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The Kinetics of Calcium Oxalate Precipitation

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At concentrations below 1 mM the rate determining step in the precipitation of calcium oxalate is a reaction in the surface of the crystals. It is apparently of an order between 3.0 and 3.5. It is shown that when the incompleteness of the dissociation of calcium oxalate is taken into account the »true» order of the reaction is 4, when the rate is expressed by the ionic concentrations, and 2, when expressed by the concentration of the undissociated calcium oxalate.

At concentrations above 1 mM the rate is determined by diffusion.

In a previous work [1] the kinetics of calcium oxalate precipitation was investigated by means of experiments with the initial concentration $c_0 = 0.75$ and 0.50 mM. It was found that the rate of formation of the precipitate — measured by the electric conductance of the aqueous solution — was proportional to the total surface area of the precipitate and to a power of the concentration of the unprecipitated calcium oxalate close to 3.5. The power was clearly larger than 3 and less than 4.

The data found in the present work where $c_0 = 1$ and 5 mM, are treated in the way described in a previous work [2] on barium sulfate and the logarithm of the growth rate, $\mathrm{d}l/\mathrm{d}t$, where l is the length of a cube of the same volume as one of the growing crystals, and t is time, is plotted as a function of the logarithm of the concentration of the calcium oxalate in the solution at that time; see Fig. 1. In the region where $c < 1$ mM the points lie close to a straight line of slope 3.3, which means that the rate is proportional to the 3.3-rd power of c. At $c > 1$ mM the rate is proportional to c. Later on we shall see that in this part of the curve the rate is diffusion controlled. But first we shall consider the steeper part of the curve.

THE ORDER OF THE SURFACE REACTION

In interpreting the power or order of the reaction it must be remembered that calcium oxalate may be incompletely dissociated at the concentrations used. When this is taken into account it turns out that the precipitation (or crystal growth) rate follows

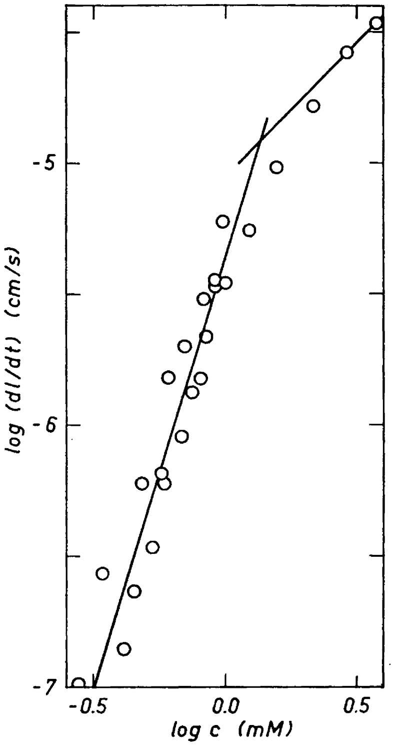

Fig. 1. The linear rate of crystal growth as function of (CaOx) in a logarithmic diagram. Below 1 mM the rate is proportional to the 3.3rd power of the concentration. Above 1 mM the rate is proportional to the concentration.

$$J_1 = k_1\ (\mathrm{CaOx})^2$$
$$J_2 = k_2\ (\mathrm{Ca}^{++})^2\ (\mathrm{Ox}^{--})^2$$
$$J\ = J_1 + J_2 = k_1\ (\mathrm{CaOx})^2 + k_2\ (\mathrm{Ca}^{++})^2\ (\mathrm{Ox}^{--})^2$$

where J is the total rate of depositing matter per unit area of the crystal surfaces.

From the law of mass action

$$(\mathrm{Ca}^{++})\ (\mathrm{Ox}^{--}) = K \cdot (\mathrm{CaOx})$$

it follows that

$$J = k_{\mathrm{I}}(\mathrm{CaOx})^2 = k_{\mathrm{II}}(\mathrm{Ca}^{++})^2(\mathrm{Ox}^{--})^2$$

where $k_{\mathrm{I}} = k_1 + k_2K$

$$k_{\mathrm{II}} = k_1/K + k_2$$

When the ionic species Ca^{++} and Ox^{--} are present in equivalent concentrations we define $c = (\mathrm{CaOx}) + (\mathrm{Ca}^{++}) = (\mathrm{CaOx}) + (\mathrm{Ox}^{--})$.

