研究简报

$Zn(AA)SO_4 \cdot H_2O$ (AA = Thr, Phe, Val, Met) 在水和丙酮混合溶剂中的结晶动力学研究

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The Crystallization Kinetics of $Zn(AA)SO_4 \cdot H_2O$ (AA = Thr, Phe, Val, Met) in Mixed Solvent of Water with Acetone

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The optimum volume ratio of $Zn(AA)SO_4 \cdot H_2O$ crystallizing from mixed solvent of water with acetone has been determined, which are 1:3, 1:9, 1:10, and 1:30 of water: acetone, respectively. The crystal growth processes of the compounds at 298.15K are investigated by microcalorimetry. The experimental results show that the processes are in accord with the Burton-Cabrera-Frank dislocation theory.

Keywords: **amino-acid zinc complexes** **mixed solvent** **crystallization kinetics** **microcalorimetry**

Zinc is a necessary life element in human body. *L*-α-amino acid is the basic unit of protein related with life. *L*-α-Thr(Threonine), *L*-α-Phe(Phenylalanine), *L*-α-Val(Valine) and *L*-α-Met(Methionine) are indispensable to life which have to be absorbed from food because they 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 solubilities of $ZnSO_4$-Thr/Phe/Val/Met-H_2O system at 298.15K have been investigated by semimicro-phase equilibrium method[6~9]. The phase diagrams are simple systems, in which the phase regions of $Zn(AA)SO_4 \cdot H_2O$ do not exist. The solid complexes of $Zn(AA)SO_4 \cdot H_2O$ have been prepared by adding acetone into the reaction solution of $ZnSO_4$ and AA (Thr, Phe, Val, Met) in literatures[6~9]. Obviously, the investigation on crystal growth processes of the complexes will provide important parameters for an understanding of the reaction mechanism and technology of synthesis.

In this paper, the kinetic equation of the crystal growth process is derived, and the optimum volume

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ratios of mixed solvent of water with acetone for $Zn(AA)SO_4 \cdot H_2O$ (AA = Thr, Phe, Val, Met) to crystallize from are determined. The total heat produced and the rate of heat production during the crystal growth process are measured using a RD496-Ⅲ type microcalorimeter. The kinetic parameters are calculated.

1 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)→	A(s)	+ heat
$t = 0$,	C_0	0	0
$t = t$,	C	m	Q
$t = \infty$,	C_∞	m_∞	Q_∞

where C is the solute concentration in the solution at time t; m is the mass of solid deposited during a certain time t; Q is the heat produced during a certain time. 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

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

and

$$\frac{C_\infty - C}{C_\infty - C_0} = \frac{m_\infty - m}{m_\infty} = \frac{Q_\infty - Q}{Q_\infty} \qquad (2)$$

From eqn. (1), we have

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

and

$$\frac{dm}{dt} = \left(\frac{m_\infty}{Q_\infty}\right)\frac{dQ}{dt} \qquad (3)$$

From eqn. (2), we obtain

$$C - C_\infty = (C_0 - C_\infty)\left(1 - \frac{Q}{Q_\infty}\right) \qquad (4)$$

According to the Burton-Cabrera-Frank (BCF) dislocation theory[10], for relatively high supersaturation, the rate of crystal growth at t time (dm/dt) may be expressed as

$$\frac{dm}{dt} = k_1 m_\infty (C - C_\infty) \qquad (5)$$

where k_1 is the rate constant of crystal growth.

The combination of eqns. (3), (4) and (5) gives

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

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

When $\left(\frac{dQ}{dt}\right)_i$ is plotted versus $\left(1 - \frac{Q}{Q_\infty}\right)_i$ by the least-squares method, giving the value of k_2 (slope) and a (intercept) in the equation (7)

$$\frac{dQ}{dt} = k_1 Q_\infty (C_0 - C_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a = k_2\left(1 - \frac{Q}{Q_\infty}\right) + a \qquad (7)$$

where

$$k_1 = \frac{k_2}{Q_\infty (C_0 - C_\infty)}$$

As $C_0 \gg C_\infty$

$$k_1 = \frac{k_2}{Q_\infty C_0} \qquad (8)$$

Equ. (8) relates k_1 to k_2.

The combination of eqns. (3), (4) and (7) gives

$$\frac{dm}{dt} = \left(\frac{m_\infty}{Q_\infty}\right)\frac{dQ}{dt} = \frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (C_0 - C_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a\right] = \frac{m_\infty}{Q_\infty}[k_1 Q_\infty (C - C_\infty) + a] = k_1 m_\infty (C - C_\infty) + \frac{a m_\infty}{Q_\infty} \qquad (9)$$

Similarly, eqn. (9) may be written as

$$\frac{dm}{dt} = k_1 m_\infty (C - C_\infty) + b \qquad (10)$$

where b is the intercept of eqn. (10).

