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Phase chemistry and thermochemistry on coordination behavior of zinc acetate with methionine

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Abstract

The solubility of $ZnAc_2$–Met–H_2O system at 298.15 K in the entire concentration range was investigated by the semimicro-phase equilibrium method. The corresponding phase diagram and refractive index diagram were constructed. The experimental results indicated that the system was a simple one; any new compounds were not obtained. The complex of $Zn(Met)Ac_2·H_2O$ was prepared by adding acetone into the reaction solution of $ZnAc_2$ and Met with the optimum volume ratio of water:acetone of 1:25. The crystal growth process of the complex at 298.15 K was investigated by microcalorimetry. The experimental results showed the process accorded with the Burton–Cabrera–Frank dislocation theory.

Keywords: Crystal growth process; Enthalpy of solution; Methionine; Ternary system; Microcalorimetry; Zinc acetate

1. Introduction

Zinc is an essential life element in living systems. Many diseases arise from a deficiency of zinc element and these have been received considerable attention. L-α-Amino acid is the basic unit of proteins related with life. The complexes of zinc salts with α-amino acids as additives have a wide application in medicine, foodstuff and cosmetics [1–3]. L-α-Methionine (Met) indispensable to life has to be absorbed from food because it could not be synthesized by organism. The study is of considerable importance in application. In our previous studies, the solubility of $ZnSO_4$–Met/Phe/His–H_2O systems at 298.15 K, the preparations and characterization of the relating complexes $Zn(AA)SO_4·H_2O$ (AA = Met, Phe, His) have been investigated [4–6].

In this paper, the solubility of the ternary system $ZnAc_2$–Met–H_2O has been investigated at 298.15 K by the semimicro-phase equilibrium method [7]. The phase regions corresponding to new compounds in the phase diagram were not discovered. Adding acetone into the reaction solution of $ZnAc_2$ with Met, the solid complex of $Zn(Met)Ac_2·H_2O$ was obtained. The crystal growth process was investigated at 298.15 K by microcalorimetry. The experimental result showed that it was in accordance with the Burton–Cabrera–Frank dislocation theory [8].

2. Derivation of the kinetic equation of the crystal growth process

In order to analyze the kinetics of the crystal growth process of the complexes of Zn^{2+} with amino acid, the following general form of the crystal growth process is used

$$A(aq) \rightarrow A(s) + \text{heat}$$

$$t = 0, \quad c_0 \quad 0 \quad 0,$$
$$t = t, \quad c \quad m \quad q, \qquad t = \infty, \quad c_\infty \quad m_\infty \quad Q_\infty$$

where c is the solute concentration in the solution at time t; m the mass of solid deposited at a certain time t; Q the heat produced at a certain time t. When $t = 0$, $c = c_0$, $m = 0$ and $Q = 0$; when $t = \infty$, $c = c_\infty$, $m = m_\infty$ and $Q = Q_\infty$.

The relationship between the energy change (i.e. the heat produced) of a reaction system and the extent (i.e. mass or concentration) of the reaction is given by

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$$\frac{Q}{Q_\infty} = \frac{m}{m_\infty} = \frac{c_0 - c}{c_0 - c_\infty} \tag{1}$$

and

$$\frac{c_\infty - c}{c_\infty - c_0} = \frac{m_\infty - m}{m_\infty} = \frac{Q_\infty - Q}{Q_\infty} \tag{2}$$

From Eq. (1), we have

$$\frac{m_\infty}{Q_\infty} Q = m$$

and

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \left(\frac{m_\infty}{Q_\infty}\right) \frac{\mathrm{d}Q}{\mathrm{d}t} \tag{3}$$

From Eq. (2), we obtain

$$c - c_\infty = (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) \tag{4}$$

According to the Burton–Cabrera–Frank (BCF) dislocation theory, for relatively high supersaturations, the rate of crystal growth ($\mathrm{d}m/\mathrm{d}t$) at time t can be expressed as

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k_1 m_\infty (c - c_\infty) \tag{5}$$

where k_1 is the rate constant of crystal growth.

The energy change brought about by the reaction progress, the combination of Eqs. (3)–(5) gives

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) = k_2 \left(1 - \frac{Q}{Q_\infty}\right) \tag{6}$$

where $k_2 = k_1 Q_\infty (c_0 - c_\infty)$.

