Preparation and Thermal Chemical Property of Complexes of Zinc Nitrate with Trytophan

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The solubility property of $Zn(NO_3)_2$-Try-H_2O system at 25 ℃ in whole concentration range has been investigated by the semi-micro phase equilibrium method. The corresponding phase diagrams and refractive index diagrams were constructed. Under the guidance of the phase equilibrium results, the incongruently soluble compounds of $Zn(Try)(NO_3)_2 \cdot 2H_2O$ (F) and $Zn(Try)_2(NO_3)_2 \cdot H_2O$ (G), which have not been reported previously, were synthesized and characterized by IR, XRD, TG-DTG, as well as chemical and elemental analyses. The constant-volume combustion energies of the compounds, $\Delta_c E$, determined by a precision rotating bomb calorimeter at 298.15 K, were (-13518.98 ± 4.99) $J \cdot g^{-1}$ and (-17690.85 ± 4.88) $J \cdot g^{-1}$, respectively. The standard enthalpies of combustion for these compounds, $\Delta_c H$, were calculated to be (-5802.36 ± 2.14) $kJ \cdot mol^{-1}$ and (-10891.59 ± 3.01) $kJ \cdot mol^{-1}$ when the standard enthalpies of formation, $\Delta_f H_m^{\ominus}$ were (-1161.18 ± 2.61) $kJ \cdot mol^{-1}$ and (-1829.71 ± 4.20) $kJ \cdot mol^{-1}$. The enthalpies of solution in condition of simulating human gastric juice (37 ℃, pH = 1, the solution of hydrochloric acid), which were also measured by a microcalorimeter, were (14.55 ± 0.04) $kJ \cdot mol^{-1}$ and (10.58 ± 0.06) $kJ \cdot mol^{-1}$, respectively.

Keywords   ternary system, zinc nitrate, trytophan, characterization, standard enthalpy of formation

Introduction

Zinc is an essential trace element to the life. Many diseases aroused from a deficiency of zinc element have received considerable attention. *L-α*-Amino acids are basic units of proteins. *L-α*-Trytophan is one of the eight species of amino acids indispensable for life, which has to be absorbed from food because it can not be synthesized in the human body. In view of the complexes of *L-α*-trytophan and essential elements as addictives widely used in such fields as foodstuff, medicine and cosmetic,[1-3] they have a broaden prospect for applications. Briefly, a better understanding of the research for the complexes of the microelements and *L-α*-trytophan is thus of considerable practical and fundamental importance.

In our previous papers, the phase chemistry of $ZnSO_4/ZnCl_2/ZnAc_2$-Try-H_2O system and the property of the corresponding solid complex have been reported.[4-6] As the further work, the solubility property of $Zn(NO_3)_2$-Try-H_2O system at 25 ℃ was investigated by the semi-micro phase equilibrium method in this paper.[7] From the phase equilibrium diagram, two new solid complexes of zinc with *L-α*-trytophan were prepared, and thermal chemical properties for these compounds were determined and discussed.

Experimental

Reagents

$Zn(NO_3)_2 \cdot 6H_2O$ was of A.R. grade from Beijing Shuanghuan Chemical Plant and *L-α*-trytophan with B.R. grade was purchased from Shanghai Kanda Ammonia Factory, and other regents were of A.R. grade. All chemicals and materials were recrystalized with the purity higher than 99.95%, which was analyzed by GC.

Experimental methods and apparatus

The temperature fluctuation of the thermostatic water bath was ±0.05 ℃; WZS-1 Abbe refractometer was made in Shanghai Shiyan Apparatus Factory, the temperature may be controlled within ±0.2 ℃. ZD-2 automatic potentiometric titrator was from the Apparatus Factory of Shanghai. IR spectra of the compounds were obtained with a BRUKER EQ UINOX-550 model infrared spectrophotometer (KBr pellet). TG and DTG data were determined by a Perkin Elmer thermogravimetric analyzer. All TG-DTG tests were performed under a dynamic atmosphere of dry oxygen at a flow rate of 60 $cm^3 \cdot min^{-1}$, the heating rate used is 10 ℃ $\cdot min^{-1}$ and sample masses are approximately 1 mg. A RBC-type II rotation bomb calorimeter[8] and a RD496-III microcalorimeter were used.[9] Carbon, hydrogen and nitrogen analyses were carried out on a 2400 type elemental analyzer (PE Company, U.S.A.).

