

Investigation of the Crystallization Kinetics of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ in Mixing Solvent by Microcalorimetry

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The crystal growth process of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ from water and acetone was investigated using a Calvet microcalorimeter. The heat and the rate of heat production during the crystal growth process at 293.15 K, 295.15 K, 298.15 K and 300.15 K were measured. On the basis of experimental and calculated results, the rate constant and the kinetic parameters (the activation energies, the pre-exponential) during the crystal growth process were obtained. The results show that the crystal growth process accorded with the Burton-Cabrera-Frank dislocation theory.

Keywords zinc sulfate, *L*- α -leucine, complex, crystallization kinetics, microcalorimetry

Introduction

Zinc is an essential trace element to organism. α -Amino acid is the basic unit of protein related with life. *L*- α -Leu (leucine) is one of eight sorts of amino acids indispensable to life which are 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 synthetic methods of the complexes of zinc salts with α -amino acid have been reviewed.^{4,5} The solubility of ZnSO_4 -Leu- H_2O system at 298.15 K has been investigated by semimicro-phase equilibrium method.⁶ The phase diagram is a simple phase, in which the phase region of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ did not exist. Interestingly, the solid complex of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ has been prepared from the reaction solution of ZnSO_4 and Leu into which 5 times volume of acetone was added as reported in literature.⁶ Evidently, how to make the solid $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ crystallizing from the solution is main concerns. Undoubtedly that a better understanding of the research for the preparation and applications of the complex is considerable practical and fundamental importance. As for the solid compound $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$, its physico-chemical, structure and thermal stability of the compound have been reported in details in literature.⁶ The standard enthalpy of formation of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ at 298.15 K has been reported in literature.⁷ The crystalliza-

tion kinetics of the compound has not been reported.

The crystal growth process from supersaturation solution or mixing solvent has been investigated by Becker⁸ and Bransom, *etc.*,⁹ and then the dislocation theory model (BCF theory) of crystal growth was established.¹⁰ The crystallization kinetics for cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) has been investigated with microcalorimetry by Chen *et al.*^{11,12}

In this paper, the crystal growth process of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ from the mixed solvent of water and acetone was designed according to the reported method.⁶ The heat and the rates of heat production at different temperature were measured with microcalorimetry. The rate constant and the kinetic parameters were calculated.

Derivation of the kinetic equation of the crystal growth process^{9,11-13}

According to the Burton-Cabrera-Frank (BCF) dislocation theory, for relatively high supersaturations, the rate of crystal growth at time t (dm/dt) may be expressed as

$$\frac{dm}{dt} = k_1 m_\infty (C - C_\infty) \quad (1)$$

where k_1 is the rate constant of crystal growth.

The combination of Eq. (1) and that reported in the literatures^{13,14} gives

$$\frac{dQ}{dt} = k_1 Q_\infty (C_0 - C_\infty) \left(1 - \frac{Q}{Q_\infty}\right) = k_2 \left(1 - \frac{Q}{Q_\infty}\right) \quad (2)$$

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

If $C_0 \gg C_\infty$, from Eq. (2), we have

$$\frac{dQ}{dt} = k_1 Q_\infty C_0 \left(1 - \frac{Q}{Q_\infty}\right) = k_3 \left(1 - \frac{Q}{Q_\infty}\right) \quad (3)$$

where $k_3 = k_1 Q_\infty C_0$.

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Received August 13, 2002; revised December 3, 2002; accepted December 15, 2002.

Project supported by the National Natural Science Foundation of China (Nos. 29871023 and 20171036).

$\left(\frac{dQ}{dt}\right)_i$ being plotted versus $\left(1 - \frac{Q}{Q_\infty}\right)_i$ by the least-squares method, k_3 or k_2 (slope) and a (intercept) are obtained, as shown in the Eqs. (4) and (5)

$$\frac{dQ}{dt} = k_3 \left(1 - \frac{Q}{Q_\infty}\right) + a \quad (4)$$

or

$$\begin{aligned} \frac{dQ}{dt} &= k_1 Q_\infty (C_0 - C_\infty) \left(1 - \frac{Q}{Q_\infty}\right) + a \\ &= k_2 \left(1 - \frac{Q}{Q_\infty}\right) + a \end{aligned} \quad (5)$$

where

$$k_1 = \frac{k_2}{Q_\infty (C_0 - C_\infty)} \xrightarrow{C_0 \gg C_\infty} \frac{k_2}{Q_\infty C_0} \quad (6)$$

