

Kinetics of calcium molybdate crystallization

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Abstract. Kinetics of crystallization of calcium molybdate from unstirred molten solutions of lithium chloride of low to medium supersaturation in platinum crucibles by the process of continuous cooling at $5^{\circ}\text{C hr}^{-1}$ from temperatures $T_0 = 700$ and 750°C are investigated. The crystal size measured by optical microscopy for different crystallization periods reveals that both crystal length and width generally increase with cooling period. The degree of crystallization α_t , also increases with cooling period, attaining a maximum of 0.90. The diffusion rate constants, K_D , at 700 and 750°C are 0.0776 and 0.1138 respectively. The effect of variation of the crystallization temperature on the crystal size and their number is also studied.

Keywords. Calcium molybdate; crystallization kinetics.

1. Introduction

Crystallization of inorganic materials from high temperature solution has been studied by many workers (Laudise 1963; Kroger 1964; White 1964; Schroedger and Linares 1966; Elwell and Scheel 1975). Alkaline earth metal molybdates and tungstates have been prepared by crystallization from lithium chloride and sodium tungstate or molybdate metals (Groot 1947; Moon 1948; Klick 1949; Anikin 1956; Van Uitert 1960; Ouwetjes 1965; Packter and Roy 1971). Packter and Roy (1973, 1974, 1975) studied some of the crystallization kinetics of alkaline earth metal compounds. Kinetics of precipitation of alkaline earth metal molybdates have also been briefly studied (Packter 1977). However, only preliminary reports on the kinetics of crystal growth of calcium molybdate are available in literature and therefore we have undertaken further studies of the crystallization kinetics of calcium molybdate from an unstirred supersaturated solution in molten lithium chloride. These results are reported here.

2. Experimental

2.1 Materials

The chemicals used were CaMoO_4 powder (ICN Pharmaceuticals, New York) and hydrated LiCl (Burgoyne, Bombay). A 100 ml platinum crucible was employed to hold the growth charge.

2.2 Solubility

Calcium molybdate solubilities in LiCl melt at 650 to 900°C were determined by supersaturation method. For this purpose, lithium chloride powder (5 g) was melted

in a platinum crucible and the temperature was measured with a chromel/alumel thermocouple and controlled using a variable voltage transformer. Increasing amounts of ground metal molybdate were then added to the molten solvent until a saturated solution was attained; the solution was considered saturated when traces of excess solute were visible at the bottom of the crucible. The solubility was thus determined from the weight of solute dissolved.

2.3 Crystallization

From the solubility data, appropriate quantities of flux and solute were weighed, mixed thoroughly using a pestle and mortar and then packed into the platinum crucible with a loosely fitting lid to prevent excessive evaporation. The saturated solutions were prepared at temperature, given by

$$T_i = T_0 + \Delta T,$$

where T_0 is the temperature at which the crystallization is intended to be studied and $\Delta T = 50^\circ\text{C}$. The charge was heated at T_i for an hour. The furnace was then rapidly cooled to the crystallization temperature T_0 and then soaked for an hour. After soaking, it was cooled at a uniform rate of 5°C hr^{-1} for different periods ranging from 1 to 17 hr, after which the crucible was withdrawn from the furnace and the undissolved crystals were separated from the solidified matrix by leaching with hot distilled water. The crystallization was studied at $T_0 = 700$ and 750°C and the crystals were characterized essentially by EDAX and XRD. Crystal sizes were measured by optical microscopy.

Crystallization was next studied at $T_0 = 650, 700$ and 750°C , but the charge was cooled from T_0 to the eutectic (550°C) at 5°C hr^{-1} . The furnace power was then turned off and the crucible allowed to cool to room temperature. The effect of variation of crystallization temperature on the final crystal sizes and number was also studied.

3. Observations and discussion

The solubility of calcium molybdate at different temperatures is shown in figure 1. The observed increase in solubility with temperature is quite favourable for the crystal growth. The charge was deliberately heated at 50°C above T_0 , to ensure removal of any undissolved excess nuclei which might have remained at T_0 ; failure to carry this out usually resulted in considerable spurious nucleation. Calcium molybdate crystallized as tetragonal bipyramids with well-developed (011) faces. The average crystal lengths l_t and widths w_t were both measured using a travelling microscope (least count 0.001 cm). The l_t (cm) vs t (hr) and the w_t (cm) vs t (hr) plots are shown in figure 2. One observes that the crystal size increases with increasing crystallization period and the growth rate is higher at larger temperatures. However, after about 10 hr of cooling the change in crystal size was very small, giving a final, almost consistent size, l_{fin} and w_{fin} . Probably, the limiting growth rate is imposed by surface kinetic processes, such as dissolution, ledge integration of kinks and steady removal of solvent molecules from the surface. At times, spontaneous nucleation of further crystals might also limit the experimental, maximum feasible, growth rate (Laudise 1963).

