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# The Influence of Complex Formation on Coprecipitation Behavior

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The relationship between the composition of macro- and micro-components and the logarithmic distribution coefficient was studied for the coprecipitation process of calcium-europium oxalate system by the addition of complex forming substances like carboxylic acids and ethylenediaminetetraacetic acid. Formic, acetic, monochloroacetic, propionic, *n*-butyric, and *iso*-butyric acids were used as monocarboxylic acids. The distribution coefficient was obtained at the pH value where each acid anion dissociated half. It increased as the decrease of the dissociation constant of the acid. Ethylenediaminetetraacetic acid was added in order to control the composition of the micro-component which was one of the most important factors in calcium-europium oxalate system.

## INTRODUCTION

When a macro-component is precipitated by precipitation from a homogeneous system, a micro-component is distributed between crystal and solution phases in two systematic ways. One is proposed by Chlopin<sup>1)</sup>, Henderson and Kracek<sup>2)</sup> and others<sup>3)</sup> and called the homogeneous distribution law, in which the ratio of a micro-component to a macro-component in the crystal is proportional to the ratio in the solution:

$$\begin{aligned} & \left( \frac{\text{A micro-component}}{\text{A macro-component}} \right)_{\text{cryst.}} \\ & = D \left( \frac{\text{A micro-component}}{\text{A macro-component}} \right)_{\text{soln.}} \end{aligned} \quad (1)$$

where  $D$  is constant in the coprecipitation process of a given system and is called the homogeneous distribution coefficient. This law is based upon the assumption that the distribution of a micro-component is in the state of true thermodynamic equilibrium in which the crystal phase is digested sufficiently to remove all concentration gradients and is homogeneous.

The other is derived by Doerner and Hoskins<sup>4)</sup> and called the logarithmic distribution law and expressed as follows:

$$\begin{aligned} \log \frac{\text{A initial micro-component}}{\text{A micro-component left in solution}} = \\ \lambda \log \frac{\text{A initial macro-component}}{\text{A macro-component left in solution}} \end{aligned} \quad (2)$$

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where  $\lambda$  is the logarithmic distribution coefficient and also constant in the coprecipitation process. This law is postulated that a replacement equilibrium is achieved on only each layer of the crystal through the precipitation process of a macro-component.

Some attempts have been made to reveal the distribution behavior of macro- and micro-components. Feibush *et al.*<sup>6)</sup> reported that each pair of rare earth oxalates coprecipitated in a logarithmic manner from a homogeneous solution. Purkayastha and Bhattacharyya<sup>6)</sup> studied the coprecipitation of yttrium and europium with calcium oxalate and observed that these ions coprecipitated obeying with the logarithmic law. In the previous papers, the coprecipitation behaviors of strontium<sup>7)</sup>, scandium<sup>8)</sup> and lanthanide<sup>9,10)</sup> with calcium oxalate were studied by the slow precipitation method, and they indicated that the most important factors affecting the coefficient were the pH value and the concentration of the organic acid. This may be caused by the fact that the acid anion forms the complex compounds with macro- and micro-components and the concentrations of the components undergo a change. In the present research, the influence of complex formation to the distribution coefficient,  $\lambda$  was investigated in calcium-europium oxalate system.

## EXPERIMENTAL

### Apparatus and Reagents

The radioactivity counting was performed with a TEN NaI (44.5 mm. in dia.  $\times$  50.8 mm.) well-type scintillation counter, model PS-300, coupled with a scaler, Model SA-230. A Hitachi-Horiba pH meter, Model M-3, was used for the pH measurements. Eu-152, 154 was supplied as chloride by The Radiochemical Centre, Amersham, England, and was diluted to make a solution  $5 \times 10^6$  cpm/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 europium solution was prepared by dissolving reagent-grade europium oxide with hydrochloric acid. The solution of ethylenediaminetetraacetic acid (0.00330M), containing its magnesium complex, was used for the determination of the calcium ion of the sample solutions. The other reagents were reagent grade materials.

### Procedure

The procedure of coprecipitation and the determination of macro- and micro-components were essentially the same as those described in the previous paper<sup>10)</sup>. The homogenous and logarithmic distribution coefficients  $D$  and  $\lambda$  were calculated from the above equations 1 and 2.

## RESULTS AND DISCUSSION

The influence of monocarboxylic acid used as a buffer agent on the coprecipitation behavior was determined. As the acid is a complex forming substance though weak, it changes the composition of macro- and micro-components, which

may have an effect on the distribution coefficient. Formic, acetic, monochloroacetic, propionic, *n*-butyric, and *iso*-butyric acids were used in the present study as monocarboxylic acids. The higher one than butyric acid in carbon chain length was not able to be used because of their solubility relatively low to an aqueous solution. This experiment was made at the pH value where each acid dissociated half to equalize the concentration of the acid anion. A micro-component coprecipitated obeying with logarithmic distribution law from each acid anion solution. An example of coprecipitating in the logarithmic manner is shown in Fig. 1.

