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THE THERMOKINETICS OF THE FORMATION REACTION OF COBALT HISTIDINE COMPLEX

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Abstract

The enthalpy change of formation reaction of cobalt(II) histidine (His) complex in water has been determined by a microcalorimeter, using cobalt chloride with *L*-α-histidine in the temperature range of 25~50°C. On the basis of experimental and calculated results, three thermodynamics parameters (the activation enthalpies, the activation entropies, the activation free energies), the rate constant, three kinetic parameters (the activation energies, the pre-exponential constant and the reaction order) are obtained. The results show that the titled reaction easily took place in the studied temperature.

Keywords: cobalt chloride, formation reaction, *L*-α-histidine complex

Introduction

Cobalt is one of essential trace elements for human body. It is the element cobalt that shows biological activity in the form of vitamin B_{12}. Cobalt-deficiency in one's body will lead to cardiovascular system diseases and anaemia deriving from DNA-synthesis disorders. *L*-α-histidine is essential to life, and its supplement has to be from food because of not being produced by one. So, it is significant to expand the research for the complex of cobalt and *L*-α-histidine. Concerning the complex of cobalt(II) and *L*-α-histidine, the properties of magnetism, oxidizing and IR spectrum are investigated by Spaca, Mihalidis, Akbarov, etc. [1–3]. The studies on stability constant in solution, NMR spectroscopy for the complex are discussed by Jitaru, Jezouska, Ismailov, etc. [4–6]. However, the formation thermokinetics of these complexes have not been reported in literature. In this paper, fundamental parameters for reaction of preparing cobalt histidine complex, including the reaction rate constant (k), the activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H_{\neq}^{0}$), the activation entropy ($\Delta S_{\neq}^{0}$), the activation free energies ($\Delta G_{\neq}^{0}$) and the enthalpies ($\Delta_r H_0$) obtained by means of a microcalorimeter, were studied. These parameters will provide a scientific basis for technological processing of preparing cobalt histidine complex.

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Experimental

Materials

$CoCl_2·6H_2O$ (A) is A.R. grade *L*-α-his*t*idine (B) is B.R. grade with the >99.5% purity. They are dissolved in distilled water. The molarities of solution A and B are 0.1000 mol L^{-1}. In our experimental, the molar ratio of both solutions, A to B is 1:2. The conductivity of the deionized water is $5.48·10^{-8}$ S cm^{-1}.

Experimental equipment and conditions

The reaction thermokinetics was studied by microcalorimeter, type RD496-III (China, Southwest Institute of Electronic Engineering), which was equipped with two 15 mL vessels (Fig. 1). After reaching equilibrium, the spacers of the sample and reference vessels were pushed down simultaneously and the samples were mixed. The microcalorimeter was calibrated by Joule effect and its sensitivity were 63.994±0.042, 64.308±0.027, 64.499±0.064, 64.638±0.078, 64.733±0.077 and 64.739±0.059 μV mW^{-1} at the experimental temperature of 298.5±0.005, 303.15±0.005, 308.15±0.005, 313.15±0.005, 318.15±0.005 and 323.15±0.005 K, respectively. The experimental precision and accuracy were checked by measuring the enthalpy of special pure crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H_m^0$ of 17.238±0.048 kJ mol^{-1} (*t* inspection, 99% believability) is excellent agreement with that of $\Delta_{sol}H_m^0$ of 17.241±0.018 kJ mol^{-1} reported in the literature [7]. This indicated that the device used in this work was reliable. The precision measured was in 0.5%.

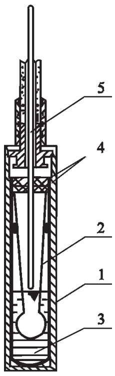

Fig. 1 Device used for the study of the formation reaction; 1 – calorimetric cell; 2 – adding tube containing cobalt chloride solution; 3 – adding tube containing histidine solution; 4 – silicone rubber cover; 5 – glass rod (on depressing the bottom of tube 2 is broken. The two solutions are mixed in the 1 and 2)

The IR spectra for cobalt histidine complex were determined by the Bruker of USA, Model EQ UINOX-550 FT-IR spectrophotometer (KBr pallet). The Zn^{2+} was determined complexometrically with EDTA. Cl^- was determined by Fajans method.

Carbon, hydrogen, and nitrogen analyses were carried out on a 1106-type elemental analyzer, Italy.

