The Coprecipitation of Calcium with Strontium Oxalate

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The distribution coefficients in the coprecipitation process of the calcium-strontium oxalate system were determined. Calcium ion coprecipitated with obeying the logarithmic distribution law. The distribution coefficient was a little affected by the pH value and the acetate concentration. This can be attributed to the fact that strontium and calcium formed complexes with the organic acid. When the complex formation component was eliminated from the present system, the distribution coefficient became constant and had a value of about 3.6.

INTRODUCTION

In our previous papers, the coprecipitation behaviors of strontium,[1] scandium[2] and lanthanide[3,4] ions with calcium oxalate were studied, and the logarithmic distribution law was obeyed in all cases of these systems. The logarithmic distribution coefficient, λ, was considerably affected by the changes of the pH value and the concentration of an organic acid in the lanthanide-calcium oxalate system. But the distribution coefficient was not almost affected by these changes in the coprecipitation process of strontium with calcium oxalate. This was caused by the fact that macro and micro components had a similar complexing ability with a carboxylic acid used as a buffering agent.

The coprecipitation process of strontium was not observed in detail, that is, the distribution coefficient observed, λ, was not very accurate, because the coefficient was considerably low (about 0.1) and the surface adsorption of a micro component was observed at the beginning of the precipitation process.

The authors were still much interested in observing the coprecipitation behavior of calcium with strontium oxalate; for example, the value of the distribution coefficient and influence by changes of the pH value and the concentration of an organic acid.

EXPERIMENTAL

Reagents. Calcium–45 was supplied as chloride in hydrochloric acid by International Chemical & Nuclear Corp., Irvine, Calf., U.S.A., and was diluted to make a solution of $\sim 1 \, \mu\text{Ci/ml}$. A stock strontium solution was prepared by dissolving reagent-grade strontium chloride with redistilled water and by standardizing it with a standard ethylenediaminetetraacetic acid (EDTA) solution. The calcium solution was prepared by dissolving dry calcium carbonate with hydrochloric acid. The standard EDTA solution (0.00330M), containing EDTA-magnesium complex, was standardized with the standard calcium solution. Reagent grade dimethyloxalate

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was purified by recrystallization from methanol. Liquid scintillator for measurement of calcium–45 was prepared by dissolving 100 ml of 1,4–bis(5–phenyloxazolyl)–benzene (POPOP), 4 g of 2,5–diphenyloxazole (DPO) and 75 g of naphthalene with dioxane and by diluting it to 1 liter with dioxane.

The other chemicals were reagent grade materials.

Apparatus. Radio-tracer measurements were made with Packard Tri-carb Liquid Scintillation Spectrometer, Model 3320. A Hitachi-Horiba pH Meter, Model F–5, was used for pH measurements.

Procedure. The procedure of the coprecipitation was essentially the same as those described in previous papers.[3,4]

At appropriate intervals of time, 1.0 ml (sample A) and 2.0 (sample B) of the samples solutions were pipetted out from the reacting solution through a sintered glass filter into conical beakers, respectively. After these samples were ashed with perchloric acid, sample A was used for the determination of calcium, sample B for the determination of strontium. As for sample A, 1 ml of 0.1 N hydrochloric acid and 15 ml of liquid scintillator were added to the beaker. After transfered into a vial, the sample was counted with a liquid scintillation spectrometer. Sample B was titrated with standard EDTA solution.

The homogeneous and logarithmic distribution coefficients, D[5,6] and λ,[7] were calculated by the following equations:

$$\left(\frac{\text{Ca}}{\text{Sr}} \right)_{\text{cryst.}} = D \left(\frac{\text{Ca}}{\text{Sr}} \right)_{\text{soln.}} \tag{1}$$

$$\log \frac{\text{Initial Ca}}{\text{Ca left in soln.}} = \lambda \log \frac{\text{Initial Sr}}{\text{Sr left in soln.}} \tag{2}$$

RESULTS AND DISCUSSION

Calcium ion coprecipitated into strontium oxalate phase typically obeying logarithmic distribution law, as shown in Fig. 1. The experimental condition was as follows: The concentrations of calcium, strontium and dimethyloxalate were 1.0×10^{-5}, 2.5×10^{-2} and 0.1M, respectively. The total volume of the reacting solution was 200 ml which was buffered with 1.0M acetate, and the temperature was kept at 75°C. The logarithmic distribution coefficient in the present system was about 2.7 and this showed that the calcium ion was enriched in the solid phase.

