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Extraction Characteristics of Niobium(V) and Tantalum(V) on Trioctylmethyl Ammonium Chloride-Impregnated Polyurethane Foam

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ABSTRACT

A reagent-impregnated polymer material has been prepared with trioctylmethyl ammonium chloride (TOMAC) and polyurethane foam as a new type of extractant for niobium and tantalum. Niobium(V) and tantalum(V) can be easily concentrated from their hydrofluoric acid solutions with TOMAC-impregnated polyurethane foam. The log *D* value for tantalum(V) is more than 4 in the HF concentration range from 0.5 to 2 mol·L^{-1}. The recovery of tantalum(V) from hydrofluoric acid solutions containing a large amount of niobium(V) has been successfully carried out by a batch technique. Extraction characteristics of the present system are similar to solvent extraction rather than to conventional anion-exchangers with respect to the dependence of the value of log *D* on hydrofluoric acid concentration.

INTRODUCTION

The recovery of niobium and tantalum from industrial waste is becoming more and more important due to the rapidly growing demand for them in many kinds of industrial fields and also to increasing concerns about global environmental pollution. Solvent extraction and ion exchange have been

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generally applied for the concentration and separation of niobium(V) and tantalum(V) from their fluoric acid solutions. Solid polymer materials which can selectively extract a certain metal ion are considered to have advantages over solvent extraction for the effective recovery of such metals because of the ease of handling as well as the high concentration ratio. Although conventional ion exchangers sometimes show excellent properties for the concentration and separation of specific metal ions, they are not satisfactory for niobium(V) and tantalum(V) in respect to adsorptivity (1). Thus, it is useful to develop new types of adsorbents whose mechanisms are different from those of ordinary ion-exchange reactions in order to produce efficient materials for the concentration of niobium(V) and tantalum(V).

Many studies (2–17) have reported the concentration of metal elements with polyurethane foam (PUF) as a solid polymer material. They have shown that PUF is a promising material for extracting many kinds of heavy metal ions from their aqueous solutions. The extraction mechanisms of these systems have also been discussed, and one of them is named the "cation-chelation mechanism" (7). It has also been reported that the concentration mechanism with PUF is sometimes based on solvent extraction, with the polymer acting as a solid extracting solvent.

Niobium and tantalum ions are poorly extracted into PUF from a thiocyanate solution (18). We, however, found and briefly reported that the impregnation of PUF with trioctylmethyl ammonium chloride gives a new type of a solid material which can extract niobium(V) from its hydrofluoric acid solution based on ion-pair extraction (18). In this report we extend our discussions to the concentration and separation of niobium(V) and tantalum(V) with the same type of solid material from their hydrofluoric acid solutions.

EXPERIMENTAL

Apparatus and Reagents

A Varian 634S spectrophotometer equipped with 1-cm quartz cells and a Seiko SPS-1200A ICP-atomic emission spectrometer were used for the determination of the metal ions. A Coleman 38A pH-meter was used for measurement of pH. A multiple wrist-action type shaker with polyethylene bottles was used for the extraction experiment.

Stock solutions (0.01 $mol \cdot L^{-1}$) of niobium(V) and tantalum(V) were prepared by dissolving their oxides in a hydrofluoric acid solution. Polyether-type polyurethane foam sheets were obtained locally and cut into cylinders (2.0 cm in diameter and 4.6 cm long) of approximately 450 mg, shaken in 1 mol·L^{-1} nitric acid for several hours, and then extensively rinsed with distilled water before use. All other chemicals were of analytical grade and used without any special purification.

Preparation of Extractant

Trioctylmethyl ammonium chloride (0.7 g) was dissolved into 100 mL acetone. Several pieces of PUF (approximately 2.4 g) were immersed in the solution for 1 hour and then filtered, followed by air-drying overnight at room temperature. The solid extractant (TOMAC-PUF) pieces were kept in a desiccator and cut to the desired size before use.

Extraction Procedure

An aliquot of the metal ion stock solution was placed in a 50-mL polyethylene bottle. The acidity of the solution was adjusted with hydrofluoric acid and diluted to the desired volume with distilled water. Several pieces of TOMAC-PUF, weighed precisely, were immersed in the solution and shaken until equilibrium was attained. The foam was then removed from the solution and the concentration of the metal ion in the solution was determined. The percentage extraction (*A*%) was calculated from the concentrations before and after extraction. The distribution ratio (*D*, mL/g) was obtained from the following equation.

$$D = \frac{\text{the amount of metal sorbed into the solid material (mmol}\cdot\text{g}^{-1}\text{)}}{\text{the amount of metal remaining in the solution (mmol}\cdot\text{cm}^{-3}\text{)}}$$

