Investigation of the Crystallization Kinetics of $Zn(Thr)Ac_2 \cdot 2H_2O$ by Microcalorimetry

S. CHEN, Y. REN, SH. GAO*, R. ZU, and Q. SHI

Department of Chemistry, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an, 710069, P. R. China
e-mail: gaoshli@nwu.edu.cn

Received 2 September 2003

The crystal growth process of $Zn(Thr)Ac_2 \cdot 2H_2O$ 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 298.15 K, 301.15 K, 304.15 K, and 307.15 K were measured. On the basis of experimental and calculated results, the thermodynamic parameters (the apparent activation enthalpy, the activation entropy, and the activation Gibbs energy), the rate constant, and the kinetic parameters (the activation energy, the pre-exponential factor) during the crystal growth process were obtained. The results showed that the crystal process was in accord with the Burton—Cabrera—Frank dislocation theory.

Zinc is an essential trace element in living systems. α-Amino acid group is the basic unit of proteins related with life. L-α-Threonine (Thr) is one of the eight sorts of amino acids indispensable for life which has to be absorbed from the diet because it cannot be synthesized in the human body. The complexes of zinc salts with α-amino acid as additive have a wide application in medicine, foodstuff industry, and cosmetics [1—3]. The synthesis methods of the complexes of zinc salts with α-amino acid have been reviewed [4—6]. The solubility of the $ZnAc_2$—Thr—H_2O system at 298.15 K has been investigated by the semimicrophase equilibrium method [7]. The phase diagram is a simple one, in which the phase region of the new compound $Zn(Thr)Ac_2 \cdot 2H_2O$ does not exist, in other words, the solid complex $Zn(Thr)Ac_2 \cdot 2H_2O$ cannot be prepared from a solution of $ZnAc_2$ and Thr in water. Obviously, how to crystallize solid $Zn(Thr)Ac_2 \cdot 2H_2O$ from the solution is the main concern.

The crystal growth process from supersaturated solution or mixed solvent was investigated by *Becker* [8] and *Bransom* [9], and the dislocation theory model (BCF theory) of crystal growth was applied successfully [10]. The crystallization kinetics for cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) has been investigated with a microcalorimeter by *Chen Xi-jun* and others [11, 12].

In the present work, the crystal growth process of $Zn(Thr)Ac_2 \cdot 2H_2O$ from the mixed solvent of water and acetone was experimentally designed and preformed. Based on calorimetry and the Burton—Cabrera—Frank (BCF) dislocation theory, the kinetic model of the crystal growth from solution has been derived. The heat produced and the rates of heat production during the process at different temperatures were measured by microcalorimetry. The thermodynamic parameters, the rate constant, and other kinetic parameters related with the crystal growth process of $Zn(Thr)Ac_2 \cdot 2H_2O$ were calculated.

THEORETICAL

As known, the value of the heat change, ΔQ, at time t can be determined experimentally by measuring the heat flow accompanying a process with a microcalorimeter. That is, a microcalorimeter allows the gains of $\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_t$ and $\left(1 - \frac{Q}{Q_\infty}\right)_t$ at time t. A linear regression of the variables $\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_t$ and $\left(1 - \frac{Q}{Q_\infty}\right)_t$ results in k_2 (slope) and a (intercept), as shown in eqns (*1*) and (*2*). Q is heat production at time t, Q_∞ total heat produced, and $\mathrm{d}Q/\mathrm{d}t$ rate of heat production at time t.

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_2 \left(1 - \frac{Q}{Q_\infty}\right) + a \qquad (1)$$

Eqn (*1*) transforms as eqn (*2*)

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

*The author to whom the correspondence should be addressed.

$$= k_2 \left(1 - \frac{Q}{Q_\infty}\right) + a \qquad (2)$$

Substituting $\frac{m}{m_\infty} = \frac{Q}{Q_\infty}$ into eqn (*2*) gives eqn (*3*)

$$\begin{aligned}\frac{\mathrm{d}m}{\mathrm{d}t} &= \left(\frac{m_\infty}{Q_\infty}\right)\frac{\mathrm{d}Q}{\mathrm{d}t} = \\ &= \frac{m_\infty}{Q_\infty}\left[k_1 Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) + a\right] = \\ &= \frac{m_\infty}{Q_\infty}[k_1 Q_\infty (c - c_\infty) + a] = \\ &= k_1 m_\infty (c - c_\infty) + \frac{a m_\infty}{Q_\infty} \qquad (3)\end{aligned}$$

where $\mathrm{d}m/\mathrm{d}t$ is the rate of crystal growth at time t, m_∞ total mass of solid deposited, c solute mass in 100 g solution, and c_∞ equilibrium saturation mass in 100 g solvent.

