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Thermochimica Acta 306 (1997) 7–12

thermochimica
acta

Calcium oxalate crystallization kinetics from calorimetric measurements

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Received 5 May 1997; accepted 20 August 1997

Abstract

The kinetics of calcium oxalate monohydrate precipitation effected by mixing aqueous solutions of calcium chloride and sodium oxalate together in the stoichiometric ratio at 25 and 37°C, were studied using an isoperibolic reaction twin calorimeter. A method for inferring the crystal growth kinetic parameters from experimental progress curve giving the time development of the integral heat evolved during the precipitation is suggested and verified. Results obtained for calcium oxalate monohydrate compare favourably with those obtained with conventional techniques for studying crystallization. © 1997 Elsevier Science B.V.

Keywords: Calcium oxalate; Crystallization kinetics; Isoperibolic reaction twin calorimeter

1. Introduction

Experimental techniques employed for studying kinetics of crystallization from aqueous solutions can be broadly divided into direct and indirect methods [1]. The direct methods, based on measurements performed on an isolated growing crystal, can be applied only to crystals exceeding a certain minimum size, say several hundreds of micrometers. Moreover, only a limited number of crystals can be studied by the direct methods and information thus obtained is hardly relevant to the industrially important mass crystallization. This type of crystallization, characterized by simultaneous growth of innumerable crystals in the system, can be studied by indirect methods based on determining the time development of a selected system property, such as solution concentration, conductivity, optical turbidity, crystal size distribution, heat evolved, etc. Calorimetry directly measures the integral heat evolved from the crystallization, the quantity that is related to the total mass of solid crystallized from the system. An isoperibolic reaction twin (hereinafter IRT) calorimeter providing compensation for additional heat effects due to dilution, stirring, heat losses, etc. represents a suitable and convenient technique for studying the crystallization kinetics [2].

This contribution presents a method of inferring the crystallization kinetics from data obtained with the IRT calorimeter. The procedure is demonstrated on calcium oxalate (hereinafter CaO*x*) crystallization, effected by mixing aqueous solutions of $CaCl_2$ and sodium oxalate together at 25 and 37°C.

2. Theoretical

Crystal growth rate, $\dot{r}$ (=d*r*/d*t* where *r* is the crystal radius), can be expressed as a function of actual

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PII S0040-6031(97)00274-8

driving force by an exponential function [1]

$$\dot{r} = k_g(c - c_{eq})^g \tag{1}$$

where k_g is the kinetic constant, g the order of crystal growth, and c and c_{eq} the actual and equilibrium concentration of crystallizing substance in the solution, respectively. The initial solution concentration, c_i, falls towards the equilibrium solubility of crystallizing substance, c_{eq}, over the time course of the batch precipitation which terminates when this solubility is reached. The integral heat, Q, released at batch crystallization is directly proportional to the amount of solute transferred into crystalline state over the same interval, i.e.

$$Q = Q_{mol}n = Q_{mol}V(c_i - c) \tag{2}$$

where Q_{mol} is the molar heat of crystallization, n the number of moles of substance transferred into crystalline state, and V the volume of crystallizing system. The total amount of heat, Q_∞, released from the batch crystallization onset to its completion is

$$Q_\infty = Q_{mol}n_\infty = Q_{mol}V(c_i - c_{eq}) \tag{3}$$

where n_∞ represents the moles of crystallizing substance in excess of equilibrium contained in a solution volume V. The actual size, r, that crystals reach at any time is determined by the amount of solute actually deposited on N crystals of initial size r_i present in a unit volume of the crystallizing system

$$n = k_v N\rho(r - r_i)^3/M_w \tag{4}$$

where k_v is the volume shape factor, ρ the solid density and M_w the molar weight. A similar expression holds for the final crystal size, r_∞, reached when the crystallization is complete. The following relation holds when number of particles, N, formed by nucleation at the process onset remains constant thereafter, i.e. the secondary nucleation is not significant, and all crystals grow with the same rate,

