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## VI. 2. Study on Selective Separation of Cesium Using a Macroporous Silica-Based Supramolecular Recognition Absorbent

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### Introduction

Recently, much attention has been given to the selective separation and recovery of Cesium(Cs)-137 from high level liquid waste (HLLW) in relation to the partitioning of radioactive nuclides and their effective utilization<sup>1-3</sup>. Cs-137 having a relatively long half-life of about 30 years exhibits high radioactivity and heat generation. In the HLLW, large amounts of Cs group (~3.6 kg/1tHU, 45 GWd/t) are contained<sup>4</sup>. Therefore, selective separation of Cs-137 from HLLW is an important environmental issue for nuclear waste management. In addition, the purified Cs is also expected for radiation and heat sources in the field of medicine and industry.

Many methods for the separation of Cs(I) such as solvent extraction, ion exchange and co-precipitation have been studied<sup>5-8</sup>. In the liquid-liquid solvent extraction process, supramolecular recognition agents are well known to have selective extraction ability to Cs(I). In order to utilize these extractants having high affinity for Cs(I), the impregnation methods have been proposed to fix the extractant on different supporting matrices<sup>9-12</sup>. 1,3-[(2,4-Diethylheptyloxy)oxy]-2,4-crown-6-calix[4]arene(Calix[4]arene-R14), a kind of supramolecular recognition composite, which shows high selectivity toward Cs(I) and excellent radiation stability, can act as one of the most promising adsorbent for the uptake of Cs(I)<sup>13</sup>. In this study, we have attempted to load the Calix[4]arene-R14 extractant and a molecule modifier 1-dodecanol into the SiO<sub>2</sub> silica based polymer support (SiO<sub>2</sub>-P) by using its high immobilizing ability for the selective separation of Cs(I) from HLLW. The present paper deals with the preparation of Calix[4] arene-R14 and dodecanol-loaded

SiO<sub>2</sub>-P ((Calix[4] + Dodecanol)/SiO<sub>2</sub>-P) , characterization and the evaluation of its uptake abilities.

## **Experimental**

### *Materials*

The 1,3-[(2,4-Diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14, 97%) was purchased from Rikoh Kagaku co. Ltd. and used without further purification. The Molecular structure of Calix[4]arene-R14 is shown in Fig. 1. 1-dodecanol was procured from Wako Pure Chemical Industries, Ltd. The SiO<sub>2</sub> silica based polymer support (SiO<sub>2</sub>-P) was synthesized by following the literature method<sup>14</sup>). Other chemicals such as CsNO<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, RE(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (RE = La, Nd, Sm, and Gd), ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O were reagent grade supplied by Kanto Chemical Co. Palladium nitrate solution (4.5wt%) and ruthenium nitrosyl nitrate solution (1.5wt%) were purchased from Sigma-Aldrich Chemical Co.

### *Preparation of (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P*

The Calix[4]arene-R14 and a molecule modifier 1-dodecanol impregnated on SiO<sub>2</sub>-P support ((Calix[4] + Dodecanol)/SiO<sub>2</sub>-P) was prepared as follows. First, the Calix[4]arene-R14 and 1-dodecanol were dissolved in dichloromethane and then mixed with the SiO<sub>2</sub>-P particles in a glass flask for approximately 0.5 h at 25°C. After that the mixture was stirred gently for 2 h at 40°C under reduced pressure by using rotary evaporator in order to enhance impregnating, and finally vacuum-dried for 1d at 40°C.

### *Characterization*

The surface morphology of (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P was observed by scanning electron microscopy (SEM, Hitachi TM-1000). Thermal stability of (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P was evaluated by thermal gravimetry and differential thermal analysis (TG-DTA, Shimadzu DTG-60) under the operation conditions of temperature range: 25 ~ 600°C and heating rate: 1°C/min.

