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Investigation of the Crystallization Kinetics of Aqua Methioninezinc (II) Sulfate by Microcalorimetry

Yan Fang, Shengli L. Gao*, **Sanping P. Chen, Rongzu Z. Hu,**
and **Qizhen Z. Shi**

Department of Chemistry, Shaanxi Key Laboratory of Physico-Inorganic Chemistry,
Northwest University, Xi'an, 710069, P.R. China

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Summary. The crystal growth process of aqua methioninezinc (II) sulfate (Zn(*Met*)$SO_4 \cdot H_2O$) from water and acetone was investigated using a Calvet microcalorimeter. The heat produced and the rate of heat production during the crystal growth process at 293.15, 295.15, 298.15, and 300.15 K were measured. On the basis of these results the rate constant, the *Eyring* parameters (the apparent activation enthalpy, the activation entropy, and the activation free energies), and the *Arrhenius* parameters (the activation energy, the pre-exponential factor) of the crystal growth process have been obtained. The results have shown that this crystal growth process accords with the *Burton-Cabrera-Frank* dislocation theory.

Keywords. Zinc sulfate; *L*-α-Methionine; Crystallization kinetics; Microcalorimetry.

Introduction

Zinc is an essential trace element in living systems. The α-amino acid group is the basic unit of proteins related with life. *L*-α-*Met* (methionine) is one of eight amino acids indispensable for life which has to be absorbed from food because it can not be synthesized in the human body. The complexes of zinc salts with an α-amino acid as additive have a wide application in medicine, foodstuff, and cosmetics [1–3]. The synthesis methods of complexes of zinc salts with α-amino acids have been reviewed [4–6]. The solubility of Zn(Met)$SO_4 \cdot H_2O$ at 298.15 K has been investigated by the semimicro-phase equilibrium method [4]. The phase diagram is a simple one, in which the phase region of aqua methioninezinc (II) sulfate (Zn(*Met*)$SO_4 \cdot H_2O$) does not exist. The solid complex of Zn(*Met*)$SO_4 \cdot H_2O$ has been prepared from a solution of $ZnSO_4$ and *Met* into which 30 times its volume of acetone was added [1, 6].

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* Corresponding author. E-mail: weizhang@nwu.edu.cn

Obviously, how to crystallize solid Zn(Met)$SO_4 \cdot H_2O$ from solution is our main concern. The physico-chemical properties, structure and thermostability, as well as the standard enthalpy of formation and the enthalpy of solution in water of the solid compound Zn(*Met*)$SO_4 \cdot H_2O$ at 298.15 K have been reported in detail [6–8], however, the crystallization kinetics of the compound has not been investigated so far.

The crystal growth process from supersaturated solution or mixed solvent was investigated by *Becker* [9] and *Bransom et al.* [10], and the dislocation theory model (*BCF* theory) of crystal growth was applied successfully [11]. The crystallization kinetics for cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) has been investigated with microcalorimetry by *Chen Xi-Jun et al.* [12, 13].

In this paper, the crystal growth process of Zn(Met)$SO_4 \cdot H_2O$ from the mixed solvent water–acetone was experimentally designed according to literature [1]. The heat produced and the rate of heat production during the process at different temperatures were measured by microcalorimetry. The thermodynamic parameters, the rate constant, and other kinetic parameters were determined.

Derivation of the Kinetic Equation of the Crystal Growth Process [9, 12–14]

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 shown in Eq. (1) where k_1 is the rate constant of crystal growth, m_∞ is the total mass of solid deposited, c (g/100 g of solvent) is the concentration of Zn(*Met*)$SO_4 \cdot H_2O$, and c_∞ (g/100 g of solvent) is the equilibrium saturation concentration.

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k_1 m_\infty (c - c_\infty) \tag{1}$$

The energy change brought about by the reaction progress, see Eq. (1), is given in Eq. (2) where $k_2 = k_1 Q_\infty (c_0 - c_\infty)$ [13, 14].