Zn^{2+} was determined complexometrically with EDTA. Trytophan was analyzed by the formalin method. The Zn^{2+} was removed by precipitating with $K_2C_2O_4$ before the titration. The solubility of L-α-trytophan was 4.46% at 25 ℃ in our experiment, and the value in Ref. 10 is 8.13% when the solubility of $Zn(NO_3)_2$ is 55.91% and the value is 55.98% in Ref. 11.

The phase diagram of the ternary system was constructed by the semi-micro phase equilibrium method. The constant volume combustion energies of the complexes have been determined by a RBC-Ⅱ type rotating-bomb calorimeter. Benzoic acid had an isothermal combustion heat of -26434 $J \cdot g^{-1}$ at 25 ℃. The calibration for the apparatus and temperature, the determination processes of the experiment and the analyses of final products were identical with the Ref. 8.

The enthalpies of solution for the complexes were obtained using a microcalorimeter, type RD496-Ⅲ (China, Southwest Institute of Electronic Engineering), which was equipped with two 15 cm^3 vessels (Fig. 1). After reaching equilibrium, the spacers of the sample and reference vessels were depressed simultaneously and the samples were mixed. The microcalorimeter was calibrated by Joule effect. The experimental precision and accuracy were checked by measuring the enthalpy of crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H_m^\ominus$ (17.238 ± 0.048) $kJ \cdot mol^{-1}$ was in good agreement with the reported value of $\Delta_{sol}H_m^\ominus$ (17.241 ± 0.018) $kJ \cdot mol^{-1}$.[12] The precision of measurement for the microcalormeter was ± 0.5%.
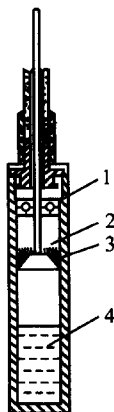

Fig. 1 Sketch of calorimetric vessels. 1. Calorimetric cell; 2. solid sample; 3. spacer; 4. solution.

Results and discussion

Preparation and composition of the complexes

The solubility property of the ternary system $Zn(NO_3)_2$-Try-H_2O has been investigated in the whole concentration by the phase equilibrium method at 25 ℃. Based on 23 sets of phase equilibrium data, the phase diagram and refractive index diagram were constructed and are shown in Fig. 2. The data of the solubility and refrac-

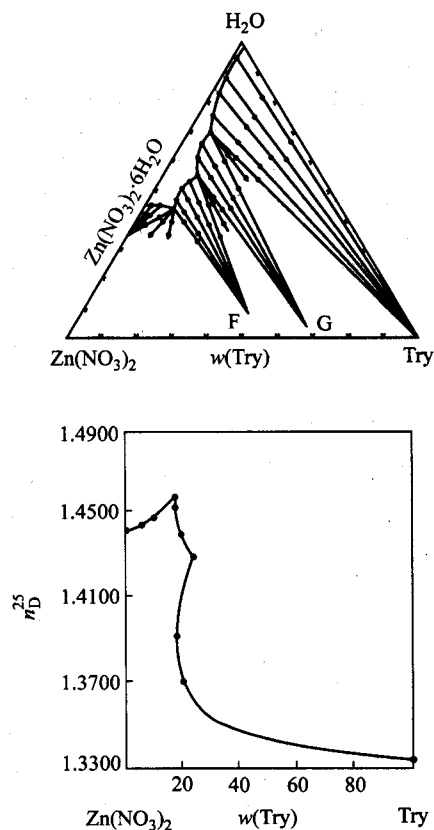tive index of the system are listed in Table 1.

Fig. 2 Solubility diagram and refractive index curve of ternary system $Zn(NO_3)_2$-Try-H_2O at 25 ℃.

