

Solid-Phase Extraction of Ga³⁺ and In³⁺ with a Hexadentate Chelating Reagent

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A new adsorption system for divalent and trivalent metal ions have been developed. The indium ion was efficiently separated from an acidic aqueous solution containing Ga³⁺, In³⁺, and Zn²⁺. The adsorption and separation material was synthesized and it was loaded onto silica gel containing chemically bonded octadecyl groups (C18). As a ligand, N,N'-bis(5-chloro-2-hydroxybenzyl)-N,N'-bis(2-methyl-pyridyl)ethylenediamine (H₂Clbbpen) was used. The separation material, containing H₂Clbbpen, was able to adsorb Ga³⁺ and In³⁺ from a Zn²⁺ containing acidic solution. In addition, when this adsorption material was applied to the column adsorption method, Ga³⁺ and In³⁺ could be adsorbed from an aqueous acidic solution containing zinc ions. The Zn²⁺ ions did not adsorb onto this separation material. After adsorption, Ga³⁺ could be eluted first using a sodium hydroxide solution. Subsequently, In³⁺ could be eluted with a nitric acid solution.

1. Introduction

Rare earth metals have been abundantly used in the high-tech industry. However, indium is a very rare mineral resource because it can only be mined for several year. Therefore, to secure a stable supply, the recycling and reuse of indium from advanced industrial products is necessary for the construction of a sustainable society. There is an abundant rare metal resource available in our country called the urban mine, which includes used and disposed electronic devices. The development of a technique to efficiently separate and collect rare metals from the urban mine is very important. In the separation and recovery process of rare metals from electronic devices, it is necessary to research separation materials with high selectivity for collecting and separating the desired metal ions. As a method to separate a metal ion from an aqueous solution, the "ion exchange method" and "solvent extraction method" are often used. These methods use the difference in metal valences, ionic radii, and complex formations between a metal ion and the extracting agent to separate metal ions with specificity. In particular, ion exchange methods will be able to support small metal separation systems because the adsorption of metal ions from the aqueous phase to the solid phase does not use harmful

organic solutions. However, the solvent extraction reagent used in the solvent extraction method has superior selectivity over that of a typical ion exchange resin for separating metal ions. Therefore, separation materials impregnated or bonded to a solvent extraction reagent with high selectivity for the separation of metal ion on a solid phase, such as silica gel, resin or natural fiber, were synthesized to study the separation of rare metal ions from an acidic aqueous solution [1–8]. For the establishment of efficient metal ion separation technology, hydrophobic silica gel (silica gel chemically bonded to a long-chain alkyl group) was considered to become a pseudo-organic phase and was used as a carrier for the solvent extraction reagent. A β -diketone was chosen as the solvent extraction reagent and the separation material was synthesized. The selectivity of this separation material was better than that of the solvent extraction method using the same loaded extraction reagent [9–11]. In addition, this separation material is available for construction of the pseudo-solvent extraction system in spite of separation system by the ion exchange reaction. Therefore, superior separation ability was developed for metal ions [9–11]. The separation of In^{3+} from Ga^{3+} and Zn^{2+} using the $\text{H}_2\text{Clbbpen}$ -loaded surface-modified silica gel (C18- H_2L) was studied.

2. Experimental

2.1 Reagents and apparatus

All reagents were used for analytical grade without further purification. Deionized water used throughout was prepared from a Milli-Q Elix Advantage3 water purification system (Millipore). Other organic materials used were obtained from Tokyo Kasei Kogyo. Inductively coupled argon-plasma optical emission spectrometry (ICP-OES) was performed using an Agilent 5100 to determine the concentration of metal ions. The pH values of aqueous solutions were measured using a pH meter (TOA-DKK M-60) equipped with a glass electrode. $\text{H}_2\text{Clbbpen}$ was synthesized according to Neves *et al.*, as shown in Figure 1 [12].

