BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1114—1119 (1966)

The Coprecipitation Behavior of Rare Earth Elements with Calcium Oxalate upon Precipitation from a Homogeneous System

By Masakazu MATSUI

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

(Received July 19, 1965)

The effects of the pH value, the concentration of organic acid and several other variables upon the distribution coefficient were studied for the coprecipitation process of the calcium-lanthanide oxalate system. The logarithmic distribution law was followed in all cases of the coprecipitation of rare earth elements. Of the several variables studied which affected the logarithmic distribution coefficient, the most important were the pH value and the concentration of an organic acid. The coefficient decreased as the acid anion content increased. This can be attributed to the fact that the acid anion formed complex compounds with lanthanide and calcium. The distribution coefficients of several rare earth elements in producing the precipitate from a similar solution were closely related to their basicity or to the solubility of their oxalate salts. The order of the magnitude of the distribution coefficient was as follows: Lu>Y>Eu>Ce; this was in the reverse order of the basicity of rare earth elements or of the solubility of their oxalate salts.

Coprecipitation has often been used for the chemical concentration or enrichment of trace elements from dilute solutions and for the chemical separation of radioisotopes. Furthermore, coprecipitation phenomena are observed in the precipitation method of gravimetric analysis and in geochemical processes.

When a macro component is precipitated, micro components in the solution are distributed between the solid and liquid phases. The initial distribution may be quite random, but structural transformation must occur in the recrystallization process of the precipitate. As equilibrium conditions are reached, an orderly rearrangement is achieved. For such a system, macro and micro components distribute themselves to obey the following equation, which was introduced by Chlopin1) and by Henderson and Kracek2):

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

where D is the homogeneous distribution coefficient and is constant for a given system. This homogeneous distribution law represents a true thermodynamic equilibrium.

Beside the homogeneous distribution in crystals, there are many possible heterogeneous arrangements. Only one of these was given by Doerner and Hoskins' distribution equation.3) It is called the logarithmic distribution law and is expressed as follows:

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

where λ is the logarithmic distribution coefficient and is also constant for a given system. It is postulated in the logarithmic law that a distribution equilibrium is attained between the ions in the solution and the ions on the solid surface as each new crystal layer is formed. A crystal formed under such circumstances retains a radial gradient of the concentration of the tracer component distributed in a logarithmic manner. If λ is larger than unity, the tracer component is enriched in the crystal and the concentration of the tracer component is the highest at the center of each crystal, decreasing gradually toward the outer part of the crystal. When λ is smaller than unity, the tracer component is enriched in the solution, and the radial concentration gradient in the crystal becomes the reverse of that of the case of values of λ greater than unity.

The coprecipitation method using calcium oxalate as a carrier is often used for the enrichment of strontium, scandium and rare earth elements from dilute solutions for the separation of those radioisotopes from the other elements.

Some attempts have been made to reveal the distribution behavior of macro and micro components. In general, due to the low solubility of oxalates, coprecipitation from a homogeneous system was used. This also gave rise to the more reproducible results.

---

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).

Feibuch, Rowly and Gordon[4] reported that the coprecipitation of pairs of rare earth oxalates obeyed the logarithmic distribution law. Purkayastha and Bhattacharyya[5] showed that the coprecipitation of yttrium and europium with calcium oxalate also followed the logarithmic distribution law. Previously, Shigematsu et al. had studied the coprecipitation behavior of scandium[6] and yttrium ions[7] with calcium oxalate from a homogeneous system and found that there were distinct differences between the two cases. In the calcium-yttrium system, the logarithmic distribution law was followed, regardless of the composition of the solutions, while the distribution of scandium deviated gradually from the logarithmic law with an increase in the pH value, and under similar conditions yttrium gave larger distribution coefficients than did scandium. On the basis of the above results, it was deduced that yttrium was more stable than scandium in the calcium oxalate crystal, because the ionic radius of bivalent calcium is closer to that of tervalent yttrium than to that of tervalent scandium.

