BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 581—585 (1966)

The Coprecipitation Behavior of Strontium with Calcium Oxalate by Precipitation from a Homogeneous System

By Masakazu MATSUI

Institute for Chemical Research, Kyoto University, Sakyo-ku, Kyoto

(Received July 19, 1965)

The coprecipitation of strontium with calcium oxalate was studied using dimethyloxalate to precipitate calcium from a homogeneous solution. The several effects of the coprecipitation conditions on the distribution coefficients were investigated in the fractional precipitation process of calcium-strontium oxalate mixtures. Regardless of the pH value, the concentration of acetic acid and other factors, the coprecipitation curves of strontium showed similar shapes in almost all cases, although the curves well shifted up and dawn to some extent. It appears to be an anomalous system, because an increase in the fraction of the calcium precipitated tends to decrease the distribution coefficients. It is considered that two coprecipitation mechanisms are involved in the coprecipitation system; one is the surface adsorption on fine crystals, while the other is a normal systematic type. When the adsorption part was removed, it was found that the modified system obeyed the Doerner and Hoskins logarithmic distribution law and that the coefficient gave nearly a constant, 0.1.

The coprecipitation with calcium oxalate is generally used to separate strontium ions from other metals in dilute solutions.

When a strontium ion is coprecipitated with a calcium oxalate, there are two systematic ways in which strontium is distributed in crystals. One type of distribution is expressed by the homogeneous distribution law proposed by Chlopin[1] and Henderson and Kracek,[2] in which the strontium-calcium ratio in the precipitated crystals is proportional to the strontium-calcium ratio in the final solution:

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

where D is defined as the homogeneous distribution coefficient. This distribution law represents a state of true thermodynamic equilibrium, one in which the solid phase has been thoroughly digested in order to remove all the concentration gradients inside a crystal.

The other type is expressed by the logarithmic distribution law proposed by Doerner and Hoskins[3] and expressed as follows:

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

where λ is the logarithmic distribution coefficient; this law is obeyed when a replacement equilibrium is achieved on each layer of the crystal during the precipitation process. When λ is smaller than unity, the tracer component is enriched in the solution, and vice versa.

Ishibashi et al.[4] carried out an experiment in which oxalates were homogeneously precipitated, with a rise in pH value due to ammonium ions uniformly generated by the hydrolysis of urea. They found that strontium was distributed in calcium oxalate in accordance with the logarithmic distribution law, and that the extrapolation of the logarithmic distribution coefficients to 0% of calcium precipitated would give a constant value of about 0.30.

The coprecipitation behavior of scandium,[5] yttrium[6] and lanthanide[7] ions with calcium oxalate was studied by Shigematsu et al. and by the present author. Their results demonstrate that the most predominant factors affecting the coefficient are the pH value of the solution and the concentration of the organic acid used as a buffering agent, because the ionic concentrations of divalent macro and tervalent micro components vary with the coprecipitation conditions; the ionic radius also plays an important role in the coprecipitation process.

According to these papers, it may be deduced that the distribution coefficient in the case of a calcium-strontium system will not be very much affected by the precipitation condition, such as the pH value and the concentration of an organic acid, because the ratio of the complexing ability of macro and micro components with an organic acid is hardly affected at all by the above-mentioned

---

[1] W. Chlopin, *Z. anorg. u. allgem. Chem.*, **143**, 97 (1925).

[2] L. M. Henderson and F. C. Kracek, *J. Am. Chem. Soc.*, **49**, 738 (1927).

[3] H. A. Doerner and W. M. Hoskins, ibid., **47**, 662 (1925).

[4] M. Ishibashi, T. Shigematsu and T. Ishida, *Annual Rep. Research Committee on the Application of Artificial Radio-isotopes*, **3**, 6 (1953/4).

[5] T. Shigematsu, M. Tabushi and M. Matsui, *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 381 (1962).

[6] T. Shigematsu, M. Tabushi and M. Matsui, This Bulletin, **37**, 1610 (1964).