The combination of Eqs. (4) and (5) gives

$$\begin{aligned} \frac{dm}{dt} &= \left(\frac{m_\infty}{Q_\infty}\right) \frac{dQ}{dt} \\ &= \frac{m_\infty}{Q_\infty} \left[k_1 Q_\infty (C_0 - C_\infty) \left(1 - \frac{Q}{Q_\infty}\right) + a \right] \\ &= \frac{m_\infty}{Q_\infty} [k_1 Q_\infty (C - C_\infty) + a] \\ &= k_1 m_\infty (C - C_\infty) + \frac{am_\infty}{Q_\infty} \end{aligned} \quad (7)$$

Similarly, Eq. (1) may be written as

$$\frac{dm}{dt} = k_1 m_\infty (C - C_\infty) + b \quad (8)$$

Where b is the intercept of Eq. (8).

Comparing Eq. (7) with Eq. (8), Eq. (9) is obtained

$$b = \frac{am_\infty}{Q_\infty} \quad (9)$$

If the constants a and b are small as compared with those of 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 experimental and calculated results, according to the literature,¹³ the rate constant and three kinetic parameters (the activation energy, the pre-exponential constant and the reaction order) are obtained at different temperatures.

Experimental

Materials

ZnSO₄·7H₂O, A. R. (made in Xi'an Chemical Company); L-α-Leu, B. R. (Shanghai Kangda Company), purity >99.9%; C₃H₆O, 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 × 10⁻⁸ S·cm⁻¹, its density is 0.99705 g·cm⁻³ at 298.15 K; the others are of

A. R. grade.

Analytic method

Zn²⁺ was determined with EDTA by complexometric titration. Leu was analyzed by the formalin method before the titration Zn²⁺ was removed by precipitating with K₂C₂O₄. SO₄²⁻ was determined by the BaSO₄ weighting method.

Experimental method

The calorimetric experiment was performed using a RD496-III type microcalorimeter.¹⁴ The microcalorimer was calibrated by Joule effect before experiment, and the sensitivities were obtained which were (63.830 ± 0.037) μV/mW, (63.932 ± 0.040) μV/mW, (63.994 ± 0.042) μV/mW and (64.000 ± 0.026) μV/mW at 293.15 K, 295.15 K, 298.15 K and 300.15 K, respectively. The enthalpy of solution in deionized water of KCl (special purity) was measured to be (17.238 ± 0.048) kJ·mol⁻¹, which was very close to (17.241 ± 0.018) kJ·mol⁻¹.¹⁵ The accuracy was 0.02% and the precision was 0.3%, which indicated that the calorimetric system was accurate and reliable. The reaction solution/solvent and the diluent were put into the stainless steel sample cell with the container of 15 cm³ (Fig. 1), separately. After equilibrium, the containers of sample and reference were pushed down simultaneously. As a result, the two liquids were mixed and the thermogram was recorded.

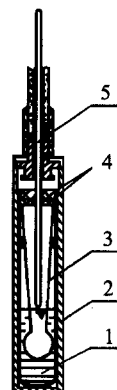


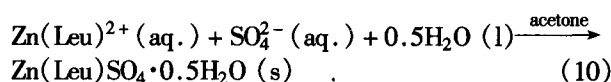
Fig. 1 Sketch used for study of the formation reaction. 1, Calorimetric cell; 2, solution of ZnSO₄ with Leu; 3, acetone; 4, silicone rubber cover; 5, glass rod.

Results and discussion

Zn(Leu)²⁺ (aq.) was produced from the reaction of ZnSO₄ with Leu in water (lg K is 4.51¹⁶) but the solubility of the complex was too big to obtain the solid complex. Adding acetone into the system to change the solvent and decrease the solubility of complex, the solution became a relatively high-supersaturated system. That is, in the phase diagram, the phase region of acid was reduced, which was separated from the phase region of salt, and the phase region of complex was

formed. Based on the above analyses, with the volume ratio of water to acetone being 1:5, the white solid compound was obtained. After suction filtration, followed by rinsing with a little acetone and drying to constant weight, the yield of the compound is 90%. The results of composition analysis indicated that the product was identified as $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$.⁶

Adding acetone into the reaction solution system of $\text{ZnSO}_4\text{-Leu}$, the crystallization process was shown in following



A typical schematic thermogram during the dilution and

crystallization was depicted in Fig. 2. The original data obtained from the TK curve are shown in Table 1. The kinetic data during the dilution/crystallization process could be obtained from Eqs. (5), (6) and (9) (Table 1).