In this research, the coprecipitation of rare earth elements with calcium oxalate was investigated. The effects of the pH values, the concentration of acetate used as the buffer solution and several other variables on the distribution coefficient were studied, using cerium-144, yttrium-91, europium-152, 154 and lutetium-177 as the radiotracers. The distribution coefficients of rare earth elements coprecipitated under the same conditions were compared.

Experimental

Apparatus and Reagents.—Radioactivity countings were made with a Phillips halogen-quenched G-M tube connected to a dekatron scaler (Metro Model D-5), and with a NaI (Tl) ($1^3/_4' \times 2'$) well-type scintillation counter (Kobe Kogyo Model PS-300) connected to a scaler (Model SA-230). A Hitachi-Horiba pH meter, Model M-3, was used for the pH measurements.

Radioisotopes were supplied as chloride in hydrochloric acid from The Radio Chemical Centre, Amersham, England. Reagent-grade dimethyl oxalate was purified by recrystallization from anhydrous methanol and was stored in a dry atmosphere to prevent it from hydrolysis by moisture. Stock solutions of rare earth elements were prepared by dissolving their reagent-grade oxides in hydrochloric acid. The calcium solution was prepared by dissolving reagent-grade calcium carbonate in hydrochloric acid. The EDTA solution (0.01 M) containing a Mg-EDTA complex was standardized with a standard calcium solution.

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

Procedure.—A representative procedure adopted in the homogeneous coprecipitation is as follows.

Twenty milliliters of a calcium chloride stock solution (2.0 M) and a suitable volume of a rare earth solution, with an appropriate amount of radioactive isotopes, are placed in a 250-ml. Erlenmeyer flask. Twenty milliliters of 10 M acetic acid or formic acid (as a buffer solution), a suitable volume of a sodium hydroxide solution, and 2.36 g. of dimethyl oxalate dissolved in water are added, the resulting solution is diluted to 200 ml., and the pH of the solution is measured. Then the flask, equipped with a reflux condenser, is placed in a thermostat, and the solution is stirred continuously with a mechanical stirrer to prevent it from supersaturation.

When the temperature of the solution rises to 60°C, 2 ml. of the solution is pipetted out into a glass counting dish 25 mm. in diameter for beta counting or into a polyethylene counting tube 12 mm. in diameter for gamma counting. After calcium ions begin to be precipitated by 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 vessel at appropriate intervals of time, and 0.2 ml. of concentrated hydrochloric acid is added immediately to stop any precipitation which may occur in cooling. The radioactivities of the liquid samples in the dish or tube are measured to determine the amount of rare earth elements in the solution phase. This solution is then washed out into a beaker with 5 N hydrochloric acid, dried slowly, and ashed by fuming it repeatedly with perchloric acid on a hot plate. After dilution with water and the addition of a buffer solution, the calcium ion is 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.

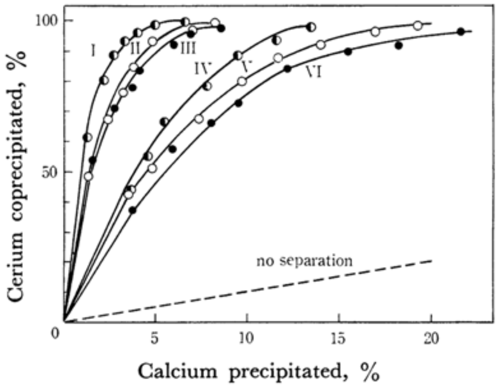

Fig. 1. Coprecipitation of cerium with calcium oxalate at several pH values.

Ca^{2+}: 0.2 M, Ce^{3+}: 10^{-6} M, Dimethyloxalate: 0.1 M, Temp: 60°C,

1 M formate: I, pH 2.92; II, pH 3.50, III, pH 4.06,

1 M acetate: IV, pH 4.08; V, pH 4.42; VI, pH 4.90

---

[4] A. M. Feibuch, K. Rowley and L. Gordon, *Anal. Chem.*, **30**, 1605 (1958).

