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THE CRYSTALLIZATION KINETICS OF $Zn(Met)SO_4 \cdot H_2O$ IN MIXED SOLVENT OF WATER WITH ACETONE

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Abstract

The crystal growth process of $Zn(Met)SO_4 \cdot H_2O$ at 298.15 K is investigated by microcalorimetry. The rate constant of heat production (k_2) and the rate constant of crystal growth (k_1) during the crystallization process are $6.79 \cdot 10^{-3}$ J s^{-1} and $11.21 \cdot 10^{-3}$ s^{-1}, respectively. The experimental results show the process accords with the Burton–Cabrera–Frank dislocation theory.

Keywords: crystallization kinetics, microcalorimetry, mixed solvent, $Zn(Met)SO_4 \cdot H_2O$

Introduction

Zinc is a necessary life element in human body. *L*-α-amino acid is the basic unit of protein related with life. *L*-α-Met (methionine) is one of eight sorts of amino acids indispensable to life which have to be absorbed from food because it can not be synthesized in human body. The complexes of zinc salts with α-amino acid as additive have a wide application in medicine, foodstuff and cosmetics [1–3]. The synthesis methods of the complexes of zinc salts with α-amino acid have been reviewed [4, 5].The solubility of $ZnSO_4$–Met–H_2O system at 298.15 K has ever been investigated by phase equilibrium method [6, 7]. The phase diagram is a simple one, in which the phase region of $Zn(Met)SO_4 \cdot H_2O$ does not exist. The solid complex of $Zn(Met)SO_4 \cdot H_2O$ has been prepared by adding acetone into the reaction solution of $ZnSO_4$ and Met in literatures [1] and [8].The physico-chemical constants, structure and thermochemical constants have also been reported in details [4, 6]. The enthalpy of solution in water of $Zn(Met)SO_4 \cdot H_2O$ at 298.15 K has been reported in literature [9]. The crystallization kinetics of the compound has not yet been reported. The crystallization kinetics of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) have been investigated with microcalorimetry by Chen Xi-Jun *et al*. [10, 11].

In this paper, the total heat produced and the rate of heat production during the crystal growth process of $Zn(Met)SO_4 \cdot H_2O$ are measured using a RD496-III type micro-

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calorimeter [12]. The kinetic parameters are calculated. The experimental results show the process accords with the Burton–Cabrera–Frank dislocation theory [13].

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

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

$T = 0, C_0$	0	0
$t = t, C$	m	Q
$t = \infty, C_\infty$	m_∞	Q_∞

where C is the solute concentration in the solution at time t; m the mass of solid deposited during a certain time t; Q the heat produced during a certain time t. When t=0, C=C_0, m=0 and Q=0; when t=∞; C=C_∞, m=m_∞, and Q=Q_∞.

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

$$\frac{Q}{Q_\infty} = \frac{m}{m_\infty} = \frac{C_0 - C}{C_0 - C_\infty} \tag{1}$$

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 at time t ($\mathrm{d}m/\mathrm{d}t$) may 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 combination of Eqs (3), (4) and (5) gives

$$\frac{dQ}{dt} = k_1 Q_\infty (C_0 - C_\infty)\left(1 - \frac{Q}{Q_\infty}\right) = k_2\left(1 - \frac{Q}{Q_\infty}\right) \quad (6)$$

where $k_2 = k_1 Q\infty(C_0 - C_\infty)$.

If $C_0 >> C_\infty$, from Eq. (6), we have

$$\frac{dQ}{dt} = k_1 Q_\infty C_0\left(1 - \frac{Q}{Q_\infty}\right) = k_3\left(1 - \frac{Q}{Q_\infty}\right) \quad (7)$$

where $k_3 = k_1 Q_\infty C_0$.

When $(dQ/dt)_i$ is plotted *vs.* $(1 - Q/Q_\infty)_i$ by the least-squares method, this gives the value of k_3 or k_2 (slope) and a (intercept) in the Eqs (8) and (9)

$$\frac{dQ}{dt} = k_3\left(1 - \frac{Q}{Q_\infty}\right) + a \quad (8)$$

or

$$\frac{dQ}{dt} = k_1 Q_\infty (C_0 - C_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a = k_2\left(1 - \frac{Q}{Q_\infty}\right) + a \quad (9)$$

where

$$k_1 = \frac{k_2}{Q_\infty (C_0 - C_\infty)} \xrightarrow{C_0 >> C_\infty} \frac{k_2}{C_\infty C_0} \quad (10)$$

Equation (10) relates k_1 to k_2. The combination of Eqs (3), (4), (8) and (9) gives

$$\frac{dm}{dt} = \left(\frac{m_\infty}{Q_\infty}\right)\frac{dQ}{dt} = \frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (C_0 - C_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a\right] = \\ = \frac{m_\infty}{Q_\infty}[k_1 Q_\infty (C - C_\infty) + a] = k_1 m_\infty (C - C_\infty) + \frac{a m_\infty}{Q_\infty} \quad (11)$$

Similarly, Eq. (5) may be written as

$$\frac{dm}{dt} = k_1 m_\infty (C - C_\infty) + b \quad (12)$$

where b is the intercept of Eq. (12).