According to 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

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k_1' m_\infty (c - c_\infty) \qquad (4)$$

where k_1' is the rate constant of crystal growth.

The energy change brought about by the reaction progress, see eqn (*4*), is given in eqn (*5*) where $k_2' = k_1' Q_\infty (c_0 - c_\infty)$ [12, 13].

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1' Q_\infty (c_0 - c_\infty)\left(1 - \frac{Q}{Q_\infty}\right) = k_2'\left(1 - \frac{Q}{Q_\infty}\right) \qquad (5)$$

If $c_0 \gg c_\infty$, from eqn (*5*) we get eqn (*6*), where $k_2' \approx k_1' Q_\infty c_0$.

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1' Q_\infty c_0 \left(1 - \frac{Q}{Q_\infty}\right) \approx k_2'\left(1 - \frac{Q}{Q_\infty}\right) \qquad (6)$$

Likewise, eqn (*4*) transforms as eqn (*7*)

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k_1 m_\infty (c - c_\infty) + b \qquad (7)$$

where b is the intercept of eqn (*5*).

Comparing eqns (*3*) with (*7*), eqn (*8*) is obtained.

$$b = \frac{a m_\infty}{Q_\infty} \qquad (8)$$

If 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 eqns (*4*) or (7).

From the experimental and calculated results, according to Ref. [13], three thermodynamic parameters (the activation enthalpy, $\Delta H^{\neq\circ}$, activation entropy, $\Delta S^{\neq\circ}$, and activation Gibbs energy, $\Delta G^{\neq\circ}$), the rate constant, k, three kinetic parameters (the activation energy, E, the pre-exponential constant, A, and the reaction order, n) are obtained.

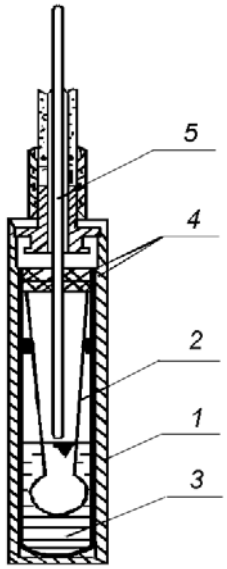

Fig. 1. Schematic diagram of the sample cell. *1.* Calorimetric cell, *2.* solution of $ZnAc_2$ with Thr, *3.* acetone, *4.* silicone rubber cover, *5.* glass rod.

EXPERIMENTAL

$ZnAc_2 \cdot 2H_2O$ was of anal. grade and made in Xi'an Chemical Company. L-α-Thr was of B. R., and purchased from Shanghai Kangda Company, with purity greater than 99.9 %. C_3H_6O was of anal. grade purchased from Xi'an Chemical Company. The conductivity of the deionized water was 5.48×10^{-8} S cm^{-1} and its density was 0.99705 g cm^{-3} at 298.15 K. The other materials, anal. grade, were commercially available and used as purchased.

Zn^{2+} was determined with EDTA by complexometric titration. Thr was analyzed by the formaldehyde method after Zn^{2+} was removed by precipitating with $K_2C_2O_4$. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin—Elmer 2400 type elemental analyzer.