[7] M. Matsui, This Bulletin, in press.

factors.

This paper will deal with the variable influences of the coprecipitation conditions on the distribution coefficient in the fractional precipitation process of calcium-strontium oxalate mixtures.

Experimental

Apparatus and Reagents. — The radioactivity counting was performed with a Phillips halogen-quenched G-M tube connected to a Metro dekatron scaler, Model D-5. A Hitachi-Horiba pH meter, Model M-3, was used for the pH measurements.

Strontium-89 was supplied as chloride in hydrochloric acid by the Oak Ridge National Laboratory, Oak Ridge, Tennessee, U. S. A., and was diluted to make a solution of ~1 μc./ml. Reagent-grade dimethyloxalate was purified by recrystallizing it from anhydrous methanol; it was then stored in a dry atmosphere in a desiccator. The calcium solution was prepared by dissolving dry calcium carbonate with hydrochloric acid. The strontium solution was prepared by dissolving reagent-grade strontium chloride with water, after which it was standardized with a standard EDTA solution. The EDTA solution (0.00330 M), containing a magnesium EDTA complex, was standardized by means of a calcium standard solution; it was used for the determination of the calcium ions of the sample solutions.

The other chemicals were chemically-pure or reagent-grade materials.

Procedure.—The procedure of the coprecipitation and the determination of the macro and micro components were essentially the same as those described in previous papers.[6,7] The calcium was titrated with a EDTA solution containing its magnesium chelate.

The strontium activity would be contaminated very slightly by yttrium-90 existing as a radioactive daughter of strontium-90 impurity. The yttrium activity was estimated by the coprecipitation method with ferric hydroxide, while the strontium activity in the solution phase was corrected by means of the distribution values of yttrium.[6] The homogeneous and logarithmic distribution coefficients, D and λ, will be calculated from Eqs. 1 and 2.

Results

The Effect of the pH Value.—The percentages of coprecipitated strontium in the fraction of the calcium oxalate precipitate at different pH values are plotted in Fig. 1. The experimental conditions were as follows: The concentrations of calcium, strontium and dimethyloxalate were 2.50×10^{-1} M, 10^{-6} M and 0.1 M respectively. The total volume of the reacting solution was 200 ml.; this solution was buffered with 1 M acetate or formate, and the temperature was kept at 75.0°C. As is shown in Fig. 1, the strontium ion content was enriched in the solution phase, and unlike as in the case of the calcium - rare earth system, the coprecipitation behavior was the same regardless of the pH value and the species of organic acid.

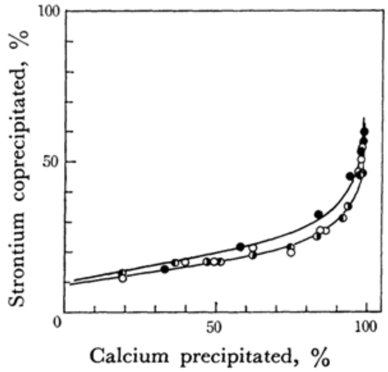

Fig. 1. The coprecipitation of strontium with calcium oxalate at different pH values.
Ca: 0.025 M, Sr: 10^{-6} M, dimethyloxalate: 0.1 M, acetate or formate: 1 M. Temp.: 75°C,
pH: ●; 2.88, ○; 3.62, ◐; 4.00, ◑; 4.79

The distribution coefficients, D and λ, were calculated from these experimental data; a few examples are presented in Table I. The results show that the increase in the amounts of precipitated calcium tends to decrease the coefficients.