At *low* concentrations we have $(\mathrm{CaOx}) \langle\langle\ (\mathrm{Ca}^{++}) = (\mathrm{Ox}^{--})$

$$(\mathrm{Ca}^{++}) = (\mathrm{Ox}^{++}) = c$$

$$\therefore J = k_{\mathrm{II}}c^4$$

At *high* concentrations $(\mathrm{CaOx}) \gg (\mathrm{Ca^{++}}) = (\mathrm{Ox^{++}})$

$$c = (\mathrm{CaOx})$$

$$\therefore J = k_{\mathrm{I}}c^2$$

If however (CaOx), $(\mathrm{Ca^{++}})$ and $(\mathrm{Ox^{--}})$ are of the same order of magnitude none of the above mentioned approximations is valid and if one writes

$$J = kc^p$$

p is only apparently a constant, $2 < p < 4$, in limited concentration ranges.
To be more precise we may define p by

$$p = \mathrm{d}\ln J/\mathrm{d}\ln c.$$

Putting $(\mathrm{CaOx}) = x$, $(\mathrm{Ca^{++}}) = (\mathrm{Ox^{--}}) = c - x$ we find

$$(c - x)^2 = Kx$$

$$\therefore \frac{\mathrm{d}x}{\mathrm{d}c} = \frac{1}{1 + (K/2(c - x))}$$

$$J = k_{\mathrm{I}}x^2$$

$$p = \frac{\mathrm{d}\ln J}{\mathrm{d}\ln c} = \frac{c}{J}\frac{\mathrm{d}J}{\mathrm{d}c} = \frac{2c}{x[1 + (K/2(c - x))]}$$

Solving the mass action law with respect to x we find

$$x = c - \frac{K}{2}\left(\sqrt{1 + \frac{4c}{K}} - 1\right)$$

$$\therefore p = \frac{2c}{[c - (K/2)(\sqrt{1 + (4c/K)} - 1)]\,[1 + (1/(\sqrt{1 + (4c/K)} - 1))]}$$

$$= \frac{2}{[1 - (1/2q)(\sqrt{1 + 4q} - 1)]\,[1 + (1/(\sqrt{1 + 4q} - 1))]}$$

Table 1.

q	p
0.001	3.989
0.01	3.961
0.05	3.826
0.1	3.690
0.2	3.491
0.5	3.155
1	2.895
2	2.667
5	2.437
10	2.312
100	2.100
1 000	2.041

where $q = c/K$. Values of p calculated by this formula are in Table 1. It is easily seen that $p \rightarrow 2$ for $q \rightarrow \infty$ and $p \rightarrow 4$ for $q \rightarrow 0$.

DETERMINATION OF THE DISSOCIATION CONSTANT

The calibration measurements were performed on solutions of $CaCl_2$, Na_2Ox and NaCl having the same compositions as the reaction mixture at different degrees of advancement during a kinetic run. From these measurements the dissociation constant may be estimated neglecting the dependence of the molar conductivities on the concentration. This is only permissible when the range of ionic strengths used is small. We write

$$10^3\varkappa = c_0(\Lambda_{\mathrm{CaOx}}(1-\alpha)\delta + 2\Lambda_{\mathrm{NaCl}})$$

$$10^3\varkappa_1 = 2c_0\Lambda_{\mathrm{NaCl}}$$

$$K = (\mathrm{Ca}^{++})(\mathrm{Ox}^{--})/(\mathrm{CaOx}) = c_0(1-\alpha)\delta^2/(1-\delta)$$

where

$\varkappa$ = specific electric conductance
c_0 = initial concentration of CaOx
Λ_{CaOx} and Λ_{NaCl} = molar conductivities
a = degree of reaction
δ = degree of dissociation of CaOx.

Eliminating δ and Λ_{NaCl} we obtain

$$\frac{c_0(1-a)}{\varkappa-\varkappa_1} = \frac{\varkappa-\varkappa_1}{K\Lambda^2_{\mathrm{CaOx}}} + \frac{1}{\Lambda_{\mathrm{CaOx}}}$$

