Distribution of cadmium between calcium carbonate and solution (part 1) " $\text{Ca}(\text{HCO}_3)_2 + \text{Cd}^{2+} + \text{bipyridine} \rightarrow \text{carbonate}$ " system

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(Received January 13, 1978)

The thermodynamic distribution coefficient of cadmium between calcite and solution has been determined from the measurement of the apparent distribution coefficient in the calcium bicarbonate solutions containing cadmium ions and bipyridine as a complexing agent with cadmium ions.

The distribution of cadmium ions for aragonite in the solution containing magnesium ions (Mg^{2+} : 1.2 g/l) has also been examined.

Thermodynamic distribution coefficient for cadmium was revealed not to be constant, although constant values were obtained for magnesium, copper, zinc, manganese, strontium, barium and other divalent ions.

INTRODUCTION

It was reported that the cadmium content of carbonate sediments is as small as 0.0n–0.0ppm (WAKITA, 1970; GONG *et al.*, 1977). The basic study on the behavior of cadmium ions at the separation of calcium carbonate is needed for understanding the geochemical balance of cadmium (KITANO, 1978).

The contents of the present study are as follows: (a) experiments to reveal the amounts of cadmium ions adsorbed on calcium carbonate suspended in a solution and also on the wall of glass container, (b) experiments to measure the change in the concentrations of calcium and cadmium ions in the calcium bicarbonate solution containing cadmium ions and bipyridine during calcium carbonate formation from the solution, (c) measurements on the activity of cadmium in a solution by using cadmium electrode, (d) determinations of the values of the apparent and thermodynamic distribution coefficients of cadmium between carbonate precipitate and solution (FUJINO *et al.*, 1976; KUMAGAI *et al.*, 1976), and (e) identification of the crystal form of calcium carbonate formed in the solution, and observation of its surface by scanning electron microscope.

EXPERIMENTAL

Reagents and solutions Calcium bicarbonate solution: Calcium carbonate suspension (200g

CaCO_3) in distilled water (20l) was bubbled with carbon dioxide gas for three hours. The filtrate of the solution contains about 400mg calcium ions per liter.

Standard cadmium solution (1,000ppm): 1.000g of cadmium metal was dissolved in a small amount of nitric acid and diluted to one liter.

Bipyridine solution: Desired amounts of bipyridine were dissolved in pure water (10^{-4} to 10^{-3} mol Bpy/l).

Experimental procedure (a) Adsorption of cadmium ions on powdered calcium carbonate: Various amounts of powdered calcium carbonate were suspended in pure water or in calcium bicarbonate solution, and cadmium solution was added stirring. The suspension was stirred for ten minutes, and filtered. Cadmium in the filtrate was determined.

(b) Coprecipitation of cadmium ions with calcium carbonate: Cadmium solution was added to the calcium bicarbonate solution containing 0 to 10^{-3} mol/l of bipyridine to adjust the concentration of cadmium ions to 2ppm. The release of carbon dioxide gas from this solution was followed by carbonate precipitation, and portions of the solution were taken to determine the decrease in the calcium, cadmium and bipyridine concentrations of the solution. Calcium ions in the solution were determined volumetrically with EDTA solution, and cadmium ions with an atomic absorption spectro-

meter. The concentration of bipyridine was measured colorimetrically with ferrous solution. (c) Measurement of the activity of cadmium in solution: The apparatus used for the measurement was a pH meter (Hitachi Horiba F5) combined with cadmium electrode (Orion 94-48A) and calomel electrode as a reference electrode. The electrode was calibrated with standard cadmium nitrate solution.

(d) Identification of the crystal form of calcium carbonate: A Rigaku Denki X-ray diffractometer was employed. Standard conditions used for the identification were as follows: voltage, 35KV; current, 15mA; scale factor, 8; multiplier factor, 1; time constant, 4; goniometer speed, $1^\circ/\text{min}$.

(e) Observation of the surface of calcium carbonate: Scanning electron microscope (Japan Electric JSM-T20) was used.

RESULTS AND DISCUSSION

1. Adsorption of cadmium ions on calcium carbonate When the calcium bicarbonate solutions containing cadmium ions (2ppm) and bipyridine ($0 - 10^{-3}\text{mol/l}$) had been kept in a glass container, any adsorption of cadmium ions on the wall of the glass container was never observed experimentally (STRUEMLER, 1973; KING *et al.*, 1974; BENES and KOPICKA, 1976). When calcium carbonate is suspended in a solution containing cadmium ions, cadmium concentration of the solution decreases. These observations suggest that the decrease in the cadmium concentration of the solution is caused by the adsorption of cadmium ions on suspended calcium carbonate.