Clearly, it was visible from the phase diagram of the system $Zn(NO_3)_2$-Try-H_2O that the solubility curves of the systems consisted of four branches which corresponded to $Zn(NO_3)_2 \cdot 6H_2O$, $Zn(Try)(NO_3)_2 \cdot 2H_2O$ (F), $Zn(Try)_2(NO_3)_2 \cdot H_2O$ (G) and L-α-Try, and F and G, the incongruently soluble compounds, were not prepared directly from water but from the mixture of acetone and water. In addition, it was very interesting that any new phase region was not formed for the phase diagrams of $ZnSO_4$/$ZnAc_2$-Try-H_2O described in the reported paper[4,6] and the incongruently soluble compound $Zn(Try)Cl_2 \cdot \frac{1}{2}H_2O$ was formed in the $ZnCl_2$-Try-H_2O system.[5] Summarizing the results of $ZnX_2(X = Cl^-, NO_3^-, SO_4^{2-}$ and Ac^-)-Try-H_2O, the new solid complexes were formed might be attributed to the solubility of the complexes of Cl^- or NO_3^- with $Zn(Try)^{2+}$ being less than that of the complexes of SO_4^{2-} or Ac^- with $Zn(Try)^{2+}$.

The complexes were prepared by the following procedures: according to the composition of the system point in the phase region of the complex F and G, the corresponding ingredients were sealed in polyethylene tubes, and put in a thermostat for more than 30 d, then the wet solid were filtered and dried under vacuum, and the target complexes of white powder were obtained. They were soluble in water, not in ethanol and acetone. The results of composi-

tional analyses are listed in Table 2.

IR *spectra of the complexes*

The principal IR data of the ligand and the complexes are shown in Table 3. Non-existence in the complexes for the characteristic absorption bands of − COOH group at 1700—1750 cm⁻¹ revealed that trytophan still maintained the structure of inner salt.[13] Wide shift of the characteristic absorption NH_3^+ and COO^- for the complexes comparing

with those of ligand indicates that valine coordinated to Zn^{2+} through N atom of amino and O atom of carboxyl as bidentate ligand. The characteristic absorption peaks of NO_3^- could not be identified from the spectra of the complexes. The wide characteristic absorption band at 3500 cm⁻¹ of $\nu^{as}(OH^-)$ reveals that H_2O molecule is comprised in the complexes, and non-existence of the characteristic peak of Zn—O at 364 cm⁻¹ indicates that the role of water in the complexes is crystallizable water, not coordinated one.[14]

Table 1 Solubility and refractive index of $Zn(NO_3)_2$-Try-H_2O system at 25 ℃

No.	Comp. of intermediate compound (%)		Comp. of liquid phase (%)		Wet residue (%)		$\dfrac{Try}{Zn(NO_3)_2 + Try} \times 100\%$	n_D^{25}	Equilibrium solid phase[a]
	$Zn(NO_3)_2$	Try	$Zn(NO_3)_2$	Try	$Zn(NO_3)_2$	Try			
1	—	—	—	1.09	—	—	100.00	1.3359	Try
2	3.50	15.01	4.00	0.98	3.00	29.04	19.68	1.3386	Try
3	9.14	15.92	10.95	1.51	7.69	32.02	12.12	1.3420	Try
4	13.02	15.10	15.07	2.35	11.09	28.00	13.49	1.3500	Try
5	18.90	13.20	21.02	4.05	16.02	26.10	16.15	1.3603	Try
6	21.51	17.96	24.89	5.88	18.96	27.53	19.11	1.3721	Try + G
7	23.69	14.36	24.85	5.86	22.65	24.08	19.11	1.3721	Try + G
8	25.60	15.03	24.81	5.82	26.08	23.67	19.11	1.3721	Try + G
9	28.96	13.09	28.75	5.22	29.04	23.89	15.37	1.3989	G
10	32.08	13.89	32.38	6.30	31.78	24.90	16.29	1.3937	G
11	34.97	13.00	35.05	10.10	34.06	22.23	22.30	1.4328	G + F
12	35.86	36.98	35.05	10.06	36.26	25.78	22.30	1.4328	G + F
13	37.00	18.01	35.10	10.08	39.02	26.55	22.30	1.4328	G + F
14	39.89	13.99	39.10	8.15	40.87	21.08	17.25	1.4312	F
15	42.18	10.88	42.07	9.56	42.56	6.96	18.52	1.4430	F
16	45.66	11.93	45.87	7.89	45.05	19.68	14.68	1.4557	F
17	47.32	13.89	47.94	8.63	46.75	20.98	15.27	1.4601	F + S
18	50.72	10.00	47.90	8.68	53.86	11.56	15.27	1.4601	F + S
19	53.00	7.51	47.91	8.62	57.48	6.88	15.27	1.4601	F + S
20	53.08	5.88	47.90	8.63	58.06	3.03	15.27	1.4601	F + S
21	57.86	2.07	50.93	4.24	59.74	1.35	7.69	1.4503	S
22	56.98	1.03	53.25	2.03	59.48	0.57	3.67	1.4408	S
23	57.96	—	55.91	—	—	—	—	1.4450	S

