Thermokinetics of the Formation Reaction of Zinc Histidine Complex

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The enthalpy change of reaction of zinc chloride with *L*-α-histidine in the temperature range of 25—50 ℃ has been determined by a microcalorimeter. On the basis of experimental and calculated results, three thermodynamics parameters (the activation enthalpy, the activation entropy, the activation free energy), the rate constant and three kinetic parameters (the activation energy, the pre-exponential constant and the reaction order) of the reaction, and the standard enthalpy of formation of $Zn(His)^{2+}(aq.)$ are obtained. The results showed that the title reaction easily took place at the studied temperature.

Keywords zinc chloride, *L*-α-histidine, complex, formation reaction, thermokinetics

Introduction

Of the various materials considered, the complexes of zinc with *L*-α-amino acid as addictive have received much attention due to its wide application in medicines, foodstuff and cosmetics.[1,2] Preparative methods of zinc amino acids reported in literatures were as follows: adjusting pH of solution,[3] adding weak acid,[4,5] treating with organic solvent,[2,6-7] and electrolytic process.[8] It is noteworthy that the yield of the complexes prepared by above-mentioned methods is low and the products are not soluble in water. Anion is not contained in these complexes. At present, our research group has investigated the solubility properties of zinc chloride-histidine-water system at 25 ℃. The results indicate that the new complex $Zn(His)Cl_2 \cdot 0.5H_2O$ formed in this system is congruently soluble in water. Based on phase equilibrium, the complex was prepared in water as well as characterized by XRD and TG-DTG technology.[9] The constant volume combustion energy of the complex was determined by a rotating-bomb calorimeter. The standard enthalpy of formation was calculated for this complex.[10] However, the thermokinetics of formation reaction of these complexes has not been reported in literatures. In this paper, fundamental parameters for reaction of preparing zinc histidine complex, including the reaction rate constant k, the activation energy E, the pre-exponential constant A, the reaction order n, the activation enthalpy $\Delta H_m^{\theta,\neq}$, the activation entropy $\Delta S_m^{\theta,\neq}$, the activation free energy $\Delta G_m^{\theta,\neq}$ and the reaction enthalpy ΔH_r^{θ} obtained by means of a microcalorimeter, are studied. They will provide a scientific basis for technological process of preparing zinc histidine complex.

Experimental

Materials

The $ZnCl_2$ (A) is of AR grade and *L*-α-histidine (B) BR grade which were recrystallized with the purity prior to 99.9%. They are dissolved in deionized water. The concentration of solutions A and B is 0.1000 mol/L. In our experiments, the molar ratio of solution A to B

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is 1:1. The conductivity of the deionized water is 5.48×10^{-8} S/cm.

Equipment and conditions

The thermokinetics of the reaction was measured by a microcalorimeter, type RD496-Ⅲ (Southwest Institute of Electronic Engineering, China), which was equipped with two 15 mL vessels. The device used for the study of the formation is shown in Fig. 1. The microcalorimeter was calibrated by Joule effect and its sensitivity was 63.994 ± 0.042, 64.308 ± 0.027, 64.499 ± 0.064, 64.638 ± 0.078, $64.733 \pm 0.077$and 64.739 ± 0.059 μV/mW at the experimental temperature of 298.5, 303.15, 308.15, 313.15, 318.15 and 323.15 K, respectively. The experimental precision and accuracy were checked by measurements of the enthalpies of solution of special purity crystalline KCl in deionized water at 298.15 K. The molar ratio of H_2O to KCl is 2000. The experimental value of $\Delta H^{\theta}_{m,sol}$ of 17.238 ± 0.048 kJ/mol (t inspection, 99% believability) is in good agreement with that of $\Delta H^{\theta}_{m,sol}$ of 17.241 ± 0.018 kJ/mol reported in the literature,[11] which indicated that the device used in this work was reliable. The precision of the measurements was in 0.5%.

