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KINETICS OF CRYSTAL GROWTH AND DISSOLUTION PROCESSES OF VARIOUS COBALT(III) COMPLEXES IN AQUEOUS SOLUTIONS

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A spectrophotometric method has been developed for studying the kinetics of crystallization and dissolution processes of metal coordination compounds. The crystal growth and dissolution of the cobalt(III) complexes are controlled by a reaction at the crystal surface. The order of the reaction is between 1 and 2 indicating the crystal growth and dissolution processes proceeded by a surface controlled mechanism.

The crystallization (including crystal growth) or the dissolution of solid materials in solution is probably the most frequently used operation in industries and in laboratories. Although many literatures [1-3] are available on the studies of crystallizations and dissolutions of inorganic and organic compounds in aqueous solutions, very little is known concerning the crystal growth and dissolution of metal coordination compounds. In order to elucidate the mechanism of crystallization and dissolution processes of the metal coordination compounds, the kinetic study described in the present work has been made spectrophotometrically by the use of a flow cell and by the seeded crystal growth and dissolution technique.

The experiments were performed in a 100 ml pyrex double-walled reaction cell. The cell was maintained at 25 °C by circulating thermostated water through the outer jacket.

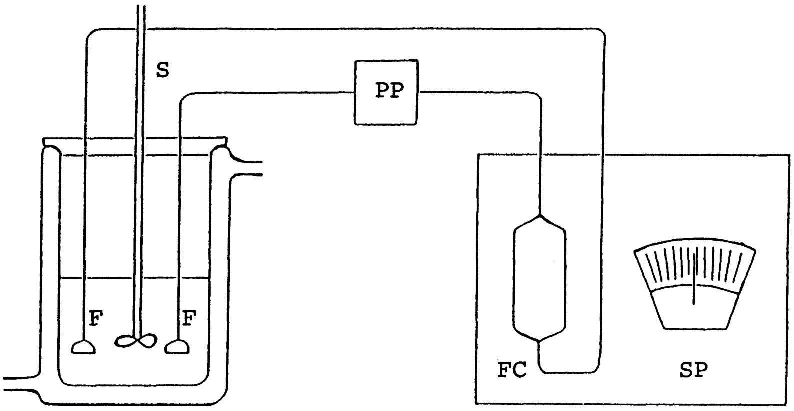

Fig. 1. Schematic diagram of the instrument. S, stirrer; F, filter; FC, flow cell; PP, peristaltic pump; SP, spectrophotometer.

Fig. 1 shows the schematic diagram of the instrument. The circulation tube(inner diameter, 0.5 mm) passing through the flow cell, has two small filters(diameter 3 mm) at both ends, which prevent crystals from entering the cell. The flow direction of the circulation is reversed by using peristaltic pump at regular intervals to avoid the clogging of the filters.

All the complexes used in the present study were prepared following the literature methods. The super- or sub-saturated solutions were prepared using distilled water and filtered (0.22 µm Millipore filter) before use. These supersaturated solutions are stable enough for a long period of time (more than one hour) without precipitation. The crystallization or dissolution was initiated when the crystals of metal complexes were added to the super- or sub-saturated solutions. Thereafter the changes in ionic concentration of the solution were measured spectrophotometrically through the flow cell.

The overall rate of crystal growth or dissolution is often represented by the following empirical expression:

$$R = k.s.\sigma^{n},$$

where k is the rate constant; s, a parameter proportonal to the total surface area of the seed crystals (correction for changes in surface area of the particles, assumed no change of the morphology during the growth or dissolution, was made by a factor $(m_t/m_0)^{2/3}$ where m_0 and m_t are the weights of solid phase present initially and at time t, respectively.4)) ; σ , the super- or sub-saturation ratio, characterized by $|C_t - C_0|/C_0$ (C_t is the concentration of the solution at time t and C_0 , the equilibrium concentration), and n is usually referred as the "effective order" of the crystal growth or dissolution process, but not necessarily an integer. For C_0 , the saturation concentration was usually used and taken as a constant, although it should depend on the ionic strength of the solution.

The experimental data were analyzed in both ways (visual method and curve fitting method using SALS 5) program). A typical smooth curve of optical density against time (shown in Fig. 2) was used to obtain the rate of crystallization. When the mole quantity plotted against time, the slope of the tangent of the curve at each point gives the rate of crystallization. A linear plot of -log (R/s) (for changes in surface area corrections are applied) against -log σ is shown in Fig. 3; the slope of the line gives n, the effective order of the reaction. After an equilibrium was reached, ten or eleven crystals were taken out at random to measure their lengths under microscope. The experimental results are summarized in Table 1.