TABLE I. DEPENDENCE OF DISTRIBUTION COEFFICIENT ON THE PRECIPITATED FRACTION OF CALCIUM

Ca: 0.025 M, Sr: 10^{-6} M, dimethyloxalate : 0.1 M
Temp.: 75°C

Reacting time min.	Ca ppted. %	Sr coppted. %	D	λ
(A) pH: 4.80, acetate: 1 M				
120	28.31	11.52	0.330	0.368
240	46.96	16.74	0.227	0.289
300	62.17	18.81	0.141	0.214
450	83.47	25.29	0.0670	0.162
600	93.85	35.00	0.0353	0.155
700	98.35	46.34	0.0145	0.152
(B) pH: 2.88, formate: 1 M				
75	33.11	14.33	0.338	0.385
100	57.88	21.89	0.209	0.286
135	83.79	32.52	0.0932	0.216
180	94.53	45.03	0.0494	0.206
240	97.81	53.18	0.0254	0.199

The Effect of the Strontium Concentration.—While keeping the other variables constant, the calcium oxalate was precipitated at pH 4.00 in solutions containing 10^{-5} M, 10^{-6} M and 10^{-7} M of strontium respectively. The effect is indicated in Fig. 2; no significant change in the coprecipitation behavior was observed.

The Effect of the Acetate and Sodium Chloride Concentrations.—The effect of the acetate concentration was examined at pH 4.00 with regard to sample solutions of 0.5 M, 1.0 M and 2.0 M acetate, while the other variables were kept constant; the effect was found to be almost not noticeable in the range investigated, as is shown in Fig. 3. In order to study the effect of the ionic concentration in a reaction solution, an effect which is concerned with the adsorption in coprecipitation, final concentrations with nil, 1.0 M and 2.0 M of sodium chloride respectively were used. Figure 4 shows that the coprecipitation of strontium behaves in a similar manner, although it is appreciably influenced at the beginning of precipitation.

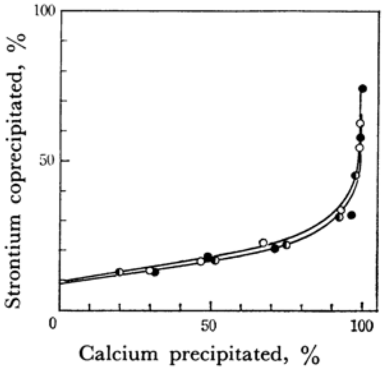

Fig. 2. The effect of the concentration of strontium.
Ca: 0.025 M, dimethyloxalate: 0.1 M, acetate: 1 M
Temp.: 75°C pH: 4.00
Sr: ○; 10^{-4} M, ●; 10^{-5} M, ◐; 10^{-6} M

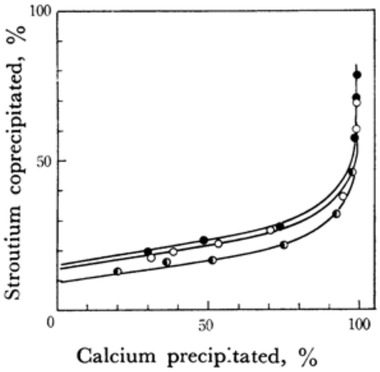

Fig. 3. The effect of acetate ion.
Ca: 0.025 M, Sr: 10^{-6} M,
Acetate: ○; 2.0 M, ◐; 1.0 M, ●; 0.5 M
Others are same to in Fig. 2.

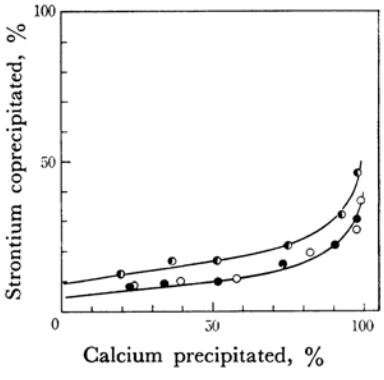

Fig. 4. The effect of sodium chloride concentration.
Ca: 0.025 M, Sr: 10^{-6} M,
NaCl: ◐; 0, ○; 1.0 M, ●; 2.0 M
Others are same to in Fig. 2.