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

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

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

Results and Discussion

The effect of the pH value on the coprecipitation was studied. The results in the calcium-cerium(III) system are shown in Fig. 1, in which the percentages of coprecipitated cerium at several pH values are plotted against the fractions of calcium precipitated. The diagram shows that the cerium ion is enriched in the precipitate in the pH range investigated, with the extent of enrichment increasing as the pH decreases. This is a similar case to that of yttrium.

The logarithmic and homogeneous distribution coefficients, λ and D, were calculated from these data, and λ was plotted against the percentage of the precipitation of a macro component (cf. Figs. 2 and 3). As Fig. 2 shows cerous ion coprecipitates obey the logarithmic law regardless of pH, and the value of λ increases with the decrease in pH, when the precipitation occurs in a 1 M formate solution. The value of λ which was obtained in a 1 M acetate solution is affected by the pH value in a similar manner, as is shown in Fig. 3. In the experiment made at a lower pH, λ does not seem to be constant; instead, it increases as the precipitation proceeds. The fact that deviation is more influenced in the more weakly-buffered pH range can be explained from the fact that the pH value is lowered and the value of λ increases as the oxalates are formed. Considering the shift of pH during the reaction progress, there is no doubt that the distribution in a 1 M acetate solution also follows the logarithmic distribution law.

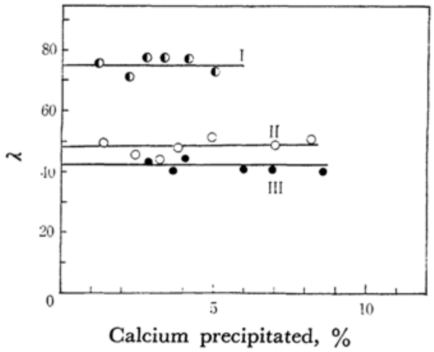

Fig. 2. Effect of pH on distribution coefficient for calcium-cerium oxalate system.
Ca^{2+}: 0.2 M, Ce^{3+}: 10^{-6} M, formate: 1 M, dimethyloxalate: 0.1 M, temperature: 60°C,
I: pH 2.92, $\lambda=75$, II: pH 3.50, $\lambda=48$,
III: pH 4.06, $\lambda=42$

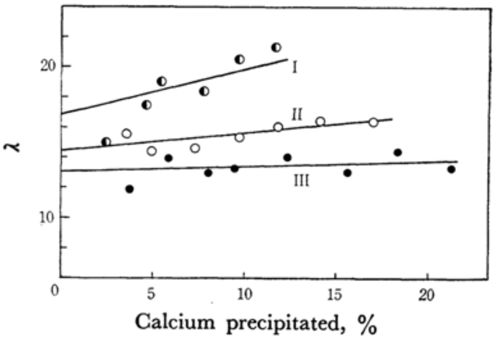

Fig. 3. Effect of pH on distribution coefficient for calcium-cerium oxalate system.
Acetate: 1 M,
I: pH 4.08, $\lambda=16.7$, II: pH 4.42, $\lambda=13.8$,
III: pH 4.90, $\lambda=12.8$,
Others are the same as in Fig. 1.

Europium and lutetium ions behave in the same way as a cerous ion does. In Fig. 4, the logarithmic distribution coefficients are plotted against the pH in calcium-cerium and calcium-lutetium systems. Although λ increases as the pH decreases, in the pH range studied these systems obey the logarithmic law. It should be pointed out that a difference was found between the distribution curves obtained in acetate and formate buffer solutions. The coefficients change monotonously with the change in pH and gradually approach a constant value in each buffer solution, though as different curves, depending upon the species of organic acid used as the buffer substance. This can be interpreted in terms of the complex formation of metal ions with those acids. The coefficients of lutetium are somewhat higher than cerium throughout the pH range investigated in Fig. 4.