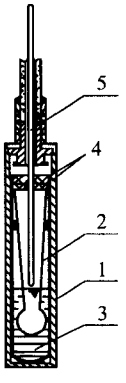

Fig.1 Sketch of device used for the study of the formation reaction: 1, calorimetric cell; 2, adding tube containing zinc chloride solution; 3, adding tube containing histidine solution; 4, silicone rubber cover; 5, glass rod (on depressing the rod, the bottom of tube 2 is broken and the two solutions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

Results and discussion

Standard enthalpy of formation, $\Delta H^{\theta}_{m,f}[Zn(His)^{2+}, aq., 298.15\ K]$

The formation reaction of zinc histidine complex can be represented as:

$$Zn^{2+}(aq.) + His(aq.) \rightarrow Zn(His)(aq.)$$

This process is an exothermic one in the experimental temperature range. The reaction enthalpy, $\Delta H^{\theta}_{m,r}$ is measured six times at 298.15 K with the mean value being -11.709 ± 0.052 kJ/mol. According to the reaction and Eq. (1) derived on the basis of the reaction, the value of $\Delta H^{\theta}_{m,f}[Zn(His)^{2+}, aq., 298.15\ K]$ of -590.51 ± 3.08 kJ/mol may be obtained from the value of $\Delta H^{\theta}_{m,r}$ obtained in this work, the value of $\Delta H^{\theta}_{m,f}(Zn^{2+}, aq., 298.15\ K) = -153.89$ kJ/mol[12] and $\Delta H^{\theta}_{m,f}(L\text{-}\alpha\text{-His}, aq., 298.15\ K) = -424.91 \pm 1.54$ kJ/mol.[13]

$$\Delta H^{\theta}_{m,f}[Zn(His)^{2+}, aq., 298.15\ K] = \Delta H^{\theta}_{m,r} + [\Delta H^{\theta}_{m,f}(Zn^{2+}, aq., 298.15\ K) + \Delta H^{\theta}_{m,f}(L\text{-}\alpha\text{-His}, aq., 298.15\ K)] \quad (1)$$

Thermokinetics of the formation reaction

The typical thermokinetic (TK) curve of the reaction is shown in Fig. 2. The original data obtained from the TK curve were shown in Table 1. These experimental data are put into Eq. (2) derived from the literature[14] by linear least-squares method.

$$\ln\left(\frac{1}{H_0}\frac{dH_i}{dt}\right) = \ln k + n\ln\left(1 - \frac{H_i}{H_0}\right) \quad (2)$$

where H_0 is the total reaction enthalpy (corresponding to the global area under the TK curve), H_i the reaction heat in a certain time (corresponding to the partial area under the curve), dH_i/dt the exothermic rate at time t, k the rate constant of reaction, n the reaction order.

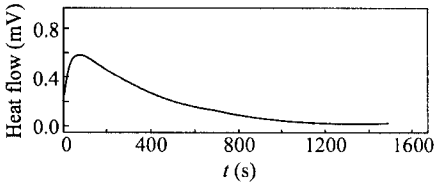

Fig.2 Thermokinetic curve of the reaction (298.15 K).

The values of k and n obtained from Eq. (1), the values of E and A obtained from Eq. (2), the value of $\Delta G^{\theta,\neq}_{m}$ obtained from Eq. (3) and the values of $\Delta H^{\theta,\neq}_{m}$ and $\Delta S^{\theta,\neq}_{m}$ obtained from Eq. (4) are listed in Table 2.

$$\ln k = \ln A - \frac{E}{RT} \quad (3)$$

$$\Delta G_m^{\theta,\neq} = RT\ln\frac{RT}{Nhk} \quad (4)$$

$$\ln\frac{k}{t} = -\frac{\Delta H_m^{\theta,\neq}}{RT} + \frac{\Delta S_m^{\theta,\neq}}{R} + \ln\frac{k_B}{h} \quad (5)$$

where A is the pre-exponential constant, E the apparent activation energy, R the gas constant, T the absolute temperature, $\Delta G_m^{\theta,\neq}$ the activation free-energy, N Avogadro number, h Planck's constant, $\Delta H_m^{\theta,\neq}$ the activation enthalpy, $\Delta S_m^{\theta,\neq}$ the activation entropy, k_B Boltzmann's constant.

The results in Table 2 clearly indicate that the higher the temperature of the reaction, the faster the reaction and the reaction is of the first order. The values of E and $\Delta H_m^{\theta,\neq}$ are very low, but $\Delta S_m^{\theta,\neq}$ is high. These facts show that the reaction can take place easily in the temperature range of 298.15—323.15 K.