[a] G, $Zn(Try)_2(NO_3)_2 \cdot H_2O$; F, $Zn(Try)(NO_3)_2 \cdot 2H_2O$; S, $Zn(NO_3)_2 \cdot 6H_2O$.

Table 2 Composition data (%) for the complexes F and G[a]

Complex	Color	Zn^{2+}	Try	C	H	N
F	white	15.24 (15.22)	47.50 (47.53)	30.80 (30.75)	3.71 (3.75)	13.06 (13.04)
G	white	10.64 (10.62)	66.38 (66.32)	42.94 (42.91)	4.25 (4.26)	13.62 (13.65)

[a] The data in brackets are calculated values.

Table 3 Principal IR data (cm⁻¹) of the ligand and the complexes

Compound	$\nu^{as}(NH_3^+)$	$\nu^s(NH_3^+)$	$\delta^{as}(NH_3^+)$	$\delta^s(NH_3^+)$	$\nu^{as}(COO^-)$	$\nu^s(COO^-)$	$\nu(OH)$	$\nu(C_8H_7N)$
L-α-Try	3403.7	3037.6	1666.6	1456.4	1590.7	1414.3	—	743.5
F	3424.7	2396.7	1633.5	1500.0	1510.0	1387.7	3498.3	751.0
G	3418.8	2290.7	1632.6	1508.0	1508.0	1389.1	3500.0	748.3

Thermo stability of the complexes

The TG-DTG curves of the complexes are shown in Fig. 3. The complexes decomposed in three steps. According to the data from the TG-DTG curves, the first decomposition stages were affirmed to be dehydration which ended at 131 ℃ and 156 ℃ corresponding to the complexes F and G, followed by the loss of 50% trytophan, and at the last step, F and G were completely decomposed into ZnO which was attested to coincide with the standard IR spectrum of ZnO by IR analysis. The products in intermediate stages were taken out and identified by IR technique analyses, IR spectra of which in the first stage were similar to those of F and G except for the characteristic absorption of water at about 3400 cm^{-1}. The experimental results of the residual amount were in well agreement with the calculated results, again confirming above conclusions.
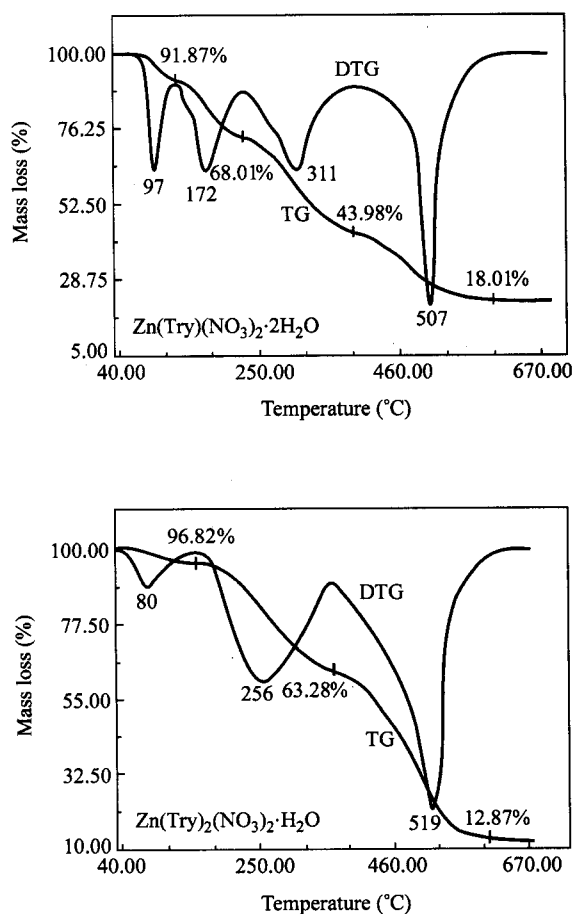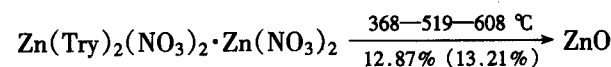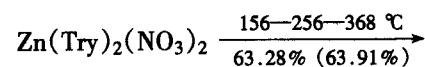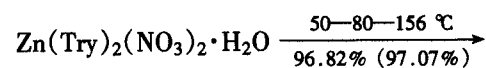
$$Zn(Try)(NO_3)_2 \cdot 2H_2O \xrightarrow[91.87\% \ (91.61\%)]{50-97-131 \ ℃}$$