The Effect of the Rate of Precipitation.—The effect of the ester was studied in order to examine the effect of the rate of precipitation. Figure 5 shows that the coprecipitation behavior almost does not change at all, except in the rapid precipitation, when the concentration of the ester changes from 0.0375 M to 0.25 M, corresponding to 1.5 and 10 times the stoichiometric quantity of calcium ions. The time required for the 90% precipitation of calcium is about 75, 580, 1350 and 2100 min. when the ratio of the ester to calcium is 10, 4, 2 and 1.5 respectively.

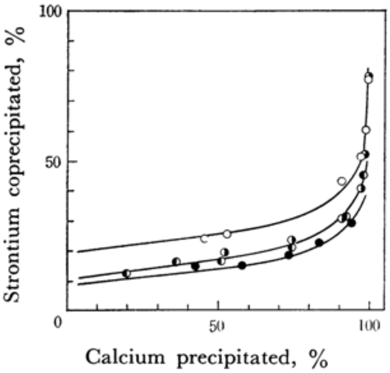

Fig. 5. The effect of the rate of precipitation.
dimethyloxalate: ◑; 0.0375 M, ●; 0.05 M,
◐; 0.10 M, ○; 0.25 M
others are same to in Fig. 2.

Discussion

As is shown in Figs. 1 to 5, the coprecipitation behavior of strontium was very similar in all cases, though the percentages of coprecipitation changed appreciably in the initial stage of the precipitation process.

The coprecipitation percentage of strontium increased very slowly to about 70 per cent, and then rapidly to the end of calcium precipitation.

An increase, in the fraction of precipitated calcium tends to decrease the distribution coefficient in all experiments, as is shown in Table I. If the decrease in λ-value is attributed to the aging of precipitate, as has been described in previous papers,[4,8] the coprecipitation behavior should be influenced by the rate of precipitation. However, the conprecipitation curves resemble each other except in the case of a very rapid precipitation.

---

[8] M. L. Salutsky, J. G. Stites, Jr., and A. W. Martin, *Anal. Chem.*, **25**, 1677 (1953).

The coprecipitation behavior in the calcium-strontium oxalate system was postulated to be as follows: When a strontium ion is coprecipitated with calcium salt, two different mechanisms are involved. One type is the surface adsorption, with very fine crystals precipitating from a supersaturated solution. The other is a normal systematic type obeying the distribution law. When the curves are extrapolated to a zero percentage of the precipitated calcium, the adsorption part of the coprecipitation can be estimated. When the effect of the latter part is corrected, the logarithmic distribution law is followed and the coefficient can be calculated. These results are shown in Tables II to VI, in which the coefficients in the range of 40 to 95 per cent of calcium precipitated are adopted in order to make the error as small as possible, because there is a risk of producing a considerable error in the determination of the precipitated calcium or coprecipitated strontium beyond the above range.

TABLE II. THE EFFECT OF pH ON λ AFTER CORRECTION OF ADSORPTION

	Ca ppted. %	Sr coppted. %	λ
(A) pH 4.80	46.96	6.74	0.110
(−10.00%)*	62.17	8.81	0.096
	83.47	15.29	0.092
	93.85	25.00	0.102
		Average	0.100
(B) pH 4.00	51.20	7.33	0.107
(−9.00%)*	74.83	12.33	0.097
	92.10	22.15	0.099
		Average	0.101
(C) pH 3.62	49.41	6.89	0.105
(−10.00%)*	62.47	10.96	0.118
	85.69	17.06	0.096
		Average	0.106
(D) pH 2.88	57.88	11.89	0.146
(−10.00%)*	83.79	22.52	0.140
	94.53	35.03	0.148
		Average	0.145

* The correction of adsorption for Sr.

TABLE III. THE EFFECT OF THE STRONTIUM CONCENTRATION AFTER CORRECTION OF ADSORPTION

	Ca ppted. %	Sr coppted. %	λ
(A) Sr: 10^{-4} M	46.77	6.23	0.102
(−10.20%)*	66.69	12.00	0.116
	92.41	23.52	0.104
		Average	0.107
(B) Sr: 10^{-5} M	49.24	6.68	0.102
(−9.00%)*	70.84	11.48	0.099
		Average	0.101
(C) Sr: 10^{-6} M see A) in Table II.			