### *Determination of Distribution Coefficient (K<sub>d</sub>)*

The distribution of metal ions for (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P was estimated by batch method. An aqueous solution (4 cm<sup>3</sup>) containing 5mM metal ions was contacted with 0.2 g of (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P at 25±1°C up to 5 h, which was found to be

sufficient for attaining equilibrium. The concentrations of Cs(I) and other metal ions were measured by atomic absorption spectrophotometry (AAS, Simadzu AA-660) and inductively coupled plasma atomic absorption spectrometry (ICP-AES, Simadzu ICPS-7510). The distribution coefficient ( $K_d$ ,  $\text{cm}^3/\text{g}$ ) of a metal ion on (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P is defined as :

$$K_d = ((C_0 - C_f) / C_f) \times V / m \quad (\text{Eq. 1})$$

where  $C_0$  and  $C_f$  are the concentration of metal ions at initial and at equilibrium, respectively;  $m$  (g) the weight of dry (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P composite,  $V$  ( $\text{cm}^3$ ) the volume of aqueous phase.

## Results and Discussion

### *Surface Morphology and Thermal Stability*

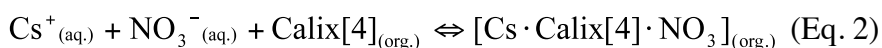
The surface morphology of (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P was examined by SEM (Fig. 2). Obvious spherical and porous particles are obtained. The particle size of (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P was estimated to be 50  $\mu\text{m}$  in diameter by the SEM image. The thermal stability was evaluated by TG/DTA analyses within the temperature range 25°~600°C (Fig. 3). The result of TG and DTA for (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P indicates three different weight loss ranges: 20-180°C, 200-330°C and 330-510°C. The first weight loss is due to the desorption of water from  $\text{SiO}_2$ -P, the second and third weight loss are due to the thermal decomposition of styrene-divinylbenzene(SDB) copolymer and organic solvents(Calix[4] + Dodecanol), respectively. These findings suggest that the (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P is thermally stable up to 200°C.

### *Uptake Rate*

In order to evaluate the equilibration time of Cs(I) and other metal ions for (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P, the effect of shaking time on  $K_d$  value was examined in the presence of 3 M  $\text{HNO}_3$  by batch method (Fig. 4). The uptake rate of Cs(I) for (Calix[4] + Dodecanol) / $\text{SiO}_2$ -P in 3 M  $\text{HNO}_3$  attained equilibrium within 0.5 h, and relatively large  $K_d$  value above 70  $\text{cm}^3/\text{g}$  was obtained. On the other hand, almost no uptake for other metal ions were observed, indicating that (Calix[4] + Dodecanol)/ $\text{SiO}_2$ -P gel is effective for the selective separation of Cs(I).

### *Effect of HNO<sub>3</sub> Concentration*

As for Cs(I), the  $K_d$  value was considerably lowered in the range of 0.1~4 M HNO<sub>3</sub>. However, the  $K_d$  value tended to increase with increasing HNO<sub>3</sub> concentration of 1 ~ 4 M HNO<sub>3</sub> and relatively large  $K_d$  value above 90 cm<sup>3</sup>/g were obtained around 4 M HNO<sub>3</sub> (Fig. 5). This effect is due to the extraction of an ion-pair species according to the following related solvent extraction reaction reported earlier<sup>13</sup>.



On the other hand, the  $K_d$  values for Sr(II), Pd(II), Ru(III), La(III), Nd(III), Sm(III), Gd(III), Zr(IV) and Mo(VI) were lower than 10 cm<sup>3</sup>/g, indicating that the (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P had excellent selectivity for Cs(I).

### *Uptake Isotherm*

In order to clarify the uptake mechanism, adsorption isotherms were obtained in a wide range of initial Cs(I) concentrations. The equilibrium amounts of Cs(I) adsorbed on (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P approached a constant value with increasing Cs(I) concentration (Fig. 6), suggesting that the uptake of Cs(I) follows a Langmuir-type adsorption equation. A fairly linear relation between  $C_{\text{eq}}/Q_{\text{eq}}$  and  $C_{\text{eq}}$  was obtained from the Langmuir plots derived from Fig. 6 and the  $Q_{\text{max}}$  value for (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P was estimated to be 0.19 mmol/g.

