The Coprecipitation of Yttrium with Calcium Oxalate

By Tsunenobu SHIGEMATSU, Masayuki TABUSHI and Masakazu MATSUI

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The coprecipitation method has been widely used for the chemical concentration or enrichment of trace elements from such extremely dilute solutions as natural water and for the chemical separation of radioisotopes.

There are two typical distribution laws in the coprecipitation mechanism. One, called the homogeneous distribution law, has been employed by Chlopin[1] and Henderson and Kracek[2]; it is expressed as follows:

$$\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{crystal}} = D\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{solution}} \qquad (1)$$

where D is the homogeneous distribution coefficient and is constant for a given system. It represents a state of true thermodynamic equilibrium, in which the crystal phase has been digested enough for it to reach a homogeneous concentration.

The other law, offered by Doerner and Hoskins,[3] is called the logarithmic distribution law; it is expressed as follows:

$$\log\left(\frac{\text{initial quantity}}{\text{quantity left in soln.}}\right)_{\text{tracer}} = \lambda \log\left(\frac{\text{initial quantity}}{\text{quantity left in soln.}}\right)_{\text{carrier}} \qquad (2)$$

where λ is the logalithmic distribution coefficient, which is constant for a given system. This law is obeyed when the rate of precipitation is slow enough to establish a replacement equilibrium on each layer of the crystal. A crystal formed in such circumstances retains a radial concentration gradient in which the tracer component is distributed throughout in a logalithmic manner. If λ is larger than unity, the tracer component is enriched in the crystal and the concentration of the tracer component is at a maximum at the center of each crystal and decreases gradually toward the outer part of the crystal; when λ is smaller than unity, the reverse is true.

It is of interest to study the coprecipitation from a homogeneous solution, because the crystals formed are large and more perfect, and because the precipitation process is more reproducible. Feibuch, Rowly and Gordon[4] reported that the coprecipitation of pairs of rare earth oxalates from homogeneous systems obeyed the logarithmic distribution law.

Calcium oxalate is often used as a coprecipitant,[5] and Purkayastha and Bhattacharyya[6] showed that the coprecipitation of yttrium and europium with calcium oxalate also followed the logarithmic distribution law. In our previous research,[7] it was observed that the coprecipitation of scandium with calcium oxalate was influenced by the conditions of the reacting solutions; in the pH range between 2.0 and 3.5, the system followed the logarithmic distribution law, whereas with a rise in pH value, it deviated gradually from the law until it began to obey the homogeneous distribution law near pH 4. The limiting distribution coefficient,[8] the value of distribution coefficients extrapolated to zero per cent of the calcium precipitated, changed with the pH value of the reacting solutions from 1.10 at an initial pH of 4.67 to about 18 at an initial pH of 2.43.

In this research the coprecipitation of yttrium with calcium oxalate was investigated. The effects of the pH value, the tracer component to the carrier ratio, the concentration of the buffer solution and several other variables on the distribution coefficient were investigated, using yttrium-91 as a tracer.

Experimental

Apparatus and Reagents. — Radioactivity countings were made with a Phillips halogen-quenched G-M tube connected to a Metro dekatron scaler, Model D-5. A Hitachi-Horiba glass electrode pH meter, Model M-3, was used for the pH measurements.

Yttrium-91 was supplied as chloride in hydrochloric acid by The Radiochemical Centre, Amersham, England, and was diluted to make a solution of 1 μc./ml. Reagent-grade dimethyl oxalate was

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[1] W. Chlopin, *Z. anorg. u. allgemg. 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] A. M. Feibuch, K. Rowley and L. Gordon, *Anal. Chem.*, **30**, 1605 (1958).

[5] T. Shigematsu, M. Tabushi, Y. Nishikawa, K. Hiraki, S. Goda and R. Inoue, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 336 (1963).

[6] B. C. Purkayastha and S. N. Bhattacharyya *J. Inorg. Nucl. Chem.*, **10**, 103 (1959).

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

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

purified by recrystallizing it from dry methanol and was stored in a dry atmosphere to prevent the hydrolysis upon contact with moisture. The yttrium solution was prepared by dissolving reagent-grade yttrium oxide in hydrochloric acid. Calcium solution (2 M) was prepared by dissolving dry calcium carbonate in hydrochloric acid and diluting it with water. The EDTA solution (0.01 M) containing a EDTA-Mg complex was standardized by means of a calcium standard solution.