$$Zn(Try)(NO_3)_2 \xrightarrow[68.01\% \ (67.86\%)]{131-172-227 \ ℃}$$

$$Zn(Try)(NO_3)_2 \cdot Zn(NO_3)_2 \xrightarrow[43.98\% \ (44.11\%)]{227-311-397 \ ℃}$$

$$Zn(NO_3)_2 \xrightarrow[24.06\% \ (23.76\%)]{397-507-600 \ ℃} ZnO$$

$$Zn(Try)_2(NO_3)_2 \cdot H_2O \xrightarrow[96.82\% \ (97.07\%)]{50-80-156 \ ℃}$$

$$Zn(Try)_2(NO_3)_2 \xrightarrow[63.28\% \ (63.91\%)]{156-256-368 \ ℃}$$

$$Zn(Try)_2(NO_3)_2 \cdot Zn(NO_3)_2 \xrightarrow[12.87\% \ (13.21\%)]{368-519-608 \ ℃} ZnO$$

Standard enthalpy of formation for the complexes

The data of constant-volume combustion energies of the complexes are listed in Table 4.

The standard enthalpies of combustion of the complexes, $\Delta_{c,coor(s)} H_m^{\ominus}$ referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.

$$Zn(C_{11}H_{11}O_2N_2)(NO_3)_2 \cdot 2H_2O \ (s) + \frac{21}{2}O_2 \ (g)$$
$$= ZnO \ (s) + 11CO_2 \ (g) + 8H_2O \ (l) + 2N_2 \ (g) \quad (1)$$

$$Zn(C_{11}H_{11}O_2N_2)_2(NO_3)_2 \cdot H_2O \ (s) + \frac{47}{2}O_2 \ (g)$$
$$= ZnO \ (s) + 22CO_2 \ (g) + 13H_2O \ (l) + 3N_2 \ (g) \quad (2)$$

$\Delta_{c,coor(s)} H_m^{\ominus}$ could be obtained from the Eq. (3)

$$\Delta_{c,coor(s)} H_m^{\ominus} = \Delta_{c,coor(s)} E + \Delta nRT \quad (3)$$

According to thermal chemical Eqs. (1) and (2), the standard enthalpies of formation of the complexes were calculated by Hess law.

$$\Delta_{f,F(s)} H_m^{\ominus} = [\Delta_{f,ZnO(s)} H_m^{\ominus} + 11\Delta_{f,CO_2(g)} H_m^{\ominus} + 8\Delta_{f,H_2O(l)} H_m^{\ominus}] - \Delta_{c,C(s)} H_m^{\ominus} \quad (4)$$

$$\Delta_{f,G(s)} H_m^{\ominus} = [\Delta_{f,ZnO(s)} H_m^{\ominus} + 22\Delta_{f,CO_2(g)} H_m^{\ominus} + 13\Delta_{f,H_2O(l)} H_m^{\ominus}] - \Delta_{c,D(s)} H_m^{\ominus} \quad (5)$$