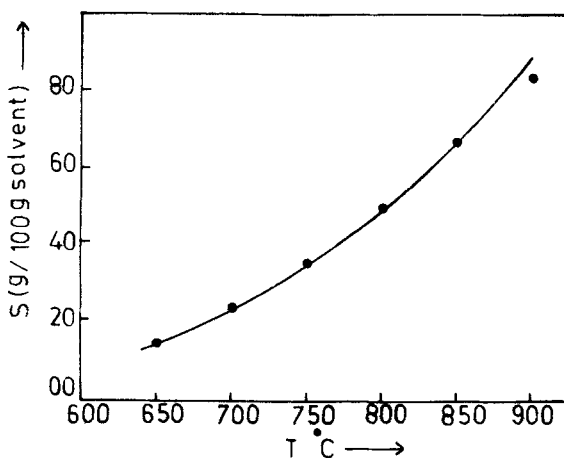


Figure 1. Solubility of CaMoO₄ in LiCl at different temperatures.

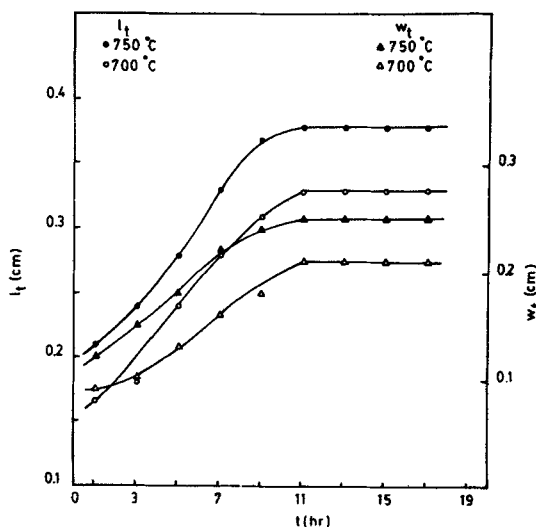


Figure 2. Variation of average crystal length and width at different cooling periods for 700° and 750°C.

The degree of crystallization, α_t , measured by the ratio between the amount of substance crystallized to the total amount able to crystallize, is defined as (Nielsen 1964)

$$\alpha_t = (C_0 - C_t) / (C_0 - S), \tag{1}$$

where C_0 is the concentration at $t=0$, C_t the instantaneous concentration and $S (= C_{sat})$ the solubility. One can also write,

$$\alpha_t = l_t^3 / l_{fin}^3 \tag{2}$$

where l_t and l_{fin} are instantaneous and final lengths, respectively. It is evident that since l_t is sensitive to the cooling time (figure 2), α_t becomes a function of the crystallization period and this relationship for 700° and 750°C is plotted in figure 3a, α_t increases monotonically with time, reaching >0.9 after about 9 hr of crystallization.

Crystal growth rates in unstirred solutions of low permeability are generally controlled by the rate of diffusion of material on different growth faces. The deposition rate of the metal salt ions on growing surfaces from low viscosity LiCl melt, at any time, would then be expressed by the relation (Mullin 1961; Nielsen 1964; Treybal 1968)

$$\frac{dl}{dt} = \frac{2 \text{Sh}\Phi_1(\epsilon)D\Delta C_t}{l_t} \frac{\rho_f}{\rho_x} \text{ cm/sec} \quad (3)$$

where Sh is the Sherwood dimensionless function, $\Phi_1(\epsilon)$ an overall shape permeability factor, D the diffusion coefficient of metal salt ion, Ca^{+2} , ΔC_t the instantaneous excess CaMoO_4 concentration expressed in g/g solution (dl/dt however depends on α_t through ΔC_t), ρ_x the crystal density and ρ_f the fluxed-melt density.

In the present case of unstirred molten solution where the natural convection is very poor, $\text{Sh} \approx 2$ (Treybal 1968), one obtains

$$dl/dt = (2 K_{Dl}\Delta C_t)/l_t \text{ cm/sec}, \quad (4)$$

where K_{Dl} is the rate constant (dependent on the permeability factor) for diffusion-controlled growth of the longer crystal-pyramid side. A general solution of equation