$$(r/r_\infty)^3 = n/n_\infty = Q/Q_\infty \tag{5}$$

Differentiating Eq. (5) with respect to time gives

$$\dot{r} = (r_\infty/3Q_\infty^{1/3}Q^{2/3})\dot{Q} \tag{6}$$

and combining this result with Eq. (1) yields

$$\dot{Q} = (3k_gQ_\infty^{1/3}Q^{2/3}/r_\infty)(c - c_{eq})^g \tag{7}$$

where $\dot{Q} = \mathrm{d}Q/\mathrm{d}t$ is the slope of the progress curve expressing the time development of the integral heat released during crystallization. At $Q = Q_\infty/3$, Eq. (7) becomes

$$\dot{Q}_{/Q=Q_\infty/3} = \frac{3^{1/3}k_gQ_\infty}{r_\infty}(c_x - c_{eq})^g \tag{8}$$

where c_x represents the solution concentration reached at the moment when the integral heat of crystallization reaches $Q_\infty/3$. At this point, one-third of the solute initially available for transfer into the crystalline state has been already crystallized, therefore, the following equations hold

$$(c_x - c_{eq}) = (2/3)(c_i - c_{eq}) \tag{9}$$

Combining Eqs. (3),(8) and (9) gives the final expression

$$\dot{Q}_{/Q=Q_\infty/3} = \frac{3^{1/3}k_gQ_{mol}V}{r_\infty}(2/3)^g(c_i - c_{eq})^{g+1} \tag{10}$$

Selection of a specific Q value ($Q_\infty/3$ in our case) at which $\dot{Q}$ is determined is quite arbitrary provided that nucleation in the system has already completely ceased at this stage.

In order to achieve a reliable estimate of the total released heat from IRT calorimeter, a theoretically substantiated function describing the progress curve should be used. Eliminating c from Eq. (2) gives

$$c_i - c_{eq} = (Q_\infty - Q)/(VQ_{mol}) \tag{11}$$

Combining Eqs. (1) and (11) yields

$$\dot{r} = k_g(Q_\infty - Q)^g/(V^gQ_{mol}^g) \tag{12}$$

Substituting

$$\dot{r} = \dot{n}V_m/A \tag{13}$$

where V_m is the solid molar volume and A the surface area of crystals present in a solution unit volume, and introducing

$$\mathrm{d}Q/\mathrm{d}t = Q_{mol}(\mathrm{d}n/\mathrm{d}t) \tag{14}$$

obtained by dividing Eqs. (2) and (3) and subsequent differentiation, into Eq. (12) provides

$$\dot{Q} = (k_g A/V_m V^g Q_{mol}^{g-1})(Q_\infty - Q)^g \qquad (15)$$

Integrating Eq. (15) for g = 2, assuming constant A yields

$$Q/Q_\infty = KQ_\infty t/(1 + KQ_\infty t) \qquad (16)$$

where

$$K = k_g A/V_m V^g Q_{mol}^{g-1} \qquad (17)$$

3. Experimental

Crystallization of CaO*x* was investigated using the IRT calorimeter shown in Fig. 1. Reaction and reference vessels of 200 ml volume (1) are situated in a thermally insulating block of polystyrene foam (2). This block is placed inside a water jacket (3) through which water of a constant temperature is circulated. The calorimeter body is constructed of a block of foam polystyrene (2). A vertically movable thermally insulating cover (4) contains mechanically coupled syringes (5), thermistors and stirrer (6). The whole calorimeter is situated in a constant temperature air box. Thermistors, inserted in the reference and reaction vessel, are connected to a differential resistance bridge with an amplifier and its voltage output is recorded as a function of time by a compensating recorder. Numerical values of actual voltage output are automatically recorded after every 1 s.

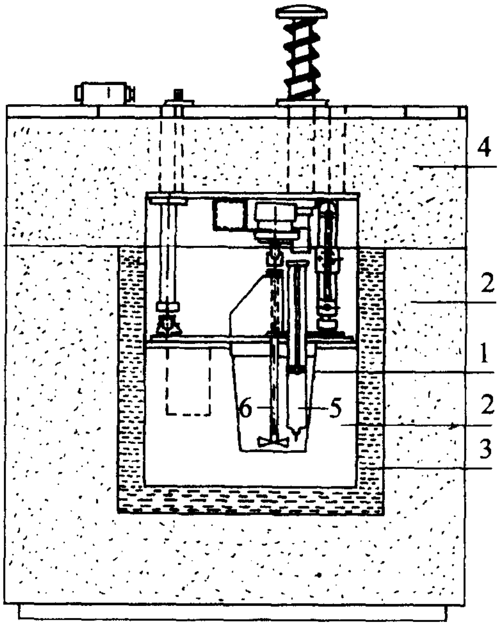

Fig. 1. A cross-section of IRT calorimeter.