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

Procedure. — An aliquot of a calcium chloride stock solution and a yttrium-91 solution with an appropriate amount of inactive yttrium is placed in a 250-ml. Erlenmeyer flask. A suitable volume of 10 N acetic acid or formic acid (as a buffer solution), a 10 N sodium hydroxide solution and a known weight of dry dimethyl oxalate in distilled water are added, the resulting solution is diluted to 200 ml., and then the pH value is measured. The flask with a reflux condenser is placed in a thermostat, and the solution is stirred continuously with a mechanical stirrer to prevent supersaturation.

When the temperature of the solution rises to a certain value, 2 ml. of the solution is pipetted out into a glass-counting dish 25 mm. in diameter. After calcium begins to precipitate with the oxalate ions released from dimethyl oxalate, 2.0 ml. of the solution is pipetted out from the reacting solution through a sintered glass filter into a counting dish at appropriate intervals of time.

The yttrium-91 activity of the liquid sample in the dish is measured in order to determine the amount of yttrium in the filtrate. The solution is then washed with hydrochloric acid into a beaker, dried slowly, and ashed by fuming it with concentrated perchloric acid on a hot plate. After adding water and a buffer solution, the calcium ions are titrated with a 0.01 M EDTA standard solution containing its magnesium chelate, using Eriochrome Black T as an indicator. The homogeneous and logarithmic distribution coefficients, D and λ, are calculated from Eqs. 1 and 2.

Results and Discussion

The Effect of the pH Value on the Coprecipitation.—The percentages of yttrium coprecipitated and of calcium precipitated in the fraction of calcium oxalate at several pH values are plotted in Figs. 1 and 2.

Figures 1 and 2 show that yttrium is enriched in the precipitate in the pH range investigated, and that the extent of enrichment increases as the pH decreases. The distribution coefficients were also calculated; a few typical examples are shown in Table I. The distribution of yttrium on the calcium oxalate obeys the logarithmic distribution law; this agrees with Purkayastha and Bhattacharyya's results,⁶⁾ which were obtained in a 3 N acetate medium. As has been previously reported,⁷⁾ the pH value of the reacting solution influenced not only the distribution coefficient, but also the type of the distribution in a scandium-calcium system. In this yttrium system, however, the logalithmic distribution law is obeyed regardless of the pH value in the given range, although the coefficient increases with a decreases in the pH value.

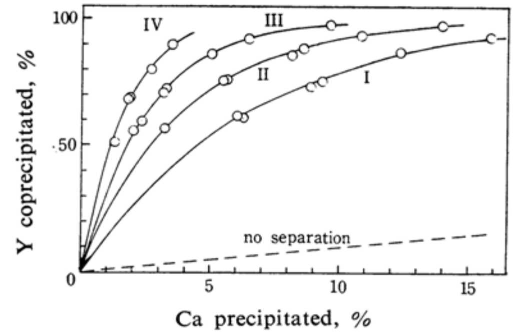

Fig. 1. Coprecipitation of yttrium with calcium oxalate in an acetate buffer solution. pH: I, 4.62; II, 4.20; III, 3.97; IV, 3.67; Y: 1.12×10^{-6} M, Ca: 0.2 M, dimethyl oxalate: 0.1 M, acetate: 1 M, temp.: 60°C. vol.: 200 ml.

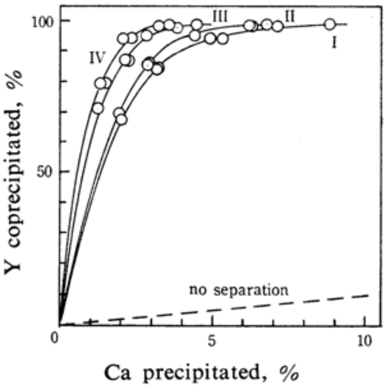

Fig. 2. Coprecipitation of yttrium on calcium oxalate in formic buffer solution. pH: I, 4.08; II, 3.42; III, 3.01; IV, 2.62; formic acid: 1 M. Others are same to in Fig. 1.