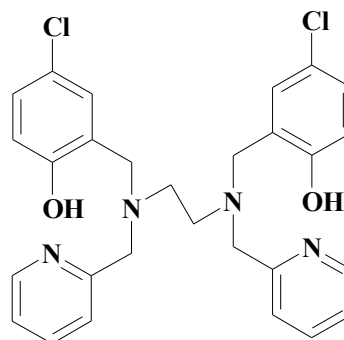


Figure 1. Structure of $\text{H}_2\text{Clbbpen}$.

2.2 Preparation of C18- $\text{H}_2\text{Clbbpen}$

The non-end-capped ODS was prepared from 60N silica gel (particle size: 40–50 μm , Kanto Chemical Co., Inc.) and octadecyl trichlorosilane according to a standard method. The separation material was prepared according to a previous method: 200 g of ODS was allowed to stand overnight in 1 dm^3 toluene solution containing 0.02 mol $\text{H}_2\text{Clbbpen}$ [10]. After standing for 24 h at 277 K, the mixed solution was filtrated, washed with methanol and deionized water, and dried in a vacuum at room temperature.

2.3 Adsorption experiment of metal ions

An aliquot of C18- H_2L was shaken with 30 cm^3 of an aqueous phase containing $[\text{M}^{n+}]$:

$1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{CH}_2\text{ClCOOH}]$: 0.02 mol dm^{-3} , and sodium salt (NaCl , NaNO_3 , or Na_2SO_4) within 12 days at $25 \pm 1 \text{ }^\circ\text{C}$. After the reaction was completed, the mixed solutions were filtered. The concentration of metal ions in the aqueous solutions was determined by ICP-OES, and the pH value of the aqueous phase was measured.

2.4 Separation of In^{3+} from Ga^{3+} and Zn^{2+} using the column method

The experimental conditions of the column method is shown: 100 cm^3 of the sample solution containing $[\text{M}^{n+}]$: $5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{NaX}]$ (X^- : Cl^- , NO_3^- , or SO_4^{2-}): 0.1 mol dm^{-3} , $[\text{CH}_2\text{ClCOOH}]$: 0.01 mol dm^{-3} and adjusted to pH: 3.0. The flow rate was $0.5 \text{ cm}^3 \text{ min}^{-1}$. Then, metal ions were adsorbed onto the column. The column was rinsed with deionized water. Thereafter, Ga^{3+} were eluted with 0.1 mol dm^{-3} NaOH solution; then, In^{3+} were eluted with 0.2 mol dm^{-3} HCl solution and dispensed in a fraction collector. The concentration of metal ions in the dispensing solution was measured using ICP-OES.

3. Results and Discussion

3.1 Adsorption behavior of the metal ions

Metal ions were adsorbed onto the C18- H_2L separation material. The relations between adsorption ratio of metal ions and pH are shown in Figure 2 and 3.