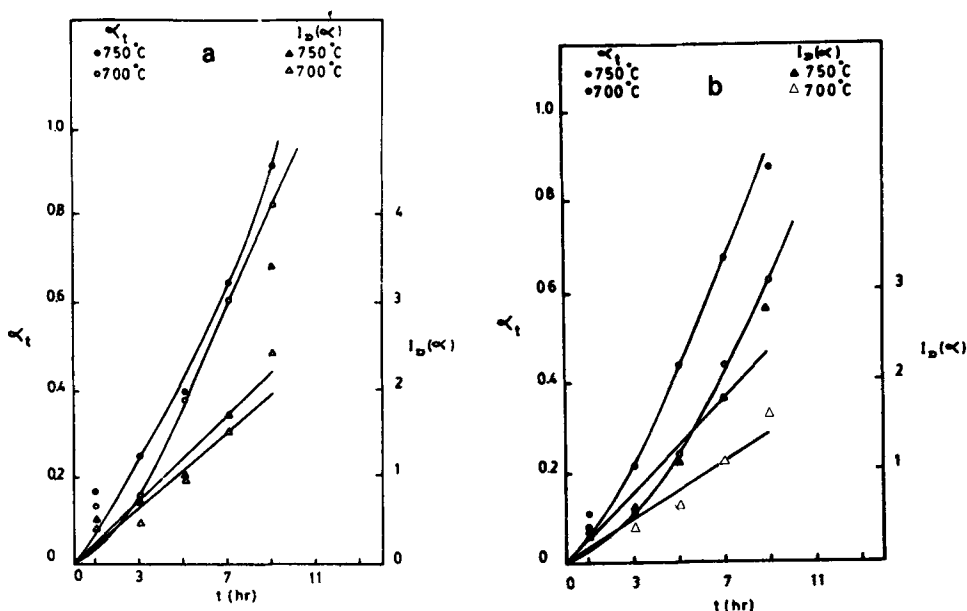


Figure 3. Degree of crystallization α_t and $I_D(\alpha)$ at different cooling periods for 700° and 750°C. a. for length b. for width.

(4) for all α_t values can be given as,

$$I_D(\alpha) = \int_0^\infty \frac{d\alpha}{\alpha^{1/3}(1-\alpha)} = \left(\frac{12K_{Di}\Delta C_0}{l_{fin}^2} \right) t = t/K_D. \quad (5)$$

The rate constant of metal salt deposition K_D , having the dimension of time, contains all physical constants of the process, including K_{Di} , ΔC_0 and l_{fin}^2 . Furthermore, $I_D(\alpha)$ is identified as the dimensionless time, or chronomal, which is a characteristic parameter for diffusion-controlled and polynuclear-layer controlled growth mechanisms. It signifies that if the size of a particle is known at a certain time, one can calculate at constant concentration the time at which it started with zero size. The integral in (5) can be solved using standard methods (Lamer and Dinegar 1950) to give

$$I_D(\alpha) = \frac{1}{2} \ln \left[\frac{(1-\alpha)}{(1-\alpha^{1/3})^3} \right] - \sqrt{3} \tan^{-1} \left[\frac{\sqrt{3}}{1+2\alpha^{-1/3}} \right]. \quad (6)$$

This equation predicts the overall kinetics of crystallization. The value of diffusion chronomal $I_D(\alpha)$ obtained with the help of Nielsen's table (Nielsen 1964) are plotted with time as shown in figure 3a for 700° and 750°C respectively. The two plots are seen to be linear upto $\alpha_t \approx 0.61$ for 700°C and $\alpha_t \approx 0.65$ for 750°C. Similarly expressing the rate of diffusion-controlled growth of the shorter side of the crystal bipyramid as

$$dw/dt = (2K_{Dw}\Delta C_i)/w_r, \text{ cm/sec} \quad (7)$$

the Nielsen's relation for this case would be

$$I_D(\alpha) = \left(\frac{12K_{Dw}\Delta C_0}{w_{fin}^2} \right) t = t/K_D, \quad (8)$$

α_t and $I_D(\alpha)$ vs t (hr) plots are shown in figure 3b. Both the plots are linear upto $\alpha_t \approx 0.44$ and $\alpha_t \approx 0.68$ for 700° and 750°C respectively.

It is interesting to find the rate constant K_{Di} and K_{Dw} at different crystallization temperatures from $I_D(\alpha)$ vs t (hr) plots using the relation,

$$K_{Di} = \frac{\text{Grad}[I_D(\alpha) \text{ vs } t \text{ plot}] \times l_{fin}^2}{12\Delta C_0} \frac{\text{cm}^2}{\text{sec}} \quad (9)$$

and

$$K_{Dw} = \frac{\text{Grad}[I_D(\alpha) \text{ vs } t \text{ plot}] \times w_{fin}^2}{12\Delta C_0} \frac{\text{cm}^2}{\text{sec}}. \quad (10)$$

The required ΔC_0 values were estimated from solubility vs temperature data (figure 1), and the results are shown in table 1.