The logarithmic distribution coefficient, λ, is plotted against the initial pH of the solution in Fig. 3. The limiting distribution coefficient of the scandium-calcium system is also shown for the sake of comparison.

There is a difference between the distribution curves obtained in acetate and in formate buffer solutions; this may be due to the property of the complex compounds of yttrium and calcium ions with acetate or formate.

The Effect of the Yttrium Concentration on the Distribution Coefficient.—The calcium oxalate was precipitated in the solutions, containing 3.37×10^{-6} M to 1.12×10^{-4} M yttrium;

TABLE I. COPRECIPITATION OF YTTRIUM WITH CALCIUM OXALATE

Ca: 0.2 M, Y: 1.12×10^{-6} M,
dimethyl oxalate: 0.1 M, temp.: 60°C

Reaction time min.	Ca pptd. %	λ
[(A) initial pH: 4.62, 1 M acetate solution]		
105	6.02	15.1
106	5.96	15.4
157	8.85	14.3
158	9.27	14.6
250	12.83	15.0
340	15.79	15.5
410	18.67	15.5
	Average	15.1
[(B) initial pH: 3.97, 1 M acetate solution]		
102	1.96	40.8
107	2.26	39.4
150	3.14	38.4
155	3.27	38.4
180	5.00	38.6
225	6.39	38.6
300	9.58	36.9
	Average	38.7
[(C) initial pH: 3.01, 1 M formate solution]		
93	1.22	102.4
120	2.11	95.4
120	2.21	92.5
152	2.79	107.9
182	3.80	100.7
195	4.45	93.4
	Average	98.7

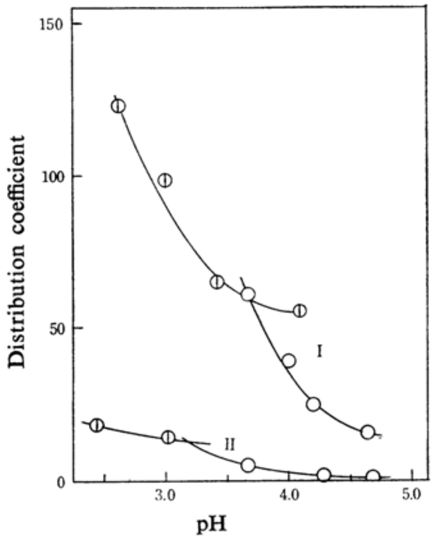

Fig. 3. The effect of pH on the distribution coefficient.
I: Y-Ca system, II: Sc-Ca system. -⦶-: 1 M formate solution, -○-: 1 M acetate solution.

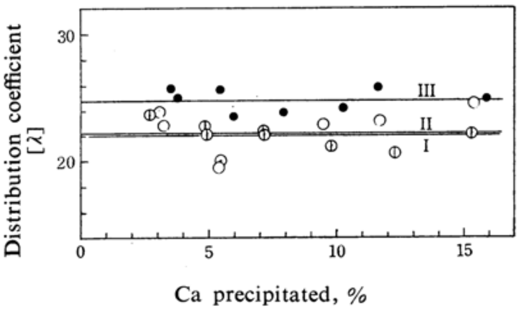

Fig. 4. The effect of yttrium concentration on distribution coefficient. pH: 4.24, I -⦶-: Y=3.37×10^{-6} M, λ=22.0; II -○-: Y=3.37×10^{-5} M, λ=22.1; III -●-: Y=1.12×10^{-4} M, λ=24.9.

the effect of the yttrium concentration is indicated in Fig. 4. No significant change in the logarithmic distribution coefficient is observed, and the mean value of λ is also in good agreement with the value (λ=23) as estimated from the curve in Fig. 3 (yttrium concentration: 1.12×10^{-6} M), at pH 4.23. This is in contrast with the scandium system, where the limiting distribution coefficient decreases as the concentration of the tracer component increases.

The Effect of the Rate of Precipitation.— Because the rate of precipitation depends upon the concentration of the dimethyl oxalate at a given pH, the effect of the latter was studied in order to examine the effect of the former.