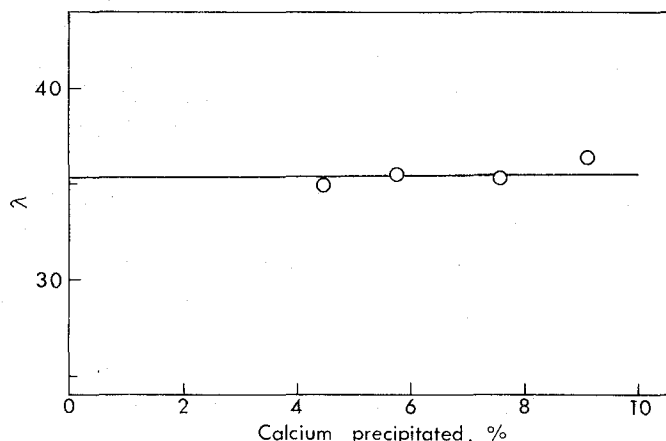


Fig. 1. Coprecipitation of europium with calcium oxalate from 2N formic acid solution.  
 Eu :  $2.5 \times 10^{-5}M$ , Ca : 0.2M, dimethyloxalate : 0.1M, temperature :  $60^{\circ}C$ ,  
 pH : 4.10~3.90

The results of the coprecipitation from several organic acid solutions are shown in Fig. 2, in which each coefficient,  $\lambda$  is plotted against the pH value. The figure

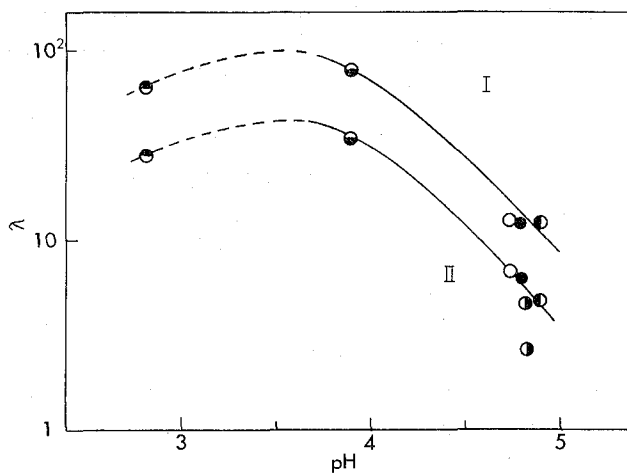


Fig. 2. The effect of monocarboxylic acids on the distribution coefficient.  
 ● : monochloroacetic acid, ◐ : formic acid, ○ : acetic acid,  
 ◑ : propionic acid, ● : *n*-butyric acid, ◒ : *iso*-butyric acid,  
 I : 1.0M, II : 2.0M.  
 Others are the same as in Fig. 1.

indicates that the coefficient is higher in the coprecipitation system of the acids with a lower dissociation constant than in the system of the other acids. This fact is explained as follows: Each acid anion forms complex compounds with europium and calcium ions, and the anion with a higher acid constant generally makes a more stable complex than that with a lower one. The ratio of the concentration of europium to that of calcium decreases as the acid anion forms stable complexes with these metal ions.

According to Chlopin's description<sup>12</sup>, the homogeneous distribution coefficient,  $D$  will practically not change if the ratio of the 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 decrease if the concentration of the micro-component decreased more rapidly than that of the macro-component. This explanation was applied successfully to the coprecipitation processes of scandium<sup>9</sup> and lanthanide<sup>9,10</sup> with calcium oxalate, where the most predominant factors affecting the logarithmic coefficient were the pH value and the concentration of the organic acid used as a buffer reagent, which varies considerably the concentration of divalent macro- and trivalent micro-components. The acid anion effect will be easily understood by applying the above explanation in the present research.

As calcium oxalate is somewhat soluble in the solution of monochloroacetic acid, the coefficient probably becomes lower than expected. The coefficient in the *iso*-butyrate system is lower a little than that in the analogical carboxylic acids system, though *iso*-butyric acid is very similar to analogical carboxylic acids in the acid dissociation constant and the stability constant with several metal ions. This may depend on the steric effect of *iso*-butyrate acid.

The influence of the strong chelating agent different from such a weak one as monocarboxylic acid on the distribution coefficient was determined. Ethylenediaminetetraacetic acid (EDTA) was added to the present coprecipitation system in order to control the composition of the micro-component. It is considered that EDTA coordinates not to calcium, but mainly to europium though the concentration ratio of calcium to europium is large, because the chelate compound of EDTA with europium is stable enough compared with the calcium chelate. Almost all europium ions also coordinate to EDTA rather than to the carboxylic acid used as a buffer agent. The concentration of EDTA added to the system is negligibly low as compared with that of calcium. Therefore, the composition of macro-component is scarcely affected by the addition of EDTA.

The effect of EDTA on the distribution coefficient was determined in the calcium-europium oxalate system buffered with 1N acetic acid. As shown in Table I, the coefficient decreases as the increase of EDTA, because EDTA brings out the decrease of the micro-component or the increase of its chelate compound. In this preliminary experiment, it is unknown whether one of the most predominant factors that effect on the coefficient is the concentration of europium ion or that of its chelate compound or both of them. Then, it was studied in detail how the composition of micro-component effected on the distribution.

