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Kinetic Studies of Crystal Growth of Sparingly Soluble Salt by the Pressure-Jump Technique

2. Lead Chloride

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The kinetics of crystallization and dissolution of lead chloride was studied using the pressure-jump technique with conductivity detection. A single relaxation was observed in an aqueous suspension of lead chloride. From examination of both kinetic and static results, the relaxation observed was attributed to the crystallization of lead chloride and the rate constants of the crystallization and dissolution were determined. The value of the equilibrium constant obtained kinetically was in good agreement with that obtained statically. © 1994 Academic Press, Inc.

INTRODUCTION

In a previous paper (1) it was proved that the pressure-jump method can be used for kinetic study of the crystal growth of sparingly soluble thallium sulfate whose solubility changes with pressure. In continuation of the previous work, it is desirable to consider in more detail the validity of the mechanism of relaxation observed in an aqueous suspension in which the concentrations of all of the species existing in saturated solution are reliable.

Lead chloride is also sparingly soluble in water and its solubility and dissociation constants obtained in two steps are known. This information motivates us to elucidate kinetically the crystal growth of lead chloride.

The purpose of the present study is to clarify kinetically the mechanism of relaxation in an aqueous lead chloride suspension from the point of view of crystal growth and to emphasize the applicability of the pressure-jump technique to the kinetic study of crystal growth.

EXPERIMENTAL

Lead chloride (reagent grade, Wako Chemical Co.) was ground into a powder by a TI-500 type vibrating mill (Heiko Seisaku Ltd.) and washed several times with distilled water to remove impurities. The particle diameter was determined with an ultramicroscope to be 3–20 μm. The sample suspension was stirred with a magnetic stirrer in the thermostat. The conductivity of the supernatant of the suspension increased with time and reached a constant value in about 10 h as shown in Fig. 1. For the relaxation measurement the sample was stirred for more than 10 h.

Kinetic measurements were carried out using the pressure-jump apparatus with an electric conductivity detecting system. The details of the pressure-jump apparatus have been described previously (1). The time constant of the pressure jump is 80 μs.

RESULTS

In an aqueous $PbCl_2$ suspension the relaxation shown in Fig. 2a was observed using the pressure-jump technique with electric conductivity detection. The direction of the relaxation indicates a decrease in the conductivity of the suspension during relaxation. Considering that the solution of $PbCl_2$ crystal in water is endothermic (2), the relaxation in Fig. 2a may be due to the association reaction between ions. On the other hand, no relaxation was observed in the supernatant solution of $PbCl_2$. These facts suggest that the $PbCl_2$ particle relates to the observed relaxation. The semilogarithmic plot of the typical relaxation curve in Fig. 2a is expressed by a straight line as shown in Fig. 2b, showing that the relaxation curve consists of a single process. Figure 3 shows the dependance of reciprocal relaxation time, τ^{-1}, on the concentration of $PbCl_2$ crystal. As can be seen from Fig. 3, the reciprocal relaxation time increases linearly with the concentration of the crystal. This fact emphasizes that the relaxation is closely related to the growth of the $PbCl_2$ crystal.

DISCUSSION

First, let us examine the following simple mechanism for relaxation:

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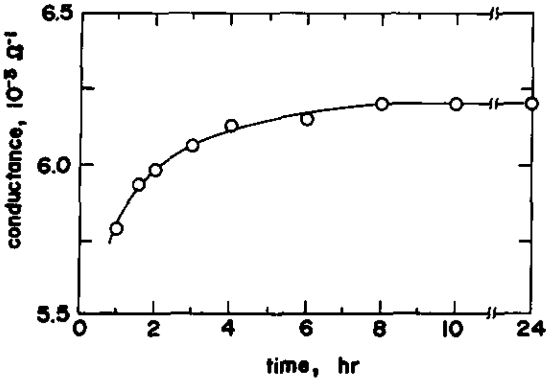

FIG. 1. Time dependence of conductance of supernatant of $PbCl_2$ suspension at concentration 3.60×10^{-1} mol dm^{-3} and 25°C.

$$Pb^{2+} \underset{Cl^-}{\rightleftarrows} PbCl^+ \underset{Cl^-}{\rightleftarrows} PbCl_2. \qquad [I]$$

Both equilibria hold in the saturated aqueous solution of $PbCl_2$. Since no relaxation could be observed in the supernatant solution of the $PbCl_2$ suspension, mechanism [I] must be easily eliminated as a possibility.

Next, the following three-step mechanism of crystal growth from the saturated solution was considered,

$$Pb^{2+} \underset{Cl^-}{\rightleftarrows} PbCl^+ \underset{Cl^-}{\rightleftarrows} PbCl_2 \longleftrightarrow (PbCl_2)_C, \qquad [II]$$

where $(PbCl_2)_C$ denotes the crystal of $PbCl_2$. In this mechanism the expression of reciprocal relaxation time for the last step is invalid for the concentration of $(PbCl_2)_C$. Thus, mechanism [II] could be also ruled out because the reciprocal relaxation time observed increases with the amount of the crystal.