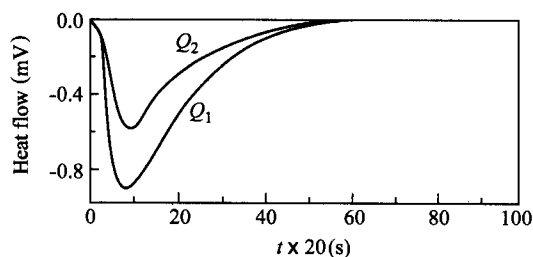


Fig. 2 Typical thermogram of the dilution/crystallization process.

Table 1 Thermokinetical data of title reaction at different temperatures

T (K)	t (s)	Total reaction process		Dilution process		Crystallization process		$Q_{3i}/Q_{\infty 3}$
		$-Q_{1i}$ (mJ)	$-(dQ/dt)_{1i} \times 10^3$ ($\text{J}\cdot\text{s}^{-1}$)	$-Q_{2i}$ (mJ)	$-(dQ/dt)_{2i} \times 10^3$ ($\text{J}\cdot\text{s}^{-1}$)	$-Q_{3i}$ (mJ)	$-(dQ/dt)_{3i} \times 10^3$ ($\text{J}\cdot\text{s}^{-1}$)	
293.15	950	3241.91	1.10	563.42	0.40	2678.49	0.71	0.8925
	975	3401.18	0.93	658.12	0.38	2743.06	0.55	0.9140
	1000	3508.91	0.79	729.48	0.34	2779.42	0.45	0.9261
	1025	3621.79	0.64	795.35	0.30	2826.44	0.34	0.9418
	1050	3738.44	0.48	867.49	0.25	2870.95	0.23	0.9566
	1075	3824.79	0.36	928.76	0.20	2896.03	0.16	0.9649
	1100	4017.20	0.29	1099.85	0.18	2917.35	0.11	0.9720
	1125	4115.47	0.23	1189.35	0.14	2926.12	0.05	0.9750
$Q_{1\infty} = -4557.111$ mJ, $Q_{2\infty} = -1555.865$ mJ, $Q_{3\infty} = -3001.246$ mJ								
295.15	725	2097.22	5.94	722.22	2.43	1374.99	3.51	0.6529
	750	2136.82	5.93	798.43	2.28	1338.39	3.65	0.6355
	775	2185.92	5.77	849.56	2.11	1336.36	3.66	0.6346
	800	2255.57	5.51	896.43	1.94	1359.14	3.57	0.6454
	825	2360.86	5.22	967.16	1.78	1393.70	3.44	0.6618
	850	2489.81	4.91	1057.47	1.62	1432.34	3.29	0.6801
	875	2577.67	4.59	1112.39	1.42	1465.28	3.16	0.6958
$Q_{1\infty} = -3527.383$ mJ, $Q_{2\infty} = -1421.388$ mJ, $Q_{3\infty} = -2105.995$ mJ								
298.15	230	1257.90	4.43	408.86	0.60	849.04	3.83	0.6108
	235	1279.44	4.34	428.43	0.53	851.01	3.81	0.6122
	240	1300.56	4.25	448.31	0.45	852.25	3.80	0.6131
	245	1321.27	4.17	468.28	0.37	852.99	3.80	0.6136
	250	1341.58	4.09	486.86	0.30	854.72	3.79	0.6148
	255	1361.48	4.01	506.02	0.22	855.46	3.78	0.6154
	260	1380.98	3.93	524.04	0.16	856.94	3.77	0.6164
	265	1400.08	3.85	541.17	0.05	858.91	3.76	0.6179
	270	1418.80	3.77	557.91	0.05	860.89	3.75	0.6193
$Q_{1\infty} = -1964.989$ mJ, $Q_{2\infty} = -574.848$ mJ, $Q_{3\infty} = -1390.141$ mJ								
300.15	1150	1002.09	1.13	201.35	0.74	800.74	0.39	0.9694
	1175	1038.27	1.01	235.47	0.65	802.80	0.36	0.9719
	1200	1083.82	0.91	279.65	0.56	804.18	0.35	0.9736
	1225	1124.76	0.81	319.49	0.47	805.27	0.34	0.9749
	1250	1174.68	0.74	367.89	0.42	806.78	0.32	0.9767
	1275	1191.73	0.66	384.26	0.35	807.47	0.31	0.9776
	1300	1222.87	0.58	415.13	0.27	807.74	0.31	0.9779
	1325	1241.78	0.49	432.53	0.20	809.26	0.29	0.9797
$Q_{1\infty} = -1293.225$ mJ, $Q_{2\infty} = -467.219$ mJ, $Q_{3\infty} = -826.006$ mJ								