* The correction of adsorption for Sr.

The consistency of the λ values obtained in Table II to VI can not be explained by assuming random error. The mean values of the coefficient nearly gave a constant, about 0.1 of λ in almost all cases. Strontium, as well as other elements,

TABLE IV. THE EFFECT OF THE ACETATE ION

	Ca ppted. %	Sr coppted. %	λ
(A) Acetate: 0.5 M	48.36	7.05	0.110
(−16.00%)*	73.62	11.91	0.095
		Average	0.103
(B) Acetate: 1.0 M	see A) in Table III		
(C) Acetate: 2.0 M	38.27	5.27	0.112
(−14.10%)*	53.06	7.99	0.110
	70.60	12.96	0.113
	94.20	23.73	0.090
		Average	0.106

* The correction of adsorption for Sr.

TABLE V. THE EFFECT OF SODIUM CHLORIDE CONCENTRATION

	Ca ppted. %	Sr coppted. %	λ
(A) NaCl: none added	see A) in Table II		
(B) NaCl: 1.0 M	57.47	7.89	0.096
(−2.60%)*	81.90	16.81	0.108
		Average	0.102
(C) NaCl: 2.0 M	51.37	7.79	0.113
(−2.00%)*	73.73	13.20	0.106
	90.33	19.15	0.091
	(96.99)	(28.91)	(0.097)
		Average	0.103

* The correction of adsorption for Sr.

TABLE VI. THF EFFECT OF THE RATE OF PRECIPITATION

	Ca ppted. %	Sr coppted. %	λ
(A) Dimethyloxalate:	52.58	9.11	0.113
0.25 M	90.96	26.27	0.130
(−17.00%)*	(96.77)	(34.02)	(0.121)
	(98.13)	(35.67)	(0.111)
		Average	0.122
(B) Dimethyloxalate: 0.1 M	see A) in Table II		
(C) Dimethyloxalate:	57.38	9.20	0.113
0.05 M	73.53	12.62	0.101
(−5.70%)*	83.12	17.04	0.105
	93.92	23.88	0.097
		Average	0.104

* The correction of adsorption for Sr.

such as scandium, yttrium and lanthanide, were also coprecipitated by calcium oxalate obeying along the logarithmic distribution law proposed by Doerner and Hoskins.(3)

Tables II and III show that, in the calcium-strontium oxalate system, λ is not influenced by the pH value and the acetate concentration, unlike as in the calcium - tervalent element system.

According to Chlopin's description,(9) the homogeneous distribution coefficient, D, will practically not change if the ratio of the ionic concentration of the micro component to that of the macro component does not vary even when the composition of the solution phase varies, while the value of D will increase if the ionic concentration of the macro component decreases more rapidly than that of the micro component, and vice versa. This explanation was applied in the calcium - tervalent metal ion system, which obeyed the logarithmic distribution law.(7) This rule can be applied to the present research, because the ratio of the ionic concentration of strontium to that of calcium scarcely does change, even if the precipitation conditions vary. The coefficient, λ, is nearly 0.1, meaning that strontium is enriched in the solution phase. The homogeneous distribution coefficient, D, of course decreased as the precipitation of calcium proceeded under all coprecipitation conditions.

When a strontium ion is brought together with the calcium oxalate carrier from the sample solutions, it may, in view of the above results, be concluded that: As the concentration of calcium left in solution phase becomes lower, the percentage of the coprecipitated strontium becomes higher. It is desirable to react with high pH values (if not influenced by the carbonate ion) and with an excess of oxalic acid in order to concentrate the strontium ions in the precipitate.

The author wishes to express his thanks to Professor Tsunenobu Shigematsu and Dr. Masayuki Tabushi for their valuable advice.

---

9) I. E. Starik, "Hoshakagaku no Kiso" (Fundamental Radiochemistry), translated from Russian by F. Ichikawa, H. Okashita and R. Ishiwatari, Nankodo, Tokyo (1962), p. 174.