The reference vessel containing 100 ml of water was placed. The reactant solution of 100 ml, placed in the reaction vessel, contained the required amount of $CaCl_2$. Then an amount of stock solution of sodium oxalate required for achieving the stoichiometric reaction conditions was added simultaneously into both the vessels through syringes to start the crystallization.

The chemicals used, of Analar grade, were dissolved in distilled water and the resulting stock solutions filtered through a membrane filter before use.

The IRT calorimeter and experimental procedures for its use are described in detail elsewhere [3].

The composition of solid was determined by X-ray diffraction.

4. Results

Crystallization of calcium oxalate, accomplished by mixing the solutions of $CaCl_2$ and sodium oxalate in a stoichiometric ratio, was observed at 25 and 37°C. Voltage output of the differential resistance bridge, experimentally determined quantity, was converted through calibration to Q. A typical progress curve giving the time development of the integral heat of precipitation ((points) and their fit to Eq. (16) (full line)) is shown in Fig. 2.

The experimental progress curves were fitted to Eq. (16) by the least square method [4]. The slope of the progress curve, $\dot{Q}$, was determined at the point where $Q = Q_\infty/3$. This point either coincided with, or was situated in the vicinity of, the progress curve inflection point.

The equilibrium solubility of CaO*x* was calculated from the solubility product: 2.0×10^{-9} at 25°C and $2.51 \times 10^{-9}\ \mathrm{mol}^2\,\mathrm{l}^{-2}$ at 37°C and the constant of calcium and oxalate ion pair formation: 1537 and 1869 $\mathrm{mol\,l}^{-1}$ at 25 and 37°C, respectively [3]. Activity coefficients were calculated from the Davies extension of the Debye–Hückel equation

$$\log \gamma_\pm = -4A\{[\sqrt{I}/(\sqrt{I} + 1) - 0.3I\} \qquad (18)$$

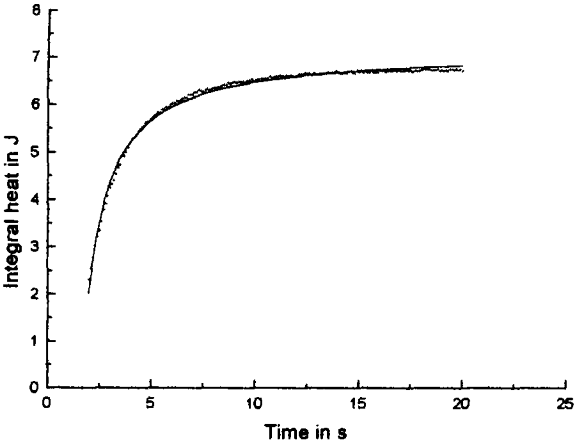

Fig. 2. A typical progress curve of CaO*x* precipitation (points) fitted by the least square method (full line).

where A equals 0.511 and 0.522 for 25 and 37°C, respectively, and the solution ionic strength is defined by

$$I = 0.5\sum c_i z_i^2 \tag{19}$$

z_i being the ionic charge.

Experimental data for CaO*x* precipitation under the stoichiometric conditions at 25 and 37°C are given in Tables 1 and 2. In these tables, c_i denotes the initial concentration of CaO*x*, V the volume crystallizing mixture, $\Delta c = c_i - c_{eq}$ the initial concentration driving force, and n_∞ the number of CaO*x* moles crystallized in the reaction vessel on the completion of crystallization. Reported values of $\dot{Q}_{/Q=Q_\infty/3}$, Q_∞ and Q_{mol} in Tables 1 and 2 give the average results of five independent experiments performed at identical conditions, i.e. temperature, c_i and V. The agreement among independent measurements is indicated by the standard deviation of resulting Q_{mol} value quoted in the last column of each Table as $Q_{mol} \pm \sigma$.

