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Thermochemical Study of a Process of Complex Formation Between *D,L*-Triptophan and Cobalt(II) Ions in Water Solution

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Abstract—Heat effects of the reactions of formation of complexes of the composition $CoTrp^+$ and $CoTrp_2$ were measured by direct calorimetry. Analysis of the effect of the ion force of the solution (0.25, 0.50, and 0.75 M KNO_3) on the heat effects of the processes of complex formation in the *D,L*-triptophan–Co(II) system at different temperatures (288.15, 298.15, and 308.15 K) was carried out. Standard thermodynamic characteristics of the reactions of formation of complexes in the system under study were evaluated.

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Metal ions play an important role in living organisms. In the combination with amino acids, protein molecules, and peptides they are included in metal-containing enzymes providing the proceeding of a great number of biochemical reactions and take part in accumulation and transportation of various substances.

Cobalt is one of the most important biogenic elements. Co^{2+} ion activates a series of enzymes and may substitute Zn^{2+} in them without the significant decrease in their activity. Excess of cobalt in organism inhibits the process of absorption of iron, blocks the iron-transporting systems and suppresses the consumption of oxygen.

Triprophan, β-indolylaminopropionic acid, is one of 20 most important natural amino acids, the components of proteins of all living organisms. It is one of the indispensable amino acids. It is the starting compound for the synthesis of many substances in organism such as melatonin, serotonin, etc. It also takes part in the reactions of metal-containing enzymes [1].

Stability constants of cobalt(II) complexes with *D,L*-triptophan in water solution are known with the sufficiently high accuracy. They are presented in [2–10] (see Table 1). For comparison of the results obtained under the different ion force values concentrational stability constants of CoL^+ and CoL_2 complexes were recalculated to the conditions of the zero ion force according to equation [11].

$$\log \beta^0 = \log \beta^c + A\Delta Z^2 \left(\frac{\sqrt{I}}{1 + 1.6\sqrt{I}} - 0.05I \right) - \delta I. \qquad (1)$$

Here β^c and β^0 are the concentrational and thermodynamic stability constants; ΔZ^2 is the difference in squares of charges of the reaction products and starting substances; A is the constant of the extreme Debye–Hükkel law equal to 0.5107 at 25°C, δ is the empirical coefficient, I is the ion force of the solution.

On the basis of critical analysis of the reported data it was possible to suggest that the most probable values of thermodynamic stability constants of complexes Co^{2+} ion with the Trp^- anion must be $\log \beta_1^0$ 5.12±0.04 and $\log \beta_2^0$ 9.44±0.03.

Reliable data on the stability constants of *D,L*-triptophan with Co^{2+} ions permit to interpret unambiguously the results of calorimetric measurements.

Data on the heat effects of processes of formation of cobalt(II) complexes with *D,L*-triptophan in water solutions are reported nowhere. The concentrational and temperature dependence of enthalpies of the reactions of complex formation in the system under investigation also was not studied previously.

The aim of this study is the direct calorimetric evaluation of heats of complex formation of *D,L*-triptophan with the cobalt(II) ion at 288.15, 298.15,

Table 1. Published data on the stability constants of cobalt(II) complexes with *D,L*-triptophan in water solution

Evaluation conditions			Stability constants				Reference
T, K	*I*	Background electrolyte	log β_1	log $\beta_1^{0\,a}$	log β_2	log $\beta_2^{0\,a}$	
308.15	0.1	KNO_3	4.39	5.72	–	–	[2]
308.15	0.1	KNO_3	4.35	5.68	–	–	[3]
308.15	0.1	KNO_3	4.55	5.88	–	–	[4]
308.15	0.1	KNO_3	4.52	5.85	–	–	[5]
308.15	0.2	KNO_3	4.10	4.37	8.01	8.28	[6]
308.15	0.1	KNO_3	4.39	5.72	–	–	[7]
298	0.1	$NaClO_4$	4.72	5.17	–	–	[8]
298	0.1	KNO_3	4.62	5.07	8.62	9.44	[9]
298	0.2	KNO_3	4.1	4.65	–	–	[10]

[a] Calculated in this work.

and 308.15 K and the ion force values 0.25, 0.50, and 0.75 (KNO_3 as background electrolyte), and also the investigation of the effect of concentration of background electrolyte and temperature on thermodynamic characteristics of processes of complex formation, and calculation of standard thermodynamic characteristics of the reactions under study.