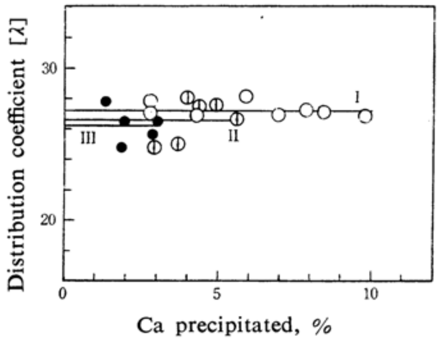

Fig. 5. The effect of the concentration of dimethyl oxalate. pH: 4.16, I -○-: 0.05 M ester, λ=27.2; II -⦶-: 0.02 M ester, λ=26.5; III -●-: 0.01 M ester, λ=26.5.

Figure 5 shows that the logarithmic distribution coefficient (measured at pH 4.16) is almost constant, even when the concentration of the ester changes from 0.01 M to 0.05 M, values which correspond to 1/20 and 1/4 of the stoichiometric quantity necessary to complete the precipitation of calcium ions. The value of λ obtained at pH 4.16 in Fig. 3 (ester concentration: 0.1 M) is 26.5, which is approximately the same as the value in Fig. 5. The time required to precipitate 3 per cent of the calcium ion was about 1540, 450, 200 and 90 min. when the concentration of the dimethyl oxalate was 0.01, 0.02, 0.05 and 0.1 M respectively.

The Effect of Acetate Ion Concentration on the Coefficient.—The effect of the acetate concentration was examined with solutions containing 1.0 M, 0.5 M and 0.25 M of acetate; the results obtained at pH 4.10 are represented in Table II. The logarithmic distribution law is obeyed, but the value of the distribution coefficient is remarkably influenced by the acetate concentration. The mean values of λ were 30 at 1.0 M, 70 at 0.5 M and 186 at 0.25 M of acetate.

TABLE II. EFFECT OF THE ACETATE ION ON DISTRIBUTION COEFFICIENT

Ca: 0.1 M, Y: 1.12×10^{-6} M, dimethyl oxalate: 0.1 M, initial pH: 4.0, temp.: 60°C

Ca pptd. %	Y copptd. %	λ
(A) 1 M acetate		
3.01	60.14	29.9
5.36	81.87	31.0
5.39	81.23	30.2
8.43	92.89	30.0
8.40	92.46	29.5
10.02	95.85	30.0
12.52	98.11	29.7
	Average	30.0
(B) 0.5 M acetate		
1.63	66.15	66.2
3.03	88.30	69.6
5.01	97.40	71.1
5.03	97.39	70.6
5.94	98.86	73.2
	Average	70.1
(C) 0.25 M acetate		
0.63	69.95	190
1.34	91.18	180
2.17	98.53	192
2.91	99.658	193
2.91	99.488	179
3.75	99.935	180
	Average	186

When the acetate concentration decreases and, consequently, the buffer action weakens, the pH-drift during the precipitation process is not negligible. However, the fact that the differences in the distribution coefficients of Experiments A, B and C are much larger than the fluctuation of data in each experiment can not be explained by such a pH-drift. It is reasonable to assume that acetate ions affect the enrichment of yttrium into the solid phase because of their complex formation.

As has been mentioned above, the distribution coefficient increases monotonically with a decrease in the pH value (see Fig. 3). One of the reasons, perhaps the major, might be also the complex formation of metal ions with acetate or formate, which dissociate more as the pH rises, although such complicated questions as the formation of a hydroxocomplex should also be taken into consideration.

It is interesting to compare the yttrium-calcium system with the scandium-calcium system. There are distinct differences between them. Firstly, in the yttrium-calcium system, the logarithmic distribution law is followed regardless of the pH in the given range, while the distribution of scandium changes gradually from logarithmic to homogeneous with an increase in the pH. Secondly, the molar ratio of the tracer component to the carrier affects the distribution coefficient in the scandium system, but not in the yttrium system. Lastly, under similar conditions yttrium gives larger distribution coefficients than does scandium.

A strict discussion is difficult, because a tervalent element coprecipitates with bivalent calcium as an oxalate and because the properties of the crystal are not clear. However, the results described above seem to show that yttrium is more stable than scandium in the calcium oxalate crystal. This may be caused by the fact that the ionic radius of bivalent calcium is nearer to that of tervalent yttrium than to that of tervalent scandium.

Institute for Chemical Research
Kyoto University
Sakyo-ku, Kyoto