Comparing eqns. (9) and (10), eqn. (11) is obtained

$$b = \frac{a m_\infty}{Q_\infty} \qquad (11)$$

If the values of the constants a and b are so 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 eqns. (5) and (6).

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

2 Experimental

2.1 Materials

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

2.2 Analysis Method

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

2.3 Experimental Method

The calorimetric experiment is performed using a RD496-Ⅲ type microcalorimeter[11] at (298.15 ± 0.005) K. The calorimetric constant is determined by Joule effect before experiment, which is (63.994 ± 0.042) $\mu V \cdot mW^{-1}$ at 298.15K. The enthalpies of solution in deionized water of KCl (spectral purity) is measured to be $(17.238 \pm 0.048) kJ \cdot mol^{-1}$, which is very close to $(17.241 \pm 0.018) kJ \cdot mol^{-1}$[12]. 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 a container of $15 cm^3$ (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 thermogram is recorded.

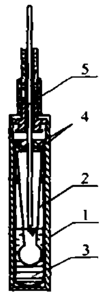

Fig. 1 Sketch used for the study of the formation reaction
1: calorimetric cell; 2: solution of $ZnSO_4$ with AA; 3: acetone; 4: silicone rubber cover; 5: glass rod.

3 Result and Discussion

3.1 Choice of the Volume Ratio of Water to Acetone in Mixed Solvent

$Zn(AA)^{2+}(aq)$ are produced from the reaction of $ZnSO_4$ with AA in water (the values of $\lg K$ are 4.43[13], 4.47[14], 4.44[15] and 4.40[15], respectively) but the solubility is too large 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, for 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 considerations, with the volume ratio of water: acetone of 1:3, 1:9, 1:10, 1:30, respectively, the white solid compound with the most yields are obtained. After suction filtration, followed by rinsing with a few of acetone and drying to constant weight. The yields of the compounds are 86%, 90%, 73% and 95%, respectively. The results of components analyses indicate that the product is identified as $Zn(AA)SO_4 \cdot H_2O$ in comparison with literatures[6-9]. The experimental results of variable volume ratios of water to acetone are shown in Table 1.

3.2 Dilution/Crystallization Kinetics

Adding acetone into the reaction solution system of $ZnSO_4$-AA, the crystallization processes begin.

$$ZnSO_4 \cdot 7H_2O(s) + AA(aq) \rightarrow Zn(AA)^{2+}(aq) + SO_4^{2-}(aq) + 7H_2O(l) \quad (12)$$

$$Zn(AA)^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l) \xrightarrow{\text{acetone}} Zn(AA)SO_4 \cdot H_2O \quad (13)$$

The typical schematic thermograms during the dilution and crystallization are depicted in Fig. 2. The original data obtained from the thermokinetical curve are shown in Table 2. Using the above data, the kinetic data during the dilution/crystallization process

Table 1 Experimental Results of Water and Acetone with the Different Volume Ratios

AA	experimental results							
Thr	volume ratio	1:1	1:2	1:3	1:4	1:10	1:20	1:30
	phenomena	turbid	turbid	gelationus precipitate	gelationus precipitate	amount of precipitate decreasing gradually		
	yield/%	—	—	86	86	80	68	54
Phe	volume ratio	1:1	1:3	1:5	1:7	1:9	1:11	1:13
	phenomena	turbid	turbid	turbid increasing	precipitate formed	mass precipitate	mass precipitate	precipitate decreasing gradually
	yield/%	—	—	—	82	90	88	86
Val	volume ratio	1:2	1:4	1:6	1:8	1:10	1:12	1:14
	phenomena	turbid	turbid	precipitate formed	amount of precipitate increasing	mass precipitate	amount of precipitate decreasing gradually	
	yield/%	—	—	—	61	73	68	51
Met	volume ratio	1:5	1:10	1:15	1:20	1:25	1:30	1:35
	phenomena	turbid	turbid	turbid increasing	precipitate formed	amount of precipitate increasing	mass precipitate	amount of precipitate decreasing
	yield/%	—	—	—	62	90	95	91