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) = k_2\left(1 - \frac{Q}{Q_\infty}\right) \tag{2}$$

If $c_0 \gg c_\infty$, from Eq. (2) we get Eq. (3) where $k_3 = k_1 Q_\infty c_0$.

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1 Q_\infty c_0\left(1 - \frac{Q}{Q_\infty}\right) = k_3\left(1 - \frac{Q}{Q_\infty}\right) \tag{3}$$

A linear regression of the variables $\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_\mathrm{i}$ and $\left(1 - \frac{Q}{Q_\infty}\right)_\mathrm{i}$ results in k_3 or k_2 (slope) and a (intercept), as shown in Eqs. (4) and (5) where k_1 is defined by Eq. (6).

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_3\left(1 - \frac{Q}{Q_\infty}\right) + a \tag{4}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a = k_2\left(1 - \frac{Q}{Q_\infty}\right) + a \tag{5}$$

$$k_1 = \frac{k_2}{Q_\infty (c_0 - c_\infty)} c_0 \geqq c_\infty \frac{k_2}{Q_\infty c_0} \tag{6}$$

As $m/m_\infty = Q/Q_\infty$ Eq. (5) gives Eq. (7).

$$\begin{aligned}\frac{\mathrm{d}m}{\mathrm{d}t} &= \left(\frac{m_\infty}{Q_\infty}\right)\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a\right] \\ &= \frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (c - c_\infty) + a\right] = k_1 m_\infty (c - c_\infty) + \frac{a m_\infty}{Q_\infty}\end{aligned} \tag{7}$$

Similarly, Eq. (1) may be written as shown in Eq. (8) where b is the intercept.

$$\frac{dm}{dt} = k_1 m_\infty (c - c_\infty) + b \tag{8}$$

From Eqs. (7) and (8) b is obtained as defined in Eq. (9)

$$b = \frac{a m_\infty}{Q_\infty} \tag{9}$$

If the constants a and b are small compared with k_2 (or k_3) and k_1, the kinetics of the crystal growth process can be expressed by Eqs. (1) and (2).

On the basis of the experimental results the rate constant, the reaction order, three *Eyring* parameters (the activation enthalpy, the activation entropy, and the activation free energy), and two *Arrhenius* parameters (the activation energy and the pre-exponential constant) have been obtained at different temperatures [14].

Results and Discussion

$Zn(Met)^{2+}$(aq) was produced from the reaction of $ZnSO_4$ with *Met* in water (lg$K$ is 4.40 [17]), but the solubility is too high to obtain the solid complex. Adding acetone to the system decreases the solubility of the complex, thus the solution becomes highly supersaturated. In the phase diagram, the phase region of acid is reduced, which separates from the phase region of salt, and the phase region of complex is formed. Based on the above analyses, with the volume ratio of water:acetone of 1:30, the white solid compound is obtained. It was filtered off, rinsed with a few milliliters of acetone, and dried to constant weight. The yield of the compound was 95%. The results of component analyses indicate that the product can be identified as aqua methioninezinc (II) sulfate [1, 6].

By adding acetone to a solution containing $ZnSO_4$ and *Met*, the solid complex $Zn(Met)SO_4{\cdot}H_2O$ crystallizes.

A typical schematic thermogram during the dilution and crystallization is depicted in Fig. 1. The original data obtained from the thermokinetical curves are shown in Table 1. The kinetic data of the dilution/crystallization process can be obtained from Eqs. (5), (6), and (9) (Table 1).