Table 1 Thermokinetic data of the reaction

t (s)	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	H_i/H_0	dH/dt ($\times 10^4$ J/s)	H_i/H_0	dH/dt ($\times 10^4$ J/s)	H_i/H_0	dH/dt ($\times 10^4$ J/s)	H_i/H_0	dH/dt ($\times 10^4$ J/s)	H_i/H_0	dH/dt ($\times 10^4$ J/s)	H_i/H_0	dH/dt ($\times 10^4$ J/s)
200	0.1922	40.05	0.3883	39.04	0.3307	51.02	0.3105	68.76	0.3499	86.57	0.3289	112.9
250	0.2729	36.99	0.4946	32.79	0.4311	44.27	0.4099	60.59	0.4491	73.45	0.4277	97.93
300	0.3425	34.13	0.5838	27.31	0.5185	37.71	0.4977	52.24	0.5343	61.89	0.5139	83.68
350	0.4046	30.35	0.6581	22.57	0.5940	31.89	0.5740	44.46	0.6072	51.93	0.5885	71.04
400	0.4641	27.00	0.7198	18.60	0.6586	26.83	0.6397	37.55	0.6693	43.51	0.6525	59.95
450	0.5206	24.00	0.7709	15.25	0.7138	22.44	0.6961	31.75	0.7222	36.47	0.7073	50.44
500	0.5741	21.55	0.8129	12.49	0.7607	18.76	0.7445	26.71	0.7675	30.59	0.7542	42.39
550	0.6258	19.68	0.8476	10.23	0.8005	15.66	0.7858	22.39	0.8061	25.67	0.7941	35.40
600	0.6706	17.01	0.8763	8.382	0.8344	13.05	0.8209	18.70	0.8391	21.48	0.8280	29.47
650	0.7159	14.84	0.8999	6.837	0.8630	10.82	0.8508	15.59	0.8672	17.87	0.8567	24.63

H_0 = 2.788 (298.15 K), 2.879 (303.15 K), 2.925 (308.15 K), 3.137 (313.15 K), 3.383 (318.15 K) and 3.512 (323.15 K) J.

Table 2 Values of n, k, A, E, $\Delta G_m^{\theta,\neq}$, $\Delta H_m^{\theta,\neq}$ and $\Delta S_m^{\theta,\neq}$ of the reaction

T (K)	Eq.(2)			Eq.(3)			Eq.(4)	Eq.(5)		
	k (10^{-3} s^{-1})	n	r^a	E (kJ/mol)	ln$A$	r^a	$\Delta G_m^{\theta,\neq}$ (kJ/mol)	$\Delta H_m^{\theta,\neq}$ (kJ/mol)	$\Delta S_m^{\theta,\neq}$ [J/(mol·K)]	r^a
298.15	1.790	0.967	0.999	31.62	6.419	0.999	88.71	29.04	−194.9	0.999
303.15	2.204	0.968	1.000				89.71			
308.15	2.632	0.986	1.000				90.78			
313.15	3.234	0.980	1.000				91.76			
318.15	3.909	0.997	1.000				92.76			
323.15	4.850	0.993	1.000				93.68			

[a] correlation coefficient.

Preparation and composition of the solid complex

The final solution collected after each experiment was concentrated in a 343.15—353.15 K water bath till crystal membrane was formed, and was put into desiccator with P_4O_{10} to remove trace water. The analytical results indicated that they had the same composition of Zn(His)$Cl_2 \cdot 0.5H_2O$. The analytical results of composition are given in Table 3.

Table 3 Analytical results of composition of the complex (%)[a]

	Zn^{2+}	Cl^-	C	H	N
Calculated values	21.76	23.60	23.99	3.35	13.99
Experimented values	21.34	23.71	24.03	3.36	13.55

[a] Zn^{2+} was determined complexometrically with EDTA. Cl^- was determined with Fajans method. Carbon, hydrogen and nitrogen analyses were carried out on a 2400 type elemental analyzer.

The IR spectra of the complex Zn(His)$Cl_2 \cdot 0.5H_2O$ and the ligand of *L*-α-His were shown in Fig. 3 (IR-440 model infrared spectrophotometer, KBr pallet, Japan). The IR absorption of main groups for the com-

plex and ligand are given in Table 4.

The IR spectrum of the complex shows that characteristic absorption peaks of amino and carboxyl groups in the complex have a great shift as compared to those in the ligand. It indicates that nitrogen and oxygen atoms in the complex coordinate to Zn^{2+} in a bidentate fashion.[15] In addition, characteristic absorption peak of imidazolyl group in the complex shifts intensively, which shows that nitrogen atom in the imidazolyl group coordinates to Zn^{2+} as well.[16] Band 3420 cm^{-1} in the IR spectrum for the complex is assigned to hydroxyl absorption of water. The existence of water molecule is believed in the complex.