Figure 1 shows the amount of cadmium ions adsorbed on suspended calcium carbonate (10–200mg) in a solution (50ml) containing cadmium ions (1ppm) at room temperature. Figure 1 indicates that in any solution (pure water and seawater) the amount of cadmium ions adsorbed on calcite was larger than that on aragonite. This seems to be in harmony with the fact that cadmium carbonate is of calcitic lattice configuration. Here, the following observed results should be noted: Copper and zinc ions are adsorbed more greatly on suspended aragonite than on suspended calcite, though copper and zinc carbonates have always a calcitic crystal form (KITANO *et al.*, 1976). The adsorption of cadmium ions on calcium carbonate suspended in calcium bicarbonate solution was examined experimentally as given in Fig. 2. The

Fig. 1. Amount of cadmium ions adsorbed on suspended calcium carbonate (10–200mg) in a solution (50ml) containing cadmium ions (initially 1ppm) at room temperature. C and A denote calcite and aragonite, respectively. S denotes the solution containing the same amounts of calcium and magnesium ions as those of seawater.

Fig. 2. Influence of pH value in calcium bicarbonate solution on the amount of cadmium ions adsorbed.

figure shows that the adsorbed amount of cadmium ions is affected by the pH value and the calcium bicarbonate concentration. With increasing pH value of the solution, the amount of cadmium ions adsorbed on calcium carbonate increases. About 10 per cent of cadmium ions present in the initial solution is adsorbed on suspended calcium carbonate.

As will be discussed later, the amount of cadmium ions adsorbed on suspended calcium

carbonate is small as compared with the amount of cadmium ions coprecipitated with forming calcium carbonate. In the calcium bicarbonate solution containing bipyridine, the adsorption of cadmium ions on suspended calcium carbonate is neglected. These facts indicate that the adsorption of cadmium ions on calcium carbonate has little significant effect on the cadmium content of calcium carbonate formed from the calcium bicarbonate solution containing cadmium ions (see section 4).

2. Coprecipitation of cadmium ions with forming calcium carbonate

Factors controlling the distribution of cadmium ions between calcium carbonate and solution are as follows (KITANO *et al.*, 1973): (a) the crystal form and the physico-chemical properties of forming carbonate crystals (b) states and concentrations of calcium and cadmium dissolved in a parent solution, and concentrations of other chemical species dissolved in the solution which control the activities of calcium and cadmium in the solution, and (c) releasing rate of carbon dioxide in the solution. The releasing rate has a great influence on the rate of crystal formation.

Figure 3 shows the decrease in the cadmium content of a parent calcium bicarbonate solution from which only calcite is formed. Cadmium ions had been removed almost completely from

Fig. 3 Decrease in the cadmium content of parent calcium bicarbonate solution from which only calcite is formed.

Fig. 4. Decrease in the cadmium content of parent calcium bicarbonate solution containing magnesium and cadmium ions (initially 1.2g/l and 2ppm, respectively), from which aragonite is formed.

the solution before 10 per cent of calcium ions in the solution was precipitated as calcite.

Figure 4 gives the decrease in the cadmium content of the parent solution during the process of aragonite formation from the calcium bicar-

Fig. 5. Decrease in the cadmium content of parent calcium bicarbonate solution containing cadmium ions (2 ppm) and bipyridine to control the activity of cadmium ions in the solution.

bonate solution containing magnesium ions (1.2 g/l) and cadmium ions (2ppm). Figure 4 indicates that the rate of decrease in the cadmium content of the solution in aragonite formation was smaller than that in calcite formation.

Figure 5 shows the decrease in the cadmium content of the calcium bicarbonate parent solution containing cadmium ions (2ppm) and bipyridine to control the activity of cadmium ions in the solution through the complex formation between cadmium ions and bipyridine. With increasing concentration of bipyridine added to the solution, the activity of cadmium ions in the solution and then the amount of cadmium ions coprecipitated with forming calcium carbonate decrease.

It was observed that the concentration of bipyridine in the solution did not change throughout the process of carbonate precipitation.

3. Effect of stirring rate of a parent solution on coprecipitation of cadmium ions with forming calcium carbonate

The stirring rate of the calcium bicarbonate parent solution controls the releasing rate of carbon dioxide from the solution and the rate of carbonate formation. When calcite was formed from the calcium bicarbonate solution containing only cadmium nitrate, significant influence of the stirring rate

Fig. 6. Decrease in the cadmium content of parent calcium bicarbonate solution containing bipyridine (0.5×10^{-3} mol/l) from which only calcite was formed.