During the interaction of solutions containing cobalt(II) ion and *D,L*-triptophan in the calorimeter the following processes are possible.

$$Co^{2+} + Trp^- = CoTrp^+, \quad (2)$$

$$Co^{2+} + 2Trp^- = CoTrp_2, \quad (3)$$

$$H^+ + Trp^- = HTrp^{\pm}, \quad (4)$$

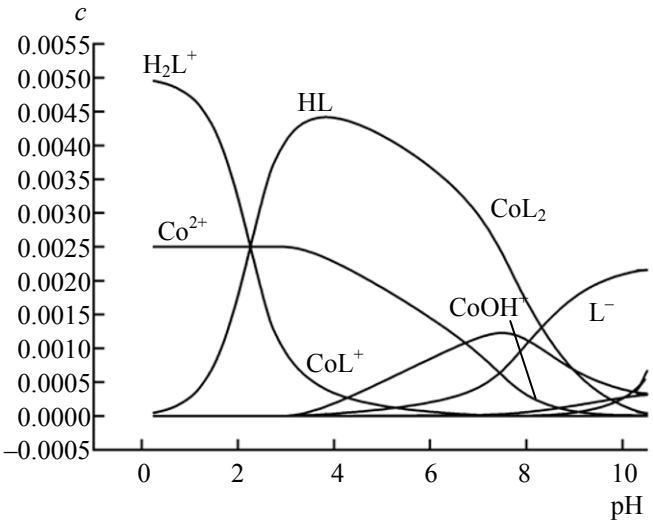

Fig. 1. Diagram of equilibria in the Co(II)–*D,L*-triptophan system at the 1:2 metal:ligand ratio, 25°C, $I = 0$.

$$2H^+ + Trp^- = H_2Trp^+, \quad (5)$$

$$Co^{2+} + H_2O = CoOH^+ + H^+, \quad (6)$$

$$H_2O = OH^- + H^+. \quad (7)$$

For the choice of optimal conditions for performing the experiment the equilibrium diagrams considering all the processes at the metal:ligand ratio 1:2, 1:5, and 1:7 were plotted with the help of the RRSU computer program [12].

In Fig. 1 the diagram of partial distribution of species in the system depending on the pH value of the medium for the 1:2 metal:ligand ratio is presented. The main goal of optimization of the conditions of calorimetric measurements is the establishing of such pH areas and such metal:ligand ratios where the yields of the processes under study are the highest and the contribution of the by-processes is the lowest.

Heat effects of the reactions of formation of complexes of the composition $CoTrp^+$ and $CoTrp_2$ were calculated by solving the system of two equations with two unknown quantities.

$$\Delta_{mix}H_1 - \Delta_{dil}H_1 = \alpha_1[CoTrp^+]\Delta_{comp}H(CoTrp^+) + \alpha_1[CoTrp_2]\Delta_{comp}H(CoTrp_2) + \alpha_1[CoOH^+]\Delta_{comp}H(CoOH^+) + \alpha_1[HL]\Delta_{ass}H_L - + \alpha_1[OH^-]\Delta_rH^w, \quad (8)$$

$$\Delta_{mix}H_2 - \Delta_{dil}H_2 = \alpha_2[CoTrp^+]\Delta_{comp}H(CoTrp^+) + \alpha_2[CoTrp_2]\Delta_{comp}H(CoTrp_2) + \alpha_2[CoOH^+]\Delta_{comp}H(CoOH^+) + \alpha_2[HL]\Delta_{ass}H_L - + \alpha_2[OH^-]\Delta_rH^w. \quad (9)$$

Here $\Delta_{mix}H$ is the heat effect (kJ mol^{-1}) of mixing solution of *D,L*-triptophan with cobalt(II) nitrate at the 1:2, 1:5, and 1:7 metal:ligand ratio; $\Delta_{dil}H$ is the heat

effect (kJ mol^{-1}) of dilution of cobalt(II) nitrate solution in the background electrolyte (KNO_3); $\Delta_{comp}H(CoTr^+)$ and $\Delta_{comp}(CoTrP_2)$ are heat effects of the reactions of formation of $CoTrp^+$ and $CoTrp_2$ complexes respectively; $\Delta_{ass}H$ is the heat effect of addition of proton to the L-anion of the amino acid [13]; Δ_rH^w is the heat effect of formation of water from the H^- and OH^- ions [14]. Contributions of the fourth and the fifth addends in the Eqs. (8)–(9) are negligible.