RESULTS AND DISCUSSION

Preparation of Solid Extractants

The optimum conditions to prepare TOMAC-impregnated PUF for the concentration of niobium(V) were examined in previous work (18). The amount of niobium sorbed into TOMAC-PUF increases with an increase in the amount of TOMAC impregnated but becomes constant for more than 0.7 g TOMAC with 2.4 g PUF. This suggests that polyurethane foam can hold a limited amount of an extractant in its polymer matrix. The release of a considerable amount of TOMAC from the solid extractant by shaking with a niobium solution containing 0.2 mol·L^{-1} hydrofluoric acid was observed for the material prepared from an excess amount of TOMAC. These results mean that efficient solid extractants cannot be obtained with an excess amount of TOMAC, which has also been observed for a similar extractant prepared from XAD-7 and trioctylamine (19). In this study we used the same method to prepare solid extractants for the concentration of tantalum. The extraction isotherms show that there is a saturation capacity at 0.25 mmol/g (Fig. 1). This capacity is considered to relate to the amount of TOMAC in PUF because PUF itself sorbs both tantalum and niobium(V) only slightly under the same conditions. If all the TOMAC impregnated in PUF is used for the extraction of tantalum(V), almost half the amount of TOMAC in the acetone solution used for this preparation method is considered to have been impregnated into PUF, or is available for complexation.

Rate of Extraction

Time-course experiments on the extraction of tantalum(V) and niobium(V) were made with a batchwise procedure. Figure 2 shows that extraction equilibrium can be attained within 90 minutes for both metals. The result suggests that this material is applicable for practical use.

Effect of HF Concentration

The effect of the concentration of hydrofluoric acid on the extractability of tantalum(V) was examined. The results are shown in Fig. 3 along with those for niobium(V). Extractability of the present solid extractant for tantalum(V) is stronger than that of conventional ion-exchangers. It is

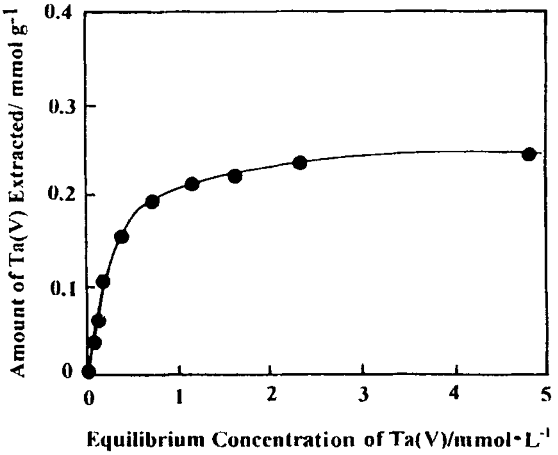

FIG. 1 Extraction of tantalum(V) with TOMAC-PUF from HF solutions with various Ta(V) concentrations. Weight of TOMAC-PUF, 100 mg; volume of solution, 20 mL; [HF] = 2 mol·L^{-1}; shaking time, 2 hours.

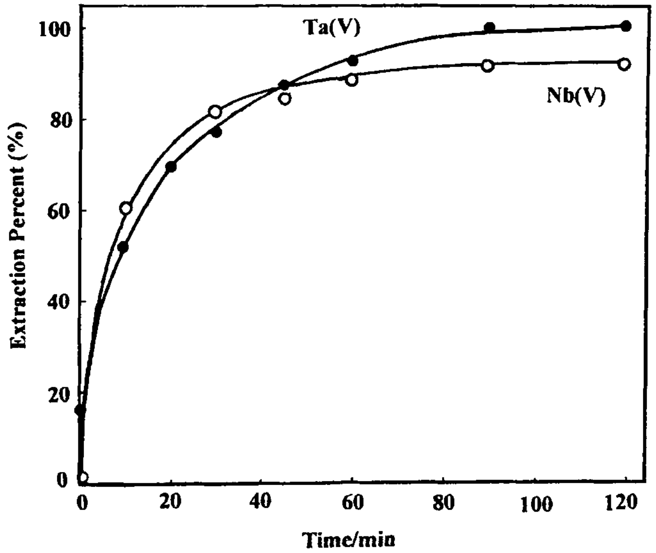

FIG. 2 Time-course of the extraction of niobium(V) and tantalum(V) with TOMAC-PUF. Weight of TOMAC-PUF, 450 mg; volume of solution, 20 mL; [metal] = 2.2×10^{-4} mol·L^{-1}; [HF] = 1 mol·L^{-1}.

also clear that tantalum(V) can be concentrated and separated successfully from niobium(V) in the low HF concentration range.

The values of log D decrease with an increase in the concentration of hydrofluoric acid above 1 mol·L^{-1} for both metals. The present solid extractant also showed somewhat different extraction characteristics for these metals from typical commercial anion-exchangers (1). This suggests that the concentration mechanisms in this system may be different from those for conventional or commercial ion-exchangers. The separation mechanisms of a reagent-impregnated polymer material with common extractants are usually very similar to those for solvent extraction rather than those for solid ion-exchangers (18). According to the solvent extraction mechanism, we can expect the following reaction for the concentration of an anion A^- from its aqueous solution with QX-impregnated PUF:

$$QX_{(o)} + A^- \rightleftharpoons QA_{(o)} + X^- \qquad (1)$$

where Q^+ is the hydrophobic cation and X^- is the counteranion, and the subscript (o) designates the species in the polymer phase. Equation (2) then holds with respect to the equilibrium constant K.

