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Solvent Extraction Behavior of Cerium(IV), Zirconium, and Thorium with Liquid Ion Exchangers

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NOTE

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Abstract

The systematic solvent extraction behavior of cerium(IV), zirconium, and thorium has been studied with the high molecular weight carboxylic acids SRS-100 and Versatic-9, with benzene as diluent. Quantitative extraction has been achieved in almost all cases. Only in the case of zirconium has incomplete extraction (73.5%) been reported with Versatic-9. Quantitative extraction requires three consecutive equilibrations at pH 2.9. The effect of metal ion concentration, solvent concentration, diluents, and the interference of the associated elements were critically examined. The percentage extraction at various ranges of pH has been studied. Exchange reaction techniques have been employed in several systems. The proposed methods are very simple, rapid, and fairly selective. They can be carried out both at micro and macro levels, and they are applicable to extraction of metal ions in the presence of other commonly interfering ions.

Extraction studies with the liquid ion exchangers SRS-100 and Versatic-9 have been extensively made in this laboratory for the extraction of various types of metals (*1*, *2*). The extraction studies have now been extended to some tetravalent metals: cerium(IV), zirconium, and thorium. This article describes the systematic study of these metals with SRS-100 and Versatic-9 and also their separations. The optimum conditions for extraction and separation have been critically studied.

The general extraction reaction of these tetravalent metal ions with the liquid ion exchangers can be expressed as

$$[M^{4+}]_{aq} + 4[HR]_{org} \rightleftharpoons [MR_4]_{org} + [4H^+]_{aq}$$

where HR represents the carboxylic acids and the subscripts aq and org refer to the aqueous and organic phases, respectively.

EXPERIMENTAL

The apparatus and reagents used were same as those reported in the previous papers (*1*, *2*).

Cerium sulfate solution (5.3 mg/ml). About 3.6 g of $Ce(SO_4)_2 \cdot 4H_2O$ (E. Merck) was dissolved in 250 ml of distilled water and 1 ml of concentrated sulfuric acid, and the solution was standardized by the iodometric method (*3*).

Zirconium nitrate solution (4.3 mg/ml). About 4.3 g of $Zr(NO_3)_4$ (E. Merck) was dissolved in 250 ml of distilled water and 8 ml of concentrated nitric acid, and the solution was standardized by complexometric titration with ethylenediaminetetraacetic acid (EDTA) using back-titration technique (*4*).

Thorium nitrate solution (7.2 mg/ml). About 4.5 g of $Th(NO_3)_4 \cdot 6H_2O$ (E. Merck) was dissolved in 200 ml of distilled water and 1 ml of concentrated nitric acid, and the solution was standardized by the complexometric titration with EDTA using xylenol orange indicator (*4*).

General Procedure

The general procedures for extraction and measurement were the same as those described in the previous papers (*1*, *2*). Equilibrations were carried out by shaking 15 ml of aqueous solution with 10 ml of organic solvent for 5 min, using benzene as diluent (solvent:diluent = 1:2 ratio). The metals from the organic phase were stripped twice with 10 ml of (2–4 *N*) sulfuric acid and estimated by standard methods (*3*, *4*). Zirconium and thorium in both phases were determined by complexometric titration with EDTA, whereas cerium(IV) was estimated by the iodometric method. Larger amounts of metals were extracted under the optimum conditions, and the metals were analyzed by the conventional gravimetric methods (*3*) after back-extraction.

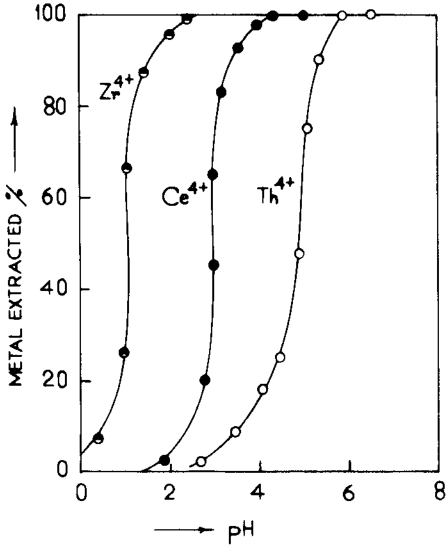

FIG. 1. Extraction with SRS-100 as a function of pH (SRS-100:benzene = 1:2).

RESULTS AND DISCUSSION

The comparative extraction behaviors of cerium(IV), zirconium, and thorium with SRS-100 and Versatic-9 in various pH ranges are represented in Figs. 1 and 2. The figures show that the extraction of all three metals increase with increasing pH, and becomes quantitative for cerium(IV) at pH 4.3, for thorium at pH 6.0, and for zirconium at pH 2.4 with SRS-100. In the case of versatic-9 the respective conditions are 6.9, 6.0, and 2.9 pH, respectively. The optimum pH ranges for quantitative extraction are cerium 4.5–6.0 (SRS-100) and 6.0–6.5 (Versatic-9), and thorium 6.0–7.0 (SRS-100 and Versatic-9). Extraction of zirconium with SRS-100 at pH 2.4 is almost quantitative (98.5%). At higher pH (>2.4) with SRS-100, zirconium undergoes hydrolysis, which leads to difficulty in phase separation. Incomplete extraction of zirconium has been achieved with Versatic-9, the maximum extraction being 73.5% at pH 2.9. Quantitative extraction requires three consecutive equilibrations at pH 2.9. The optimum shaking period for extraction is 2 to 3 min for Versatic-9 and 4 min for SRS-100. This shows that the rate of extraction is more rapid in the case of Versatic-9.