Completeness of formation of complex species was calculated as follows:

$$\alpha_1 = [CoTrp^+]/c^0_{Co}, \quad (10)$$

$$\alpha_2 = [CoTrp_2]/c^0_{Co}, \quad (11)$$

where $[CoTrp^-]$ and $[CoTrp_2]$ are the equilibrium concentrations of $CoTrp^+$ and $CoTrp_2$ species; c^0_{Co} is the total concentration of cobalt(II) solution introduced with the ampule accounting for the dilution to the volume of the calorimetric liquid.

Data on the heat effects of the reactions of formation of complex $CoTrp^+$ and $CoTpr_2$ species at different ion force values permit to calculate the standard heat effects of formation of the amino acid complexes with cobalt(II) ion by the equation with one individual parameter [11].

$$\Delta H - \Delta Z^2\Psi(I) = \Delta H^0 + bI. \quad (12)$$

Here ΔH is the heat effect of the reaction of complex formation (kJ mol^{-1}) at the fixed ion force value; ΔH^0 is the enthalpy release in the corresponding process at the ion force equal to zero (kJ mol^{-1}); ΔZ^2 is the difference in squares of charges of the reaction products and starting substances; $\psi(I)$ is the theoretically calculated ion force function; b is the empiric coefficient; I is the ion force of the solution.

Graphic evaluation of heats of the reactions of formation of $CoTrp^+$ and $CoTrp_2$ complexes at different temperatures on the basis of Eq. (12) is presented in the Fig. 2. As is seen, the points satisfactory lay on the straight lines, and the fragments cut on the ordinate axis correspond to the standard enthalpies of the reactions of formation of cobalt(II) complexes with *D,L*-triptophan.

Heats of the reactions of formation of $CoTrp^+$ and $CoTrp_2$ complexes under standard conditions and in different salt solutions were estimated in this work for the first time.

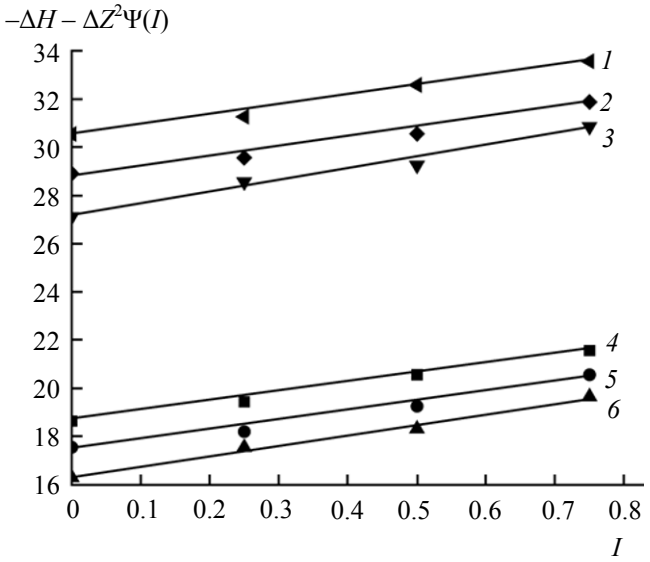

Fig. 2. Graphic evaluation of standard heats of the reactions of formation of (*4–6*) $CoTrp^+$ and (*1–3*) $CoTrp_2$ complexes at different temperatures, K: (*1, 4*) 288.15, (*2, 5*) 298.15, and (*3, 6*) 308.15.

In Table 2 thermodynamic characteristics of the reactions of complex formation of cobalt(II) ion with *D,L*-triptophan are presented.

It is seen from Fig. 2 that the heat evolution during the formation of Co(II) complexes with *D,L*-triptophan increases with the increase in the concentration of the background electrolyte. In contrast, at the increase in temperature heat effects of the reactions of complex formation decrease in absolute value. Thermodynamic characteristics of the reactions of complex formation of cobalt(II) ion with *D,L*-triptophan were obtained in this work for the first time.

