



## **EFFECT OF COEXISTING SODIUM ION ON EXTRACTIVE SEPARATION OF METAL IONS WITH CALIX[4]ARENE TETRACARBOXYLIC ACID**

Keisuke OHTO<sup>\*</sup>), Akikazu SHIOYA, Hirotaka HIGUCHI,  
Tatsuya OSHIMA and Katsutoshi INOUE

Department of Applied Chemistry, Faculty of Science and Engineering,  
Saga University, 1-Honjo, Saga 840-8502, Japan

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### **ABSTRACT**

Solvent extraction of metal ions with calix[4]arene tetracarboxylic acid has been carried out to elucidate effect of coexisting sodium ion. Extraction of metal ions examined, Pb(II), Fe(III), Cu(II), Zn(II), Ni(II), and Co(II), is enhanced by the addition of sodium ion. The enhancement degree of the metal extraction is not necessarily in proportion to the added sodium concentration. The addition of trace amount of sodium ion is necessary to specifically complex for calix[4]arene tetracarboxylic acid and to enhance the extraction ability. However, the addition of excessive amounts of sodium suppresses the extraction of other metal ions, since they act as a competitive ion with other metal ions; The relation between extractive  $pH_{1/2}$  of metal ions and sodium concentration is shown.

Mutual separation of metal ions by using additional sodium ion is also investigated. Although complete mutual separation of three metal ions, Pb(II), Cu(II), and Zn(II), has not been achieved, the possibility that the sodium addition will enhance not only the extraction ability but also the separation efficiency is suggested.

Keywords: calix[4]arene, metal separation, coexisting sodium ion, solvent extraction

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### **INTRODUCTION**

Calixarenes are phenolic, cyclic, and attractive oligomers. A number of studies have been conducted on the recognition properties of calixarenes such as ionic and molecular recognition[1,2] and a number of their specific

\* Corresponding author

behavior have been reported. Especially, there are many studies on sodium uptake, because calix[4]arene compound provides a cavity preorganized for sodium recognition.

Among the studies, coextraction of sodium and the other metal ions with calix[4]arene tetracarboxylic acids is also notable. As reported by Ludwig *et al.* [3,4] and other authors [5,6], during coextraction of sodium and other metal ions with calix[4]arene tetracarboxylic acid, sodium ion would play a very important role. The above opinion was strongly supported by self-coextraction of sodium ions reported in our previous paper [7]. There are two ways of extracting sodium ions. The first sodium ion was specifically extracted with calix[4]arene tetracarboxylic acid by surrounding with phenoxy and carbonyl oxygens and a carboxyl group. The second sodium ion was just ion-exchanged with one carboxyl group among the rest ones in the enhanced extractant by the first complexation. Since the complexation of the second sodium ion should not be so strong, if other metal ions coexist, such ions with high affinity would be selectively extracted. The self-coextraction mechanism of sodium ions and the coextraction mechanism of sodium and other metal ions with calix[4]arene tetracarboxylic acid are shown in Fig. 1.



Fig. 1. Self-coextraction mechanism of sodium ions and coextraction mechanism of sodium and other metal ions with calix[4]arene carboxylic acid.

However, excessive amounts of sodium ion should act as the second ion. Consequently, they should compete with other metal ions. Two ways of complexing sodium that acts as promoter in trace amount and as suppressor in excessive amount to other metal extraction is remarkably specific. However, the relation between the enhanced metal extraction and the

addition of the sodium ion has not been reported in detail. If the hypothesis is correct, for a certain metal the extractability should be the different extent at the different additional amount of the sodium ion. For different metals, the extractabilities should be also different at the same addition sodium.

In the present paper, we report the effect of sodium concentration on metal extraction, together with the mutual separation of three metal ions by adding of sodium salt as an industrial application.

## MATERIALS/METHODS/PROCEDURES

### Reagents

25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethyl-butyl)calix[4]arene (cone conformation) was synthesized in a similar manner to that described in the previous paper [8]. The chemical structure of the extractant was shown in Fig.1.