The experimental results in Table 2 are obtained based on the principle presented as block diagram in Fig. 2 where $(dQ/dt)_{1i}$ 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. Thus, 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

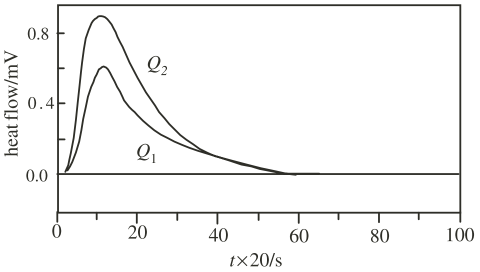

Fig. 1. Typical thermogram of the dilution/crystallization process

Table 1. Thermokinetical data of the crystallization kinetics of aqua methioninezinc (II) sulfate

T/K	t/s	Total reaction process		Dilution process		Crystallization process		
		$Q_{1\mathrm{i}}/\mathrm{mJ}$	$(\mathrm{d}Q/\mathrm{d}t)_{1\mathrm{i}}\cdot 10^3/\mathrm{J\,s^{-1}}$	$Q_{2\mathrm{i}}/\mathrm{mJ}$	$(\mathrm{d}Q/\mathrm{d}t)_{2\mathrm{i}}\cdot 10^3/\mathrm{J\,s^{-1}}$	$-Q_{3\mathrm{i}}/\mathrm{mJ}$	$-(\mathrm{d}Q/\mathrm{d}t)_{3\mathrm{i}}\cdot 10^3/\mathrm{J\,s^{-1}}$	$Q_{3\mathrm{i}}/Q_{\infty 3}$
293.15	500	5153.07	9.43	9924.77	10.75	4771.71	1.33	0.7554
	525	5290.84	8.66	10180.9	9.90	4890.04	1.24	0.7741
	550	5399.43	7.97	10416.4	9.11	5016.98	1.15	0.7942
	600	5568.13	6.76	10832.5	7.72	5264.40	0.97	0.8333
	630	5657.31	6.13	11050.8	7.00	5393.50	0.87	0.8538
	650	5705.26	5.75	11184.8	6.56	5479.56	0.81	0.8674
	700	5841.06	4.91	11484.1	5.60	5643.07	0.69	0.8933
	735	5929.40	4.41	11667.1	5.03	5737.74	0.62	0.9083
	750	5963.24	4.21	11739.7	4.81	5776.47	0.59	0.9144
	800	6066.53	3.64	11959.2	4.15	5892.65	0.51	0.9328
	805	6071.67	3.59	11979.4	4.09	5907.71	0.50	0.9351
	850	6152.60	3.17	12148.5	3.60	5995.92	0.43	0.9491
	$Q_{1\infty}=15001.34\,\mathrm{mJ}$, $Q_{2\infty}=21318.57\,\mathrm{mJ}$, $Q_{3\infty}=-6317.23\,\mathrm{mJ}$							
295.15	200	4321.29	25.3	6326.37	29.8	2014.08	4.55	0.3945
	210	4560.45	24.8	6898.56	29.0	2338.11	4.22	0.4580
	220	4803.57	24.3	7456.50	28.1	2652.92	3.90	0.5196
	230	5041.51	23.8	8032.29	27.3	2990.77	3.55	0.5858
	240	5274.17	23.2	8569.01	26.5	3294.84	3.24	0.6453
	250	5501.36	22.7	9068.02	25.6	3566.66	2.97	0.6986
	255	5612.90	22.4	9320.84	25.2	3707.94	2.82	0.7263
	260	5723.07	22.1	9563.08	24.8	3840.01	2.69	0.7522
	270	5939.26	21.6	10031.1	24.0	4091.86	2.43	0.8015
	280	6149.87	21.0	10476.7	23.2	4326.82	2.19	0.8475
	290	6354.89	20.4	10895.2	22.4	4540.29	1.98	0.8893
	300	6554.30	19.9	11294.2	21.7	4739.93	1.77	0.9284
	$Q_{1\infty}=18801.31\,\mathrm{mJ}$, $Q_{2\infty}=23906.66\,\mathrm{mJ}$, $Q_{3\infty}=-5105.35\,\mathrm{mJ}$							
298.15	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
	$Q_{1\infty}=17769.97\,\mathrm{mJ}$, $Q_{2\infty}=22292.64\,\mathrm{mJ}$, $Q_{3\infty}=-4522.67\,\mathrm{mJ}$							
300.15	1700	11631.8	1.12	13890.7	4.15	2258.90	3.03	0.7526
	1750	11800.4	1.03	14087.6	3.99	2287.16	2.96	0.7620
	1800	11927.2	0.95	14276.3	3.74	2349.09	2.80	0.7827