For the analysis of values of thermodynamic characteristics of the reactions of complex formation with bioligands an approach based on the notions of Gurney thoroughly described in [15] occurs to be useful. Variation in enthalpy during the process of complex formation may be presented as a sum of temperature-dependent (Δ_rH_d) and temperature-independent (Δ_rH_{id}) factors:

$$\Delta_rH = \Delta_rH_d + \Delta_rH_{id}. \quad (13)$$

The process of complex formation of copper(II) ions with *D,L*-triptophan under the same conditions was thoroughly studied previously [16]. It is interesting to compare the data on the temperature-dependent and temperature-independent increments of thermodynamic characteristics of processes of com-

Table 2. Thermodynamic characteristics of the reactions of complex formation of cobalt(II) ion with *D,L*-triptophan at different values of ion force and temperature

Process	I	$\log \beta_n$	$-\Delta_{comp}G$, kJ mol^{-1}	$-\Delta_{comp}H$, kJ mol^{-1}	$\Delta_{comp}S$, J mol^{-1} K^{-1}
			288.15 K		
$Co^{2+} + Trp^- = CoTrp^+$	0.00	6.30±0.08	34.70±0.44	18.64±0.14	55.73±1.6
	0.25	6.01±0.08	33.10±0.44	19.43±0.14	47.44±1.2
	0.50	5.96±0.08	32.80±0.44	20.56±0.09	42.48±1.6
	0.75	5.93±0.08	32.66±0.44	21.56±0.20	38.52±1.7
$Co^{2+} + 2Trp^- = CoTrp_2$	0.00	10.64±0.09	58.60±0.50	30.54±0.13	97.38±1.8
	0.25	10.35±0.09	57.00±0.50	31.26±0.06	89.33±1.8
	0.50	10.30±0.09	56.73±0.50	32.58±0.13	83.78±1.8
	0.75	10.27±0.09	56.56±0.50	33.56±0.19	79.82±1.9
			298.15 K		
$Co^{2+} + Trp^- = CoTrp^+$	0.00	5.12±0.08	28.18±0.44	17.56±0.14	35.62±1.6
	0.25	4.83±0.08	27.52±0.44	18.20±0.14	31.26±1.2
	0.50	4.78±0.08	27.24±0.44	19.26±0.09	26.77±1.6
	0.75	4.75±0.08	27.07±0.44	20.56±0.20	21.83±1.7
$Co^{2+} + 2Trp^- = CoTrp_2$	0.00	9.44±0.09	53.80±0.50	28.90±0.13	83.52±1.8
	0.25	9.15±0.09	52.14±0.50	29.56±0.06	75.73±1.8
	0.50	9.10±0.09	51.86±0.50	30.55±0.13	71.47±1.8
	0.75	9.07±0.09	51.69±0.50	31.88±0.19	66.44±1.9
			308.15 K		
$Co^{2+} + Trp^- = CoTrp^+$	0.00	4.21±0.08	24.80±0.44	16.30±0.14	27.58±1.6
	0.25	3.92±0.08	23.09±0.44	17.56±0.14	17.88±1.2
	0.50	3.87±0.08	22.79±0.44	18.32±0.09	14.51±1.6
	0.75	3.84±0.08	22.62±0.44	19.65±0.20	9.64±1.7
$Co^{2+} + 2Trp^- = CoTrp_2$	0.00	8.56±0.09	50.42±0.50	27.12±0.13	75.61±1.8
	0.25	8.27±0.09	48.71±0.50	28.56±0.06	65.39±1.8
	0.50	8.22±0.09	48.41±0.50	29.25±0.13	62.18±1.8
	0.75	8.19±0.09	48.24±0.50	30.86±0.19	56.40±1.9

plex formation in the systems metal(II)–*D,L*-triptophan (Table 3).

