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用可溶性冠醚萃取铀和钍的研究

A STUDY OF SOLVENT EXTRACTION OF
URANIUM AND THORIUM WITH A CROWN
ETHER CARBOXYLIC ACID



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用可离解冠醚萃取铀和钍的研究

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摘 要

以均二苯基-16-冠-5-氧代乙酸 (E) 作为一种新型萃取剂, 研究了 UO_2^{2+} 和 Th^{4+} 的溶剂萃取行为。结果指出, 其萃取效率受水相酸度的影响很大, 在 $\text{pH} \approx 3.5$ 时, Th^{4+} 可以接近定量地被萃取, 而 UO_2^{2+} 则几乎全部留在水相。保持水相酸度不变, 得到 UO_2^{2+} 和 Th^{4+} 的分配比与有机相中 E 浓度的对数关系是线性的, 斜率分别为 1 和 2, 表明在萃取过程中, 它们分别同 E 形成了 1:1 和 1:2 的萃合物。建立了以 E 为萃取剂的分离 U 和 Th 的溶剂萃取方法, 该法简单、方便、可迅速地分离得到高纯 U 和 Th。在分析化学和核工业领域有良好的应用前景。

A STUDY OF SOLVENT EXTRACTION OF URANIUM AND THORIUM WITH A CROWN ETHER CARBOXYLIC ACID

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ABSTRACT

The solvent extraction of uranium and thorium with a new type of extractant sym-dibenzo-16-crown-5-oxyacetic acid in chloroform has been studied. The extraction efficiencies for both elements depend strongly on pH. At pH 3.5, UO_2^{2+} is not extractable, whereas Th^{4+} is extracted with greater than 98% efficiency. The dependence of the distribution ratios of UO_2^{2+} and Th^{4+} on the concentration of sym-dibenzo-16-crown-5-oxyacetic acid are linear and the slopes are 1 and 2 respectively. The results suggest that uranium and thorium appear to form a 1 : 1 and 1 : 2 extraction complex with ligand. A new method for separating U and Th is established, and U and Th with high purity can be obtained. This method have important application to analytical chemistry and nuclear industry.

INTRODUCTION

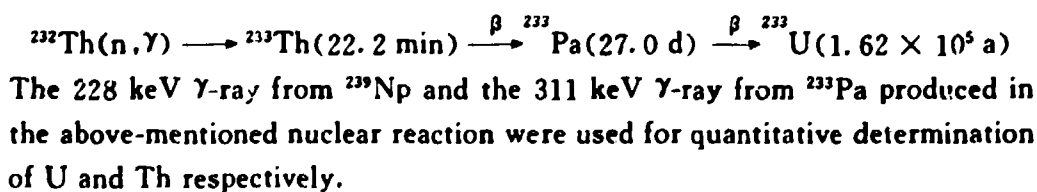
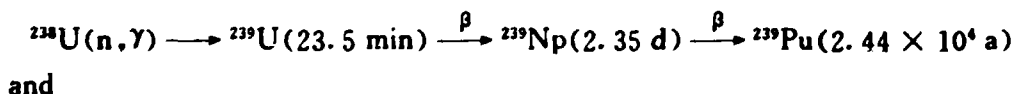
The separation of uranium and thorium by solvent extraction is of considerable interest in nuclear chemistry industry. The key to further improvement of such separations is the development of new, more effective extractants. In 1981, Bartsch et al. [1-4] synthesised the crown ether carboxylic acid and explored its application in the extraction of alkali metal and alkaline earth cations. Subsequently studies were carried out by Wai et al. for the extraction of lanthanides by crown ether carboxylic acid [5-7]. This type of ionizable crown ether possesses with distinct advantage over closely related neutral crown ether compounds in that the extraction efficiency and selectivity of the metal cations are superior and independent of the aqueous phase anions [5,6]. Furthermore, the extraction is readily reversible with respect to pH. The studies of solvent extractions with crown ether carboxylic acids have been primarily limited to alkali metal, alkaline earth and lanthanide cations. In the present work, the extraction of uranium and thorium from aqueous acetate buffers by sym-dibenzo-16-crown-5-oxyacetic acid is investigated. A new method for separating uranium and thorium is established.

1 EXPERIMENTAL

The sym-dibenzo-16-crown-5-oxyacetic acid (crown ether carboxylic acid or E) was synthesised by the reported procedure [2]. The $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ was obtained from Mallinckrodt Inc. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and other chemicals used in this study were Baker Analytical Grade. Deionized water was prepared by passing distilled water through an ion exchange column (Barnstead ultra-pure water purification cartridge) and a 0.2 μm filter assembly (Pall Corporation, Utipor DFA). The containers used in this study were cleaned by soaking in 10% (V/V) HNO_3 , rinsed with deionized water and dried in a class 100 clean hood equipped with a vertical laminar flow filter (CCI). Standards solutions of U and Th were prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ respectively in 0.1 mol/L HNO_3 . The equipment for activity measurements consisted of a large-volume coaxial ORTEC Ge(Li) detector with a resolution of about 2.3 keV at 1332 keV γ -ray from ^{60}Co . The detector output was fed into a EG & G ORTEC ADCAM multichannel analyser. The data from the analyser were processed by EG & G ORTEC software on an