A linear regression of the variables $(\mathrm{d}Q/\mathrm{d}t)_i$ and $(1 - Q/Q_\infty)_i$ results in k_2 (slope) and a (intercept) in Eq. (7)

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a = k_2 \left(1 - \frac{Q}{Q_\infty}\right) + a \tag{7}$$

where

$$k_1 = \frac{k_2}{Q_\infty (c_0 - c_\infty)} \overset{c_0 \gg c_\infty}{=} \frac{k_2}{Q_\infty c_0} \tag{8}$$

As $m/m_\infty = Q/Q_\infty$, the combination of Eqs. (3), (4) and (7) gives

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \left(\frac{m_\infty}{Q_\infty}\right) \frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a\right] = \frac{m_\infty}{Q_\infty}[k_1 Q_\infty (c - c_\infty) + a] = k_1 m_\infty (c - c_\infty) + \frac{a m_\infty}{Q_\infty} \tag{9}$$

Similarly, Eq. (5) may be written as

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k_1 m_\infty (c - c_\infty) + b \tag{10}$$

where b is the intercept of Eq. (11).

When (9) and (10) are equated, Eq. (11) is obtained

$$b = \frac{a m_\infty}{Q_\infty} \tag{11}$$

If the values of the constants a and b are small as compared with those of k_2 and k_1, the kinetics of the crystal growth process can be expressed by Eqs. (5) and (6).

Eqs. (5) and (6) are known as the thermokinetic equations of the crystal growth process.

3. Experimental

3.1. Materials and experimental equipments

$ZnAc_2{\cdot}2H_2O$ and L-α-methionine are BR grade reagents with a purity better than 99.5% and the others are AR grade. The conductivity of deionized water used in the experiments is $5.48 \times 10^{-8}\,\mathrm{S\,cm^{-1}}$. The thermostat had a temperature variation of ±0.05 °C. WZS-1 type Abbe refractometer made by Shanghai ShiYan Apparatus Factory, it had a temperature fluctuation of ±0.2 °C. ZD-2 type automatical potential titrator and RD496-III type microcalorimeter were used [9].

3.2. Analysis method

Zn^{2+} was determined with EDTA by complexometric titration. Met was analyzed by the formalin method, Zn^{2+} was removed by precipitation with $K_2C_2O_4$ before titration. The solubility of Met at 298.15 K is 3.31% from the result of experiments when that in the literature is 3.10% [10]. The solubility of $ZnAc_2$ at 298.15 K is 25.38%, compared with 25.74% in literature [11].

3.3. Experimental method

The soluble property of the system was investigated by the semimicro-phase equilibrium method. The system came to equilibrium after 30 days. The composition of the sample including liquid phase and wet solid phase was analyzed by the methods described above and the refractive index of each saturation liquid phase was determined.

The calorimetric experiment during the crystal process was performed using an RD496-III type microcalorimeter at 298.15 ± 0.005 K. The calorimetric constant was determined by the Joule effect before each experiment, and was 63.994 ± 0.042 μV mW^{-1}.The enthalpy of solution of KCl (spectral purity) in deionized water was measured as 17.238 ± 0.048 kJ mol^{-1}, which was very close to 17.241 ± 0.018 kJ mol^{-1} in Ref. [12]. The accuracy was 0.02% and the precision was 0.3%, which indicated that the calorimetric system was accurate and reliable. In the dilution/crystallization experiments, the reaction solution/solvent and diluent were put into the adding tubes 2 and 3 in Fig. 1, respectively. After equilibrium, the bottom

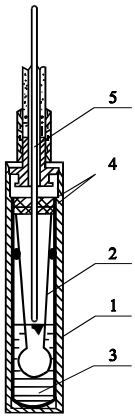

Fig. 1. Sketch used for measuring the crystallization kinetics. 1: calorimetric cell; 2: adding tube containing solution/solvent; 3: adding tube containing diluent; 4: silicone rubber cover; 5: glass rod.

of the tube 2 was broken and the two solutions on depressing the rod were mixed together in the tubes 2 and 3, and the thermogram was recorded.