Fig. 7. Rate of decrease in the calcium and cadmium contents of the calcium bicarbonate solution containing bipyridine (10^{-4} mol/l).

of the solution was not observed on the rate of the coprecipitation of cadmium ions with the forming calcite.

Figure 6 shows the decrease in the cadmium content of the solution containing bipyridine from which only calcite was formed. The figure indicates that the rate of coprecipitation of cadmium ions was larger on vigorous stirring than on moderate stirring. When the parent solution was kept still without stirring, as shown in Fig. 7, the rate of decrease in the calcium and cadmium contents of the solution was remarkably different from one portion to the other in a container, although the releasing rate of carbon dioxide gas and the formation rate of calcium carbonate are higher in the upper layer than in

Fig. 8. Rate of decrease in the calcium and cadmium contents of the calcium bicarbonate solution containing bipyridine (10^{-3} mol/l).

the lower layer of the solution.

However, Fig. 8 indicates that throughout any portion of the solution containing a large amount of bipyridine, any difference was not observed in the rate of decrease in the calcium and cadmium contents.

4. Distribution coefficient of cadmium between calcium carbonate and solution

4-1 $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + $\text{Cd}(\text{NO}_3)_2$ (Cd^{2+} : 2ppm) $\rightarrow$ calcite

Figure 9 shows the obtained values of the apparent distribution coefficient (K^s) of cadmium between calcium carbonate and solution, by use of the Doerner Hoskins' equation, from the measurement of decrease in calcium and cadmium concentrations in the parent solution during the process of calcium carbonate formation. The figure indicates that a constant value of K^s of about 20 is observed throughout the process of carbonate formation in this solution system. And also in the solutions containing 0.5 and 1ppm cadmium ions, a constant K^s value of 20 was obtained. The value is considered to be the value of the thermodynamic distribution coefficient, as will be discussed later in 4-3. And the constant value may support that cadmium carbonate is present as a solid solution with calcitic calcium carbonate formed in this solution system.

Fig. 9. Values of the apparent distribution coefficient (K^s) of cadmium between calcite and the calcium bicarbonate solution containing cadmium ions (initially 2ppm).

Fig. 10. Values of the apparent distribution coefficient (K^s) of cadmium between aragonite and calcium bicarbonate solution containing cadmium and magnesium ions (initially 2ppm and 1.2g/l, respectively).

4-2 $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + MgCl_2 (Mg^{2+} : 1.2g/l) + $\text{Cd}(\text{NO}_3)_2$ (Cd^{2+} : 2ppm) $\rightarrow$ Aragonite

Figure 10 gives the value of the apparent distribution coefficient of cadmium between aragonite and solution. An abnormal and high value of the distribution coefficient was observed at the early stage of carbonate formation (KITANO *et al.*, 1971). At the later stage, however, the apparent value reaches about 1.5 in the calcium bicarbonate solution containing 1.2 g/l of magnesium ions. Cadmium is not captured in the crystal lattice of aragonite, because cadmium carbonate has always a calcitic crystal form. Although the value of the distribution coefficient of cadmium between aragonite and solution has no physico-chemical meaning, the value is convenient to express the amount of cadmium ions coprecipitated with aragonite.

4-3 $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + Bpy (Bpy: 10^{-4} to 10^{-3} mol/l) + $\text{Cd}(\text{NO}_3)_2$ (Cd^{2+} : 2ppm) $\rightarrow$ calcite

Figure 11 shows the value of the apparent distribution coefficient which varies with the different concentrations of bipyridine in a parent solution. The value decreases with increasing concentration of bipyridine added to the solution, owing to the decrease in the activity of cadmium ions in the solution by the complex formation between cadmium ions and bipyridine.

Fig. 11. Values of the apparent distribution coefficient (K^s) of cadmium between calcite and the calcium bicarbonate solution containing cadmium ions (initially 2ppm) and bipyridine.

An apparent distribution coefficient K^s is expressed in equation (1):

$$K^s = \frac{1}{1 + \alpha} \cdot \frac{1}{\lambda_{\text{CdCO}_3}^s} \cdot K^{T,S} \quad (1)$$

where $\lambda_{\text{CdCO}_3}^s$ denotes the activity coefficient of CdCO_3 in solid solution, α refers to the relative extent of the complex formation of cadmium ions with bipyridine in the parent solution, and $K^{T,S}$ denotes the thermodynamic distribution coefficient.

