Short communication

Sulfinylcalix[4]arene-impregnated Amberlite XAD-7 resin for the separation of niobium(V) from tantalum(V)

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Abstract

Amberlite XAD-7 resin was impregnated with *p-tert*-butylsulfinylcalix[4]arene. Niobium(V) was collected on the impregnated resin in yields of more than 90% around pH 5.4, whereas tantalum(V) was negligibly collected. The collected niobium(V) was desorbed with 9 M sulfuric acid nearly quantitatively, hence the separation of niobium(V) from tantalum(V) was successfully achieved.
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1. Introduction

The development of functional materials which react selectively with a desired metal ion or molecule is an important theme in the field of separation science. Impregnating, coating, or loading a solid support with a chelating reagent offers a facile preparation of a sorbent for metal ions [1–6]. The impregnation method is free from difficulties encountered in chemically linking a chelating reagent to a support matrix, hence there is a wide choice of reagents for desired selectivity.

Recently, thiacalixarenes, a new class of macrocyclic ligand, generally made up of phenol units linked by sulfur moieties, have attracted considerable attention in broad fields of supramolecular chemistry [7–9]. Since our first report of a practical synthesis of *p-tert*-butylthiacalix[4]arene [10], we have demonstrated the potential and utility of thiacalixarenes

[7], including their use as analytical reagents for metal ions [11–14]. During the course of such efforts, the sulfinyl analog, in which the sulfide linkages are oxidized to sulfoxides, has been found to react with niobium(V) in preference to tantalum(V) [15], though their chemical properties are very similar [16,17].

Stimulated by this finding, herein an attempt has been made to prepare a niobium-selective sorbent by the impregnation of an Amberlite XAD resin with *p-tert*-butylsulfinylcalix[4]arene (SOCA, see Fig. 1). Unlike most of other existing methods for the chemical separation of niobium(V) and tantalum(V) [4,16–18], the SOCA-impregnated XAD resin affords their separation without addition of a high concentration of highly hazardous hydrofluoric acid, which is an attractive feature of the present sorbent.

2. Experimental

2.1. Materials

Amberlite XAD-7 resin (methacrylate-based polymer material, particle size of 0.3–0.9 mm, Rohm and Haas, Philadelphia, PA, USA) was washed with acetone, dried

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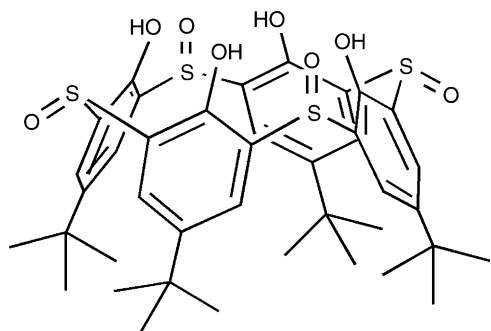*E-mail addresses:* h-matsu@numse.nagoya-u.ac.jp (H. Matsumiya), iki@orgsynth.che.tohoku.ac.jp (N. Iki).

Fig. 1. Chemical structure of *p-tert*-butylsulfinylcalix[4]arene (SOCA).

in vacuo (2–4 mmHg), and soaked in chloroform before use. The chelating reagent, *p-tert*-butylsulfinylcalix[4]arene (SOCA), was synthesized as described in the literature [15]. Commercial 1000 ppm standard solutions of niobium and tantalum (1 M HF solutions) were purchased from Wako Pure Chemicals (Osaka, Japan) and diluted to appropriate concentrations with water (by factors of 22–430) before use. Other reagents and solvents used were of guaranteed-reagent-grade. Deionized water purchased from Daiwa Chemicals (Sendai, Japan) was used throughout this study.

2.2. Preparation of SOCA-impregnated XAD-7 resin

In a 300 ml glass flask, 2.4 g (3.0 mmol) of SOCA was dissolved in 150 ml of chloroform with stirring. A 30 g amount of XAD-7 was added to the solution and gently stirred for 1 h. Subsequently, the chloroform was gradually removed off with a rotary vacuum-evaporator in a water bath at 40 °C: the pressure was kept at 340 mmHg until dryness, and then reduced to 55 mmHg for an additional 10 min. The resin was washed with a small amount of chloroform, dried in vacuo (2–4 mmHg), and stored in air. The impregnated resin was conditioned with an appropriate pH buffer solution before use.