Comparing Eqs (11) and (12), a relationship [Eq. (13)] is obtained

$$b = \frac{a m_\infty}{Q_\infty} \quad (13)$$

Equation (13) relates b to a.

If the values of the constants a and b are small as comparison with those of k_2 (or k_3) and k_1, the kinetics of the crystal growth process can be expressed by Eqs (5) and (6).

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

Experimental

Materials

$ZnSO_4 \cdot 7H_2O$, A.R. (made in Xi'an Chemical Company); *L*-α-Met, B.R. (Shanghai Kangda Company), purity >99.9%; C_3H_6O, A.R. (made in Xi'an Chemical Company), its density is 0.79 g cm^{-3} at 298.15 K; the conductivity of the demonized water is $5.48 \cdot 10^{-8}$ S cm^{-1}, its density is 0.99705 g cm^{-3} at 298.15 K; the others are A.R. grade.

Analysis method

Zn^{2+} is determined with EDTA by complexometric titration. Met is analyzed by the formalin method, before which Zn^{2+} is removed by precipitating with $K_2C_2O_4$. SO_4^{2-} is determined by the $BaSO_4$ gravimetric method.

Experimental method

The calorimetric experiment is performed using a RD496-III type microcalorimeter at 298.15±0.005 K. The calorimetric constant is determined by Joule effect before experiment, which is 63.994±0.042 μV mW^{-1} at 298.15 K. The enthalpies of solution in deionized water of KCl (spectral purity) is measured to be 17.238±0.048 kJ mol^{-1}, which is very close to 17.241±0.018 kJ mol^{-1} [14]. The accuracy is 0.02% and the precision is 0.3%, which indicates that the calorimetric system is accurate and reliable. The reaction solution/solvent and the diluent are put into the stainless steel sample cell with the container of 15 mL (Fig. 1), separately. After equilibrium, the containers of sample and reference are pushed down simultaneously. As a result, the two liquids are mixed and the calorimetric curve is recorded.

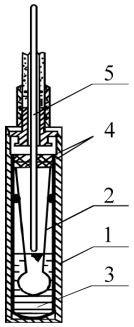

Fig. 1 Sketch used for study of the formation reaction; 1 – calorimetric cell; 2 – solution of $ZnSO_4$ with Met; 3 – acetone; 4 – silicone rubber cover; 5 – glass rod

Results and discussion

$Zn(Met)^{2+}(aq)$ is produced from the reaction of $ZnSO_4$ with Met in water (lg$K$ is 4.40 [15]) but the solubility is too big to obtain the solid complex. If adding acetone into the system to change the solvent and decrease the solubility of complex, the solution becomes a relatively high supersaturated system. That is, in the phase diagram, the phase region of acid is reduced, which separates with the phase region of salt, and the phase region of complex is formed. Based on the above principle, with the volume ratio of water:acetone of 1:30, the solid compound is obtained. After suction filtrated, followed by rinsing with a few of acetone and drying to constant weight. The yield of the compound is 95%. The results of component analysis indicate that the product is $Zn(Met)\ SO_4 \cdot H_2O$ in comparison with literature [1, 6, 7, 9].

Adding acetone into the reaction solution system of $ZnSO_4$–Met, the crystallization process begins.

$$ZnSO_4 \cdot 7H_2O(s)+Met(aq) \rightarrow Zn(Phe)^{2+}(aq)+SO_4^{2-}(aq)+7H_2O(l) \quad (14)$$

$$Zn(Met)^{2+}(aq)+SO_4^{2-}(aq)+H_2O(l) \xrightarrow{\text{acetone}} Zn(Met)SO_4 \cdot H_2O(s) \quad (15)$$

A typical schematic calorimetric curve during the dilution and crystallization is depicted in Fig. 2. The original data obtained from the TK curve are shown in Table 1. Using the above data, the kinetic data during the dilution/crystallization process can be obtained from Eqs (9), (10) and (13) (Table 2).