(*continued*)

Table 1 (*continued*)

T/K	t/s	Total reaction process		Dilution process		Crystallization process		
		Q_{1i}/mJ	$(\mathrm{d}Q/\mathrm{d}t)_{1i} \cdot 10^3/\mathrm{J\,s^{-1}}$	Q_{2i}/mJ	$(\mathrm{d}Q/\mathrm{d}t)_{2i} \cdot 10^3/\mathrm{J\,s^{-1}}$	$-Q_{3i}/\mathrm{mJ}$	$-(\mathrm{d}Q/\mathrm{d}t)_{3i} \cdot 10^3/\mathrm{J\,s^{-1}}$	$Q_{3i}/Q_{\infty 3}$
	1850	12044.6	0.89	14452.6	3.53	2408.01	2.64	0.8022
	1900	12215.9	0.83	14623.9	3.47	2408.01	2.64	0.8023
	1950	12317.1	0.79	14787.0	3.27	2469.94	2.48	0.8229
	2000	12453.5	0.75	14941.5	3.19	2487.98	2.43	0.8289
	2050	12555.1	0.73	15092.4	3.03	2537.28	2.31	0.8454
	2100	12639.7	0.70	15234.1	2.86	2594.40	2.16	0.8644
	2150	12778.5	0.67	15369.9	2.84	2591.39	2.17	0.8634
	2200	12863.7	0.64	15503.2	2.68	2639.50	2.04	0.8794
	2250	12937.8	0.62	15627.8	2.53	2690.00	1.91	0.8962
	$Q_{1\infty} = 15878.25\,\mathrm{mJ}$, $Q_{2\infty} = 18879.69\,\mathrm{mJ}$, $Q_{3\infty} = -3001.44\,\mathrm{mJ}$							

Table 2. The experimental results of the dilution/crystallization kinetics at different temperatures

T/K	Solute (Zn(*Met*)$SO_4 \cdot H_2O$)/g	Solvent (H_2O)/g	Diluent (C_3H_6O)/g	$-Q_\infty/\mathrm{J\,g^{-1}}$	$k_2 \cdot 10^3/\mathrm{J\,s^{-1}}$	$a \cdot 10^4/\mathrm{J\,s^{-1}}$	r	$k_1 \cdot 10^3/\mathrm{s^{-1}}$	$b \cdot 10^7/\mathrm{g\,s^{-1}}$
293.15	0.0033	0.0997	2.3700	2015	4.53	2.50	0.999	5.46	1.24
295.15	0.0033	0.0997	2.3700	1625	5.22	7.67	0.996	7.66	4.72
298.15	0.0033	0.0997	2.3700	1446	6.79	4.85	0.999	11.21	3.60
300.15	0.0033	0.0997	2.3700	954	7.81	9.00	0.999	19.54	9.43

Q_∞: total heat produced; k_2: rate constant of crystal growth; a: constant of *BCF*; k_1: rate constant of crystal growth; b: constant of *BCF*

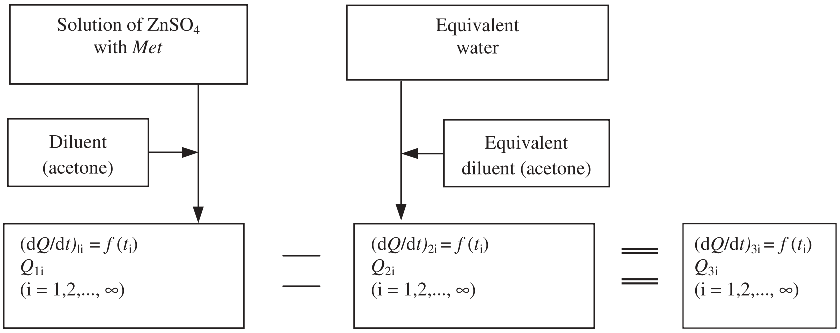

Fig. 2. Block diagram of the process of studying dilution/crystallization kinetics

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 different temperatures is shown in Table 2.