4. Results and discussion

4.1. Phase equilibrium results

The ternary system $ZnAc_2$–Met–H_2O has been investigated at 298.15 K by the semimicro-method. The solubility and refractive index data of the system are presented in Table 1. The phase diagram of system and the curve of refractive index *vx* composition of dry salt are shown in Fig. 2. The eutonic point of phase diagram corresponds with the breakpoint of the refractive index *vx* composition curve. As shown in Fig. 2, this system is a simple one. The solubility

Table 1
Solubility data and refractive index of ternary system $ZnAc_2$–Met–H_2O at 298.15 K

Composition of liquid phase (wt.%)		Composition of synthetic phase (wt.%)		Composition of wet solid phase (wt.%)		$\frac{\text{Met}}{ZnAc_2 + \text{Met}} \times 100\%$	Refractive index	Equilibrium solid phase
$ZnAc_2$	Met	$ZnAc_2$	Met	$ZnAc_2$	Met			
25.38	–	–	–	–	–	0.00	1.3704	S
26.72	4.43	50.13	2.81	73.98	0.82	14.28	1.3847	S
26.56	6.32	51.67	3.98	58.85	3.01	19.22	1.3891	S
26.09	8.93	41.62	6.03	68.35	2.49	29.75	1.3936	S
25.96	10.21	46.54	7.68	68.74	3.00	28.23	1.3948	S + Met
25.26	13.11	51.26	8.32	71.88	2.76	34.17	1.3960	S + Met
26.09	12.98	38.52	17.55	54.81	24.07	33.22	1.3959	S + Met
25.56	13.32	36.29	28.16	42.44	37.70	34.26	1.3960	S + Met
25.31	13.37	23.99	32.92	22.72	46.88	34.75	1.3961	S + Met
25.66	13.50	19.24	33.83	12.95	56.14	34.47	1.3960	S + Met
23.98	11.34	15.88	38.87	10.05	60.12	32.11	1.3898	Met
21.37	9.78	15.89	34.00	9.76	56.84	37.68	1.3868	Met
16.21	7.72	10.96	34.00	6.92	55.82	35.17	1.3680	Met
10.03	5.56	7.34	30.18	4.38	60.16	35.66	1.3662	Met
6.06	4.43	4.80	35.42	2.34	61.74	41.40	1.3505	Met
–	3.31	–	–	–	–	100.00	1.3390	Met

S = $ZnAc_2 \cdot 2H_2O$.

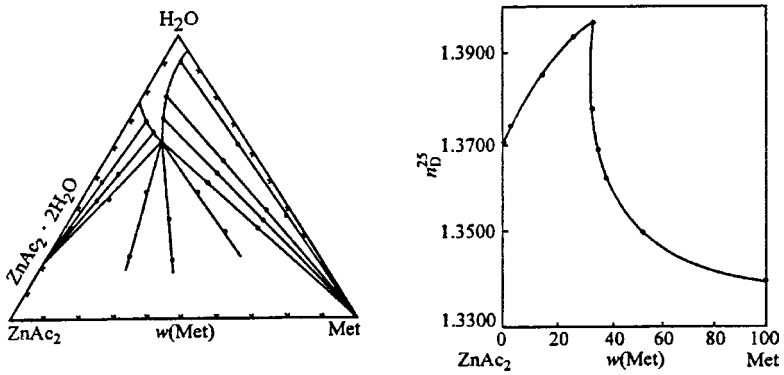

Fig. 2. Phase diagram and refractive index curves of saturated solutions of ternary system $ZnAc_2$–Met–H_2O at 298.15 K.

Table 2
Experimental results with the different volume ratio of water and acetone

Volume ratio	Phenomena	Yield (%)
1:10	Turbid	50
1:15	Turbid	54
1:20	Precipitate	58
1:25	Precipitate	76
1:28	Precipitate	68
1:30	Decreasing	60
1:33	Gradually	50

curves consist of two branches, corresponding to solid phase of $ZnAc_2{\cdot}2H_2O$ and Met. That is, methionine zinc cannot be prepared from $ZnAc_2$ with Met in the whole concentration range at 298.15 K.