Where,

$$\Delta_{f,ZnO(s)} H_m^{\ominus} = (-350.46 \pm 0.27) \ kJ \cdot mol^{-1},$$

$$\Delta_{f,CO_2(g)} H_m^{\ominus} = (-393.51 \pm 0.13) \ kJ \cdot mol^{-1},$$
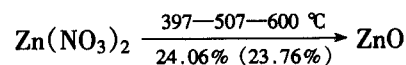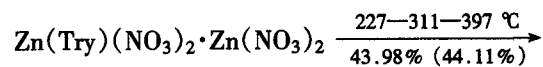
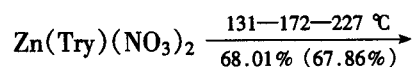$$\Delta_{f,H_2O(l)} H_m^{\ominus} = (-285.83 \pm 0.042) \ kJ \cdot mol^{-1}.[15]$$
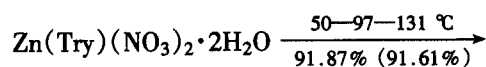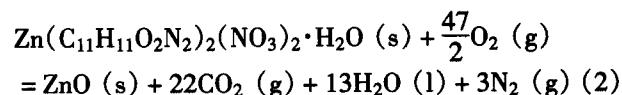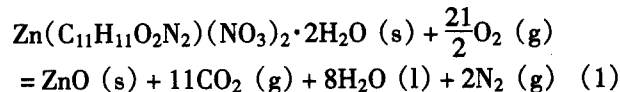

Fig. 3　TG-DTG curves of the complexes.

In accordance with the results of IR spectra and TG-DTG experiments described above, it was preliminarily assumed that the thermal decomposition processes for these complexes were as follows:

Enthalpy of solution for the complexes

The Standard combustion enthalpy and standard enthalpy of formation of the complexes are showed in Table 5.

Under the condition of simulating human gastric juice (37 ℃, pH = 1), the complexes dissolved completely in the solution of hydrochloric acid, and the mole ratio of the solvent to the complex [n (H_2O)/n (complex)] was more than 4000. The solution enthalpies were thus obtained in limitless dilution solution. The solution was an endothermic reaction and the heat produced by the complex F in solution process was greater than that of the complex G.

Table 4　Constant-volume combustion energy of the complexes

Complex	No.	Mass of complex m (g)	Calibrated heat of combustion wire q_c (J)	Calibrated heat of acid q_N (J)	Calibrated ΔT (K)	Combustion energy $-\Delta_c E$ (J·g^{-1})
F	1	1.04260	10.80	46.28	0.7862	13519.16
	2	1.00325	11.70	44.53	0.7556	13501.23
	3	1.01436	12.60	45.03	0.7659	13534.76
	4	1.16055	12.60	51.52	0.8746	13510.23
	5	1.00769	12.60	44.73	0.7600	13519.25
	6	1.01053	12.60	44.86	0.7627	13529.22
	Mean					13518.98 ± 4.99
G	1	1.14290	12.60	62.77	1.1270	17684.34
	2	1.12375	12.60	68.89	1.1080	17675.90
	3	0.97326	12.60	46.29	0.9605	17704.20
	4	0.95045	11.70	52.20	0.9381	17699.58
	5	1.00236	12.60	55.06	0.9883	17680.72
	6	1.01068	12.60	55.51	0.9976	17700.36
	Mean					17690.85 ± 4.88

Table 5　Standard combustion energy, standard combustion enthalpy and standard enthalpy (kJ·mol^{-1}) of formation of the complexes

Complex	$-\Delta_{c,coor(s)}E$	$-\Delta_{c,coor(s)}H_m^{\ominus}$	$-\Delta_{f,coor(s)}H_m^{\ominus}$
F	5808.56 ± 2.14	5802.36 ± 2.14	1161.18 ± 2.61
G	10895.31 ± 3.01	10891.59 ± 3.01	1829.71 ± 4.20

Table 6　Enthalpy of solution for the complexes under the simulating juice condition

Complex	Weight of sample m (mg)	$\Delta_{sol}H_m^{\ominus}$(kJ·mol^{-1})	Mean of $\Delta_{sol}H_m^{\ominus}$(kJ·mol^{-1})
F	20.55, 30.48, 41.19 52.66, 64.08, 74.40	14.59, 14.50, 14.52 14.55, 14.54, 14.60	14.55 ± 0.04
G	20.49, 30.86, 38.41 44.26, 57.20, 63.89	10.59, 10.67, 10.58 10.50, 10.59, 10.53	10.58 ± 0.06

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