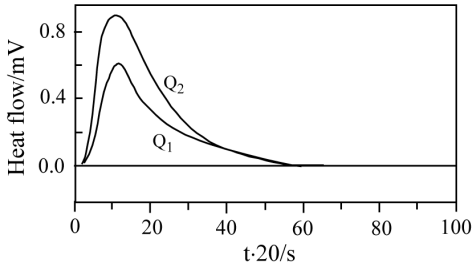

Fig. 2 Typical calorimetric curve of the dilution/crystallization process

The experimental results in Table 2 are obtained based on the principle presented as a block diagram in Fig. 3. In Fig. 3, $(dQ/dt)_{1i}$ 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}, 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 crystal growth process and the rate constant at 298.15 K are shown in Table 2.

Because the values of the constants a and b are small as comparison with those of k_2 and k_1, the kinetics of the crystal growth process of $Zn(Met)SO_4 \cdot H_2O$ can be expressed by Eqs (5) and (6). This fact indicates that the crystal growth process of $Zn(Met)SO_4 \cdot H_2O$ accords with the BCF dislocation theory model.

Table 1 Thermokinetical data of the titled reaction

t/s	Total reaction process		Dilution process		Crystallization process		
	Q_{1i}/mJ	$(dQ/dt)_{1i} \cdot 10^2$/J s^{-1}	Q_{2i}/mJ	$(dQ/dt)_{2i} \cdot 10^2$/J s^{-1}	Q_{3i}/mJ	$(dQ/dt)_{3i} \cdot 10^3$/J s^{-1}	$Q_{3i}/Q_{\infty 3}$
200	4925.14	2.009	4934.31	2.738	–9.18	–7.286	0.002
225	5540.08	1.849	5595.13	2.574	–55.06	–7.246	0.012
250	6128.68	1.681	6213.89	2.401	–85.21	–7.200	0.019
275	6645.14	1.519	6789.34	2.230	–144.20	–7.110	0.032
300	7204.62	1.348	7322.60	2.063	–117.98	–7.150	0.026
325	7653.79	1.194	7818.04	1.902	–161.24	–7.084	0.036
350	8091.91	1.045	8268.23	1.752	–176.32	–7.061	0.039
375	8471.84	0.909	8684.86	1.610	–213.02	–7.005	0.047
400	8839.75	0.778	9067.20	1.476	–227.44	–6.983	0.050
415	8840.52	0.736	9280.99	1.402	–440.47	–6.658	0.097
425	8760.01	0.721	9417.43	1.354	–657.43	–6.327	0.145
450	8987.17	0.623	9738.32	1.241	–751.16	–6.184	0.166

$Q_{\infty 1}$=17769.97 mJ, $Q_{\infty 2}$=22292.64 mJ, $Q_{\infty 3}$=–4522.67 mJ

Table 2 The experimental results of the dilution/crystallization kinetics

Solute/g	Solvent/g	Diluent/g	$-Q_\infty$/J g^{-1}	$dQ/dt=k_2(1-Q/Q_\infty)+a$			$dm/dt=k_1(C-C_\infty)+b$	
				$k^2\cdot10^3$/J s^{-1}	$a\cdot10^4$/J s^{-1}	r	$k_1\cdot10^3$/s^{-1}	$b\cdot10^7$/g s^{-1}
$Zn(Met)SO_4·H_2O$	H_2O	C_3H_6O	1443	6.80	5.00	0.999	11.25	3.47
(0.0033)	(0.0997)	(2.3700)	1440	6.79	4.50	0.997	11.26	3.13
			1450	6.77	5.20	0.997	11.15	3.59
			1447	6.82	5.30	0.998	11.25	3.66
			1444	6.80	4.70	0.995	11.24	4.71
			1449	6.75	4.40	0.999	11.12	3.04
		mean	1446	6.79	4.85		11.21	3.60

Q_∞, total heat produced/(J g^{-1}); dQ/dt, rate of heat production 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/100 g solvent); C_∞, equilibrium saturation concentration/(g/100 g solvent); b, constant of BCF/(g s^{-1})

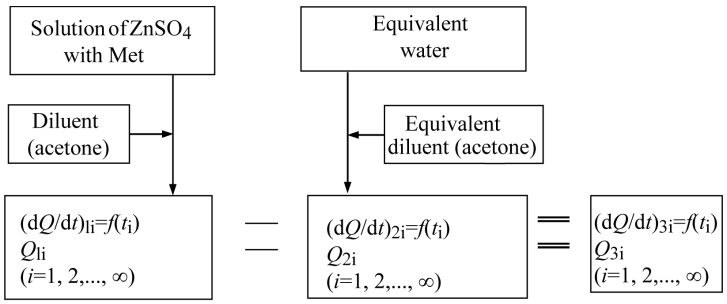

Fig. 3 Block diagram of the process of studying dilution/crystallization kinetics

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