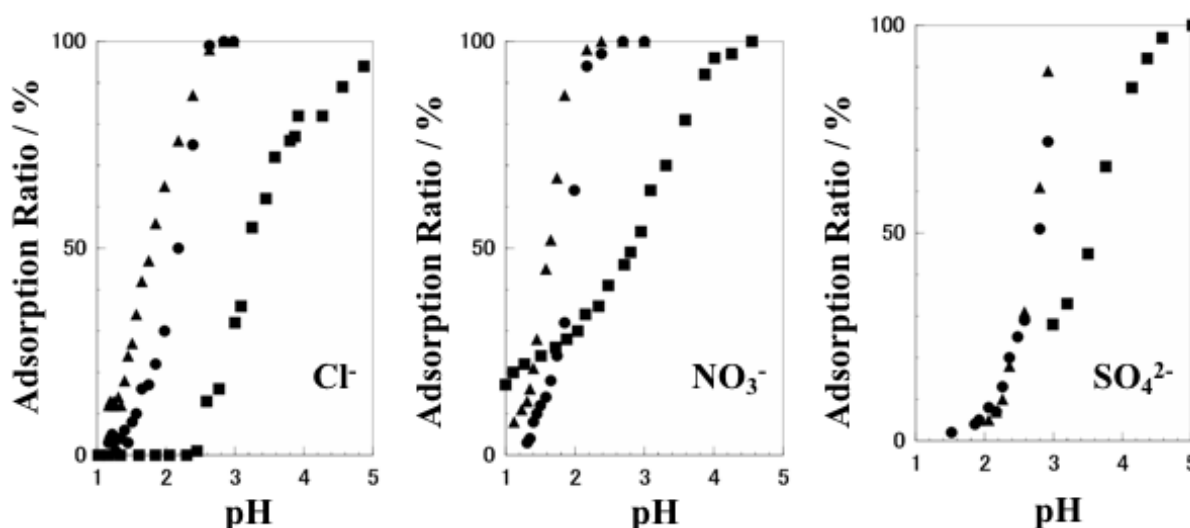


Figure 2. Adsorption ratios of Ga^{3+} , In^{3+} , and Zn^{2+} using C18- H_2L separation material. \blacktriangle : In^{3+} , \bullet : Ga^{3+} , \blacksquare : Zn^{2+} , $[\text{M}^{n+}]$: $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaCl}]$, $[\text{NaNO}_3]$ or $[\text{Na}_2\text{SO}_4]$: 0.1 mol dm^{-3} , C18- H_2L : $0.3 \text{ g}/30 \text{ cm}^3$. Shaking time: 8 days.

The value of adsorption ratio E was defined as follows:

$$E = \{[\text{M}^{n+}]_{\text{init}} - [\text{M}^{n+}]_{\text{eq}}\} / [\text{M}^{n+}]_{\text{init}} \times 100 (\%) \quad (1)$$

In this equation, $[\text{M}^{n+}]_{\text{init}}$ was the initial concentration of the metal ion and $[\text{M}^{n+}]_{\text{eq}}$ was the concentration of metal ions after adsorption. The adsorption behavior of Ga^{3+} , In^{3+} , and Zn^{2+} are shown in Figure 2 and that of Cu^{2+} , Co^{2+} , and Ni^{2+} are shown in Figure 3. In the case of adsorption of Zn^{2+} ,

Cu^{2+} , Co^{2+} and Ni^{2+} with Na_2SO_4 was already published [13]. In this result, mutual separation of between Ga^{3+} and In^{3+} from the adsorption curves was difficult.