Analysis of the results obtained permitted revealing some rules in the variation of thermodynamic parameters of the reactions of complex formation with bioligands. Firstly, the values of temperature-dependent components of thermodynamic characteristics of the processes of formation of complexes of the composition $CuTrp^+$ and $CuTrp_2$ ($\Delta_{comp}H_d^0$, $\Delta_{comp}S_d^0$) increase with temperature, while in the case of the cobalt(II)-triptophan system the reversed trend, that is, the decrease of $\Delta_{comp}H_d^0$ and $\Delta_{comp}S_d^0$ values is observed. Secondly, for the system copper(II)–*D,L*-triptophan $\Delta_{comp}G^0$ values decrease in going from 288.15 K to 308.15 K, while for the cobalt(II)–*D,L*-triptophan system the increase in the corresponding values takes place. Finally, it can be noted that in the processes of summary addition of ligands temperature-dependent increments of enthalpy and entropy increase with the increase in the number of ligands. At the addition of the second ligand $\Delta_{comp}H_d^0$ increases approximately two times.

EXPERIMENTAL

Chromatographically homogenous *D,L*-triptophan from Reanal (Hungary) was used without further purification. Before preparing the solutions crystalline amino acid was dried at 353 K until the constant mass. *D,L*-triptophan solution of given concentration was prepared by dissolution of the weighed amount of the

Table 3. Temperature-dependent (d) and independent (id) components of thermodynamic characteristics of processes of formation of cobalt(II)–*D,L*-triptophan and copper(II)–*D,L*-triptophan complexes.

Process	Temperature, K	A	$-\Delta_{comp}G^0_d$, kJ mol^{-1}	$-\Delta_{comp}G^0_{id} = -\Delta_{comp}H^0_{id}$, kJ mol^{-1}	$\Delta_{comp}H^0_d$, kJ mol^{-1}	$\Delta_{comp}S^0_d$, J mol^{-1} K^{-1}
$Cu^{2+} + Trp^- = CuTrp^+$	288.15	6281	23.27	34.15	7.21	105.78
	298.15	6448	25.00	33.56	8.88	113.63
	308.15	6635	26.92	32.78	10.79	122.38
$Cu^{2+} + 2Trp^- = CuTrp_2$	288.15	11161	41.36	66.77	12.81	178.7
	298.15	10665	41.36	68.35	14.69	187.99
	308.15	11187	45.40	70.52	18.19	206.36
$Co^{2+} + Trp^- = CoTrp^+$	288.15	5347	19.62	24.69	6.08	89.19
	298.15	3920	15.20	23.93	5.40	69.1
	308.15	3310	13.43	21.65	5.38	61.04
$Co^{2+} + 2Trp^- = CoTrp_2$	288.15	9757	36.15	41.68	11.20	164.32
	298.15	8537	33.10	40.60	11.76	150.46
	308.15	7728	31.36	39.62	12.57	142.56

amino acid in bidistilled water directly before performing the calorimetric measurement. Starting pH value was adjusted by addition of the calculated amount of KOH solution to the solution of amino acid. Titrated KOH solution was prepared from the "chemically pure" grade reagent according to the routine procedure [17]. For adjusting the ion force potassium nitrate crystallized from bidistillate was used [18]. Measurements of the heats of mixing and dilution of the cobalt(II) nitrate solution with the solution of triptophan were carried out in a calorimeter with the isothermal jacket and the automatic recording of the temperature-time curve [16]. The calorimeter was calibrated by current. The volume of calorimetric liquid was 50.10 ml. Batches of the solutions were weighted on the VRL-200 scales with the accuracy 5×10^{-5} g.

Experiments were carried out at 288.15, 298.15, and 308.15 K and the ion force values 0.25, 0.50, and 0.75 on the background of potassium nitrate. In the measurements of the formation enthalpies of complex species of the Co^{2+} ion with triptophan 50.10 ml of a solution of ligand with the given ion force value (KNO_3) and pH 8 was used as a calorimetric liquid. Values of enthalpies of mixing (ΔH_{mix}) and dilution (ΔH_{dil}) were found as the arithmetic mean values from three to five experiments, and the error was calculated as the mean square deviation. Metal to ligand ratio at the end of calorimetric experiment was 1:2, 1:5, and 1:7 respectively. pH values in the course of calorimetric experiment were controlled by the IPL-311 pH-meter. Close coincidence of the experimental and calculated pH value (±0.10–0.20 pH units) indicated the validity of the interpretation of the results of calorimetric measurements.

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