Experimental slopes $\dot{Q}_{/Q=Q_\infty/3}$ fitted to Eq. (10) were rearranged into

$$\log(\dot{Q}_{Q=Q_\infty/3}/V) = a + b\log\Delta c \tag{20}$$

where $a = 3^{1/3}k_g Q_{mol}/r_\infty$ and $b = g + 1$ using the least square method. Calculated parameters a and b together with the respective correlation coefficient, *c.c.*, are reported in Table 3.

Table 1
Crystallization of CaO*x* at 25°C

$c_i \times 10^3$ (mol l^{-1})	V (l)	$\dot{Q}_{Q=Q_\infty/3}$ (J s^{-1})	Q_∞ (J)	$\Delta c \times 10^3$ (mol l^{-1})	$n_\infty \times 10^4$ (mol)	Q_{mol} (kJ mol^{-1})
1.176	0.102	0.030	2.49	1.117	1.139	21.84 ± 2.65
1.747	0.103	0.169	3.58	1.686	1.736	20.64 ± 1.50
2.308	0.104	0.373	4.56	2.245	2.334	19.53 ± 1.14
2.857	0.105	0.638	5.47	2.786	2.929	18.68 ± 1.36
3.396	0.106	1.249	6.53	3.329	3.530	18.64 ± 0.60
3.925	0.107	2.558	8.19	3.857	4.127	19.84 ± 1.28
4.444	0.108	3.731	8.71	4.374	4.724	18.45 ± 0.31
4.954	0.109	6.719	11.21	4.883	5.332	21.02 ± 1.03

Table 2
Crystallization of CaO*x* at 37°C

$c_i \times 10^3$ (mol l^{-1})	V (l)	$\dot{Q}_{Q=Q_\infty/3}$ (J s^{-1})	Q_∞ (J)	$\Delta c \times 10^3$ (mol l^{-1})	$n_\infty \times 10^4$ (mol)	Q_{mol} (kJ mol^{-1})
1.747	0.103	0.166	3.08	1.677	1.727	17.81 ± 2.28
2.308	0.104	0.640	3.88	2.235	2.324	16.69 ± 1.72
2.857	0.105	0.779	4.73	2.782	2.921	16.20 ± 0.26
3.396	0.106	1.167	5.75	3.319	3.518	16.34 ± 0.32
3.925	0.107	1.725	6.63	3.847	4.116	16.10 ± 0.55
4.444	0.108	2.916	7.88	4.364	4.713	16.72 ± 1.26
4.950	0.109	3.641	9.00	4.872	5.311	16.94 ± 1.68

Table 3
Parameters of Eq. (20)

T	*a*	*b*	*c.c.*
25	9.76	3.47	0.992
37	7.66	2.65	0.969

$CaO_x \cdot H_2O$ precipitated as a single solid phase under studied conditions, as determined by X-ray diffraction.

5. Discussion

The kinetics of CaO*x* crystal growth from an aqueous solution of low ionic strength were determined in the supersaturation range $\Delta c = (1.18 - 4.95) \times 10^{-3}$ mol l^{-1} at 25°C and $\Delta c = (1.7 - 5.4) \times 10^{-3}$ mol l^{-1} at 37°C, or in terms of the supersaturation ratio ($S = c/c_{eq}$) $S \in (20, 76)$ and (25, 66), respectively. The crystal growth order, calculated according to $g = b - 1$ using b values reported in Table 3, is 2.47 at 25°C and 1.65 at 37°C. A value of $g = 2$ has been reported for conditions similar to those used in this study [5,6]. Even for conditions differing from this study, for instance with non-stoichiometric solutions, lower S values and higher solution ionic strength, g was invariably determined to be about 2, both at 25 and 37°C, for all three existing hydrates of CaO*x* [6–12]. Hence, $g = 2$ should also apply in this work. Slight variation of the calculated g values around 2 is a consequence of the statistical treatment of imprecise experimental data.

