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SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS A COMPLEXING AGENT. PART 5. EXTRACTION OF NEPTUNIUM AND SEPARATION FROM URANIUM

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Extraction of neptunium with benzyl alcohol solutions of tetracycline is studied as a function of the pH of the aqueous phase. Separation of neptunium from uranium with tetracycline-benzyl alcohol solution is presented.

INTRODUCTION

In previous works the behaviour of the antibiotic tetracycline (TC) as a complexing and extracting agent for uranium, thorium, scandium and the lanthanide elements as well as the determination of stability constants of the lanthanide-TC complexes have been reported.[1-4] This paper presents the study of neptunium extraction into a TC-benzyl alcohol solution as a function of the pH of the aqueous phase, as well as the separation of ^{239}Np from neutron irradiated natural uranium.

EXPERIMENTAL

^{239}Np used in the extraction experiments was obtained by irradiation of 10 mg of U_3O_8 with epithermal neutrons, for about 8 hours, in the swimming pool IEA-R1 research reactor. Cooling time was about 16 hours. The epithermal neutron flux was equal to 6×10^{10} n cm^{-2} sec^{-1}.

Two mm thickness cadmium containers were used to irradiate the U_3O_8 in order to minimize, or practically to eliminate, the thermal neutron fission of ^{235}U.

^{239}Np purification

The ^{239}Np solution used to study the percentage of metal extracted, was separated from thermal neutron irradiated uranium by coprecipitation of trivalent neptunium with lanthanum fluoride.[5] Reduction of neptunium to +III oxidation state was carried out with hydroxylamine hydrochloride instead of SO_2. After precipitation of lanthanum fluoride, the precipitate was dissolved in a mixture of HNO_3 and H_3BO_3, and neptunium was oxidised with $KBrO_3$ and H_2SO_4. The lanthanum ions were eliminated from the solution by repeated precipitation as LaF_3. The supernatant solution contained the oxidised neptunium. Radioactive purity was checked by half-life determination (integral mode γ-ray counting) and by γ-ray spectrometry with a Ge(Li) detector. The half-life corresponded to 2.35 days in agreement with the tabulated half-life of ^{239}Np. The γ-ray spectrum presented only the ^{239}Np photopeaks.

Extraction experiments

The organic phase was prepared of a 10^{-2}M TC solution in benzyl alcohol (p. a. grade, Carlo Erba). The benzyl alcohol used had been previously washed with distilled water. Sodium chloride solution was added to two milliliters of the aqueous phase containing the neptunium and the final volume adjusted to give a 1.0M NaCl solution.

The extraction systems consisted of 5.0 ml of the organic-TC solution and 5.0 ml of the neptunium-NaCl or of neutron irradiated uranium (UO_2^{2+})-NaCl aqueous solution. The pH of the aqueous phase was adjusted to the desired values by adding diluted solution of NaOH. Both phases

were then equilibrated by shaking mechanically at 25°C. The phases were then separated, centrifuged and the pH of the aqueous phases measured again. Previous experiments had shown that extraction equilibrium was reached within 15 min for low pH values and at about 40 min for pH values around 4.0 or higher.

In the case of neptunium extraction, aliquots of one milliliter of both phases were taken for counting in a 5x4.4 cm well-type NaI(Tl) detector coupled to a single-channel γ-ray spectrometer. The concentration of uranium in both phases was determined by epithermal neutron activation analysis.[6] Fig. 1 presents the results of the extraction experiments. From this figure it is seen that neptunium can be separated from irradiated uranium if the organic phase containing both elements is stripped at a pH value around 2.0 or if extraction if formely carried out at this pH value.

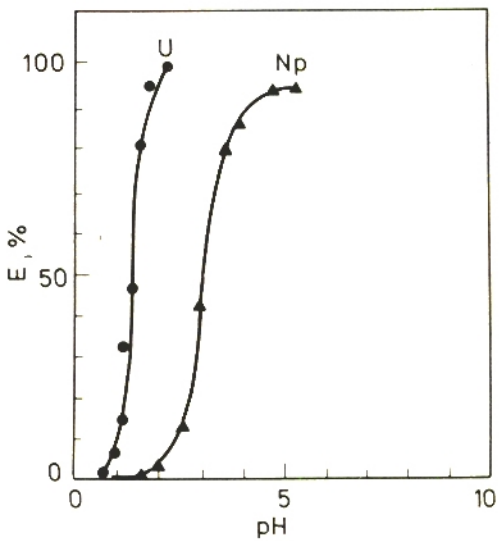

Fig. 1. Uranium and neptunium extraction curves. TC-Benzyl alcohol solution: 10^{-2}M. NaCl solution: 2.0 M. Uranium (UO_2^{2+}) solution: $5x10^{-5}$M. ^{239}Np: carrier-free

TABLE 1

Separation of neptunium from uranium

Equilibrium pH	Percent metal in organic phase U	Np
1.90	96	2.5
2.00	97	5.0
2.50	99	10
4.35	97	95
4.70	98	95

To study the separation procedure 1.68 mg of U_3O_8 was irradiated and cooled as described before and dissolved in 4M HNO_3 solution. Dilutions were made using 1.0M NaCl solution so that a 5×10^{-5}M solution of irradiated uranium was obtained. A 10.0 ml aliquot of this aqueous neptunium-uranium-NaCl solution, was equilibrated with 10.0 ml of the 10^{-2}M TC-benzyl alcohol solution in the same way as described previously. After separation of the phases by centrifugation, aliquots of 2.0 ml of both phases were withdrawn for ^{239}Np counting using a Ge(Li) detector coupled to a 4096-channel analyser and counting the 106 keV, 228 keV and 277 keV photopeaks for ^{239}Np. Uranium was analysed by taking 10 µl of each phase and irradiating them with epithermal neutrons and counting the 74.6 keV photopeak for ^{239}U.[6] Results are presented in Table 1.

To be sure that neptunium had been extracted as the Np-TC complex a set of experiments was carried out in which the ^{239}Np solution was agitated (25°C, for 15 min) with benzyl alcohol alone, i. e., in the absence of TC. The pH of the aqueous phase at which the experiments had been carried out were 2.80, 3.75 and 4.70 and the percent extraction values obtained in each case were 0.3%, 0.14% and 0.3%, respectively. These extraction values show that in the absence of TC molecule, neptunium

remains virtually totally in the aqueous phase. The very low percent extraction values found were probably due to the slight miscibility between benzyl alcohol and water. Previous work had also shown that uranium (uranyl ion) was not extracted by benzyl alcohol in the absence of TC.

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REFERENCES

1. M. J. C. Nastasi, F.W. Lima, Radiochem. Radioanal. Lett., 11 (1972) 69.

2. M. Saiki, F. W. Lima, Radiochem. Radioanal. Lett., 21 (1975) 371.

3. M. J. C. Nastasi, F. W. Lima, J. Radioanal. Chem. (in the press)

4. M. Saiki, F. W. Lima, J. Radioanal. Chem., (in the press)

5. P. Fields. in The Transuranium Elements, Research Papers, Paper 15. 10. NNES-IV, 14-B. G. T. Seaborg, J. J. Katz, W. M. Manning (Eds), McGraw Hill Book Co., Inc. New York, 1949.

6. L. T. Atalla, F. W. Lima, J. Radioanal. Chem., 20 (1974) 607.