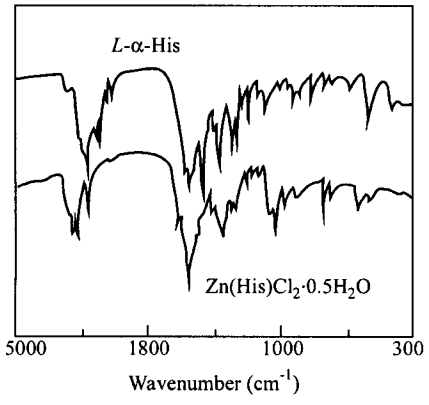

Fig. 3 IR spectra of the complex and ligand.

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

Assignment	*L*-α-His	$Zn(His)Cl_2 \cdot 0.5H_2O$
$\nu_{as}(-NH_2)$ $\nu_{as}(-NH_3^+)$	3025	3150
$\nu_s(-NH_2)$ $\nu_s(-NH_3^+)$	2860	3000
$\delta_{as}(-NH_2)$ $\delta_{as}(-NH_3^+)$	1590	1590
$\delta_s(-NH_2)$ $\delta_s(-NH_3^+)$	1456	1456
$\nu_{as}(-COO^-)$	1635	1600
$\nu_s(-COO^-)$	1415	1400
$\nu(-OH)$	–	3420
$\nu_{as}(CCN)$	1315	1110
$\nu_s(CCN)$	744	970

Conclusion

1. On the basis of experimental and calculated results, the reaction rate of the formation of $Zn(His)Cl_2 \cdot 0.5H_2O$ in the studied temperature range was found to be of the first order. And the reaction was exothermic. The enthalpy was -11.709 ± 0.052 kJ/mol, the standard enthalpy of formation of $Zn(His)^{2+}(aq)$ was -590.51 ± 3.08 kJ/mol.

2. The activation energy of the formation reaction of $Zn(His)Cl_2 \cdot 0.5H_2O$ in the temperature range of 298.15—323.15 K was very low but the entropy was high. The title reaction easily took place in the temperature range of 298.15—323.15 K.

References

1 Mahmoud, M.; Monem, A. *US Patent 4 039 681*, **1977**-08-02.
2 Taguchi, S.; Inokuchi, M.; Nakajima, N.; Inomata, M.; Naitoh, Y. *WO Patent 10 178*, **1992**-06-25.
3 Kentaro, T. *J. Pharm. Bull.* **1959**, *79*, 737.
4 Harvey, H.; Ashmed, K. U. *US Patent 4 830 716*, **1989**-05-16.
5 Sushama, C. A.; Mala, N. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2922,.
6 Mcauliffe, C. A.; Quagliano, J. V.; Vallarinol, L. M. *Inorg. Chem.* **1966**, *5*, 1996.
7 Best, S. A.; Brant, P.; Feitham, R. D. *Inorg. Chem.* **1977**, *16*, 1976.
8 Harvey, H.; Ashmed, K. U. *US Patent 4 599 152*, **1986**-07-08.
9 Liu, J. R.; Hou, Y. D.; Gao, S. L.; Ji, M.; Shi, Q. Z. *Acta Chim. Sin.* **1999**, *57*, 485.
10 Liu, J. R.; Yang, X. W.; Hou, Y. D.; Gao, S. L.; Shi, Q. Z. *Thermochim. Acta*. **1999**, *329*, 123.
11 Marthala, V. K. *J. Res. Nat. Bur. Stand* **1980**, *85*, 467.
12 Atkins, P. W. *Physical Chemistry* 5th Edition, Freeman, New York, **1994**, p.99.
13 Gao, S. L.; Hou, Y. D.; Ji, M.; Chen, S. P.; Shi, Q. Z. *Thermochim. Acta* **2000**, *351*, 47.
14 Shi, Q. Z.; Zhao, F. Q.; Yan, H. K.; Hu, R. Z. *Thermoanalysis Kinetics and Thermokinetics* Shaaxi Science-technology Press, Xi'an, **2001**, p.74.
15 Fang, F. R.; Zhang, X. L.; Guo, X. L. *Chemistry* **1997**, 40.
16 Gao, S. L.; Hou, Y. D.; Liu, J. R.; Ji, M.; Chen, S. P. *Acta Chim. Sin.* **2000**, *58*, 65.

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