Because 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 of Zn(Met)$SO_4 \cdot H_2O$ can be expressed by Eqs. (1) and (2). Thus, the crystal growth process of Zn(Met)$SO_4 \cdot H_2O$ accords with the *BCF* dislocation theory model.

Table 3. Kinetic parameters of methioninezinc (II) sulfate crystallization

T/K	$k{\cdot}10^3/\mathrm{s}^{-1}$	r	$E/\mathrm{kJ\,mol}^{-1}$	$\ln(A/\mathrm{s}^{-1})$	r	$\Delta G^{\theta}_{\neq}/\mathrm{kJ\,mol}^{-1}$	$\Delta H^{\theta}_{\neq}/\mathrm{kJ\,mol}^{-1}$	$\Delta S^{\theta}_{\neq}/\mathrm{J\,mol}^{-1}$	r
293.15	7.50	0.999	23.16	4.61	0.997	83.679	20.68	-214.86	0.996
295.15	8.11	0.999				84.078			
298.15	8.82	0.999				84.752			
300.15	9.40	0.999				85.173			

Finally, the *Arrhenius* and the *Eyring* parameters of the crystal growth process were calculated [14] and summarized in Table 3.

From Table 3, it is evident that the rate of reaction increases with increasing temperature and the reaction is first order when the values of E and $\Delta H^{\theta}_{\neq}$ are very low and $\Delta S^{\theta}_{\neq}$ is high, which shows that the coordination reaction is spontaneous over the temperature range 293.15–300.15 K.

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 $0.79\,\mathrm{g\,cm}^{-3}$ at 298.15 K; the conductivity of the deionized water is $5.48\times10^{-8}\,\mathrm{S\,cm}^{-1}$, its density is $0.99705\,\mathrm{g\,cm}^{-3}$ at 298.15 K; the other reagents are A. R. grade.

Analysis Method

Zn^{2+} was determined by complexometric titration with EDTA. *Met* was analyzed by the formalin method, after Zn^{2+} was removed by precipitation with $K_2C_2O_4$. $SO_4{}^{2-}$ was determined gravimetrically as $BaSO_4$.

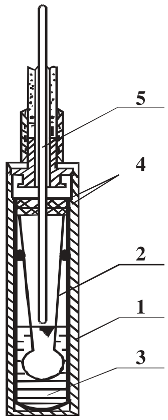

Fig. 3. Sketch of instrument used to study the formation reaction; 1. calorimetric cell; 2. solution of $ZnSO_4$ with *Met*; 3. acetone; 4. silicone rubber cover; 5. glass rod

Experimental Method

The calorimetric experiment was performed using a RD496-III type microcalorimeter [15]. The microcalorimeter was calibrated by the Joule effect before each experiment, and the following sensitivities were obtained: 63.830 ± 0.037, 63.932 ± 0.040, 63.994 ± 0.042, and $64.000 \pm 0.026\,\mu\text{VmW}^{-1}$ at 293.15, 295.15, 298.15, and 300.15 K, respectively. The enthalpies of solution in deionized water of KCI (spectral purity) was measured to be $17.238 \pm 0.048\,\text{kJ}\cdot\text{mol}^{-1}$, which is very close to $17.241 \pm 0.018\,\text{kJ}\cdot\text{mol}^{-1}$ [16]. 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 $15\,\text{cm}^3$ (Fig. 3), separately. After equilibrium, the containers of sample and reference are pushed down simultaneously. As a result, the two liquids are mixed and the thermogram is recorded.

Acknowledgements

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