2.3. Sorption of metals on SOCA-impregnated XAD-7 resin

To a 30 ml glass tube were added 0.30 g of the SOCA-impregnated XAD-7 and 20 ml of an aqueous solution containing niobium(V) and tantalum(V) (25 μM–0.25 mM) as well as an appropriate pH buffer (20 mM): formic acid–NaOH for pH 3.5–4.3, acetic acid–NaOH for pH 4.3–5.5, 2-morpholinoethanesulfonic acid (MES)–NaOH for pH 5.5–6.5, 3-morpholinopropanesulfonic acid (MOPS)–NaOH for pH 6.5–7.2. After the mixture was shaken for a given time at 125 strokes/min, the supernatant solution was analyzed with a Seiko SPS-7800 inductively coupled plasma atomic emission spectrometer (Chiba, Japan) to determine the sorption yields of niobium(V) and tantalum(V). The pH of the supernatant solution was also measured with a Horiba D-14 pH meter (Kyoto, Japan). All procedures were performed at room temperature.

3. Results and discussion

3.1. Impregnation of XAD-7 resin with SOCA

For the impregnation of chelating reagents, macroporous organic-polymer beads of Amberlite XAD series are regarded as a good support material because of their high surface-area and good mechanical stability [1–6]. Among them, XAD-7 was reported to be particularly suitable in terms of the metal-sorption efficiency of the resulting sorbent [3]. In the present study, therefore, XAD-7 was employed as a support material. XAD-7 was also reported to retain various metal ions non-selectively when pretreated with sodium hydroxide, or even sodium carbonate [19], hence XAD-7 should not be treated under alkaline conditions for avoiding the potential non-selective sorption. In the present study, XAD-7 was simply washed with acetone, as described in the Section 2.1.

The impregnation was carried out by a dry-method [2,3]: XAD-7 was soaked in a chloroform solution containing SOCA, and then the solvent was gradually removed off by evaporation. The resulting resin contained 0.064 mmol g^{-1} of SOCA, which was determined by gravimetry. The SOCA-impregnated XAD-7 required no special condition for storage, such as a nitrogen atmosphere; the impregnated resin was stable in air at least for three months, showing no marked decrease in the metal-sorption ability.

For a comparison, another type of XAD resin, XAD-4 (styrene-divinylbenzene copolymer), was used for the impregnation of SOCA. Compared with XAD-7, XAD-4 is regarded as more hydrophobic. The amount of SOCA loaded on XAD-4, however, was somewhat smaller, 0.047 mmol g^{-1}. Therefore, we focused our minds on the use of the SOCA-impregnated XAD-7 for the separation of niobium(V) and tantalum(V).

3.2. Separation of niobium(V) from tantalum(V) with SOCA-impregnated XAD-7

The sorption characteristics of the SOCA-impregnated XAD-7 were examined by a conventional batch-extraction method. Under the experimental conditions used here, the sample solutions were stable at least for 24 h; any precipitation did not occur, and no marked decrease in the metal-concentration was observed.

First, the effect of the solution pH on the sorption yield was investigated for niobium(V) and tantalum(V). As shown in Fig. 2, niobium(V) was collected on the present sorbent in yields of more than 90% around pH 5.4. In contrast, the sorption yields of tantalum(V) were negligibly small, less than 6%, over the pH range tested (pH 3.5–7.1). The blank resin, i.e., XAD-7 without SOCA, retained neither niobium(V) nor tantalum(V), suggesting that this selective sorption of niobium(V) was caused by its selective complexation with the loaded SOCA.
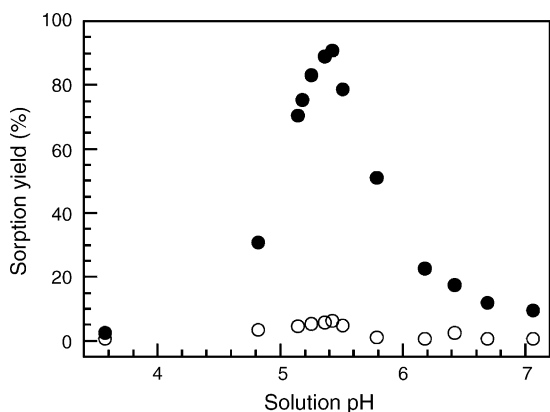
Fig. 2. The effect of the solution pH on the sorption yield: initial concentration, 0.10 mM each of Nb (●) and Ta (○); solution-volume, 20 mL; SOCA-impregnated XAD-7, 0.30 g; contact-time, 22 h.
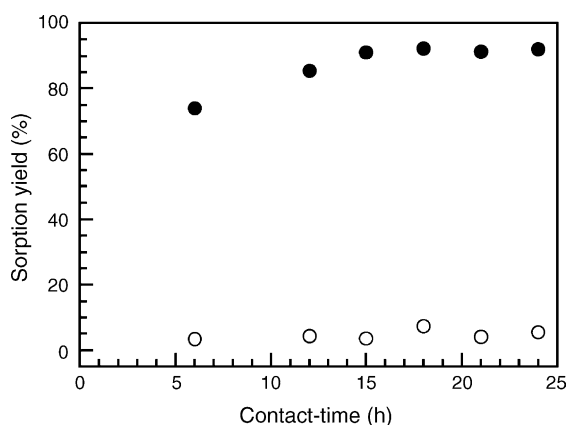