In order that a crystal may grow from solution, the solute must essentially be transported through the solution to the growing surface, desolvated and arranged in conformity with the crystal structure. Therefore, both diffusion and convection are important in controlling the growth velocity. But, when the crystal was relatively smaller than say about 10 μ , convection may be neglected in view of the very low velocity of growth fronts in normal gravity fields. At this stage, when convection is insignificant, crystal growth takes place principally due to Fick's steady diffusional

concentration gradients. The fact that this state is established around the crystal at a much faster rate than the rate at which the solution in its close vicinity would be replenished, has been proved by Nielsen (1964). This also explains the initially faster growth rate. Such a situation, on an average, exists in the present case upto about 63% (corresponding to $\alpha_i \approx 0.61$ at 700° and 0.65 at 750°C) and the remaining growth may, however, be surface-reaction-controlled, approximated by

$$l_i^3 = l_0^3 + K_R(t - t_0),$$

where K_R is the surface-reaction rate constant.

The fact that the remaining 37% of growth occurs by surface-reaction needs confirmation. This could not be done experimentally because it is not possible to measure the surface tension of solid substances, though some attempts have been made in this direction (Kuznetsov 1957) with non-convincing results. Nonetheless, the fact that the lateral growth rate is diffusion-controlled to only about 44% is corroborative of the pyramidal morphology of the crystal with its C -axis much larger than either lateral axis.

Further, to understand the effect of crystallization temperature on the final crystal size and the crystal numbers, the final crystal lengths (l_{fin}) and widths (w_{fin}) were measured, and the number N of crystals that grew from 100 g solution was

Table 1. Initial excess solute concentration ΔC_0 and rate constant at different temperatures

Temp. ($^\circ\text{C}$)	ΔC_0 (g/g solution)	Rate constant ($\text{cm}^2 \text{sec}^{-1}$)	
		$10^{-4}K_{Di}$	$10^{-4}K_{Dw}$
700	0.069	0.0776	0.0234
750	0.071	0.1138	0.0526

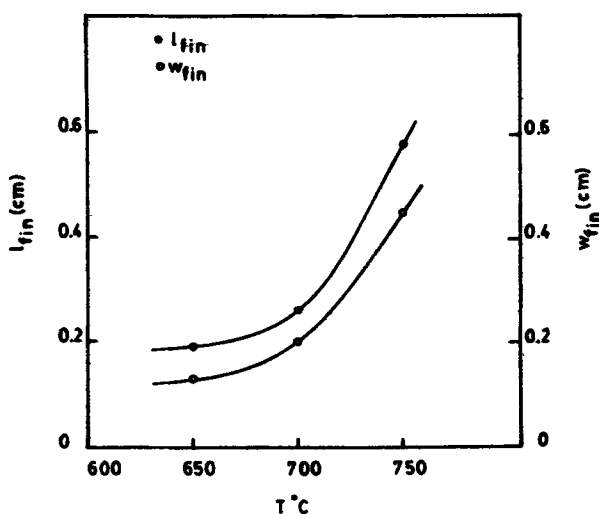


Figure 4. Variation of final crystal length and width at different crystallization temperatures.

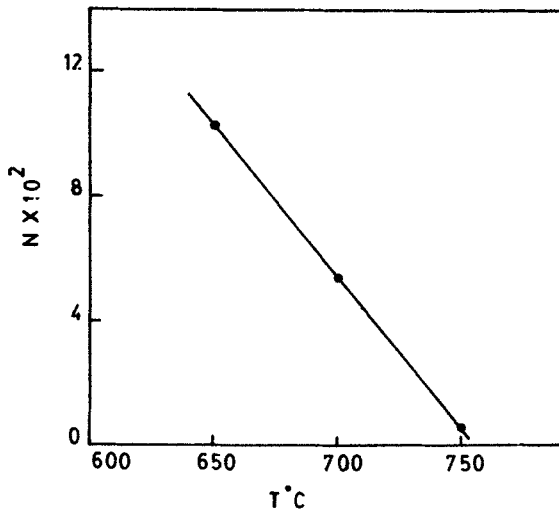


Figure 5. Variation in crystal numbers at different crystallization temperatures.

determined from the average crystal lengths using the relation (Roy and Packter 1980)

$$N = (\Delta w_{\text{tot}} / \rho_x f_s l_{\text{fin}}^3) 100 \text{ g solution}^{-1}, \quad (11)$$

where Δw_{tot} is the total weight of crystals forming from 100 g solution cooled over the temperature range T_0 to T_{eut} (eutectic temperature = 550°C), ρ_x is the crystal density and f_s is the shape factor determined by the volume V ,

$$V = f_s l^3. \quad (12)$$

The effect is shown graphically in figures 4 and 5, revealing that the crystal size increases while the crystal number decreases with increasing crystallization temperature. This supports the general expectation that the smaller the crystal nuclei concentration the larger will be the crystal size in a growth process.

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