4.2. Preparation of the complex

$Zn(Met)^{2+}(aq)$ is produced by the reaction of $ZnAc_2$ with Met in water ($\lg K = 4.40$) [13]. The solubility is too big to obtain the solid complex. Adding acetone to the system changes the solvent and decreases the solubility of complex, thus the solution highly supersaturates and the solid complex can be prepared. In the phase diagram, the phase region of the acid is reduced, which separates from the phase region of salt, and the phase region of complex is formed. Based on the above consideration, with the volume ratio of water:acetone of 1:25, the white solid compound was obtained. It was filtrated by suction, rinsed with a few milliliters of acetone and dried to constant weight in vacuum. The compound was soluble in water and insoluble in alcohol, acetone or other organic solvents. The yield was 76%. The elementary analyses result were Zn 18.82%, Met 42.17%, C 30.69%, H 5.88% and N 4.12%, which showed that the compound was $Zn(Met)Ac_2{\cdot}H_2O$ as compared with the theoretical value—Zn 18.65%, Met 42.55%, C 30.82%, H 5.46% and N 3.99%. The experimental result on variable volume ratio of water to acetone is summarized in Table 2.

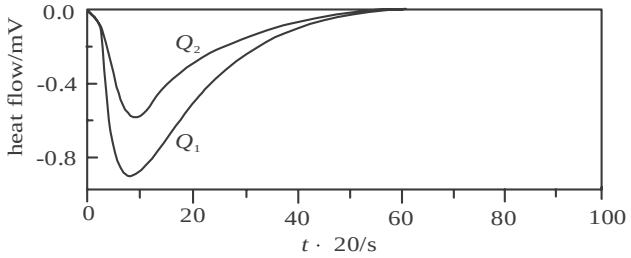

Fig. 3. Typical thermogram obtained during dilution/crystallization.

4.3. Dilution/crystallization kinetics

Adding acetone into the reaction solution containing $ZnAc_2$ and Met, the crystal process is expressed in reactions (12):

$$Zn(Met)^{2+}(aq) + 2Ac^{-}(aq) + H_2O(l) \xrightarrow{\text{acetone}} Zn(Met)Ac_2 \cdot H_2O(s) \quad (12)$$

A typical schematic thermogram during the dilution and crystallization is depicted in Fig. 3. The original data obtained from the *T–K* curve are shown in Table 3. Using the above data, the kinetic data during the dilution/crystallization process can be obtained from Eqs. (7), (8) and (11) (Table 4).

The experimental results in Table 4 are obtained based on the presentation as a block diagram in Fig. 4. In Fig. 4 $(dQ/dt)_{1i}$ is the rate of total heat production at time *t*, including $(dQ/dt)_{2i}$, the rate of the heat of mixing produced between solvent and diluent at time *t*, and $(dQ/dt)_{3i}$, the rate of the heat of crystallization of the crystal at time *t*; and Q_{1i} is the total heat produced during a certain time including Q_{2i}, Q_{2i} the heat of mixing produced between solvent and diluent during a certain time, and Q_{3i}, the heat of crystallization of the crystal during a certain time. The total heat produced during the crystal growth process and the rate constant at 298.15 K are shown in Table 3.

Table 3
Thermokinetical data of the titled reaction

t (s)	Total reaction process		Dilution process		Crystallization process		$Q_{3i}/Q_{3\infty}$
	$-Q_{1i}$ (mJ)	$-(dQ/dt)_{1i}$ ($\times 10^2$ J s^{-1})	$-Q_{2i}$ (mJ)	$-(dQ/dt)_{2i}$ ($\times 10^2$ J s^{-1})	$-Q_{3i}$ (mJ)	$-(dQ/dt)_{3i}$ ($\times 10^3$ J s^{-1})	
175	4348.268	2.6831	4940.224	3.1831	591.956	5.0000	0.4399
200	4992.980	2.4924	5694.979	2.9471	701.999	4.5470	0.5217
225	5589.902	2.3018	6394.383	2.7143	804.481	4.1250	0.5978
250	6140.192	2.1205	7038.520	2.4830	898.328	3.6250	0.6675
275	6647.480	1.9533	7628.351	2.2783	980.871	3.2500	0.7289
300	7114.681	1.7955	8167.200	2.0861	1052.520	2.9070	0.7821
325	7544.371	1.6517	8659.495	1.9049	1115.120	2.5310	0.8286
350	7939.690	1.5189	9105.060	1.7330	1165.370	2.1410	0.8660
375	8302.922	1.3923	9511.086	1.5876	1208.160	1.9530	0.8978
400	8635.836	1.2798	9880.520	1.4626	1244.680	1.8280	0.9249
425	8942.115	1.1782	10216.550	1.3439	1274.430	1.6560	0.9470
450	9224.312	1.0876	10522.430	1.2407	1298.110	1.5310	0.9646