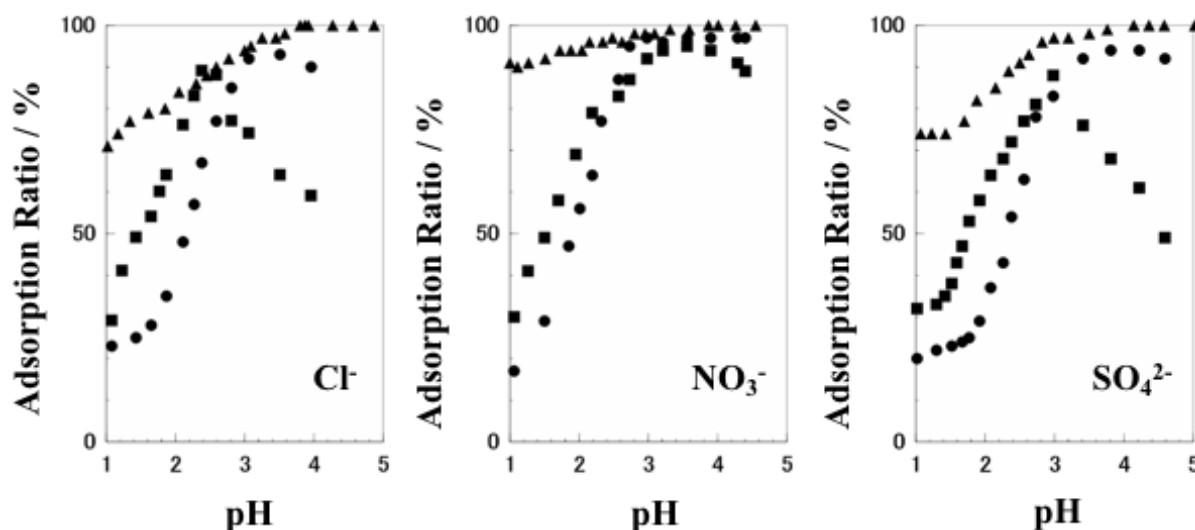


Figure 3. Adsorption ratios of Ni^{2+} , Co^{2+} , and Cu^{2+} using C18-H₂L separation material. \blacktriangle : Cu^{2+} , \bullet : Co^{2+} , \blacksquare : Ni^{2+} , $[\text{M}^{n+}]$: $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaCl}]$, $[\text{NaNO}_3]$ or $[\text{Na}_2\text{SO}_4]$: 0.1 mol dm^{-3} , C18-H₂L: $0.3 \text{ g}/30 \text{ cm}^3$. Shaking time: 8 days.

Ga^{3+} and In^{3+} were shown to have the same adsorption behavior in the case where NaNO_3 was the counter anion. When Cl^- or SO_4^{2-} was used as the counter anion, the adsorption ability of In^{3+} was better than that of Ga^{3+} . The selectivity between Ga^{3+} or In^{3+} and Zn^{2+} with NaCl was better than that with Na_2SO_4 . In the future, zinc will be used in the transference electrode for electronic device touch panels. Therefore, the development of mutual separation techniques from acidic zinc solutions containing Ga^{3+} and/or In^{3+} is necessary. On the other hand, Cu^{2+} was adsorbed from the strongly acidic solution with all kinds of counter anions.

The copper ion was adsorbed with all examined counter anions from the acid solution. Adsorption ability at the same behavior was Ga^{3+} and In^{3+} . In the case of a Cl^- , adsorption ability of Ni^{2+} was higher than that of Ga^{3+} and In^{3+} . In the case of a NO_3^- , adsorption ability of Ni^{2+} was lower than that of Ga^{3+} and In^{3+} . In the case of a SO_4^{2-} , adsorption ability of Ga^{3+} and In^{3+} was lower than that of Ni^{2+} and Co^{2+} . The mutual separation of Ga^{3+} and In^{3+} using the batch method was difficult; however, from such a characteristic, thought that mutual separation of the high efficiency construction could be expected by applying separation materials to the column method.

3.2 Separation of In^{3+} from the acid water solution

Acidic solutions containing Ga^{3+} , In^{3+} , and Zn^{2+} were passed through a column filled with the C18-H₂L separation material. Zn^{2+} could not be adsorbed on this separation material under this condition. Ga^{3+} was eluted using 0.1 mol dm^{-3} NaOH solution. The adsorbed Ga^{3+} was completely eluted. Then, In^{3+} was eluted with 0.02 mol dm^{-3} HNO_3 solution. The adsorbed In^{3+} was also completely eluted. The elution curve is shown in Figure 4. When the eluent was passing through the

column, Ga^{3+} was completely eluted approximately 600 cm^3 after the adsorbed metal ions. Under these conditions, In^{3+} was not eluted. Afterward, it was observed that In^{3+} was eluted when a nitric acid solution was passed through the column. In addition, Zn^{2+} was able to set this condition that was not adsorbed by a column from the result of the batch method on this condition. Selective separation of Ga^{3+} and In^{3+} from a simulated urban mine metal-ion-containing solution was accomplished. However, improvements will be necessary because the exchange capacity of the adsorption materials was small and the adsorption rate was also slow.