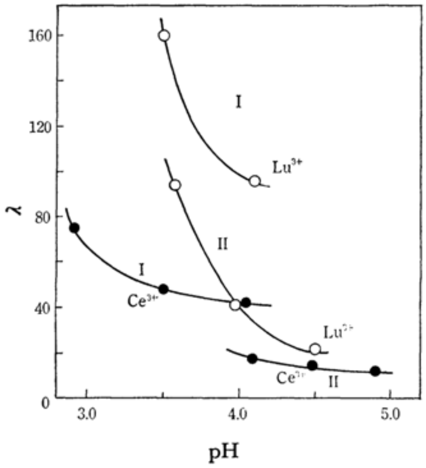

Fig. 4. Effect of pH on distribution coefficient.
I: 1 M formate, II: 1 M acetate,
Others are the same as in Fig. 1.

The effect of the organic acid concentration on the coefficient was examined in the calcium-cerium system. The precipitations were carried out on solutions containing 2.0, 1.0 and 0.5 M of acetate at pH 4.50, a value which was suitable for the estimation of λ. Although the coefficient increases slightly in the process of the precipitation, much as in Fig. 3, the distribution must obey the logarithmic law, taking account of shift in pH mentioned above.

The values extrapolated to zero percent of calcium on the coefficient-precipitated calcium curve are taken as the exact coefficient at pH 4.50. The results are represented in Fig. 5, where it is evident that the coefficient is remarkably increased by the decrease in the acetate concentration.

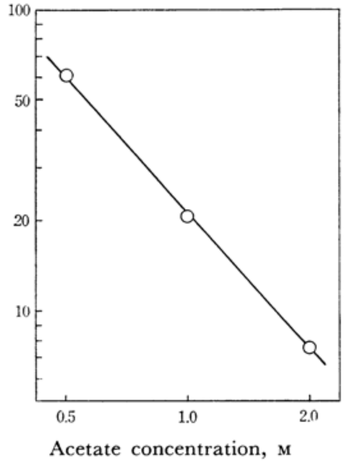

Fig. 5. Effect of acetate concentration on distribution coefficient for calcium-cerium system.

pH: 4.50, Others are the same as in Fig. 1.

The effects of other such variables as the concentration of coexisting ions and the concentration of micro component will be discussed below, although they are not so evident. To examine the effect of the ionic concentration, sodium chloride was added to make the final concentration nil, 1.0 and 2.0 M at pH 4.50 in the calcium-lutetium system. The experiment was performed in a 0.5 M acetate solution, which was selected as being suitable in respect to ionic concentration and buffer action. The results shown in Fig. 6 indicate that the coefficient is scarcely influenced by the ionic concentration. The influence of the concentration of a micro component was also hardly recognized in the calcium-lutetium system. The value of λ at pH 4.50 in 1 M acetate was 19.3 at 10^{-7} M and 19.5 at 10^{-5} M of lutetium ions respectively. As has been mentioned above, it is obvious that the factors influencing the coefficient are the pH of the solution and the concentration of a coexisting organic acid.

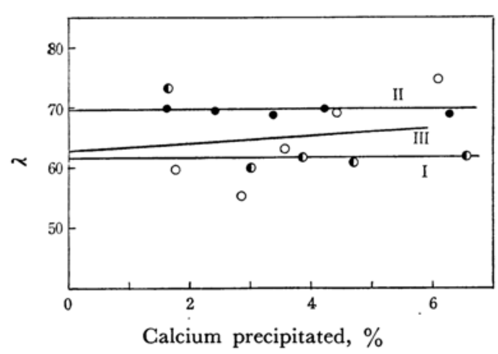

Fig. 6. Effect of ion concentration on distribution coefficient for calcium-lutetium system.

NaCl added: I, none, II, 1 M, III, 2 M,
Acetate: 0.5 M, pH: 4.50,
Others are the same as in Fig. 1.

