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Short communication

The enthalpies of solution in water of complexes of zinc with histidine

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Abstract

The enthalpies of solution in water of L-α-histidine and its zinc complexes $Zn(His)SO_4 \cdot H_2O$, $Zn(His)X_2 \cdot 1/2H_2O$ ($X=NO_3^-$, OAc^-, Cl^-) have been measured at 298.15 K. The standard enthalpies of formation of His(aq) and $Zn(His)^{2+}$(aq) have been calculated. The reliability of the experiment has been discussed.

Keywords: L-α-Histidine; Zinc salts; Enthalpies of solution; Enthalpies of formation

1. Introduction

Zinc is one of the necessary trace elements in human body. Amino acids are basic units of proteins. The complexes of zinc with α-amino acids as addictives have a wide application in medicine, foodstuff and cosmetics [1,2]. The preparation of the complexes of zinc with amino acids has been reported in the literature [1–4]. The combustion energy of L-α-histidine has been measured and the enthalpy of its formation has been calculated [5]. In the literature [6], the preparation, combustion energies, and enthalpies of formation of $Zn(His)SO_4 \cdot H_2O$, $Zn(His)(NO_3)_2 \cdot 1/2H_2O$, $Zn(His)(OAc)_2 \cdot 1/2H_2O$ and $Zn(His)Cl_2 \cdot 1/2H_2O$ has been reported, while studies of the enthalpies of solution in water for lemplexes of zinc with histidine have not been reported in the literature.

In this paper, the enthalpies of solution in water of zinc complexes with L-α-histidine have been determined using heat conduction microcalorimeter. The standard enthalpies of formation of L-α-His(aq) and $Zn(His)^{2+}$(aq) have been calculated through thermochemical equation.

2. Experimental

2.1. Preparation and composition of the complexes

Referring to the literature [5], L-α-histidine (B.R., purity >99.9%, made in Shanghai Kanda) was recrystallized and analyzed. Its purity and density were 99.99% and 1.136 g cm^{-3}, respectively. It decomposed at 277°C. Referring to the literature [4], four solid complexes of zinc with histidine of mole ratio 1:1 were prepared and put into a desiccator containing P_4O_{10} until the weight of the complexes became constant. The analytical results are summarized in Table 1. Zn^{2+} was determined complexometrically

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Table 1
Analytical results related to the composition of the complexes (in %)[a]

Complexes	Zn^{2+}	His	C	H	N
$Zn(His)SO_4{\cdot}H_2O$	19.38(19.54)	46.12(46.37)	21.37(21.54)	3.42(3.31)	12.63(12.56)
$Zn(His)(NO_3)_2{\cdot}1/2H_2O$	18.47(18.49)	43.74(43.88)	20.48(20.38)	2.81(2.85)	19.74(19.81)
$Zn(His)(OAc)_2{\cdot}1/2H_2O$	18.95(18.81)	44.98(44.63)	34.90(34.55)	4.49(4.35)	12.26(12.09)
$Zn(His)Cl_2{\cdot}1/2H_2O$	21.34(21.76)	51.73(51.64)	24.03(23.99)	3.36(3.35)	13.55(13.99)

[a] The data in brackets are calculated values.

with EDTA. Histidine was analyzed by the formalin method. The Zn^{2+} was removed by precipitating with $K_2C_2O_4$ before it was titrated. Carbon, hydrogen, and nitrogen analyses were carried out on a 1106-type elemental analyzer.

2.2. Experimental equipment and conditions

All measurements were carried out using a heat conduction microcalorimeter, type RD496-II [7] (Southwest Institute of Electron Engineering, China) and operated at 298.15±0.005 K.

The experimental precison and accuracy of enthalpies of solution were checked frequently by measurement of the enthalpies of solution ($\Delta_{sol}H^{\theta}_{\infty}$) of crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H^{\theta}_{\infty}$ of 17.224±0.024 kJ mol^{-1} is an excellent accord with that of 17.234 kJ mol^{-1} reported in the literature [8]. This shows that the device for measuring the enthalpy of solution used in this work is reliable.