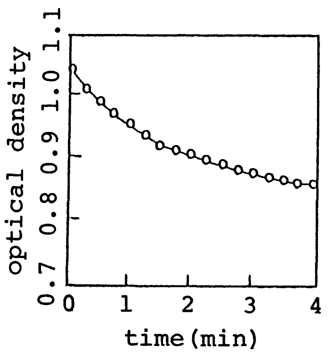

Fig. 2. Plot of optical density against time for the crystallization of *cis*-$[Co(NO_2)_2(en)_2]NO_3$.

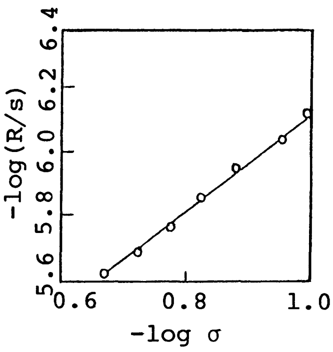

Fig. 3. Plot of -log(R/s) against -log σ for the crystallization of *cis*-$[Co(NO_2)_2(en)_2]NO_3$.

Table 1. The effective orders of crystallization of cobalt(III) complexes a)

No.	Complex	Crystal size (length/mm)	Range of sigma for analysis	Order, n (visual method)	Order, n (curve fitting)
1.	*cis*-$[Co(NO_2)_2(en)_2]NO_3$	needle shape	0.23-0.11	1.53	1.66
2.	*trans*-$[Co(NO_2)_2(en)_2]NO_3$	Sufficient supersaturation was not possible.			
3.	$[Co(ox)(en)_2]I\cdot H_2O$	1.3	0.45-0.23	1.70	1.68
4.	$[Co(en)_3]I_3\cdot H_2O$	1.8	0.19-0.09	1.51	1.39

a) The values were reproduced within ±10% on repeated runs.

A typical plot of the optical density as a function of time for the dissolution process is shown in Fig. 4. The rate of dissolution at each point is calculated from the slope of the tangent of mole quantity vs. time curve. A linear plot of -log (R/s) against -log σ is shown in Fig. 5. The experimental results are summarized in Table 2.

The effective orders of crystallization and dissolution for all the complexes studied in the present work are between 1 and 2, suggesting surface controlled crystallization and dissolution 6) processes such as the formation of unit pits on the surface of the crystal. The experiments were also performed at varying stirring speeds (between 300 and 700 revolutions per minute). They gave practically the same rates of crystallization and dissolution within the experimental error indicating that fluid dynamics have no effect upon the rates of crystallization and dissolution.

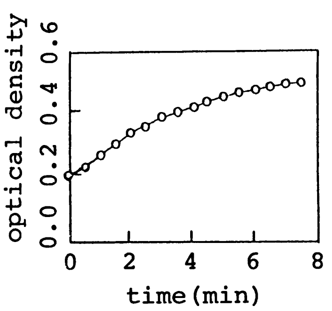

Fig. 4. Plot of optical density against time for the dissolution of *trans*-$[Co(NO_2)_2(en)_2]NO_3$.

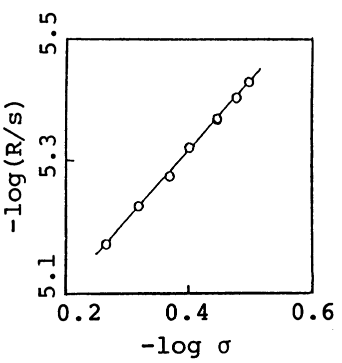

Fig. 5. Plot of -log(R/s) against -log σ for the dissolution of *trans*-$[Co(NO_2)_2(en)_2]NO_3$.

Table 2. The effective orders of dissolution of cobalt(III) complexes$^{a)}$

No.	Complex	Crystal size (length/mm)	Range of sigma for analysis	Order, n (visual method)	Order, n (curve fitting)
1.	*cis*-$[Co(NO_2)_2(en)_2]NO_3$	needle shape	0.25-0.13	1.80	1.90
2.	*trans*-$[Co(NO_2)_2(en)_2]NO_3$	2.4	0.42-0.17	1.06	1.08
3.	$[Co(ox)(en)_2]I\cdot H_2O$	1.2	0.51-0.23	1.35	1.20
4.	$[Co(en)_3]I_3\cdot H_2O$	1.7	0.26-0.09	1.28	1.13

a) The values were reproduced within ±10% on repeated runs.

Studies on the rates of the crystal growth and dissolution for some diastereoisomers of cobalt(III) complexes and optically active cobalt(III) complexes are currently under way.

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