### Distribution study

Organic solutions were prepared by diluting each extractant into an analytical grade of chloroform to  $5 \text{ mmol dm}^{-3}$ . Aqueous solutions were prepared by dissolving metal chloride or nitrate salts into  $0.1 \text{ mol dm}^{-3}$  nitric acid or  $0.1 \text{ mol dm}^{-3}$  HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) buffer solution to  $0.1 \text{ mmol dm}^{-3}$ . Sodium nitrate was added into these two stock solutions to the desired concentration, such as 0.05, 0.1, and  $0.5 \text{ mol dm}^{-3}$ . For higher pH regions over 5, sodium hydroxide was also added into these stock solutions so as to maintain sodium concentration. Equal volumes ( $10 \text{ cm}^3$ ) of both phases were mixed in an Erlenmeyer flask with a stopper and shaken at 303 K for several hours. After phase separation, the pH and the metal concentration of the aqueous solutions were measured with a pH meter (Beckman, £ 45) and atomic absorption spectrophotometer (Seiko Instrument, SAS 7500), respectively.

For mutual separation of three metal ions, aqueous solutions were prepared by dissolving three nitrate salts of lead, copper, and zinc into mixtures of  $0.1 \text{ mol dm}^{-3}$  nitric acid and HEPES buffer solutions. The pH of the solution was adjusted so that only the lead among all three metal ions was completely removed. Equal volumes ( $15 \text{ cm}^3$ ) of the aqueous solution and above-mentioned organic solution were mixed with in an Erlenmeyer flask and shaken at 303 K. After several hours,  $5 \text{ cm}^3$  of both phases were sampled. Sodium nitrate was added to the left solutions so that sodium concentration was adjusted to  $0.05 \text{ mol dm}^{-3}$ . The mixture was shaken at 303 K. After several hours, the pH and the metal concentration of the first and second equilibrated aqueous solutions were measured by pH meter and atomic absorption spectrophotometer, respectively.

The stripping of loaded lead and copper ions was also carried out with dilute acidic eluents. It was carried out in a similar manner to that described in the previous paper [9].

## RESULTS AND DISCUSSION

### Distribution study

As described above, although sodium ion affects the metal extraction, the extent has not been described. It would be significant to elucidate the effect of sodium concentration and metal type on the extent affected by sodium. The effects of pH on extractability, %*E*, of six metal ions, Pb(II), Fe(III), Cu(II), Zn(II), Ni(II), and Co(II), in various sodium concentration are shown in Fig. 2(a) - (f), respectively. The extractability, %*E*, is defined by equation (1),

$$\%E = \frac{[\text{Metal ion}]_{\text{org}}}{[\text{Metal ion}]_{\text{ini}}} \times 100 \quad (1)$$

where  $[\text{Metal ion}]_{\text{org}}$  and  $[\text{Metal ion}]_{\text{ini}}$  represent the extracted and the initial metal concentrations, respectively. For all metal ions, the addition of sodium ion shifts their extraction pH region lower compared with no additional sodium.

From these results, the half extraction pH values,  $\text{pH}_{1/2}$ s are estimated for each metal at each sodium concentration where the half-extraction pH value,  $\text{pH}_{1/2}$ , is defined as the pH where 50% of the metal ions are extracted into organic phase under the present condition. Relation between the half-extraction pH value,  $\text{pH}_{1/2}$ , of metal ion and sodium concentration is shown in Fig. 3. As the  $\text{pH}_{1/2}$  values correspond with the extractability, the inversion of the values at vertical axis are taken. As seen from Fig. 2(a) - (f), the plots from the experiments without sodium addition for all metal ions are the lowest compared with the plots with sodium additions, except for zinc ion. It should be attributed that the original calix[4]arene extractant free from sodium has poor affinity to zinc and sodium-loaded extractant has also extraction ability due to the coordination geometry and number of zinc ion, stoichiometry of zinc and the tetrameric extractant. For iron and copper ions, adequate addition of sodium ion enhances the extraction ability, whereas excess addition weakens the ability.