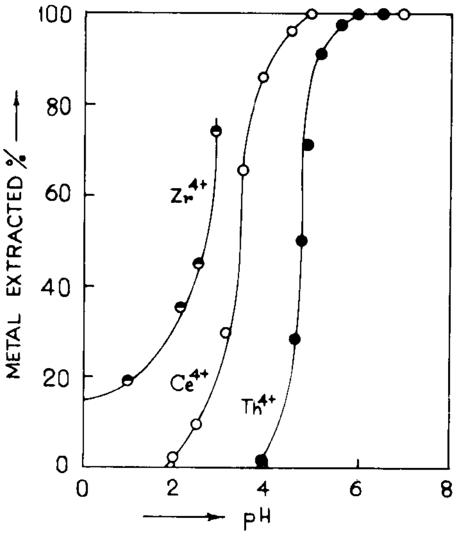

FIG. 2. Extraction with Versatic-9 as a function of pH (Versatic-9:benzene = 1:2).

TABLE 1

Percentage Extraction of Metals as a Function of Solvent Concentration

Solvent (SRS-100): benzene ratio	Cerium(IV) (%)	Zirconium(IV) (%)	Thorium(IV) (%)
1:2	100	98.5	100
1:4	98.5	81.4	99
1:9	75.3	68.7	82

TABLE 2

Effect of Diluent on Percentage Extraction of Metals

Diluent	Dielectric constant	Ratio solvent: diluent	Cerium (IV) (%)	Zirconium (IV) (%)	Thorium (IV) (%)
Benzene	2.3	1:2	100	98.5	100
Xylene	2.4	1:2	99.5	98.2	99.2
Toluene	2.4	1:2	99.0	97.2	99.5
Diisopropyl ether	3.9	1:2	97.3	95.4	98.6
Butanol	16.1	1:2	95.4	88.7	96.4

It was found that the recommended procedure holds good when the metal ion concentration was varied from 5 to 25 mg under optimum conditions. This indicates the absence of polymerization in the organic phase. The effect of solvent concentration was studied by varying the concentration of SRS-100 from 1:2 to 1:9, using benzene as diluent. The results are tabulated in Table 1. From the table it is clear that dilution of SRS-100 lowers the extraction to an appreciable extent. In the case of pure solvent the tendency for emulsion formation increases. To minimize this emulsion tendency, most of the extraction has been carried out using solvent:diluent in a 1:2 ratio. Benzene has been used as a diluent.

In order to investigate the role of the diluent in extraction, the nature of the diluent was varied from benzene to toluene, xylene, diisopropyl ether, butanol, etc. The results are tabulated in Table 2. The table shows that the nature of diluent had very little effect on extraction. Xylene and toluene show extraction almost similar to benzene, whereas butanol and diisopropyl ether behave a little bit differently. In the latter case extraction decreases. A qualitative selectivity scale of extraction can be drawn from the optimum conditions obtained with SRS-100 and Versatic-9, the order being $Zr^{4+} > Ce^{4+} > Th^{4+}$.

EXTRACTIVE SEPARATIONS AND EXCHANGE REACTIONS

Exchange reactions have also been adopted in cases where the coextraction of the interfering metal seriously limits extractive separations. The exchange reaction procedure is very simple. An aliquot of the test solution containing the metal M_1 was extracted by 10 ml solvent (SRS-100) with benzene diluent under optimum pH conditions of M_1. The aqueous phase was separated and the metal M_1–loaded organic phase was again equilibrated for 10 min with 15 ml of buffer solution containing the metal (M_2) to be exchanged, the pH of the latter being adjusted to the optimum value of extraction of M_2. After equilibration, the two phases were allowed to settle and were then separated. The metal M_1 present in the aqueous phase was estimated. The metal ion M_2 in the organic phase was stripped with (2–4 *N*) sulfuric acid and estimated.

Zirconium has been separated from thorium, tin, lead, palladium, platinum, gallium, indium, thallium, molybdenum, tungsten, bismuth, antimony, chromium, lanthanum, cobalt, nickel, copper, zinc, cadmium, mercury, manganese, silver, aluminum, barium, and strontium. Iron(III) interferes during extraction. The interference due to cerium(IV) has been eliminated by exchange reaction. In this case 98.4% exchange of zirconium with cerium has been achieved.

Cerium(IV) has been separated from tin, lead, palladium, platinum, lanthanum, thallium, antimony, molybdenum, tungsten, zinc, cadmium, mercury, cobalt, nickel, manganese, strontium, barium, and silver. The interfering ions are iron, copper, gallium, indium, and chromium. The interference due to copper has been eliminated by masking copper with thiosulfate. The interference of thorium has been removed by carrying out the separation through an exchange reactions. Quantitative (100%) exchange of cerium with thorium has been achieved.

Thorium has been separated from palladium, platinum, molybdenum, tungsten, cobalt, nickel, calcium, magnesium, strontium, barium, and mercury. The interference of iron(III) and zirconium has been eliminated by preliminary extraction with SRS-100 at pH 3.10 and 2.4, respectively. The interference of copper is removed by masking copper with thiosulfate. The interfering ions are chromium, gallium, indium, thallium, and bismuth. Exchange reaction techniques have also been successfully adopted in the presence of cerium and zirconium.

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