3. Results

3.1. Enthalpies of solution in water of L-α-histidine and its complexes with zinc

Results for the enthalpy of solution of L-α-histidine and its four complexes with zinc in deionized water at 298.15 K are given in Table 2, where r is the molar ratio $n(H_2O)/n$(L-α-His), $n(H_2O)/n(Zn(His)SO_4{\cdot}H_2O)$ or $n(H_2O)/n(Zn(His)X_2{\cdot}1/2H_2O$, ($X{=}NO_3^-$, OAc^-, Cl^-). Under experimental conditions, the pH of the final solutions were 5–6, which indicated that Zn^{2+} coordinated with histidine in water with a mole ratio of 1:1 [9], and no solid residue was observed in the solution after calorimetry. The solubility of L-α-histidine in water at 298.15 K is 4.87% [4]. After the completetion of dissolution of the samples, the solutions are far from saturation. Therefore, the dissolution processes of the samples can be expressed as follows:

$$\text{L-}\alpha\text{-His(s)} \xrightarrow{\Delta_{sol.(1)}H^{\theta}_{m}} \text{L-}\alpha\text{-His(aq,}\infty) \quad (1)$$

$$Zn(His)SO_4\cdot H_2O(s) \xrightarrow{\Delta_{sol.(2)}H^{\theta}_{m}} Zn(His)^{2+}(aq,\infty) + SO_4^{2-}(aq,\infty) + H_2O(l) \quad (2)$$

$$Zn(His)(NO_3)_2\cdot\tfrac{1}{2}H_2O(s) \xrightarrow{\Delta_{sol.(3)}H^{\theta}_{m}} Zn(His)^{2+} \times (aq,\infty) + 2NO_3^-(aq,\infty) + \tfrac{1}{2}H_2O(l) \quad (3)$$

$$Zn(His)(OAc)_2\cdot\tfrac{1}{2}H_2O(s) \xrightarrow{\Delta_{sol.(4)}H^{\theta}_{m}} Zn(His)^{2+} \times (aq,\infty) + 2OAc^-(aq,\infty) + \tfrac{1}{2}H_2O(l) \quad (4)$$

$$Zn(His)Cl_2\cdot\tfrac{1}{2}H_2O(s) \xrightarrow{\Delta_{sol.(5)}H^{\theta}_{m}} Zn(His)^{2+}(aq,\infty) + 2Cl^-(aq,\infty) + \tfrac{1}{2}H_2O(l) \quad (5)$$

Under experimental conditions, the greater values of r were used and the $\Delta_{sol}H^{\theta}_{m}$ remained unchanged with the weight of the sample. Therefore, the mean of $\Delta_{sol}H^{\theta}_{m}$ in Table 2 can be considered at infinite dilution.

3.2. Standard enthalpies of formation of L-α-His(aq) and $Zn(His)^{2+}$(aq)

According to Hess's Law, the standard enthalpies of formation of L-α-His(aq) and $Zn(His)^{2+}$(aq) were calculated through Eqs. (1) and (2):

$$\begin{aligned}\Delta_{f,\text{L-}\alpha\text{-His(aq)}}H^{\theta}_{m} &= \Delta_{sol.(1)}H^{\theta}_{m} + \Delta_{f,\text{L-}\alpha\text{-His(s)}}H^{\theta}_{m} \\ &= [(10.48 \pm 0.05) \\ &\quad + (-435.39 \pm 1.54)]\ \text{kJ mol}^{-1} \\ &= -424.91 \pm 1.54\ \text{kJ mol}^{-1}\end{aligned}$$

Table 2
Enthalpies of solution in water of L-α-histidine and complexes at 298.15 K