The small addition of sodium ion as the first sodium to the extractant is necessary to enhance the ability, and excessive amounts of sodium act as competitive ions with other metal ions. Since the sodium-loaded extractant shows different extraction behavior from the original extractant free from sodium ion, it would be regarded as different extractant from the original. Effective and significant use of the extractant with specific behavior should be capable of completely separating three metal ions by addition of sodium ion without pH adjusting.

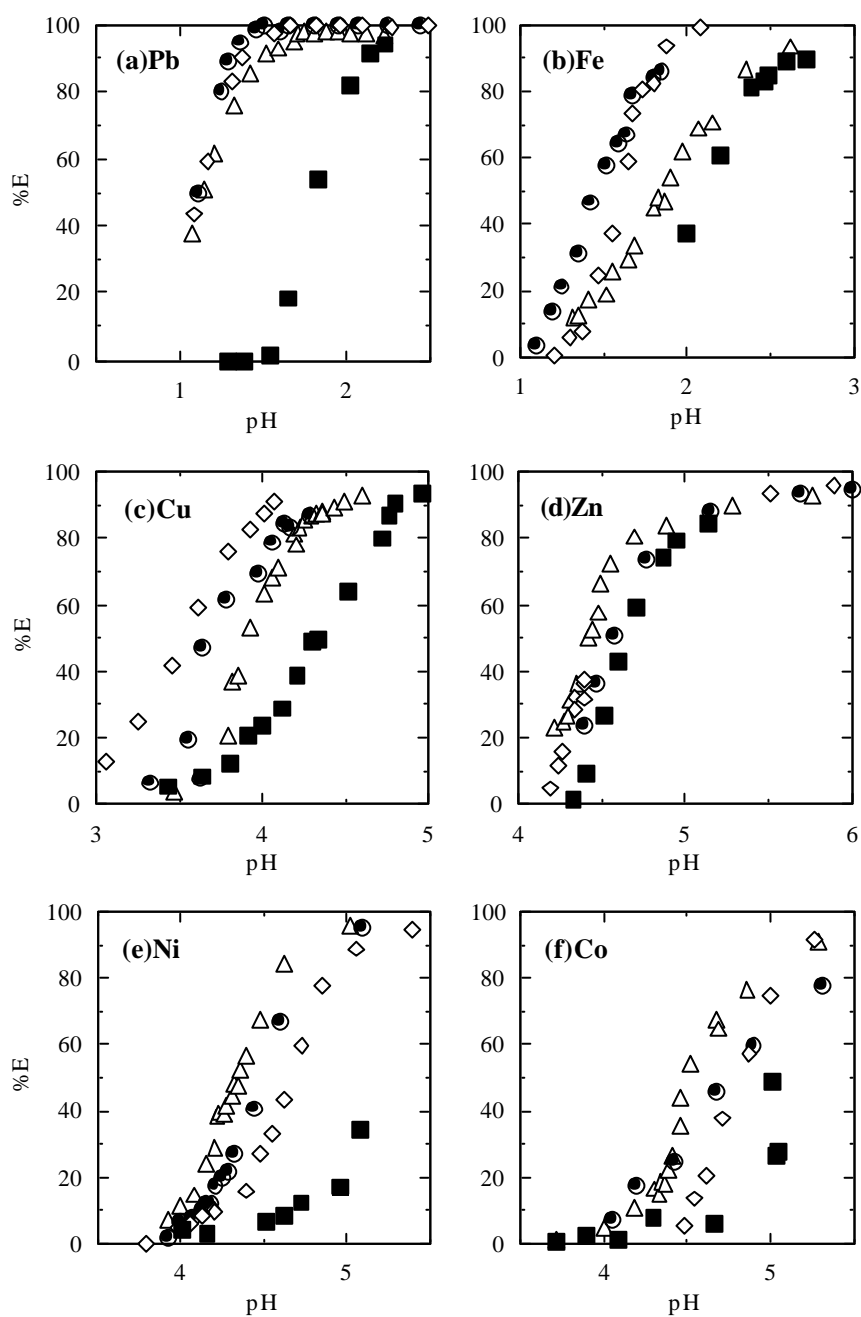


Fig. 2. Effect of pH on extractability of six metal ions in various sodium concentrations. (a) Pb(II), (b) Fe(III), (c) Cu(II), (d) Zn(II), (e) Ni(II), (f) Co(II). [Metal] =  $0.1 \text{ mmol dm}^{-3}$ , [extractant] =  $5 \text{ mmol dm}^{-3}$ , [sodium] = (■) 0 M, (◇) 0.05 M, (●) 0.1 M, (△) 0.5 M.