Chlopin[8] offered the following explanation for the relation between the composition of a solution and the homogeneous distribution coefficient, D: if the ratio of the ionic concentration of a micro component to that of a macro component does not vary, even when the composition of the solution varies, the value of D will practically not change. When a complex or an insoluble compound is formed with a change in the composition of the solution, or when the ionic concentration of a macro or micro component undergoes a change separately, the value of D will increase if the ionic concentration of a macro component decreases more rapidly than that of a micro component, and vice versa.

This explanation can be applied to the system studied, which obeyed the logarithmic distribution law. When the pH becomes higher or when the concentration of organic acid used as a buffering agent becomes higher, the ionic concentration of the organic acid increases. The acid anion forms complex compounds with rare earth and calcium, the former complex being more stable than the latter. Then, as the ionic concentration of the acid anion increases, the decrease in the concentration of calcium ions will be less than that of rare earth ions, although the situation is complicated by the formation of a hydroxo complex or by other factors which should also be taken into consideration. Therefore, the logarithmic coefficient will gradually decrease.

The coprecipitation of several rare earth elements was examined by conducting the precipitation under identical conditions; the distribution coefficient of these elements were then compared. The results are summarized in Figs. 7 and 8. Figure 7 shows the relationship between the ionic radii of several rare earth ions and their distribution coefficients obtained at pH 3.50 in a 1 M formate solution. The coefficients of several elements in Fig. 8 are obtained in the same way at pH 4.50 in 1 M acetate. The ionic radii of tervalent rare earth ions are quoted from the numerical values obtained by Goldschmidt. A

---

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

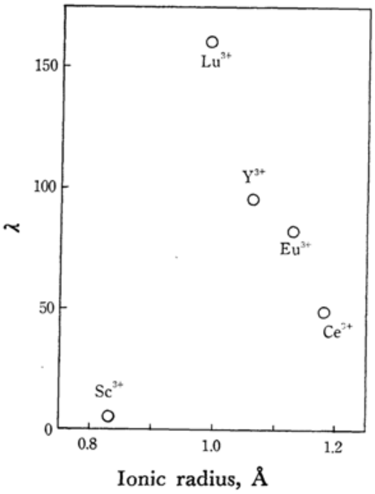

Fig. 7. Relation between ionic radius and λ at pH 3.50.

Formate: 1.0 M, Others are the same as in Fig. 1.

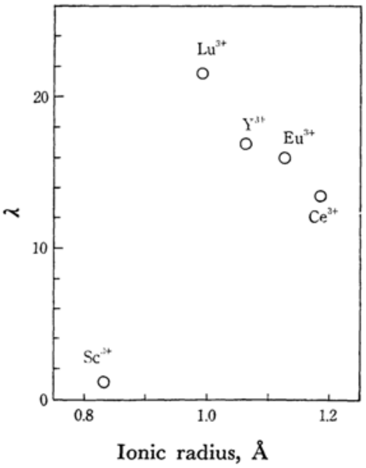

Fig. 8. Relation between ionic radius and distribution coefficient at pH 4.50.

Acetate: 1.0 M, Others are the same as in Fig. 1.

divalent calcium ion is equal in ionic radius to a tervalent yttrium ion. The limiting distribution coefficient of the calcium-scandium system in these figures was cited from the previous paper⁶⁾ for the sake of comparison. As is shown in the figures, the distribution coefficients of rare earth ions, the ionic radii of which come closer to that of divalent calcium, are closely related to their basicity or to the solubility of their oxalate salts. The order of the basicity of rare earth elements or of the solubility of their oxalate salts is as follows: Ce>Eu>Y>Lu, which is the reverse of the order of the distribution coefficients found in the present work.

Scandium ion constitutes an exception. Although it has a weaker basicity than rare earth elements, scandium is rather unstable in a calcium oxalate crystal and shows a smaller coefficient. This may be caused by the fact that the difference between the ionic radius of tervalent scandium and that of divalent calcium is quite large. This fact is a typical example showing that the ionic radius plays an important role in the coprecipitation process.

