Delta_r S(CoL^+) = 31.0$ J/(mol K) confirms this assumption. At the same time, a fairly large positive value of $\Delta_r S$ is observed during the formation of the *bis*-complex of cobalt(II) with L-histidine $\Delta_r S(CoL_2) = 87.9$ J/(mol K), undoubtedly associated with the release of water molecules from the coordination sphere of the CoL_2 complex.

It can be seen from the figure that an increase in the exothermicity of the processes of complexation with the growth in the ionic strength of the solution is observed for the CoL_2 complex. As the concentration of the background electrolyte rises, the number of free water molecules in the solution falls, reducing the endothermic contribution from the process of desolvation to the value of $\Delta_r H$. At the same time, the exothermicity of the thermal effect of the formation of the CoL^+ complex decreases with the growth in the ionic strength. The coordination of the water molecules around the complex-forming ion is apparently complicated during the formation of this complex after an increase in the concentration of KNO_3. During the formation of the CoL^+ particle, greater destruction of the hydration structure occurs as the concentration of the background electrolyte rises than in the formation of CoL_2.

The *tris*-complex of cobalt(II) with L-histidine is formed at high concentrations of the ligand. Judging by the value of $\Delta_r H(CoL_3^-)$ (Table 4), the third ligand is coordinated monodentately (presumably by the amino group) via the displacement of the carboxylic group of one of the ligands of the *bis*-complex from the coordination sphere. The process of the stepwise addition of the third ligand is accompanied by a slight change in entropy.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research, project no. 14-03-00360. It was performed at the Scientific Research Institute for the Thermodynamics and Kinetics of Chemical Processes, Ivanovo State University of Chemistry and Technology.

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Translated by E. Boltukhina