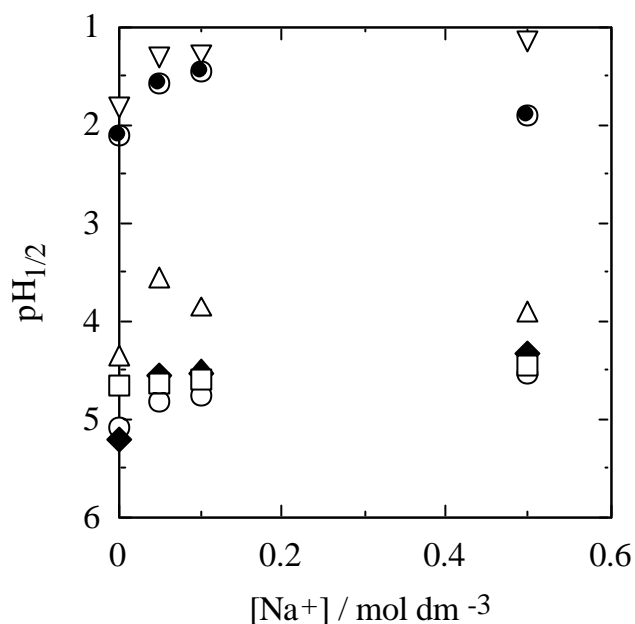


Fig. 3. Relation between half-extraction pH,  $pH_{1/2}$ , for metal ions and sodium concentration. ( $\nabla$ ) Pb(II), ( $\bullet$ ) Fe(III), ( $\Delta$ ) Cu(II), ( $\square$ ) Zn(II), ( $\blacklozenge$ ) Ni(II), ( $\circ$ ) Co(II).

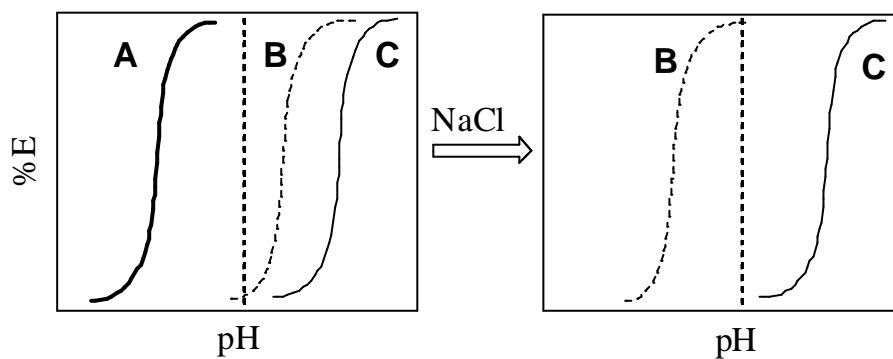


Fig. 4. Conceptual figure for mutual separation of metal ions by change of extraction pH region with addition of sodium ion: metal A - thick curve, B - broken curve, C - solid curve.

Conceptual figure for mutual separation of three metal ions by change of extraction pH region with additional sodium ions are shown in Fig. 4. The pH value is adjusted as shown by the broken straight line. At first, easily extracted Metal, A, (represented by thick curve line) is completely extracted without sodium addition at the pH. After removal A, new or

metal-stripped organic phase is added to left aqueous phase. When sodium salt is added to the mixture, if the extraction pH region of only Metal B (represented by broken curve line) is shifted lower and the region of Metal C (represented by solid curve line) is hardly changed, mutual separation of three metal ions without pH adjustment would be completed.