The percentages of coprecipitated calcium in the fraction of the strontium oxalate were plotted at 0.5, 1.0 and 2.0M of the acetate concentration in Fig. 2. The diagram indicated that calcium ion coprecipitated into strontium oxalate with decreasing the extent of enrichment as the acetate increased. The logarithmic distribution coefficient, λ, was calculated from these data. The mean values of λ were 2.97 at 0.5M, 2.71 at 1.0M and 2.22 at 2.0M of acetate. By the pH value was also affected the logarithmic distribution coefficient which was observed in a 1.0M acetate solution, as seen in Fig. 3. These results show that acetate ion affected
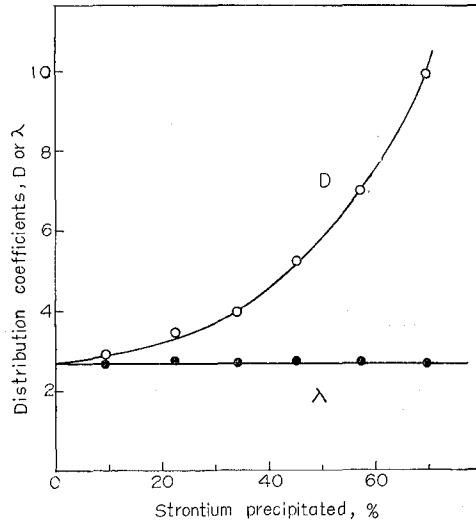
Fig. 1. The coprecipitation of calcium.
Sr: 0.025 M, Ca: 10^{-6}M, dimethyloxalate: 0.1M,
acetate: 1.0M, pH: 4.00, Temp.: 75°C

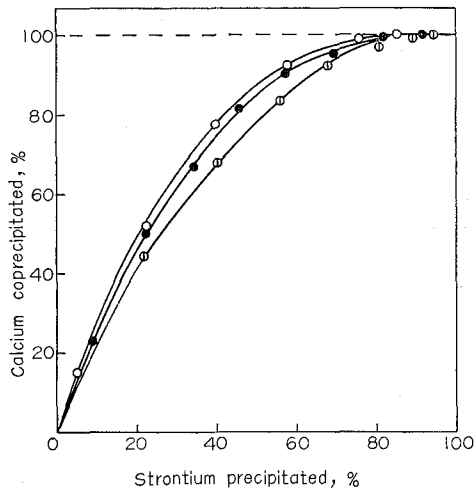Fig. 2. The effect of acetate ion.
Sr: 0.025M, Ca: 10^{-6}M, pH: 4.00
acetate: -○-; 0.5M, $\lambda=2.97$, -●-; 1.0M, $\lambda=2.71$,
-○-; 2.0M, $\lambda=2.22$

the enrichment of calcium ion into strontium oxalate phase because of the complex formation with the acetate ion.

Accordingly, it is preferable to eliminate the complex formation factor from this system. The distribution coefficient was corrected by calculating the concentrations of the free calcium and strontium ions which were easily obtained from the values of their stability constants.[8] The results are shown in Table 1.
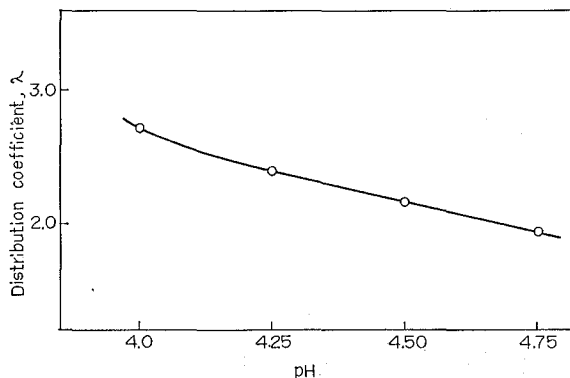
Fig. 3.   The coprecipitation of calcium at different pH values.
Sr: 0.025M,   Ca: 10^{-6}M,   acetate: 1.0M

Table 1.   The Correction of the Distribution Coefficient by the Complex Formation

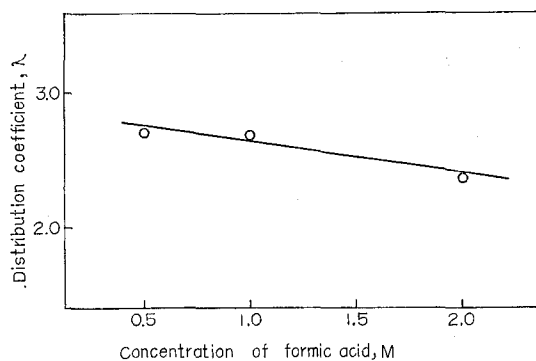| total acetate, M	pH	distribution coefficient	
		uncorrected value	corrected value
0.5	4.00	2.97	3.62
1.0	4.00	2.71	3.71
2.0	4.00	2.22	3.47
(1.0)	(4.00)	(2.71)	(3.71)
1.0	4.25	2.39	3.63
1.0	4.50	2.16	3.64
1.0	4.80	1.93	3.59
		average	3.61

Sr: 0.025M, Ca: 1.0×10^{-5}M

Fig. 4.   The effect of formate concentration.
Sr: 0.025M, Ca: 10^{-6}M, pH: 4.00

As seen in the table, the distribution coefficient became constant, though rough, by connecting the concentration of the complexing species, and had the mean value of 3.61.   In cases in which strontium coprecipitated in calcium oxalate phase, the

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distribution coefficient gave nearly a constant, 0.1. As the product of these coefficients, the value of 0.36 was obtained, and was much lower than could be expected. This may be caused by the fact that ionic radii of calcium and strontium ions and the properties of their oxalate crystals are a little different.