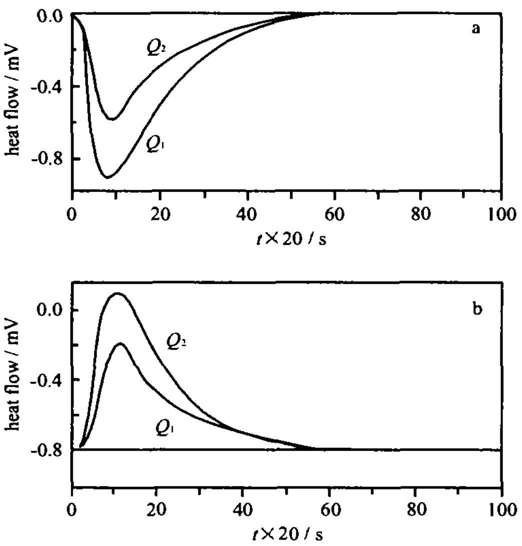

Fig. 2 Typical thermokinetical graph of the dilution/crystallization process
a. Thr; b. Phe, Val and Met

can be obtained from equations (**7**), (**8**) and (**11**) (Table 3).

The experimental results in Table 3 are obtained based on the principle presented according to a block diagram in Fig. 3. In Fig. 3, $(\mathrm{d}Q/\mathrm{d}t)_{1i}$ is the rate of total heat production at time t, including $(\mathrm{d}Q/\mathrm{d}t)_{2i}$, the rate of the heat production of mixing between solvent and diluent at time t, and $(\mathrm{d}Q/\mathrm{d}t)_{3i}$, the rate of

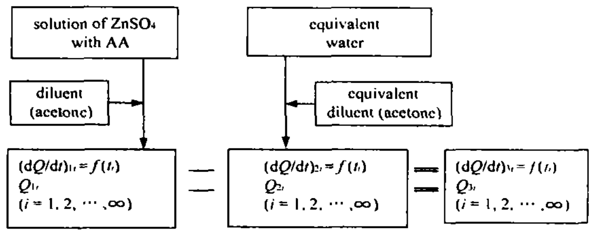

Fig. 3 Block diagram of the process of studying dilution/crystallization kinetics

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 298.15K are shown in Table 3.

Because the values of the constants a and b are enough small in comparison with those of k_2 and k_1, the kinetics of the crystal growth process of $Zn(AA)SO_4 \cdot H_2O$ can be expressed by eqns. (**5**) and (**6**). This fact indicates that the crystal growth processes of $Zn(AA)SO_4 \cdot H_2O$ are in accord with the BCF dislocation theory model.

Table 2　Thermokinetical Data of the Titled Reaction

AA	t/s	total reaction process		dilution process		crystallization process		
		$Q_{1,t}$/mJ	$(dQ/dt)_{1,t}\cdot 10^3/(J\cdot s^{-1})$	$Q_{2,t}$/mJ	$(dQ/dt)_{2,t}\cdot 10^3/(J\cdot s^{-1})$	$Q_{3,t}$/mJ	$(dQ/dt)_{3,t}\cdot 10^4/(J\cdot s^{-1})$	$Q_{3,t}/Q_{3\infty}$
Thr	365	6358.26	1.3541	3536.17	1.2209	2822.09	1.332	0.8534
	370	6430.56	1.3497	3598.03	1.2192	2832.53	1.305	0.8565
	375	6501.40	1.3447	3659.80	1.2165	2841.60	1.282	0.8593
	380	6570.90	1.3390	3721.39	1.2128	2849.51	1.262	0.8617
	385	6638.97	1.3337	3782.79	1.2092	2856.18	1.245	0.8637
	390	6705.69	1.3296	3844.04	1.2065	2861.65	1.231	0.8653
	395	6771.11	1.3254	3905.15	1.2034	2865.96	1.220	0.8666
	400	6835.19	1.3209	3966.09	1.1996	2869.10	1.212	0.8676
	$Q_{1\infty}$ = −13814.14mJ, $Q_{2\infty}$ = −10507.16mJ, $Q_{3\infty}$ = −3306.98mJ							
Phe	620	3795.91	4.84	5386.55	5.05	−1590.64	−4.94	0.942
	630	3823.86	4.69	5427.43	4.94	−1603.57	−4.55	0.950
	640	3852.81	4.55	5467.24	4.84	−1614.43	−4.22	0.956
	650	3882.81	4.41	5506.03	4.74	−1623.22	−3.95	0.962
	660	3908.71	4.28	5543.83	4.64	−1635.12	−3.59	0.969
	670	3935.22	4.15	5580.68	4.55	−1645.46	−3.28	0.975
	680	3958.76	4.04	5616.63	4.46	−1657.87	−2.91	0.982
	690	3980.38	3.92	5651.70	4.38	−1671.32	−2.50	0.990
	700	4002.75	3.80	5685.96	4.30	−1683.21	−2.14	0.997
	$Q_{1\infty}$ = 16894.82mJ, $Q_{2\infty}$ = 18582.69mJ, $Q_{3\infty}$ = −1687.87mJ							
Val	150	1624.91	16.56	3810.29	22.45	2185.38	5.90	0.4025
	160	1792.22	16.59	4045.13	22.36	2252.91	5.78	0.4149
	170	1959.57	16.57	4279.84	22.22	2320.27	5.66	0.4273
	180	2126.43	16.50	4505.43	22.05	2379.01	5.55	0.4381
	190	2292.37	16.38	4721.98	21.84	2429.62	5.46	0.4474
	200	2456.97	16.23	4929.55	21.61	2472.58	5.38	0.4554
	210	2619.86	16.04	5128.57	21.36	2508.71	5.32	0.4620
	220	2780.68	15.82	5319.29	21.08	2538.61	5.27	0.4675
	230	2939.17	15.57	5501.99	20.80	2562.82	5.22	0.4720
	240	3095.11	15.31	5676.98	20.50	2581.87	5.19	0.4755
	250	3248.26	15.02	5844.56	20.18	2596.30	5.16	0.4781
	$Q_{1\infty}$ = 15494.524mJ, $Q_{2\infty}$ = 20924.576mJ, $Q_{3\infty}$ = −5430.052mJ							
Met	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
	$Q_{1\infty}$ = 17769.97mJ, $Q_{2\infty}$ = 22292.64mJ, $Q_{3\infty}$ = −4522.67mJ							