From Fig. 2, the results for lead, copper, and zinc, were taken up again. The effects of pH on extractability of them in the absence and presence of sodium ions are shown in Fig. 5(a) and (b), respectively.

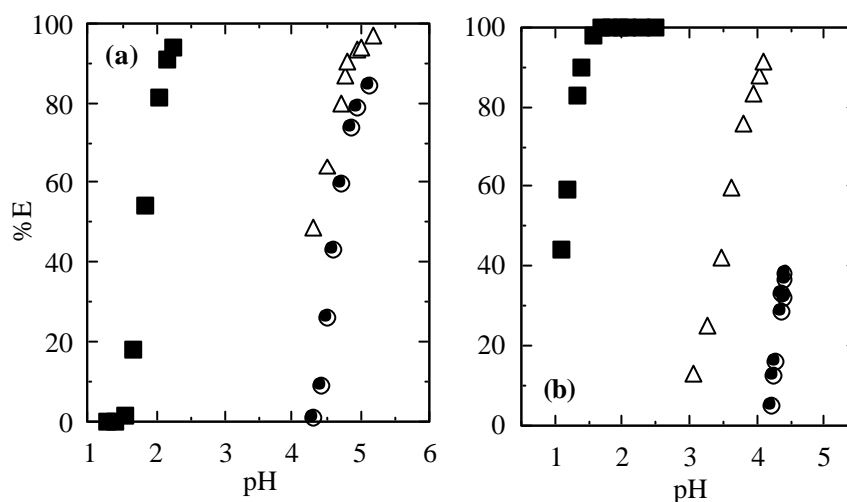


Fig. 5. Effect of pH on extractability of three metal ions in the absence (a) and presence (b) of sodium. [Sodium]:  $0.05 \text{ mol dm}^{-3}$ , (■) Pb(II), (△) Cu(II), (●) Zn(II).

These three metals may be applicable to the concept shown in Fig. 4. The results for the mutual separation of lead, copper, and zinc ions before and after the addition of sodium chloride, artificial sea-salt, and sodium acetate, are shown in Fig. 6(a) - (c), respectively. The first extraction before sodium addition is shown in the blank area and the second extraction after sodium addition is shown in the diagonal area. Ideally speaking, lead should be extracted at the first extraction and copper at the second, while zinc should not be extracted. From these results, the complete separation of these three metal ions without changing the pH and with only sodium addition has not been realized. However, the present calix[4]arene tetracarboxylic acid provides two-faced extraction behavior, consequently it should achieve the mutual separation of some metals.

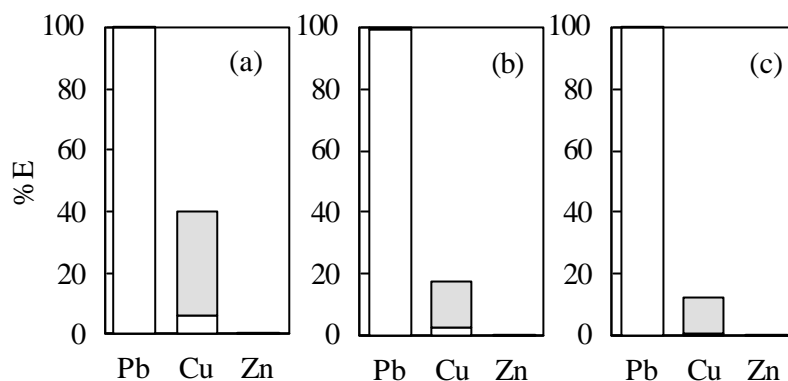


Fig. 6. Mutual separation of three metal ions before and after addition of sodium chloride, artificial sea-salt, and sodium acetate. [metal] –  $0.1 \text{ mmol dm}^{-3}$ , [sodium at addition] –  $0.05 \text{ mol dm}^{-3}$ , blank area – first extraction before sodium addition, dialog area – second extraction after sodium addition.