The experimental results in Table 2 were 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} , 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 different temperature are shown in Table 2.

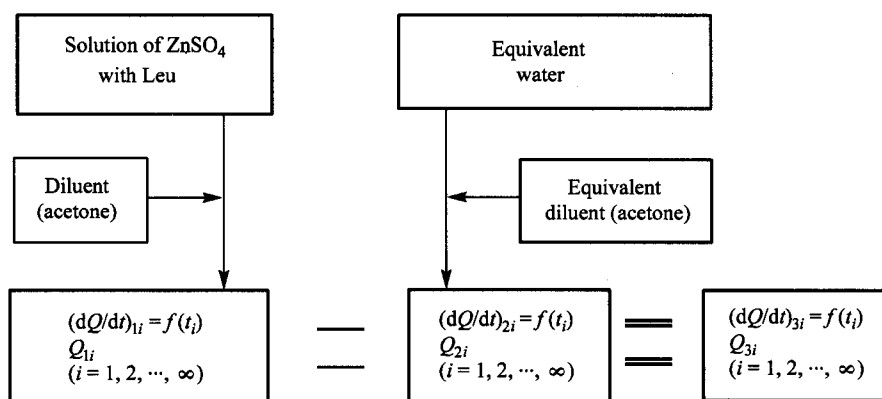


Fig. 3 Block diagram of the process of studying dilution/crystallization kinetics.

Table 2 Experimental results of the dilution/crystallization kinetics at different temperatures

T (K)	Solute (g)	Solvent (g)	Diluent (g)	$-Q_{\infty}$ ($J \cdot g^{-1}$)	$\frac{dQ}{dt} = k_2 \left(1 - \frac{Q}{Q_{\infty}}\right) + a$			$\frac{dm}{dt} = k_1(C - C_{\infty}) + b$	
					$k_2 \times 10^3$ ($J \cdot s^{-1}$)	$a \times 10^4$ ($J \cdot s^{-1}$)	r	$k_1 \times 10^3$ (s^{-1})	$b \times 10^5$ ($g \cdot s^{-1}$)
293.15	Zn(Leu)SO ₄ ·0.5H ₂ O (0.0905)	H ₂ O (0.2991)	C ₃ H ₆ O (1.1850)	36.8	7.50	-1.00	0.999	0.410	-0.27
				36.2	7.44	5.00	0.995	0.414	1.38
				36.8	7.49	6.00	0.998	0.410	1.63
				36.5	7.52	4.00	0.989	0.415	1.10
				36.7	7.48	7.00	0.990	0.410	1.91
				36.4	7.43	-5.00	0.996	0.411	-1.37
				mean	36.6	7.48	2.67	0.996	0.412
295.15				25.9	8.10	7.00	0.995	0.630	2.70
				25.6	8.05	6.00	0.998	0.633	2.34
				25.8	8.11	2.00	0.999	0.633	0.78
				25.9	8.12	4.00	0.994	0.631	1.54
				25.7	8.07	5.00	0.992	0.632	1.95
				26.0	8.13	-1.00	0.990	0.630	-0.38
				mean	25.8	8.97	3.83	0.994	0.632
298.15				17.1	8.80	4.00	0.994	1.04	2.34
				17.5	8.84	3.60	0.99	1.02	2.06
				17.4	8.81	2.00	0.99	1.02	1.15
				17.6	8.79	3.80	0.98	1.01	2.16
				17.6	8.82	5.00	0.99	1.01	2.84
				17.0	8.85	4.40	0.99	1.05	2.59
				mean	17.4	8.82	3.80	0.994	1.02
300.15				10.1	9.40	1.00	0.996	1.87	0.99
				10.0	9.38	5.00	0.995	1.89	5.00
				9.9	9.37	2.00	0.998	1.91	2.02
				9.5	9.41	5.00	0.997	1.99	5.26
				9.8	9.43	4.00	0.995	1.94	4.08
				10.2	9.40	4.00	0.989	1.86	3.92
				mean	9.92	9.40	3.50	0.994	1.91