$$K = [QA]_{(o)}[X^-]/[A^-][QX]_{(o)} \qquad (2)$$

Equation (2) can be simplified by using the relation $D = [QA]_{(o)}/[A^-]$ and transforming the result to a logarithmic form:

$$\log D = \log K - \log[X^-] + \log[QX]_{(o)} \qquad (3)$$

Equation (3) means that the value of log D is constant if the concentrations of both X^- and $QX_{(o)}$ are constant. It is clear from Eq. (2) that an increase in the amount of $QA_{(o)}$ in the solid phase inevitably leads to a decrease in the amount of $QX_{(o)}$ in the same phase. Equation (3) also shows the effect of the concentration of X^- on the distribution ratio, and it is consistent with the experimental data obtained with various concentrations of hydrofluoric acid (Fig. 3). As discussed above, a tantalum fluoro-complex can also be considered to be extracted into TOMAC-PUF as an ion-pair with the trioctylmethyl ammonium cation, as is also the case for the niobium fluoro-complex.

Extraction of Tantalum(V) in the Presence of Niobium(V)

Concentration of a small amount of tantalum(V) from hydrofluoric acid solutions containing niobium(V) was carried out with a batchwise method. The results are summarized in Table 1. A concentration of coexisting

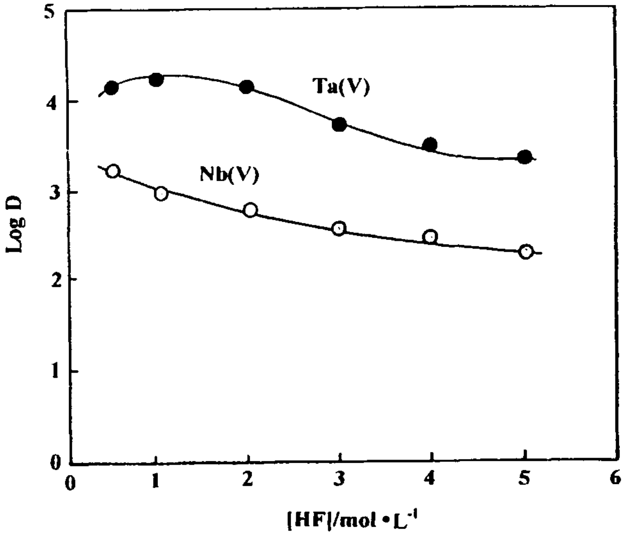

FIG. 3 Extraction of niobium(V) and tantalum(V) with TOMAC-PUF from hydrofluoric acid solutions. Weight of TOMAC-PUF, 450 mg; volume of solution, 20 mL; [metal] = 2.2×10^{-4} mol·L^{-1}; shaking time, 2 hours.

TABLE 1
Extraction of Tantalum(V) in the Presence of Niobium(V)[a]

Initial concentration ($mol \cdot L^{-1}$)		Residual concentration ($mol \cdot L^{-1}$)	
Tantalum(V)	Niobium(V)	Tantalum(V)	Niobium(V)
2.75×10^{-5}	1.1×10^{-4}	N.D.[b]	2.9×10^{-5}
2.75×10^{-5}	2.2×10^{-4}	N.D.	4.7×10^{-5}
2.75×10^{-5}	5.5×10^{-4}	N.D.	1.3×10^{-4}
2.75×10^{-5}	1.1×10^{-3}	2.8×10^{-8}	3.2×10^{-4}
5.5×10^{-5}	2.2×10^{-3}	N.D.	4.8×10^{-4}
5.5×10^{-5}	4.4×10^{-3}	N.D.	1.6×10^{-3}
5.5×10^{-5}	6.6×10^{-3}	5.5×10^{-8}	2.6×10^{-3}
5.5×10^{-5}	8.3×10^{-3}	3.7×10^{-7}	3.1×10^{-3}

[a] Weight of TOMAC-PUF, 450 mg; volume of the aqueous phase, 20 mL; [HF] = 2 $mol \cdot L^{-1}$; shaking time, 2 hours.

[b] N.D.: Not detected.

niobium(V) at least 150 times larger hardly affects the extraction of tantalum(V) from its dilute solution. The result is in agreement with the data shown in Fig. 1.

CONCLUSION

Niobium(V) and tantalum(V) can be easily concentrated from their hydrofluoric acid solution with TOMAC-impregnated polyurethane foam. In particular, the log *D* value for tantalum(V) is more than 6 in the HF concentration range from 0.5 to 2 $mol \cdot L^{-1}$. The recovery of tantalum(V) from hydrofluoric acid solutions containing a large amount of niobium(V) has been successfully carried out by a batch technique. The extraction characteristics of the present system are similar to the corresponding solvent extraction rather than to conventional anion-exchangers or "cation-chelation mechanism" with respect to the effect of hydrofluoric acid concentration on the value of log *D*.

The general approach of impregnation of hydrophobic cations into polyurethane foam is a promising way to produce effective extractants for many anionic metal complexes, including the niobium and tantalum complexes discussed in this paper.

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