(a)  $\text{pH}_{\text{ini}}=3.56$ ,  $\text{pH}_{\text{eq1}}=3.54$ ,  $\text{pH}_{\text{eq2}}=3.38$

(b)  $\text{pH}_{\text{ini}}=3.40$ ,  $\text{pH}_{\text{eq1}}=3.32$ ,  $\text{pH}_{\text{eq2}}=3.20$

(c)  $\text{pH}_{\text{ini}}=3.25$ ,  $\text{pH}_{\text{eq1}}=3.24$ ,  $\text{pH}_{\text{eq2}}=3.07$

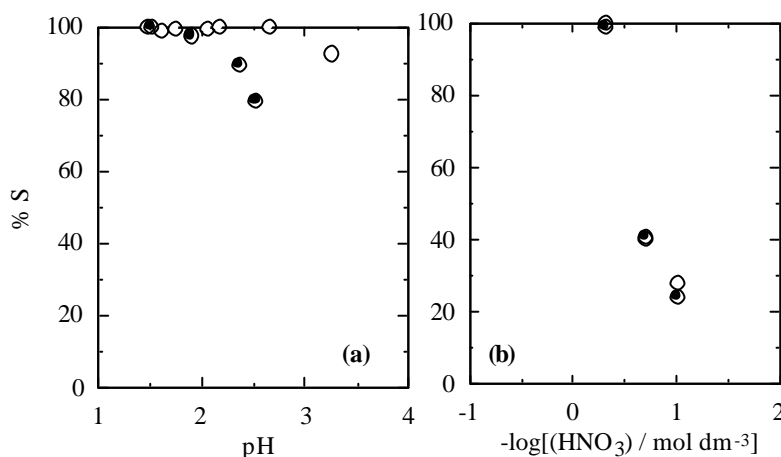


Fig. 7. Effect of pH or acid concentration on percentage of stripping for divalent ions; (a) Cu, (b) Pb, [metal] -  $0.1 \text{ mmol dm}^{-3}$ .

Easy stripping is also important from the industrial point of view. However, since most metal extractions become easier by addition of sodium ion, the stripping of metals should become more difficult. In this sense, the stripping of metal ions in the absence or the presence of sodium ions has been carried out. The percentage stripping of divalent copper and lead ions in absence or presence of sodium ion ( $0.1 \text{ mol dm}^{-3}$ ) are shown in Fig. 7(a) and (b),



respectively. Nitric acid concentration required for complete copper stripping in the presence of sodium ion is much higher than that in the absence of sodium, whereas for lead ion both acid concentrations are almost same. The difference would be attributed to the relation of extraction pH regions between sodium and divalent metal ions. That is, the extraction pH region of sodium ion is apart from that of copper, while for lead ion both regions are close. As described above, the sodium addition, in other words, the complexation of first sodium ion, makes the extraction pH region shift lower. It means that if the first sodium ion is stripped, since the pH region of metal extraction should get back to the original region in the absence of sodium ion, the difference of percentage stripping between free and sodium systems should be dependent on the extent of sodium stripping. The first sodium ion is complexed with the extractant from pH 1 at  $0.1 \text{ mol dm}^{-3}$  sodium concentration, is saturated up to pH 1.5. The acid concentration requiring complete sodium stripping should be reduced, because sodium ion is free in the stripping solution. Since the extraction region of copper ion is much higher than that of sodium, significant difference of acid concentration required complete copper stripping was observed. On the other hands, the extraction region of lead is close to that of sodium, little difference of acid concentration required complete copper takes place in both media.

### CONCLUSION

Solvent extraction of metal ions with calix[4]arene tetracarboxylic acid has been carried out to elucidate the effect of coexisting sodium ion. Extraction of all metal ions examined is enhanced by addition of sodium. Since the sodium-loaded extractant would act as a newly prepared extractant compared with the original extractant free from sodium ion, the present calix[4]arene tetracarboxylic acid provides a two-faced extraction behavior. Consequently it should achieve the mutual separation of some metals with or without the sodium ions. It is suggested that the addition of trace amount of sodium ions may improve the mutual separation of the metal ions.

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