Table 3 Experimental Results of the Dilution/Crystallization Kinetics

AA	solute/g	solvent/g	diluent/g	$-Q_\infty$ /(J·g^{-1})	$\frac{dQ}{dt}=k_2\left(1-\frac{Q}{Q_\infty}\right)+a$			$\frac{dm}{dt}=k_1 m_\infty (C-C_\infty)+b$	
					$k_2\cdot10^3$/(J·s^{-1})	$a\cdot10^4$/(J·s^{-1})	r	$k_1\cdot10^3$/s^{-1}	$b\cdot10^7$/(J·s^{-1})
Thr	Zn(Thr)$SO_4\cdot H_2O$	H_2O	C_2H_6O	258	8.4	1	0.99	2.87	3.88
	(0.0149)	(0.4990)	(1.1850)	255	8.36	2	0.99	2.86	7.84
				264	8.45	3.5	0.98	2.89	1.33
				260	8.41	2.7	0.97	2.87	1.04
				250	8.39	4.1	0.99	2.87	1.64
				251	8.47	1.5	0.98	2.89	5.98
			mean	256	8.41	2.47		2.88	3.62
Phe	Zn(Phe)$SO_4\cdot H_2O$	H_2O	C_2H_6O	272	5.1	2	0.998	7.09	7.35
	(0.0069)	(0.1994)	(1.4200)	268	5	2.5	0.997	7.05	9.33
				269	5.3	1.8	0.999	7.45	6.69
				270	5.6	2.8	0.998	7.84	10.37
				275	5.5	1.9	0.995	7.56	6.91
				272	4.9	2.4	0.997	6.81	8.82
			mean	271	5.23	2.23		7.3	8.25
Val	Zn(Val)$SO_4\cdot H_2O$	H_2O	C_2H_6O	1261	9.7	1	0.99	5.39	0.93
	(0.0059)	(0.1994)	(1.5800)	1264	9.75	1.5	0.99	5.4	1.19
				1259	9.72	2	0.99	5.41	1.59
				1266	9.69	4	0.97	5.36	3.16
				1258	9.68	3.7	0.98	5.39	2.94
				1260	9.74	2.6	0.99	5.41	2.06
			mean	1261	9.71	2.47		5.39	1.98
Met	Zn(Met)$SO_4\cdot H_2O$	H_2O	C_3H_6O	1443	6.8	5	0.999	11.25	3.47
	(0.0033)	(0.0997)	(2.3700)	1440	6.79	4.5	0.997	11.26	3.13
				1450	6.77	5.2	0.997	11.15	3.59
				1447	6.82	5.3	0.998	11.25	3.66
				1444	6.8	4.7	0.995	11.24	4.71
				1449	6.75	4.4	0.999	11.12	3.04
			mean	1446	6.79	4.85		11.21	3.6

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 a certain time/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}; , total mass of solid deposited/g; C, solute concentration in the solution (g/100g solvent); , equilibrium saturation concentration (g/100g solvent); b, constant of BCF/(g·s^{-1}).

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