Bipyridine forms the three complexes with cadmium ions in solution (CABANI and SCROCCO, 1958):

The value of α is calculated from equation (7) by use of the values of the stability constants of cadmium-bipyridine complexes (equations (2), (3) and (4)) and the concentrations of total bipyridine (equation (5)) and total cadmium (equation (6)) dissolved in the solution.

$$[\text{Bpy}, T] = [\text{Bpy}] + [\text{Cd}(\text{Bpy})^{2+}]$$

$$+ 2[\text{Cd}(\text{Bpy})_2^{2+}] + 3[\text{Cd}(\text{Bpy})_3^{2+}] \quad (5)$$

$$\begin{aligned} [\text{Cd}, T] &= [\text{Cd}^{2+}] + [\text{Cd}(\text{Bpy})^{2+}] \\ &+ [\text{Cd}(\text{Bpy})_2^{2+}] + [\text{Cd}(\text{Bpy})_3^{2+}] \\ &= [\text{Cd}^{2+}] \cdot (1 + \alpha) \end{aligned} \quad (6)$$

$$\begin{aligned} \alpha &= K_1 \cdot [\text{Bpy}] + K_1 \cdot K_2 \cdot [\text{Bpy}]^2 \\ &+ K_1 \cdot K_2 \cdot K_3 \cdot [\text{Bpy}]^3 \end{aligned} \quad (7)$$

where $[\text{Bpy}, T]$ and $[\text{Cd}, T]$ are the molar concentrations of total bipyridine and total cadmium dissolved in a solution, respectively, and $[\text{Cd}^{2+}]$ and $[\text{Bpy}]$ are the concentrations of free cadmium ions and free bipyridine in a solution, respectively.

Table 1 shows the calculated value of α against the concentration of bipyridine.

Table 1. Calculated and observed α values at the different concentrations of bipyridine

Bpy ($\times 10^{-3}$ mol/l)	α	
	observed	calculated
0.1	2	2.1
0.5	20	24
1.0	100	86

The value of the thermodynamic distribution coefficient, $K^{T,S}$, is obtained by putting into equation (1) calculated α , assumed $\lambda_{\text{CdCO}_3}^s$, and experimentally determined K^s . Figure 12 shows the obtained value of the thermodynamic distribution coefficient in the parent solution containing 10^{-3} mol/l of bipyridine. The figure indicates that the obtained value of the thermodynamic distribution coefficient, $K^{T,S}$, is affected by the stirring rate of a parent solution. Moderate stirring leads easily to give a constant value of the distribution coefficient. Such a trend appears for other concentrations of bipyridine.

The value of $K^{T,S}$ must be constant independently of the concentration of bipyridine in a parent solution, when the following conditions are satisfied: (a) The stability constants of cadmium-bipyridine complexes are correct, (b) The presence of cadmium ions, bipyridine and cadmium-bipyridine complexes in a solution has no influence on the physico-chemical properties of the surface of forming calcite, (c) Carbonate formation occurs under an equilibrium condition, (d) The cadmium carbonate is present

Fig. 12. Values of the thermodynamic distribution coefficient ($K^{T,S}$) of cadmium between calcite and the calcium bicarbonate solution containing cadmium ions and bipyridine (initially 2ppm and 10^{-3} mol/l, respectively).

Fig. 13. The values of the thermodynamic distribution coefficient ($K^{T,S}$) of cadmium between calcite and the calcium bicarbonate solution containing various amounts of bipyridine.

as a solid solution with calcitic calcium carbonate.

However, Fig. 13 shows that the different values of $K^{T,S}$ were obtained at the different concentrations of bipyridine in a parent solution. This suggests that some of the above conditions are not satisfied. An equilibrium condition seems to be maintained in a moderate stirring system, because the individual value of the apparent distribution coefficient is nearly constant throughout the process of carbonate formation at any definite concentration of bipyridine.

To check the values of the stability constants of cadmium-bipyridine complexes, the activity of cadmium dissolved in the solution was measured by using cadmium electrode. The change in the activity of cadmium in a solution was measured during the process of calcium carbonate formation in the calcium bicarbonate solution containing cadmium ions and no bipyridine. Almost all cadmium dissolved in calcium bicarbonate solution was deduced to be present as cadmium ions from the e.m.f. measurement. Thus, apparent distribution coefficient K^S of cadmium described in 4-1 solution system is considered to be thermodynamic distribution coefficient $K^{T,S}$.