The calorimetric experiment was performed using an RD496-III type microcalorimeter (Southwest Institute of Electronic Engineering, China) [14]. The microcalorimeter was calibrated by Joule effect before each experiment and the following sensitivities were obtained: (63.994 ± 0.042) μV mW^{-1}, (64.190 ± 0.028) μV mW^{-1}, (64.299 ± 0.064) μV mW^{-1}, and (64.399 ± 0.072) μV mW^{-1}, at 298.15 K, 301.15 K, 304.15 K, and 307.15 K, respectively. The enthalpy of solution of KCl in deionized water (spectral 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 %, indicating that the calorimetric system was accurate and reliable. The schematic diagram of the sample cell is shown in Fig. 1. The reaction solution + solvent and the diluent were put into the adding tubes *2* and *3*,

Table 1. Thermokinetic Data of the Title Reaction at Different Temperatures

T	t	Total reaction process		Dilution process		Crystallization process		$Q_{3t}/Q_{\infty 3}$
		Q_{1t}	$(dQ/dt)_{1t} \cdot 10^3$	Q_{2t}	$(dQ/dt)_{2t} \cdot 10^3$	$-Q_{3t}$	$-(dQ/dt)_{3t} \cdot 10^3$	
K	s	mJ	J s^{-1}	mJ	J s^{-1}	mJ	J s^{-1}	
298.15	150	1624.17	11.30	1722.04	19.12	97.87	7.82	0.0578
	200	2125.73	8.90	2716.46	13.95	591.08	5.57	0.3488
	250	2511.42	6.78	3662.77	9.93	1151.35	3.15	0.6794
	300	2800.57	5.06	4034.93	7.70	1234.36	2.64	0.7284
	350	3011.88	3.72	4296.31	6.08	1284.43	2.35	0.7579
	400	3162.60	2.68	4578.92	4.56	1416.32	1.89	0.8358
	450	3266.27	1.89	4789.90	3.28	1523.63	1.39	0.8991
	500	3334.47	1.30	4943.58	2.28	1609.11	1.00	0.9495
	550	3378.17	0.95	5072.36	1.67	1694.20	0.72	0.9997
	600	3404.34	0.53	5097.30	0.99	1692.96	0.65	0.9990
	$Q_{1\infty}$ = 4606.02 mJ, $Q_{2\infty}$ = 6310.64 mJ, $Q_{3\infty}$ = −1694.63 mJ							
301.15	125	659.64	6.07	1219.78	11.58	560.15	5.52	0.4740
	150	803.27	5.61	1495.09	10.46	691.82	4.85	0.5854
	175	935.18	5.13	1740.28	9.29	805.10	4.16	0.6812
	200	1054.79	4.64	1957.63	8.16	902.85	3.52	0.7639
	225	1162.26	4.18	2145.28	7.07	983.02	2.90	0.8317
	250	1258.53	3.75	2309.77	6.09	1051.23	2.35	0.8894
	275	1344.72	3.36	2449.03	5.32	1104.31	1.95	0.9343
	300	1421.17	3.00	2573.21	4.63	1152.03	1.62	0.9748
	325	1489.49	2.70	2678.36	4.12	1188.87	1.42	1.0059
	350	1550.39	2.43	2776.34	3.67	1225.95	1.24	1.0373
	$Q_{1\infty}$ = 6921.66 mJ, $Q_{2\infty}$ = 8103.52 mJ, $Q_{3\infty}$ = −1181.87 mJ							
304.15	150	1329.50	10.27	1646.11	16.28	316.60	6.01	0.2399
	175	1576.88	9.38	1968.75	14.92	391.87	5.54	0.2970
	200	1800.25	8.42	2260.32	13.53	460.07	5.11	0.3486
	225	2001.40	7.58	2520.40	12.32	519.01	4.74	0.3933
	250	2181.84	6.80	2747.98	11.23	566.14	4.44	0.4290
	275	2343.25	6.05	2948.51	10.24	605.25	4.19	0.4587
	300	2837.18	3.96	3532.73	7.59	695.55	3.63	0.5271
	325	2932.34	3.60	3648.05	7.10	715.71	3.50	0.5424
	350	3018.73	3.29	3757.18	6.65	738.44	3.36	0.5596
	375	3098.33	3.05	3851.39	6.31	753.06	3.26	0.5707
	400	3071.89	2.81	3941.67	5.97	769.77	3.16	0.5833
	500	3240.47	2.70	4019.22	5.80	778.76	3.10	0.5901
	525	3310.85	2.90	4098.87	5.94	788.03	3.04	0.5972
	$Q_{1\infty}$ = 7293.75 mJ, $Q_{2\infty}$ = 8513.36 mJ, $Q_{3\infty}$ = −1319.61 mJ							
307.15	100	1434.29	19.72	1445.98	28.10	11.69	8.38	0.0137
	125	1917.65	18.57	1962.05	26.62	44.40	8.05	0.0521
	150	2364.55	16.96	2453.73	24.55	89.18	7.59	0.1046
	175	2769.96	15.29	2909.57	22.37	139.61	7.08	0.1637
	200	3134.49	13.70	3325.65	20.25	191.15	6.55	0.2242
	225	3460.95	12.31	3701.31	18.36	240.37	6.05	0.2819
	250	3754.05	11.06	4037.69	16.67	283.64	5.61	0.3327
	275	4018.33	10.03	4338.03	15.56	319.70	5.24	0.3750
	300	4257.66	9.13	4605.33	14.09	347.68	4.95	0.4078
	325	4475.49	8.31	4842.74	13.07	367.25	4.75	0.4307
	350	4675.47	7.67	5053.88	12.30	378.41	4.64	0.4438
	375	4860.22	7.11	5241.77	11.72	381.55	4.61	0.4475
	$Q_{1\infty}$ = 8697.50 mJ, $Q_{2\infty}$ = 9550.12 mJ, $Q_{3\infty}$ = −852.61 mJ							