Results and discussion

Determination of $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}$ *and calculation* $\Delta_{\mathrm{f,Co(His)_2^{2+}(aq)}}H^0_{\mathrm{m}}$

The following equation could represent the formation reaction of cobalt histidine complex:

$$\mathrm{Co}^{2+}(aq)+2\mathrm{His}\,(aq)\rightarrow \mathrm{Co(His)}_2^{2+}(aq) \tag{a}$$

Within the range of the experimental temperature, the reaction is an exothermic one. $\Delta_{\mathrm{r}}H^0_{\mathrm{m}}$ of the reaction was measured six times, at 298.15 K. It was –12.878, –12.824, –12.785, –12.763, –12.760 and –12.709 kJ mol^{-1}, respectively, mean values was –12.787±0.058 kJ mol^{-1}. According to Hess' law, the standard enthalpy of formation of $\mathrm{Co(His)}_2^{2+}(aq)$ were calculated through Eq. (a):

$$\begin{aligned}\Delta_{\mathrm{f,\,(Co(His)_2^{2+}(aq)}}H^0_{\mathrm{m}} &= \Delta_{\mathrm{r}}H^0_{\mathrm{m}}+(\Delta_{\mathrm{f,\,CO^{2+}(aq)}}H^0_{\mathrm{m}}+2\Delta_{\mathrm{f},\,L-\alpha-\mathrm{His(aq)}}H^0_{\mathrm{m}})\\ &=[(-12.787\pm0.058)+(-58.2)+2(-424.91\pm1.54)]\ \mathrm{kJ\ mol^{-1}}\\ &=-920.81\pm3.08\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Here, $\Delta_{\mathrm{f,Co^{2+}(aq)}}H^0_{\mathrm{m}}$ is from the literature [8], $\Delta_{\mathrm{f},\,L\text{-}\alpha\text{-His(aq)}}H^0_{\mathrm{m}}$ is from the literature [9].

The thermokinetics calculation of the formation reaction

The typical thermokinetic (TK) curve of the reaction was shown in Fig. 2. The original data obtained from the TK curve were shown in Table 1. These experimental data were used in Eq. (1) and the reaction order and rate constant were obtained.

$$\ln\left[\frac{1}{H_0}\frac{\mathrm{d}H_{\mathrm{i}}}{\mathrm{d}t}\right]=\ln k+n\ln\left[1-\frac{H_{\mathrm{i}}}{H_0}\right] \tag{1}$$

where H_0 was the total reaction heat (corresponding to the global area under the TK curve); H_{i}, the reaction heat in a certain time (corresponding to the partial area under

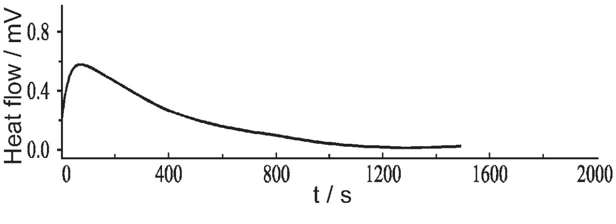

Fig. 2 Typical thermokinetic curve of the reaction (298.15 K)

Table 1 Thermophysical data of the reaction

t/s	298.15 K H_0=3.211 J		303.15 K H_0=3.520 J		308.15 K H_0=3.590 J		313.15 K H_0=3.619 J		318.15 K H_0=3.836 J		323.15 K H_0=4.066 J	
	H_t/H_0	dH/dt^*	H_t/H_0	dH/dt^*	H_t/H_0	dH/dt^*	H_t/H_0	dH/dt^*	H_t/H_0	dH/dt^*	H_t/H_0	dH/dt^*
200	0.4053	22.39	0.4172	31.53	0.3929	42.69	0.4109	52.91	0.4085	72.09	0.3467	107.1
250	0.4897	19.37	0.5027	26.72	0.4742	37.16	0.4905	46.07	0.4851	62.16	0.4227	96.64
300	0.5636	16.61	0.5769	22.50	0.5452	32.18	0.5592	40.01	0.5516	53.60	0.4921	84.63
350	0.6278	14.20	0.6410	18.92	0.6069	27.84	0.6186	34.71	0.6095	46.31	0.5539	74.00
400	0.6835	12.08	0.6963	15.96	0.6605	24.09	0.6698	30.11	0.6599	40.17	0.6090	64.65
450	0.7314	10.26	0.7440	13.49	0.7070	20.85	0.7138	26.11	0.7041	34.79	0.6579	56.41
500	0.7726	8.729	0.7851	11.41	0.7473	18.07	0.7518	22.68	0.7428	30.33	0.7012	49.33
550	0.8080	7.428	0.8205	9.674	0.7822	15.63	0.7845	19.70	0.7770	26.55	0.7397	43.32
600	0.8384	6.348	0.8509	8.239	0.8123	13.62	0.8128	17.18	0.8074	23.25	0.7740	38.10
650	0.8646	5.471	0.8770	7.052	0.8385	11.94	0.8372	14.97	0.8344	20.39	0.8043	33.49

$^*dH/dt\cdot10^4$/J s^{-1}

Table 2 The values of n, k, A, E, $\Delta G_{\neq}^{0}$, $\Delta H_{\neq}^{0}$ and $\Delta S_{\neq}^{0}$ of the reaction