A diagram of $c_0(1-a)/(\varkappa-\varkappa_1)$ as function of $\varkappa-\varkappa_1$ should thus yield a straigth line intersecting the ordinate axis at $1/\Lambda_{\mathrm{CaOx}}$ and having the slope $1/K\Lambda^2_{\mathrm{CaOx}}$. From Fig. 2 we see that a straigth line is really found in this way, and that

$$\Lambda_{\mathrm{CaOx}} = 192;\ K = 0.00162\ \mathrm{M}.$$

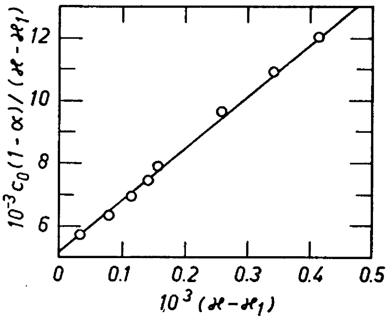

Fig. 2. A plot of $c_0(1-a)/(\varkappa-\varkappa_1)$ as function of $\varkappa-\varkappa_1$. From the slope of the straight line the dissociation constant of calcium oxalate can be determined (Units: mM, Ω and cm).

This number is, within the uncertainties and errors of approximations, the concentration dissociation constant. The activity dissociation constant K_a (or, the former extrapolated to ionic strength zero) can be estimated in the following way. The ionic strength is

$$I = \frac{1}{2} \Sigma c_i z_i^2 = 2c_0(1 + 2(1 - \alpha)\delta)$$

Assuming values of K, c_0 and α, δ can be calculated from

$$\delta^2/(1 - \delta) = K/c_0(1 - \alpha)$$

With $K = 0.001$ M, $c_0 = 0.001$ M, $\alpha = 0.8$, we find the lowest ionic strength used: $I_{\min} = 0.0027$ M; with the same K, $c_0 = 0.005$ M and $\alpha = 0$ we find the highest ionic strenth $I_{\max} = 0.017$. Using furthermore the Debye-Hückel equation in the Güntelberg formulation [3]

$$\log f_z = -0.5\, z^2 \sqrt{I}/(1 + \sqrt{I})$$

we find that f_2, the activity coefficient of a doubly charged ion lies between 0.59 and 0.80; now $K_a = K f_2^2$. Since the mean value of 0.59^2 and 0.80^2 is near to 0.50 we may estimate

$$K_a = 0.0008 \text{ M}$$

This may be compared with the value 0.0010 M reported by Davies [4].

DISCUSSION OF THE KINETICS

In Fig. 1 the range of concentrations corresponding to the steeper part of the curve is $0.0003 < c < 0.001$ M. Since $q = c/K$ where $K = 0.0016$ we have $0.2 < q < 0.6$ and consequently (see Table 1) $3.5 > p > 3.1$. We may therefore conclude from the experimental slope 3.3 that the surface reaction controlling the rate of growth of the calcium oxalate crystals is of the fourth order in the ionic concentration or, which is equivalent, of the second order in the concentration of the undissociated calcium oxalate.

This is similar to the result obtained in experiments on the precipitation of barium sulfate [2,5]. For $BaSO_4$ it has been shown [5] that $K > 0.004$ M, and most probably K is about 0.008 M. The surface reaction is rate determining for the precipitation of barium sulfate when $c < 0.4$ mM. When $q = c/K < 0.05$ Table 1 shows that $3.8 < p < 4.0$ which is just what has been found.

In the high concentration end of the curve on Fig. 1 the slope approaches 1. This is easily explained since at these high concentrations the diffusion of the matter from the bulk of the solution to the surface becomes rate determining — as explained in greater detail in the papers on barium sulfate [4]. From the electric mobilities $l_+ = 5.9 \times 10^{-4}$ and $l_+ = 7.4 \times 10^{-4}$ cm²/s·V we calculate the diffusion coefficient

$$D = 2kTl_+l_-/(l_+ + l_-)q = 8.5 \times 10^{-6} \text{ cm}^2/\text{s}$$

and the diffusional growth rate should consequently follow, in CGS-units:

$$\mathrm{d}l/\mathrm{d}t = 2.60\ vDc/l = 0.00147\ c/l$$

With the value of l in the highest point on Fig. 1, $l = 3.12 \times 10^{-4}$, cm we find $\mathrm{d}l/\mathrm{d}t = 4.7\ c$; the experiments give $(\mathrm{d}l/\mathrm{d}t) = 8.9\ c$. The reason why the growth rate is larger than calculated, is probably that the particles are not — as assumed in the calculations — spheres or cubes, but show the shape of small »stars» when viewed in a microscope. The rate of growth depends — in case of diffusion — rather on the largest corner to corner dimensions of the particles than of the volume. There is no doubt, therefore, that the rate is mainly controlled by diffusion at $c > 1$ mM.

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