Q_{∞} , Total heat produced ($J \cdot g^{-1}$); dQ/dt , rate of heat production at time t ($J \cdot s^{-1}$); k_2 , rate constant of crystal growth ($J \cdot s^{-1}$); Q , heat production at time t (J); a , constant of BCF ($J \cdot s^{-1}$); dm/dt , rate of crystal growth at time t ($g \cdot s^{-1}$); 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 ($g \cdot s^{-1}$).

Because the values of the constants a and b were small as compared with those of k_2 and k_1 , the kinetics of the crystal growth process of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ could be expressed by Eqs. (1) and (2), which indicated that the crystal growth process of $\text{Zn}(\text{Leu})\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$ accorded with the BCF dislocation theory model.

Finally, the kinetics parameters during the crystal growth process were calculated,¹³ which are summarized in Table 3.

Table 3 Kinetic parameters of the crystal growth process

T (K)	$k \times 10^3$ (s ⁻¹)	r	E (kJ·mol ⁻¹)	$\ln A$ (s ⁻¹)	r
293.15	7.50	0.999	23.16	4.61	0.997
295.15	8.10	0.995			
298.15	8.80	0.994			
300.15	9.40	0.996			

References

- Mohmoud, M.; Abdel-Monem, S.; Paul, M. *US 4 039 681*, **1977** [*Chem. Abstr.* **1977**, *87*, 157196].
- Taguohi, S.; Inokuchi, M.; Makajima, N.; Inomata, M.; Naitoh, Y. *WO 10 178*, **1992** [*Chem. Abstr.* **1992**, *117*, 258218].
- Harvey, H. A.; Ashmed, K. U. *US 4 830 716*, **1989** [*Chem. Abstr.* **1989**, *110*, 219070].
- Gao, S.-L.; Liu, J.-R.; Ji, M.; Yang, X.-W.; Zhang, F.-X.; Li, Z.-J. *Chin. Sci. Bull.* **1998**, *43*, 1527.
- Gao, S.-L.; Hou, Y.-D.; Liu, J.-R.; Chen, S.-P.; Ji, M.; Zhang, X.-Y. *Chemistry* **1999**, *11*, 30 (in Chinese).
- Yang, X.-W.; Zhang, X.-Y.; Gao, S.-L. *Acta Phys.-Chim. Sinica* **2000**, *16*, 850 (in Chinese).
- Gao, S.-L.; Zhang, X.-Y.; Yang, X.-W.; Ji, M.; Chen, S.-P.; Shi, Q.-Z. *Chemical Journal on Internet* **2000**, *2*, 12.
- Becker, R. *Discussions Faraday Soc.* **1949**, *5*, 55.
- Bransom, S. H.; Dunning, W. J.; Millard, B. *Discussions Faraday Soc.* **1949**, *5*, 83.
- Burton, W. K.; Cabrera, N.; Frank, F. C. *Transactions of the Royal Society of Tropical Medicine and Hygiene*, London, **1951**, *243*, 299.
- Chen, X.-J.; Li, Z.-B.; Hu, R.-Z. *Thermochim. Acta* **1995**, *260*, 243.
- Chen, X.-J.; Li, Z.-B.; Hu, R.-Z. *Thermochim. Acta* **1990**, *173*, 193.
- Gao, S.-L.; Chen, S.-P.; Hu, R.-Z.; Li, H.-Y.; Shi, Q.-Z. *Chin. J. Inorg. Chem.* **2002**, *18*, 362 (in Chinese).
- Ji, M.; Liu, M.-Y.; Gao, S.-L.; Shi, Q.-Z. *Instrum. Sci. Technol.* **2001**, *29*, 53.
- Kilday, M. V. *J. Res. Natl. Bur. Stand.* **1980**, *85*, 467.
- Hallman, P. S.; Perrin, D. D.; Watt Ann, E. J. *Biochemistry* **1971**, *121*, 54.

(E0208137 CHENG, B.; DONG, H. Z.)