T/K	Eq. (1)			Eq. (2)			Eq. (3)	Eq. (4)		
	$k\cdot 10^3$ s^{-1}	n	r^*	E/ kJ mol^{-1}	ln$A$/s^{-1}	r^*	$\Delta G_{\neq}^{0}$/ kJ mol^{-1}	$\Delta H_{\neq}^{0}$/ kJ mol^{-1}	$\Delta S_{\neq}^{0}$/ J mol^{-1} K^{-1}	r^*
298.15	1.145	0.964	0.999	40.17	9.424	0.998	89.81	37.60	–175.2	0.998
303.15	1.471	0.970	0.999	–	–	–	90.73	–	–	–
308.15	1.921	0.970	0.998	–	–	–	91.58	–	–	–
313.15	2.472	0.984	0.998	–	–	–	92.46	–	–	–
318.15	3.112	0.997	0.999	–	–	–	93.36	–	–	–
323.15	4.016	0.981	0.998	–	–	–	94.19	–	–	–

the curve); dH_i/dt, the exothermic rate at time t; k, the rate constant of reaction; n, the reaction order.

The values of k and n obtained by Eq. (1), the values of E and A obtained by Eq. (2), the value of $\Delta G_{\neq}^{0}$ obtained by Eq. (3) and the values of $\Delta H_{\neq}^{0}$ and $\Delta S_{\neq}^{0}$ obtained by Eq. (4), which were all listed in Table 2.

$$\ln k=\ln A-\left[\frac{E}{RT}\right] \tag{2}$$

$$\Delta G_{\neq}^{0}=RT\ln\left[\frac{RT}{Nhk}\right] \tag{3}$$

$$\ln\left[\frac{k}{T}\right]=-\frac{\Delta H_{\neq}^{0}}{RT}+\frac{\Delta S_{\neq}^{0}}{R}+\ln\left[\frac{k_B}{h}\right] \tag{4}$$

where A was the pre-exponential constant; E, the apparent activation energy; R, the gas constant; T, the absolute temperature; $\Delta G_{\neq}^{0}$, the activation free-energy; N, Avogadro number; h, Planck's constant; $\Delta H_{\neq}^{0}$ the activation enthalpy; $\Delta S_{\neq}^{0}$, the activation entropy; k_B, Boltzmann's constant.

The results in Table 2 clearly indicate that the higher the temperature of the reaction is, the faster the rate of the reaction takes place and the titled reaction is of the first order. While that values of E and $\Delta H_{\neq}^{0}$ are very low and $\Delta S_{\neq}^{0}$ is high. These facts showed that the titled reaction easily took place in the temperature range of 298.15–323.15 K.

Preparation and composition of the complex

The final solution collected from each experiment and the solution with the same mole rate as the reaction were concentrated on a 343.15–353.15 K water bath till crystal membrane formed on the surface, and then, it was put into a containing P_4O_{10} desiccator to remove trace water. The analytical results indicated that they had the same composition of $Co(His)_2Cl_2{\cdot}H_2O$. The analytical results of composition are given in Table 3.

Table 3 Analytical results of composition of complex/%

	Co^{2+}	Cl^{-}	C	H	N
Calculated values	11.35	13.66	31.46	4.40	18.34
Experimental values	11.42	13.69	31.53	4.47	18.48

The IR absorption of main groups for complex and ligand are given in Table 4.

Table 4 IR absorption of main groups for complex and ligand/cm^{-1}

Compound	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	ν_{OH}	ν^{as}_{CCN}	ν^{s}_{CCN}
L-α-His	3025	2860	1590	1456	1635	1415	–	1315	744
$Co(His)_2Cl_2\cdot H_2O$	3119	3032	1635	1407	1500	1336	3415 827	1146	966

The IR spectrum for the complex shows that characteristic absorption peaks of amino and carboxyl groups have a great shift as compared to those in the ligand. It indicates that nitrogen and oxygen atoms in the complex coordinate to Co^{2+} in a bidentate fashion [10]. In addition to above, characteristic absorption peak of imidazolyl group in the complex shifts intensively. This shows that nitrogen atom in the imidazolyl group coordinates to Co^{2+} as well [11]. 3415 and 827 cm^{-1} in the IR spectrum for the complex are assigned to hydroxyl absorption of water. The existence of water molecule is believed for the complex.

Conclusions

1. On the basis of experimental and calculated results, the reaction rate of the formation of $Co(His)_2Cl_2\cdot H_2O$ in the studied temperature range was found to be of first order. The reaction was exothermic. The enthalpy was (–12.787±0.058) kJ mol^{-1}, the standard enthalpy of formation of $Co(His)_2^{2+}$ (*aq*) was (–920.81±3.08) kJ mol^{-1}.
2. The activation energy of the formation reaction $Co(His)_2Cl_2\cdot H_2O$ in the temperature range of 298.15–323.15 K was rather low; and the entropy of the formation reaction of $Co(His)_2Cl_2\cdot H_2O$ in the studied temperature was high. It means that the titled reaction easily took place in the temperature range of 29.15–323.15 K.

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