When the difference between the concentration of total europium and that of total EDTA is constant (the former is higher than the latter), the concentration

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Table I. The effect of EDTA concentration.

EDTA ( $\times 10^{-5}M$ )	$\lambda$
0	7.0
1	4.7
5	3.7
10	2.1

Eu:  $1.7 \times 10^{-5}M$ , Ca: 0.2M, HAcO: 2.0M, dimethyl oxalate: 0.15M, pH: 4.90, temp.: 60°C

of free europium ion should be constant, because the stability of its chelate is considerably large. The effect of the europium chelate with EDTA on the distribution coefficient was studied when the concentration of free europium was kept constant ( $1.7 \times 10^{-5}M$ ). As shown in Table II, the coefficient decreases as the con-

Table II. The effect of Eu-EDTA chelate.

Eu <sup>3+</sup> ( $\times 10^{-5}M$ )	EDTA ( $\times 10^{-5}M$ )	$\lambda$
1.7	0	15.6
2.7	1	14.5
6.7	5	8.6
11.7	10	4.6

HAcO: 1.0M, others are the same as in Tab. I.

centration of the chelate increases. It suggests that the europium chelate formed prevents the coprecipitation of europium ion. This fact is found out in the present work.

In order to examine the influence of the concentration of free europium ion on the distribution, the concentration of europium was changed under the condition of the constant concentration of the europium-EDTA chelate ( $1 \times 10^{-4}M$ ). As shown in Fig. 3 the logarithmic distribution coefficient increases as the concentration of free europium ion increases. In the previous paper, the effect of the concentration of yttrium had been examined<sup>9)</sup> in its solution containing  $3.37 \times 10^{-6}M$  to  $1.12 \times 10^{-4}M$ . The effect was found to be hardly noticeable in the range investigated. However, the distribution of the micro-component was affected by the concentration of its free ion, when the chelate compound of the micro-component existed by the addition of the chelating agent.

The effect of the ratio of the concentration of europium ion to that of europium-EDTA chelate on the distribution coefficient was examined. Each of the concentrations was changed, but the ratio was kept in the constant 2. Though the coefficient is roughly constant as shown in Table III, it seems bold to say that if the ratio of the concentration of europium ion to that of europium-EDTA chelate is constant, the coefficient is constant, because complicated factors may be contained and reproducibility is not sufficient in the present system. However,

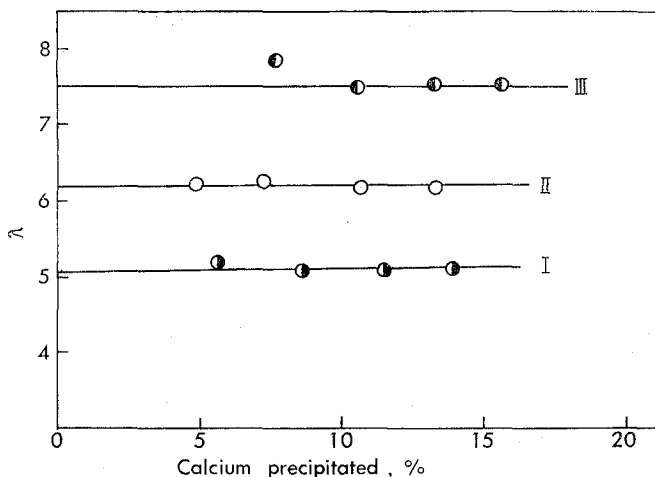


Fig. 3. The effect of the concentration of free europium ion.  
 EDTA :  $1.0 \times 10^{-3}M$ , pH 4.80, acetic acid 1.0M.  
 I : Eu  $1.0 \times 10^{-3}M$ ,  $\lambda=7.5$ , II : Eu  $2.0 \times 10^{-4}M$ ,  $\lambda=6.2$ ,  
 III : Eu  $1.0 \times 10^{-4}M$ ,  $\lambda=5.1$ .  
 Others are the same as in Fig. 1.

Table III. The effect of the concentration ratio of europium.

acetic acid (M)	Eu <sup>3+</sup> (M)	EDTA (M)	Eu/EDTA	$\lambda$
1	$1 \times 10^{-4}$	$5 \times 10^{-5}$	2	6.7
1	$2 \times 10^{-4}$	$1 \times 10^{-4}$	2	6.1
0.25	$4 \times 10^{-5}$	$2 \times 10^{-5}$	2	39
0.25	$1 \times 10^{-4}$	$5 \times 10^{-5}$	2	30
0.25	$2 \times 10^{-4}$	$1 \times 10^{-4}$	2	34

from the results mentioned above, the complex compound formed, as well as the ratio of the concentration of micro-component to that of macro-component described by Chlopin<sup>11)</sup>, is one of the most important factors in the coprecipitation of trivalent elements with calcium oxalate from the homogeneous solution.

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