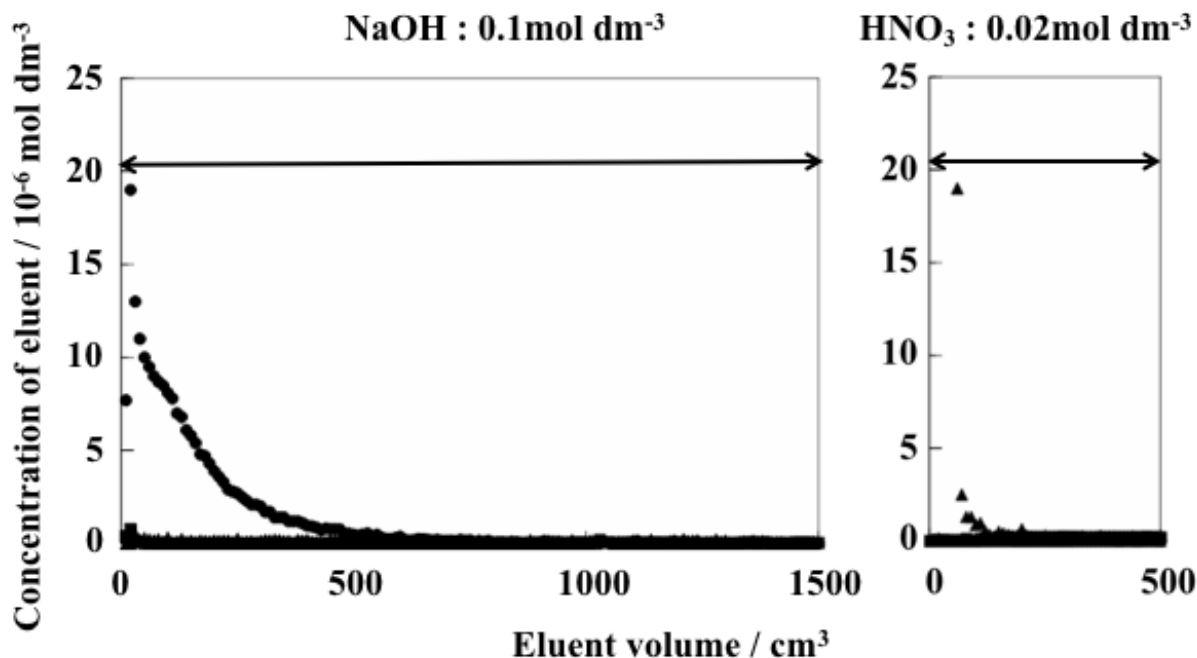


Figure 4. Elution behavior of Ga^{3+} and In^{3+} Coulum : 20cm, internal diameter : 1.0 cm, C18- H_2L : 8.0 g Adsorption condition pH : 3.0 , $[\text{M}^{n+}]$: $5.0 \times 10^{-5} \text{ mol dm}^{-3}$, Flow rate : 0.5 cm min^{-1} [Na_2SO_4] : 0.1 mol dm^{-3} , Flow Volume : 200 cm^3 .

4. Conclusion

We have developed a new adsorption system for divalent and trivalent metal ions using the C18- H_2L sorbent, which $\text{H}_2\text{Clbbpen}$ was directly loaded ODS. Relations between the adsorption ratio E (%) and pH showed that the metal ions could be absorbed from an acidic solution. The C18- H_2L system was found to have good mutual selectivity for In^{3+} - Zn^{2+} for separation. This is important because Zn^{2+} is included in the touch panel of electronic devices.

This new method has an advantage in that a chelating agent can be effectively used to remove metal ions from an aqueous solution without organic solvents. This separation material can be easily synthesized by simply loading the extraction reagent onto hydrophobic silica gel. Therefore, the application of this method is easily possible with many kinds of extraction reagents. The utilization of the extraction reagent with higher selectivity is widely enabled.

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