separately. After equilibrium, the bottom of the tube *2* was broken on depressing the rod. As a result, the two liquids were mixed and the thermogram was recorded.

RESULTS AND DISCUSSION

$Zn(Thr)^{2+}$ (aq) is produced from the reaction of $ZnAc_2 \cdot 2H_2O$ with Thr in water (lg K is 4.43) [16]. The solubility is too great to obtain the solid complex. By adding acetone to the system to decrease the solubility of the complex, the solid complex could be prepared. In the phase diagram, the phase region of the acid is reduced and separates from the phase region of salt, and the phase region of the complex is formed. Based on the above consideration, with the optional volume ratio of water to acetone of 1:9, the white solid compound is obtained, wherein variation in the yield of $Zn(Thr)Ac_2 \cdot 2H_2O$ as a function of the

Table 2. The Experimental Results of the Dilution/Crystallization Kinetics at Different Temperatures

T/K	m(Solute) / g	m(Solvent) / g	m(Diluent) / g	$-Q_\infty$ / J g^{-1}	$\frac{dQ}{dt} = k_2\left(1-\frac{Q}{Q_\infty}\right)+a$: $k_2 \cdot 10^3$ / J s^{-1}	$a \cdot 10^4$ / J s^{-1}	r	$\frac{dm}{dt} = k_1(c-c_\infty)+b$: $k_1 \cdot 10^2$ / g s^{-1}	$b \cdot 10^7$ / g s^{-1}
298.15	$Zn(Met)Ac_2 \cdot H_2O$	H_2O	C_3H_6O	1466.0	7.60	6.00	0.999	1.07	4.09
	(0.00701)	(0.0997)	(1.9800)	1463.0	7.50	2.00	0.990	1.06	1.36
				1465.0	7.20	5.00	0.970	1.02	3.41
				1468.0	7.90	2.20	0.990	1.11	1.50
				1467.0	7.80	9.00	0.980	1.10	6.14
				1467.0	7.70	11.00	0.990	1.08	7.50
			Mean	1466.0	7.62	5.87		1.07	4.00
301.15				1022.0	8.00	15.00	0.998	1.62	14.70
				1020.0	7.92	5.00	0.998	1.60	4.90
				1018.0	7.86	1.00	0.999	1.59	0.98
				1015.0	7.68	12.00	0.995	1.55	11.80
				1026.0	8.59	11.00	0.997	1.74	10.70
				1031.0	8.50	26.00	0.999	1.72	25.20
			Mean	1022.0	8.09	11.67		1.64	11.40
304.15				1142.0	8.30	3.00	0.999	1.50	2.63
				1140.0	8.10	1.00	0.997	1.64	0.88
				1138.0	8.00	3.00	0.999	1.62	2.64
				1143.0	8.40	12.00	0.989	1.70	10.50
				1145.0	8.50	16.00	0.999	1.72	14.00
				1144.0	7.90	8.00	0.980	2.21	6.99
			Mean	1142.0	8.20	2.17		1.66	1.90
307.15				738.0	8.70	2.00	0.990	2.44	2.71
				740.0	8.80	1.00	0.998	2.47	1.35
				735.0	8.30	9.00	0.999	2.33	12.20
				739.0	8.20	1.30	0.998	2.30	1.76
				741.0	9.00	6.00	0.995	2.52	8.10
				741.0	8.90	1.00	0.999	2.49	1.35
			Mean	739.0	8.65	3.38		2.42	4.58