$Q_{1\infty} = -13814.14$ mJ, $Q_{2\infty} = -10507.16$ mJ, $Q_{3\infty} = -3306.98$ mJ.

Table 4
Total heat produced and crystal growth kinetics of $Zn(Met)Ac_2 \cdot H_2O$

Solute (g)	Solvent (g)	Diluent (g)	$-Q_\infty$ ($J\,g^{-1}$)	$dQ/dt = k_2(1 - Q/Q_\infty) + a$			$dm/dt = k_1 m_\infty (c - c_\infty) + b$	
				k_2 ($\times 10^3\,J\,s^{-1}$)	a ($\times 10^4\,J\,s^{-1}$)	r	k_1 ($\times 10^2\,s^{-1}$)	b ($\times 10^6\,g\,s^{-1}$)
$Zn(Met)Ac_2 \cdot H_2O$ (0.0070)	H_2O (0.1000)	C_2H_6O (1.9800)	257	6.80	1.20	0.996	1.50	1.50
			255	6.75	2.80	0.992	1.49	3.50
			253	6.84	1.30	0.980	1.51	1.62
			254	6.81	4.50	0.990	1.51	5.62
			250	6.79	3.90	0.999	1.50	4.87
			251	6.83	1.10	0.986	1.51	1.37
Mean			253	8.41	2.47		1.50	3.08

Q_∞, total heat produced ($J\,g^{-1}$); dQ/dt, rate of heat production at time t ($J\,s^{-1}$); k_2, rate constant of crystal growth ($J\,s^{-1}$); Q, heat production at time t (J); a, constant of BCF ($J\,s^{-1}$); dm/dt, rate of crystal growth at time t ($g\,s^{-1}$); k_1, rate constant of crystal growth (s^{-1}); m_∞, total mass of solid deposited (g); c, solute concentration in the solution (g per 100 g solvent); c_∞, equilibrium saturation concentration (g per 100 g solvent); b, constant of BCF ($g\,s^{-1}$).

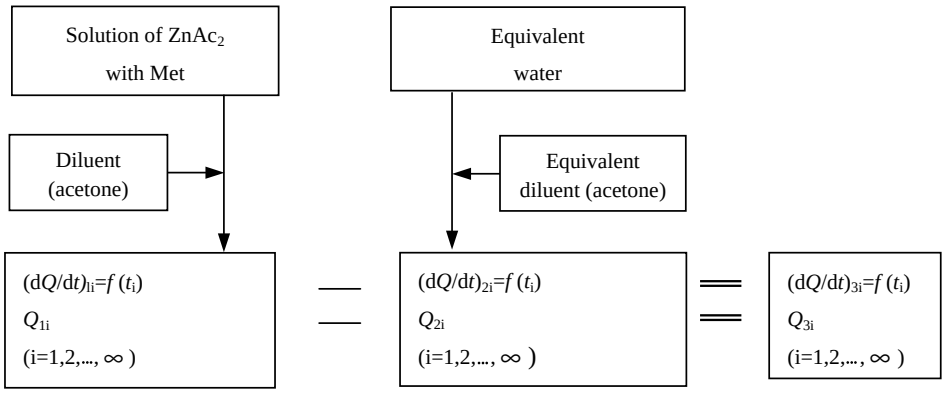

Fig. 4. Block diagram of the process of studying dilution/crystallization kinetics.

Because the values of the constants a and b are far small as compared with those of k_2 and k_1, the kinetics of the crystal growth process of $Zn(Met)Ac_2 \cdot H_2O$ can be expressed by Eqs. (5) and (6). This fact indicates that the crystal growth process of $Zn(Met)Ac_2 \cdot H_2O$ accords with the BCF dislocation theory model.

Acknowledgements

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