Fig. 3. The effect of the contact-time on the sorption yield: initial concentration, 0.10 mM each of Nb (●) and Ta (○); solution pH, 5.4; solution-volume, 20 mL; SOCA-impregnated XAD-7, 0.30 g.

Fig. 3 shows the effect of the contact-time on the sorption yields of niobium(V) and tantalum(V). The sorption yield of niobium(V) increased with increasing the contact-time, and reached to a constant value (92% at pH 5.4) after 15 h, whereas the sorption yield of tantalum(V) did not increased even after 24 h.

The selective sorption of niobium(V) was performed using sample solutions containing niobium(V) and tantalum(V) at different concentrations. As summarized in Table 1, the

Table 1
Selective sorption of niobium(V) at different concentrations

Run no.	Initial concentration (mM)		Sorption yield (%)	
	Nb(V)	Ta(V)	Nb(V)	Ta(V)
1	0.10	0.10	92	5
2	0.25	0.10	80	6
3	0.25	0.25	78	7
4	0.10	0.25	91	6
5	0.025	0.25	97	6
6	0.025	0.025	96	7

Sample solution: 20 mL, pH 5.4; SOCA-impregnated XAD-7: 0.30 g; contact-time: 22 h.
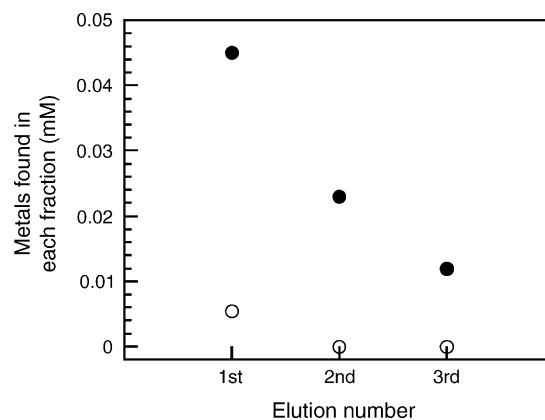

Fig. 4. Typical elution profile. After a sample solution (20 mL, $[Nb]_T = [Ta]_T = 0.10$ mM) was applied to SOCA-impregnated XAD-7 (0.30 g), the elution was performed with 9 M H_2SO_4 (20 mL × 3). The marks denote the same metal as in Figs. 2 and 3.

present sorbent retained niobium(V) selectively, irrespective of the initial concentrations of niobium(V) and tantalum(V). For 0.25 mM of niobium(V), its sorption yields decreased to 78–80% (runs 2 and 3).

The niobium(V) collected on the present sorbent was efficiently desorbed with sulfuric acid. Typically, a nearly complete (87%) recovery of niobium(V) was successfully achieved with an enrichment factor of 15 by washing the sorbent with 9 M sulfuric acid three times (washing-time, 1 h each) after a solution containing 0.1 mM each of niobium(V) and tantalum(V) had been applied to the sorbent (Fig. 4); the enrichment factor (F) is defined by the following equation: $F = (Q_1/Q_2)/(Q_1^0/Q_2^0)$, where Q^0 and Q are the quantities of the element before and after the separation, respectively, and the subscripts 1 and 2 denote the elements desired and not desired, respectively [20].

4. Conclusion

In the present study, a niobium-selective sorbent has been prepared by the impregnation of Amberlite XAD-7 resin with a sulfinyl-type calix-ligand, SOCA. Generally, the chemical properties of niobium and tantalum are very similar, hence they occur together in nature [16,17]. Their close chemical similarities also make their mutual separation difficult. In commonly performed separations of niobium and tantalum, highly hazardous hydrofluoric acid at a high concentration level (typically, more than 1 M) is frequently required for their sufficient separation [4,16–18]. In contrast, the present sorbent allows the separation of niobium(V) and tantalum(V) without addition of a high concentration of hydrofluoric acid, which is preferable in terms of human-health safety. Niobium and tantalum are rare elements and play important roles in nuclear technology [16,17], hence the novel selectivity of the present sorbent is potentially promising for their purification purposes.

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