Compounds	Mass (mg)	r	$\Delta_{sol}H_m^\theta$ (kJ mol^{-1})	Mean (kJ mol^{-1})
L-α-His	5.952	11574	10.48	
	6.484	10624	10.44	
	7.396	9315	10.51	
	8.660	7955	10.47	
	8.758	7866	10.42	
	8.808	7821	10.55	10.48±0.05
$Zn(His)SO_4{\cdot}H_2O$	9.74	15255	−35.73	
	20.66	7192	−35.61	
	28.91	5139	−35.67	
	39.93	3721	−35.61	
	40.89	3634	−35.71	
	41.28	3599	−35.70	−35.67±0.05
$Zn(His)(NO_3)_2{\cdot}1/2H_2O$	11.70	13417	−5.88	
	15.97	9855	−5.89	
	17.93	8750	−5.93	
	18.82	8341	−5.87	
	24.86	6315	−5.97	
	26.96	5823	−5.97	−5.92±0.04
$Zn(His)(OAc)_2{\cdot}1/2H_2O$	20.77	7431	−82.84	
	24.26	6362	−82.90	
	27.25	5664	−82.63	
	29.63	5209	−82.78	
	34.15	4520	−82.82	
	39.67	3891	−82.85	−82.80±0.09
$Zn(His)Cl_2{\cdot}1/2H_2O$	7.48	11837	−132.47	
	12.32	10830	−132.63	
	16.52	8077	−132.55	
	18.47	7224	−132.61	
	18.69	7139	−132.64	
	21.42	6229	−132.68	−132.60±0.08

$$\begin{aligned}
&\Delta_{f,Zn(His)^{2+}(aq)}H_m^\theta \\
&\quad = \Delta_{sol.(2)}H_m^\theta + \Delta_{f,Zn(His)SO_4\cdot H_2O(s)}H_m^\theta \\
&\qquad - \Delta_{f,SO_4^{2-}(aq)}H_m^\theta - \Delta_{f,H_2O(l)}H_m^\theta \\
&\quad = [(35.67 \pm 0.05) \\
&\qquad + (-1795.30 \pm 3.43) \\
&\qquad - (909.60 \pm 0.40) \\
&\qquad - (-285.830 \pm 0.042)]\,\mathrm{kJ\,mol^{-1}} \\
&\quad = -635.54 \pm 3.45\,\mathrm{kJ\,mol^{-1}}
\end{aligned}$$

Here, $\Delta_{sol.(1)}H_m^\theta$ and $\Delta_{sol.(2)}H_m^\theta$ are from Table 2, $\Delta_{f,L\text{-}\alpha\text{-}His(s)}H_m^\theta$ is from the literature [5], $\Delta_{f,Zn(His)SO_4\cdot H_2O(s)}H_m^\theta$ is from the literature [6], $\Delta_{f,SO_4^{2-}(aq)}H_m^\theta$ and $\Delta_{f,H_2O(l)}H_m^\theta$ are from the literature [10].

4. Discussion

The standard enthalpies of formation of $Zn(His)^{2+}(aq)$ were also calculated through Eqs. (3)–(5). The results are −631.52±2.99, −632.89±3.28 and −634.79±3.96 kJ mol^{-1}, respectively. The $\Delta_{sol.(3)}H_m^\theta$, $\Delta_{sol.(4)}H_m^\theta$ and $\Delta_{sol.(5)}H_m^\theta$ were from Table 2. $\Delta_{f,Zn(His)(OAc)_2\cdot 1/2H_2O}H_m^\theta = -1665.02 \pm 3.28$ kJ mol^{-1} [6], $\Delta_{f,Zn(His)(NO_3)_2\cdot 1/2H_2O}H_m^\theta = -1182.13 \pm 2.88$ kJ mol^{-1} [6], $\Delta_{f,Zn(His)Cl_2\cdot 1/2H_2O}H_m^\theta = -979.26 \pm 1.95$ kJ mol^{-1} [6], $\Delta_{f,NO_3^-(aq)}H_m^\theta = -206.81 \pm 0.41$ kJ mol^{-1} [11], $\Delta_{f,OAc^-(aq)}H_m^\theta = -486.01$ kJ mol^{-1} [12], $\Delta_{f,Cl^-(aq)}H_m^\theta = -167.080 \pm 0.088$ kJ mol^{-1} [9]. The values of $\Delta_{f,Zn(His)^{2+}(aq)}H_m^\theta$ were compared with each other and the error are 0.54, 0.47, 0.52 and 0.62%, respectively. This indicated that the results of the experiment are reliable. Therefore, we suggest that the $\Delta_{f,Zn(His)^{2+}(aq)}H_m^\theta$ use the average value -633.69 ± 3.42 kJ mol^{-1}.

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