Gordon has questioned whether the logarithmic distribution equation (Eq. 2) can be justifiably applied to coprecipitation systems in which the charges of the ions are different; he has thus proposed an equation in which the charges of ions were taken into account.⁹,¹⁰⁾

The present system is an example of the coprecipitation of the tervalent cation with divalent calcium salt. The equilibrium is represented by the following equation:

$$3\mathrm{Ca}^{2+}{}_{\mathrm{cryst.}} + 2\mathrm{M}^{3+}{}_{\mathrm{aq.}} = 3\mathrm{Ca}^{2+}{}_{\mathrm{aq.}} + 2\mathrm{M}^{3+}{}_{\mathrm{cryst.}}$$

The equilibrium constant, D^1, is defined as follows:

$$D' = \frac{[\mathrm{Ca}^{2+}]^3{}_{\mathrm{aq.}}[\mathrm{M}^{3+}]^2{}_{\mathrm{cryst.}}}{[\mathrm{M}^{3+}]^2{}_{\mathrm{aq.}}[\mathrm{Ca}^{2+}]^3{}_{\mathrm{cryst.}}}$$

When the equation proposed by Gordon⁹⁾ is applied to the above system, the following equation is obtained:

$$\log \frac{\mathrm{M}_{\mathrm{initial}}}{\mathrm{M}_{\mathrm{final}}} = 0.8686\,\lambda_g(\mathrm{Ca}_{\mathrm{final}}{}^{-1/2} - \mathrm{Ca}_{\mathrm{initial}}{}^{-1/2}) \tag{3}$$

TABLE I. EFFECT OF THE INITIAL CARRIER CONCENTRATION ON λ AND λ_g

Eu^{3+}: 10^{-5} M, acetic acid: 2 M, pH: 4.50, Temp.: 60°C

Ca pptd. %	Eu coppted. %	λ	λ_g
(A) Ca^{2+}: 0.1 M, dimethyloxalate 0.05 M			
5.86	42.07	9.04	2.81
6.91	56.57	11.65	3.62
10.12	71.50	11.77	3.62
13.47	82.25	11.92	3.64
19.68	90.51	10.75	3.22
23.79	92.82	9.70	2.86
	Average	10.81	3.30
(B) Ca^{2+}: 0.4 M, dimethyloxalate 0.2 M			
12.77	49.40	5.00	3.05
17.91	62.33	4.95	2.98
23.77	75.12	5.12	3.03
29.40	84.64	5.39	3.12
35.79	91.58	5.59	3.16
39.85	94.22	5.60	3.11
	Average	5.28	3.07

---

9) L. Gordon, M. L. Sulutsky and H. H. Willard, "Precipitation from Homogeneous Solution," John Wiley & Sons, New York (1959), p. 132.

10) J. Block and L. Gordon, *Talanta*, **10**, 351 (1963).

where $M_{initial}$ and $Ca_{initial}$ represent the initial concentrations in a solution; M_{final} and Ca_{final} represent the final concentrations in a solution, and λ_g is the distribution coefficient of this system.

Equation 3 suggests that when the ions have different charges the distribution coefficient is dependent upon the initial calcium concentration. Therefore, the effect of the initial calcium concentration on λ and λ_g was examined. It is represented in Table I. The results show that λ and λ_g are about equally constant throughout the reaction process, and λ is more extensively affected than λ_g by the initial calcium concentration. However, it is doubtful from these data whether Eq. 3 is valid for the present system. Further research is needed to justify the applicability of Eq. 3 to systems involving differently-charged ions.

In this paper, λ was calculated by means of the logarithmic distribution equation of Doerner and Hoskins (Eq. 2), because the coprecipitation behavior shows the same tendency, whichever coefficient is used, and also because the applicability of λ_g still remains to be studied.

The author wishes to thank Professor Tsunenobu Shigematsu and Dr. Masayuki Tabushi for their kind and valuable advice throughout this study.