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 mass in 100 g solution (g);c_∞ – equilibrium saturation mass in 100 g solvent (g); b – constant of BCF (g s^{-1}).

volume ratio of acetone to water is depicted in Fig. 2. After suction filtration, followed by rinsing with a few drops of acetone and drying to constant mass in vacuum, the white powder is obtained. The compound is soluble in water, but insoluble in alcohol, acetone, and other organic solvents. The yield of the compound is 34 %. The elemental analyses results are w_i(found): 19.62 % Zn, 35.35 % Thr, 28.08 % C, 5.31% H, and 4.12 % N, which shows the compound is $Zn(Thr)Ac_2 \cdot 2H_2O$ compared with the calculated values w_i(calc.): 19.31 % Zn, 35.18 % Thr, 28.38 % C, 5.66 % H, and 4.14 % N. The experimental result on variable volume ratio of water to acetone is depicted in Fig. 2.

The crystal process is expressed in reactions (A) and (B).

$$ZnAc_2 \cdot 2H_2O(s) + Thr(aq) \rightarrow \rightarrow Zn(Thr)^{2+}(aq) + 2Ac^-(aq) + 2H_2O(l) \qquad (A)$$

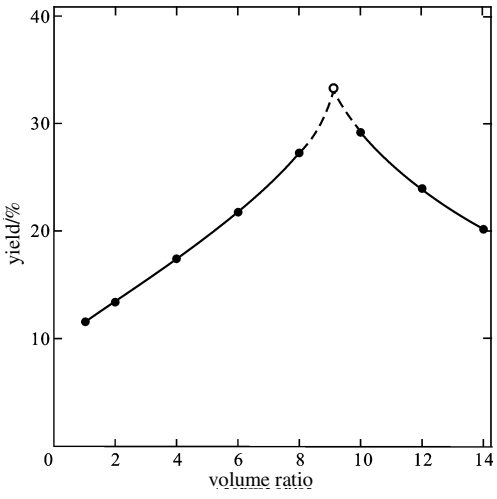

Fig. 2. Variation in the yield of $Zn(Thr)Ac_2 \cdot 2H_2O$ as a function of the volume ratio V(acetone) : V(water).

Table 3. Kinetic and Thermodynamic Parameters of the Title Reaction

T/K	$k \cdot 10^2$ / s^{-1}	r	E / kJ mol^{-1}	$\ln(A/s^{-1})$	r	$\Delta G^{\neq\circ}$ / kJ mol^{-1}	$\Delta H^{\neq\circ}$ / kJ mol^{-1}	$\Delta S^{\neq\circ}$ / J mol^{-1}	r
298.15	7.60	0.999	11.23	1.95	0.997	−79.41	8.71	−237.10	0.990
301.15	8.00	0.996				−79.31			
304.15	8.30	0.999				−79.24			
307.15	8.70	0.999				−79.15			

r – the linear correlation coefficient.

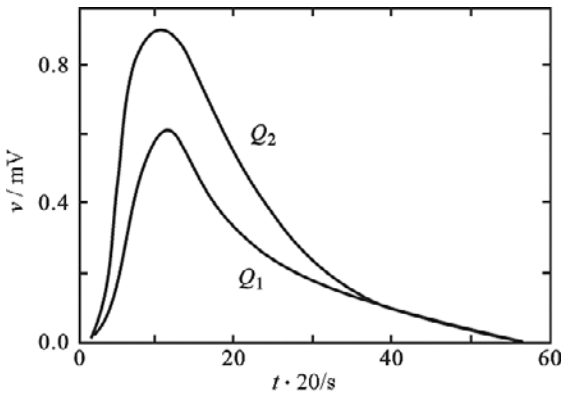

Fig. 3. Typical thermogram of the dilution/crystallization process.

$$Zn(Thr)^{2+}(aq) + 2Ac^{-}(aq) + 2H_2O(l) \xrightarrow{\text{acetone}} \xrightarrow{\text{acetone}} Zn(Thr)Ac_2 \cdot 2H_2O(s) \qquad (B)$$

A typical schematic thermogram during the dilution and crystallization is depicted in Fig. 3. The original data obtained from the TK curve are shown in Table 1. Following from those data, the kinetic data during the dilution/crystallization process can be obtained from eqns (*2*) and (*6*), and are shown in Table 1.