Fig. 14. Change in the activity of cadmium in the calcium bicarbonate solution containing bipyridine (10^{-4} mol/l) from which calcite is formed on slow (▲) and vigorous (△) stirring.

Figure 14 shows the change in the activity of cadmium in the calcium bicarbonate solution containing bipyridine (10^{-4} mol/l) from which calcite is formed. The measured values of cadmium activity in the solution could examine whether or not the values of the stability constants of cadmium-bipyridine complexes given in equations (2), (3) and (4) are correct. The comparison of α value obtained by the measurement of the activity (see Fig. 14) with the value calculated from the stability constants of cadmium-bipyridine complexes (see Table 1) indicates that both values are well in accord. This leads us to conclude that the values of the stability constants of cadmium-bipyridine complexes in equations (2), (3) and (4) are correct. One of the most probable reasons for the different values of the thermodynamic distribution coefficient at the varying concentrations of bipyridine in a parent solution is considered to exist in the abnormal physico-chemical properties of the surface of carbonate caused by the presence of cadmium ions, bipyridine and/or cadmium-bipyridine complexes in the parent solution.

The presence of cadmium ions in a parent solution does not seem to have significant influence on the property of the surface of carbonate, because a nearly constant value of the distribution coefficient was obtained throughout the process of carbonate formation in the solution system without bipyridine (see 4-1). But this should be examined more exactly.

The constant values of the thermodynamic distribution coefficient of trace metals such as Zn^{2+} , Cu^{2+} , Sr^{2+} , Ba^{2+} and UO_2^{2+} have been obtained satisfactorily throughout the formation process of calcium carbonate from the calcium bicarbonate solution containing inorganic and/or organic materials as complexing agents with the metal ions (HOLLAND *et al.*, 1964; CROCKET and WINCHESTER, 1966; KITANO *et al.*, 1968, 1971, 1973; KITANO and OOMORI, 1971; RAINSWELL and BRIMBLECOMBE, 1977).

It should be noted that the present study shows that, in the calcium bicarbonate solution containing bipyridine as a complexing agent, the constant value of the thermodynamic distribution coefficient of cadmium ions can not be obtained from the observed value of the apparent distribution coefficient even with the aid of exact stability constants of the complexes.

Finally, the surface of calcium carbonate has been observed by means of scanning electron microscope. The pictures of the surface of

calcite crystals formed in the calcium bicarbonate solutions containing varying amounts of cadmium ions are given in Photos 1 to 3, which indicate that with increasing concentration of cadmium ions in the parent solution the smoothness of their surface decreases.

The surface of calcite crystal formed from calcium bicarbonate solution containing only

— 0.5 μ Photo 1

— 1 μ Photo 2

— 1 μ Photo 3

— 1 μ Photo 4

— 1 μ Photo 5

Photo 1. Pure calcite: $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm)

Photo 2. Calcite: $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + Cd ($\text{NO}_3)_2$ (Cd^{2+} : 0.5ppm)

Photo 3. Calcite: $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + Cd ($\text{NO}_3)_2$ (Cd^{2+} : 2ppm)

Photo 4. Calcite: $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + Bpy (Bpy: 10^{-3} mol/l)

Photo 5. Calcite: $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 400ppm) + Bpy (Bpy: 10^{-3} mol/l) + Cd($\text{NO}_3)_2$ (Cd^{2+} : 2ppm)

bipyridine is similar to that of calcite formed from calcium bicarbonate solution without any other material (Photo 4).

The surface of calcite formed from calcium bicarbonate solution containing both cadmium ions and bipyridine is rough, as seen from Photo 5. It remains to be clarified whether or not the property of the surface of calcium carbonate precipitates has some influence on the distribution of trace metal between precipitate and solution. To make clear the reason why the value of thermodynamic distribution coefficient of cadmium ions can not be obtained in the present experiment, the authors are studying the distribution of cadmium ions between calcite and solution for calcium bicarbonate solution containing cadmium ions and chloride ions, which form complexes with cadmium ions. The result will be shown in another paper to answer that question.

SUMMARY

The value of the thermodynamic distribution coefficient of cadmium between calcite and solution is estimated to be about 20. When the amount of cadmium coprecipitated with aragonite is expressed in terms of distribution coefficient, the value for aragonite is about 1.5.

The thermodynamic distribution coefficient of cadmium could not be obtained from the apparent distribution coefficient observed in the calcium bicarbonate solution containing bipyridine and cadmium ions, even with the aid of exact stability constants of the complexes between cadmium ions and bipyridine.

Acknowledgement—This study was supported by a grant from the Ministry of Education.

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