The kinetic constant k_g in Eq. (1) can be calculated from

$$k_g = 10^a r_\infty (3/2)^2/(3^{1/3} Q_{mol}) \qquad (21)$$

where a is determined by the statistical data treatment according to Eq. (20) assuming $b = 3$, i.e. $g = 2$. '*a*' thus determined slightly differs from results reported in Table 3, acquiring values of 9.76 at 25°C, and 7.66 at 37°C. k_g calculated for 25°C from Eq. (21), taking $r \sim 1 \times 10^{-6}$ m and $Q_{mol} = 19.81$ kJ mol^{-1} (see below), is 0.090 m l^2 s^{-1} mol^{-1}; at 37°C, $Q_{mol} = 16.69$ kJ mol^{-1} (see below) and k_g equals 4.27×10^{-3} m l^2 s^{-1} mol^{-1}. The k_g constant for 25°C can be compared with the kinetic constant $k_2 = 5 \times 10^{-11}$ m s^{-1} for CaO*x* precipitated from an aqueous solution at 25°C and $S \in (1, 8)$ reported in Ref. [5]. Comparing Eq. (1) with Eq. (11) in Garside et al. [5] yields

$$k_g = k_2/c_{eq}^2 \qquad (22)$$

Taking c_{eq} (25°) $= 6 \times 10^{-5}$ mol l^{-1}, k_g calculated from the above reported k_2 using Eq. (22) equals 1.39×10^{-2} m l^2 s^{-1} mol^{-2} is identical to our k_g value. k_g at 37°C can be estimated from results reported in [6] as $k_2 = 2.9 \times 10^{-11}$ m s^{-1}. Taking $c_{eq} = 7 \times 10^{-5}$ mol l^{-1}, k_g calculated using Eq. (22) is 5.92×10^{-3} m l^2 s^{-1} mol^{-2}. This value is again almost identical with k_g determined in this work.

Homogeneous nucleation of CaO*x* prevails at $S > 100$ [13,14]. Precipitate under the conditions studied in this paper was formed by heterogeneous nucleation, since the initial supersaturation in this study did not exceed 76. Therefore, the number of crystals formed during the heterogeneous nucleation is only weakly dependent on initial supersaturation and no additional surge of new crystal formation, i.e. secondary nucleation is expected during the precipitation. This is especially true if the level of supersaturation is falling as the crystallization progresses as in this work [1]. Hence, determining $\dot{Q}$ at an extent of reaction equal to one-third is justifiable, since nucleation has ceased by that time. Therefore, the principal condition for Eq. (10) i.e. a constant number of crystals present in the system, is satisfied. A close agreement of crystal growth constants g and k_g inferred from calorimetric measurements with values determined by other crystallization techniques indicates the reliability of IRT calorimetry for studying precipitation. Moreover, the molar reaction heat of CaO*x* precipitation can be evaluated by averaging results reported in Tables 1 and 2 as Q_{mol} (25°) = (19.83 ± 1.24) and Q_{mol} (37°) = (16.69 ± 0.58) kJ mol^{-1}, in correspondence with the literature data [7]. This correspondence also substantiates the method for deriving kinetic parameters from calorimetric results suggested in this paper.

The only phase formed in experimental conditions confirmed by X-ray diffraction measurement is CaO*x*·H_2O though the precipitation of CaO*x*·$3H_20$, either pure or in a mixture with CaO*x*·H_2O [5] and the formation of all three existing hydrates, i.e. mono-, di- and trihydrate was also reported [15].

An undisputable advantage of calorimetric determination of crystallization kinetic data over conventional methods represents measuring quantity directly related to the process. Evaluation of such results requires introducing only a minimum number of assumptions and this considerably increases reliability of inferred kinetics of precipitation.

6. Conclusions

The isoperibolic reaction twin (IRT) calorimeter represents a reliable and convenient technique for studying precipitations effected by mixing reactant solutions together. The crystal growth kinetics can be inferred from experimental progress curves exhibiting the time development of the integral heat of precipitation determined by the IRT calorimeter.

Acknowledgements

Financial support by 'AKTION, Austria-Czech Republic' No. 4w6 is gratefully acknowledged.

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