### **Conclusions**

The uptake properties of Cs(I), characterization and dynamic adsorption properties were investigated by using (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P. The uptake of Cs(I) for (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P was fairly fast in the initial stage and the uptake equilibrium attained within 0.5 h. The  $K_{d, \text{Cs}}$  was increase with increasing HNO<sub>3</sub> concentration and relatively large  $K_d$  values above 90 cm<sup>3</sup>/g were obtained around 4 M HNO<sub>3</sub>. The uptake isotherm of Cs(I) followed a Langmuir-type adsorption equation. Thus, the Calix[4]arene-R14 and a molecule modifier 1-dodecanol impregnated on SiO<sub>2</sub>-P support is effective for the selective separation and recovery of Cs(I).

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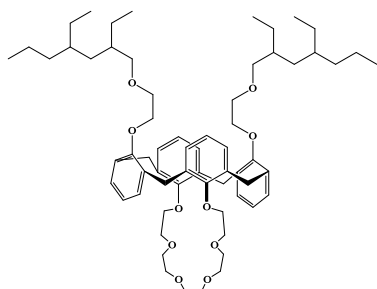


Figure 1. Molecular structure of Calix[4].

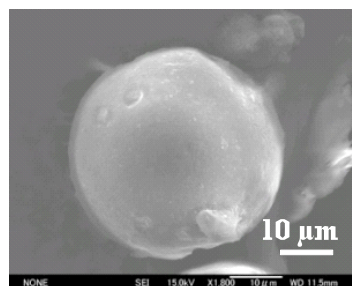


Figure 2. SEM image of the surface of (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P.

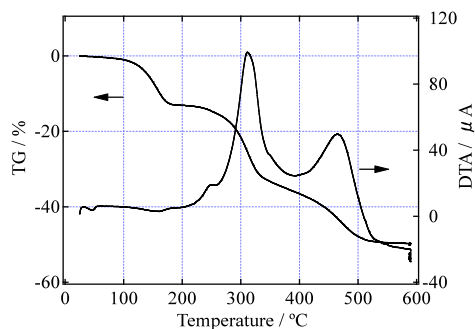


Figure 3. TG / DTA curves for (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P.

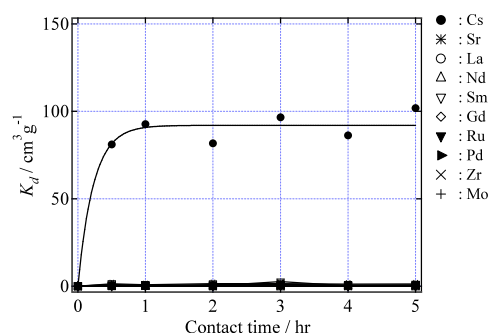


Figure 4. Effects of shaking time on  $K_d$  of different metal ions.  $V/m$ : 20 cm<sup>3</sup>/g, [Metal]: 5mM, 3 M HNO<sub>3</sub>: 25°C.

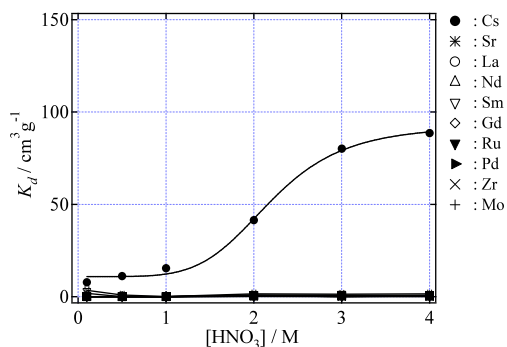


Figure 5. Effects of HNO<sub>3</sub> concentration on  $K_d$  of different metal ions.  $V/m$ : 20 cm<sup>3</sup>/g, [Metal]: 5mM, 25°C.

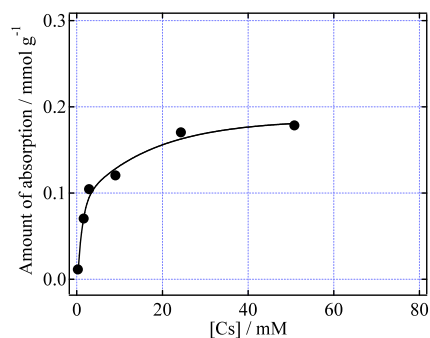


Figure 6. Uptake isotherm of Cs(I) for (Calix[4] + Dodecanol)/SiO<sub>2</sub>-P.  $V/m$ : 20 cm<sup>3</sup>/g, 3 M HNO<sub>3</sub>: 25°C.