The experimental results of the dilution/crystallization kinetics over the temperature range 298.15—307.15 K are presented in Table 2, where $(dQ/dt)_{1t}$ is the rate of total heat production at time t, including $(dQ/dt)_{2t}$ – the rate of the heat of mixing produced between solvent and diluent at time t, and $(dQ/dt)_{3t}$ the rate of the heat of crystallization of the crystal at time t. Q_{1t} is the total heat produced during a certain time including Q_{2t}, Q_{2t} the heat of mixing produced between solvent and diluent during a certain time and Q_{3t} the heat of crystallization of the crystal during a certain time.

Because the values of the constants a and b are small in comparison with those of k_2 and k_1, the kinetics of the crystal growth process of $Zn(Thr)Ac_2 \cdot 2H_2O$ can be expressed by eqns (*4*) and (*5*) or (*7*). So, the crystal growth process of $Zn(Thr)Ac_2 \cdot 2H_2O$ is in accord with the BCF dislocation theory model.

Finally, the kinetic and the thermodynamic parameters during the crystal growth process were calculated according to Ref. [13] and they are summarized in Table 3. It is evident that the rate of reaction increases with increasing temperature and the reaction is of the first order when the values of E and $\Delta H^{\neq\circ}$ are very low and $\Delta S^{\neq\circ}$ is high, which shows that the complexation reaction is spontaneous over the temperature range 298.15—307.15 K.

Acknowledgements. We thank the National Science Foundation of China (No. 29871023 and 20171036) for financial support.

REFERENCES

1. Mahmoud, M., Abdel-Monem, S., and Paul, M., *U.S.* 4093681 (1977).
2. Taguohi, S., Inokuchi, M., and Makajima, N., *W.O.* 10178 (1992).
3. Harvey, H. A. and Ashmed, K. U., *U.S.* 4830716 (1989).
4. Gao, Sh., Liu, J., Ji, M., Yang, X., Zhang, F., and Li, Zh., *Chin. Sci. Bull. 43*, 1527 (1998).
5. Gao, Sh., Guo, L., Zhang, F., and Ma, Y., *J. Chin. Phys. Chem. 17*, 573 (2001).
6. Fan, Ch., Ma, Sh., Guo, D., and Chen, J., *Chem. J. Chin. Univ. 7*, 546 (1986).
7. Guo, L., Zhang, F., Tang, X., and Gao, Sh., *J. Northwest Univ. (Nat. Sci. Edu.) 32*, 29 (2002).
8. Becker, R., *Discuss. Faraday Soc. 5*, 5 (1949).
9. Bransom, S. H., Dunning, W. J., and Millard, B., *Discuss. Faraday Soc. 5*, 83 (1949).
10. Burton, W. K., Cabrera, N., and Frank, F. C., *Trans. R. Soc. Trop. Med. Hyg.* (London) *243*, 299 (1951).
11. Chen, X., Li, Zh., and Hu, R., *Thermochim. Acta 260*, 243 (1995).
12. Chen, X., Li, Zh., and Hu, R., *Thermochim. Acta 173*, 193 (1990).
13. Gao, Sh., Chen, S., Hu, R., and Shi, Q., *Chin. Inorg. Chem. 18*, 362 (2002).
14. Ji, M., Liu, M., Gao, Sh., and Shi, Q., *Instrum. Sci. Technol. 29*, 53 (2001).
15. Martha, V. K., *Res. N. B. S. 85*, 467 (1980).
16. Hallman, P. S., Perrin, D. D., and Watt, A. E., *J. Biochem. 121*, 54 (1971).