Finally, we considered another type of three-step mechanism for the crystal growth,

$$Pb^{2+} \underset{Cl^-}{\overset{K_1}{\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}}} PbCl^+ \underset{Cl^-}{\overset{K_2}{\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}}}} PbCl_2 \underset{(PbCl_2)_{C1}}{\overset{K_3}{\underset{k_{-3}}{\overset{k_3}{\rightleftarrows}}}} (PbCl_2)_{C2}. \qquad [III]$$

Here, $(PbCl_2)_{C1}$ and $(PbCl_2)_{C2}$ are two kinds of $PbCl_2$ crystal, and k and K denote the rate and equilibrium constants, respectively. Under the assumption that both crystals have the same characteristics and are numerically equal, and the first and second steps equilibrate much more rapidly than the third step, the reciprocal relaxation time, τ^{-1}, for the slow step is given by

$$\tau^{-1} = A[\overline{PbCl_2}]_{C1} + k_3[\overline{PbCl_2}] + k_{-3} \qquad [1]$$

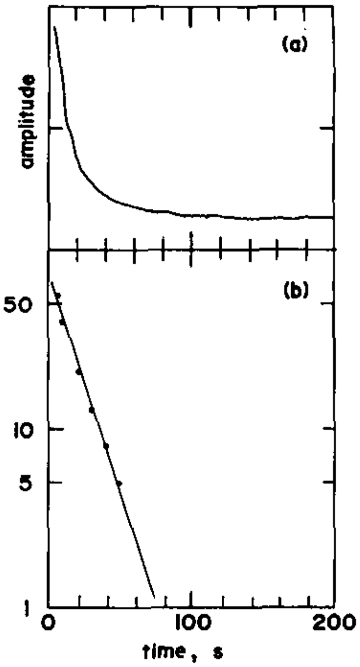

FIG. 2. (a) Typical relaxation curve for the $PbCl_2$ system observed using the pressure-jump technique with conductivity detection at concentration 5.00×10^{-1} mol dm^{-3} and 25°C. (b) Semilogarithmic plot of relaxation curve.

with.

$$A = \left\{ k_3 \frac{K_2\{2[\overline{PbCl^+}] + K_1[\overline{Cl^-}](2[\overline{Pb^{2+}}] + [\overline{Cl^-}] + [\overline{PbCl^+}])\}}{1 + K_1([\overline{Pb^{2+}}] + [\overline{Cl^-}]) + K_2\{2[\overline{PbCl^+}] + K_1[\overline{Cl^-}](2[\overline{Pb^{2+}}] + [\overline{Cl^-}] + [\overline{PbCl^+}])\}} \right\},$$

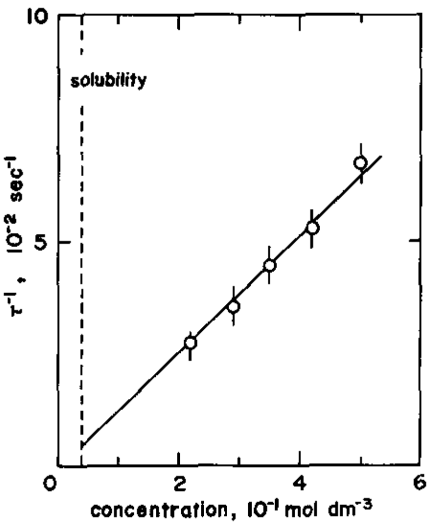

FIG. 3. Dependence of τ^{-1} on the concentration of $PbCl_2$ at 25°C; the dotted line indicates the solubility of $PbCl_2$.

where the bar over the concentration symbols, [ ], denotes equilibrium concentration. Equation [1] indicated the linearity of the plots of τ^{-1} versus $(PbCl_2)_{Cl}$, supporting the plausibility of mechanism [III]. In order to determine kinetically the values of the rate constants, k_3 and k_{-3}, from Fig. 3 using Eq. [1], the concentrations of all of the species in the saturated solution and the values of the equilibrium constants, K_1 and K_2, are required. Here we selected the data in three references to calculate these values (3)–(5). The values of k_3 and k_{-3} were obtained from the slope and intercept in Fig. 3 and are listed in Table 1. The equilibrium constant, K_{3D}, calculated kinetically from the ratio of the obtained rate constants is also shown in Table 1 along with K_{3S}, both cases determined statically. As can seen in Table 1 the value of K_{3D} is in good agreement with K_{3S}. This fact confirms the validity of mechanism [III].

Similar kinetic studies are in progress for the various sparingly soluble salts and the results will be reported in due course.

TABLE 1

Rate and Equilibrium Constants of Crystal Growth and Dissolution of $PbCl_2$ at 25°C

	$10\ k_3$ ($mol^{-1}\ dm^3\ s^{-1}$)	$10^3\ k_{-3}$ (s^{-1})	$10^2\ K_{3D}$ ($mol^{-1}\ dm^3$)	$10^2\ K_{3S}$ ($mol^{-1}\ dm^3$)
A	9.45	2.33	4.05	4.17
B	4.34	1.91	2.27	1.61

Note. (A) Based on the values in Ref. (3). (B) Based on the values in Refs. (4, 5).

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