The effect of formate ion was essentially the same as that of acetate ion. As indicated in Fig. 4, the effect was a little, compared with that of acetate. It was
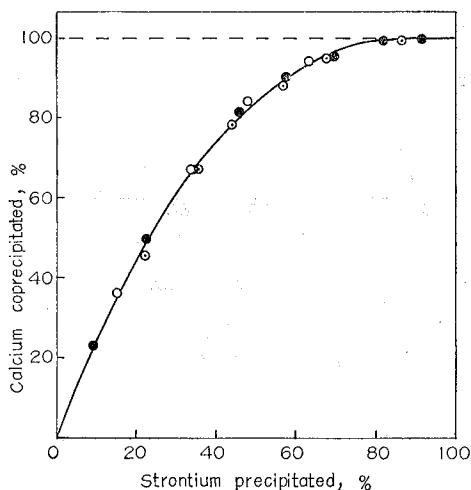

Fig. 5. The effect of the micro-component.
Sr: 0.025M,   pH: 4.00,   acetate: 1.0M
Ca: -⬤-; 10^{-6}M, $\lambda=2.71$,   -◯-; 10^{-5}M, $\lambda=2.78$,
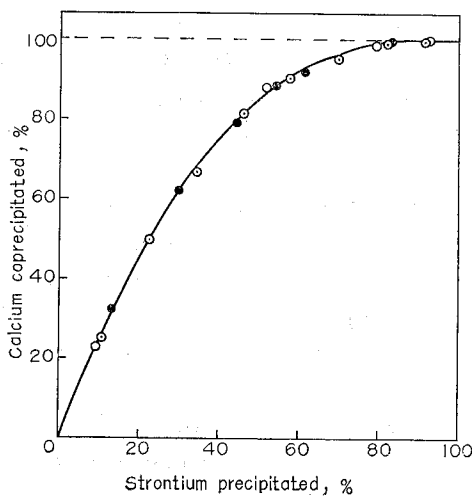   -⊙-; 10^{-4}M, $\lambda=2.65$

Fig. 6. The effect of ionic strength.
Sr: 0.025M,   Ca: 10^{-6}M,   acetate: 1.0M, pH: 4.00
NaClO$_4$: -⊙-; 0, $\lambda=2.71$,   -⬤-; 1.0M, $\lambda=2.73$,
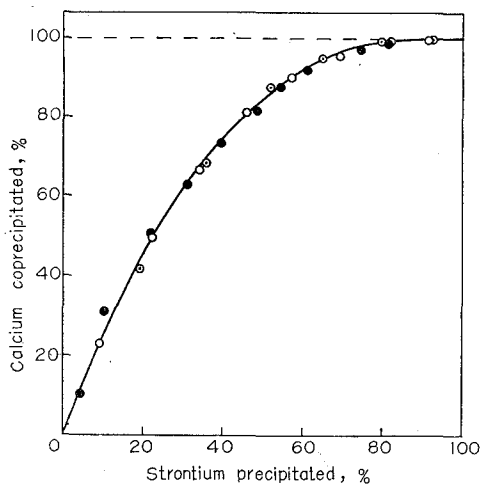   -◯-; 2.0M, $\lambda=2.81$

Fig. 7. The effect of precipitation rate.
   Sr: 0.025M,   Ca: 10^{-6}M,   acetate: 1.0M, pH: 4.00
   dimethyloxalate: $-\odot-$; 0.20M, $\lambda=2.73$, $-\bigcirc-$; 0.10M,
   $\lambda=2.71$, $-\bullet-$; 0.05M, $\lambda=2.65$

attributed to the smaller differences in stability constants of strontium and calcium formates than the differences in those of the acetates (the values of K, are 0.66 for SrForm, 0.80 for CaForm, 0.44 for SrAc and 0.77 for CaAc, respectively).[8]

The strontium oxalate was precipitated from the solutions containing 10^{-4}, 10^{-5} and 10^{-6}M of calcium, respectively, to check the effect of a micro component. The effect is shown in Fig. 5; no significant change was observed in the coprecipitation behavior.   In order to study the effect of the ionic strength in a reacting solution, nil, 1.0 and 2.0M solution of sodium perchlorate, respectively, were used.   The results shown in Fig. 6 indicated that the coprecipitation in the system was scarcely influenced by the ionic strength.   These facts suggest that the coprecipitation process of calcium into strontium oxalate crystal was not concerned with the adsorption or occlusion phenomena.

The effect of the amount of dimethyloxalate was studied in order to examine the influence of the precipitation rate.   Figure 7 shows that the coprecipitation of calcium was not almost affected by this factor, when the ester concentration changed from 0.05M to 0.20M.   The time required for the 80% precipitation of strontium was about 3.5, 12 and 45 hours when the ratio of the ester to strontium is 8.0, 4.0 and 2.0, respectively.

Previously, the authors reported that the complexing species formed in reacting solution affected the coprecipitation of a micro component.[9]   However, in the present system, when complex formation components were removed, as described above, the distribution coefficient did not get affected by the complex formation factor, in other words, acetate or formate complexes formed in this system did not affect the distribution of a micro component.

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