2 EXTRACTION PROCEDURES

Equal volumes (10.0 ml) of the aqueous phase containing UO_2^{2+} and/or Th^{4+} ions in 5×10^{-3} mol/L NaOAc and the organic phase (5.0×10^{-3} mol/L E in chloroform) were placed in a 50 ml ground-glass stoppered flask. Dilute HNO_3 and LiOH solutions were used for pH regulation. The flask was shaken vigorously for 30 min at room temperature ($24 \pm 1^\circ\text{C}$) on a wrist-action mechanical shaker (Burrell Model 75). The phases were allowed to separate and the equilibrium pH of the aqueous phase was measured with Orion research model 701 pH meter with an Orion model 91-03 semimicro combination glass electrode. A 1.00 ml sample of the aqueous phase was pipetted into a 2.5 dram polyethylene vial and heat-sealed for neutron irradiation. A 2.00 ml volume of the organic phase was shaken with 2.00 ml of 0.1 mol/L HNO_3 for 10 min. After the phase separation, 1.00 ml of the aqueous phase was heat-sealed in a 2.5 dram polyethylene vial for neutron irradiation. The remainder of the organic phase was removed and diluted with chloroform and the concentration of E in the organic phase was determined by measuring the ultraviolet absorption at 273 nm. All samples were irradiated for 2 h in a 1 MW TRIGA reactor at a steady neutron flux of 6×10^{12} n \cdot cm $^{-2}$ \cdot s $^{-1}$. A standard and a blank were run in the same manner and under the same conditions. The neutron-irradiated aliquots were subjected to γ -ray detection after an appropriate cooling time. the nuclear reaction used for the detection of uranium and thorium are



3 RESULTS AND DISCUSSION

3.1 Effect of pH on extraction efficiency of Uranium and Thorium

The dependence of the extraction efficiency of UO_2^{2+} and Th^{4+} from an aqueous acetate buffer by a 5.0×10^{-3} mol/L solution of E in chloroform on pH was measured (Fig. 1). The extraction of both species depend strongly on

creased at $\text{pH} > 7$. A similar dependence of the extraction of uranium on pH was observed. However, the extraction of thorium reached maximum at a lower pH and showed a broader plateau than did the extraction of uranium. The decrease of the extraction at high pH value may be due to the hydrolysis of UO_2^{2+} and Th^{4+} which are susceptible to hydrolysis at $\text{pH} \leq 3$. When the hydroxocomplexes $\text{M}(\text{OH})_i$ are formed in the aqueous phase, the distribution ratio (D) decreases according to the following equation:

$$D = \frac{M L_n}{[M^{n+}] + \sum_{i=1}^n M(\text{OH})^{n-i} + \dots}$$

where $M^{n+} = \text{UO}_2^{2+}$ or Th^{4+} .

The decrease of extraction of uranium and thorium may also be partly due to a decrease of the equilibrium concentration of the crown ether carboxylic acid in the organic phase at higher pH as showed in Fig. 2. Similar results were also observed by Strzelbicki and Bartsch for alkali-metal cations^(2,3).

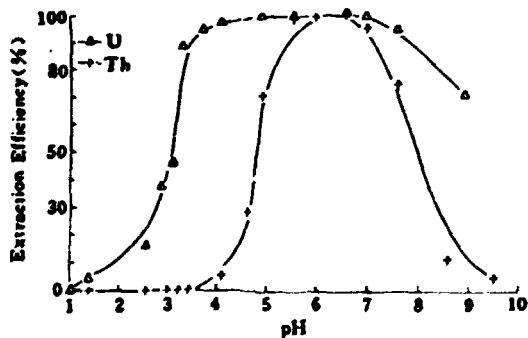


Fig. 1 Dependence of extraction efficiency of uranium and thorium with 5.0×10^{-3} mol/L E on pH

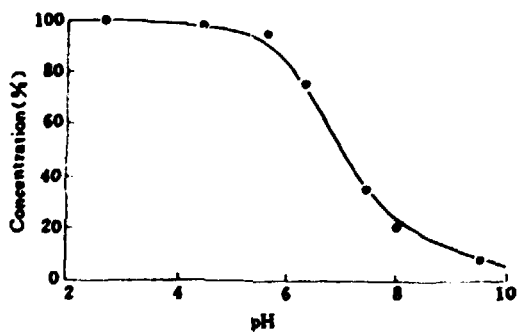


Fig. 2 Dependence of the concentration of E on pH

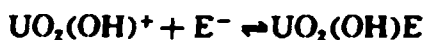
3.2 Effect of E concentration on the distribution ratio (D) of uranium and thorium

The distribution ratios of uranium and thorium were determined for extractions with varying concentrations of E while the equilibrium pH of the aqueous phase was maintained at 5. Figs. 3 and 4 show that the plots of $\log D_U$ and $\log D_{Th}$ vs. the log of the concentration of E were all linear. The slopes

were approximately 1 and 2, respectively. This suggests that the hydrolysed species were extracted into the organic phase. According to the Ref. [8], the hydrolysis products of UO_2^{2+} and Th^{4+} are expected to be predominantly $\text{UO}_2(\text{OH})^+$ and $\text{Th}(\text{OH})_2^{2+}$ at pH 5 and a concentration of UO_2^{2+} and Th^{4+} being 10^{-5} mol/L. Therefore, a 1 : 1 (U : E) and 1 : 2 (Th : E) complexes are expected to be the most stable forms. Accordingly, the extraction of UO_2^{2+} and Th^{4+} by E can be represented as follows:



for UO_2^{2+} :



for Th^{4+} :

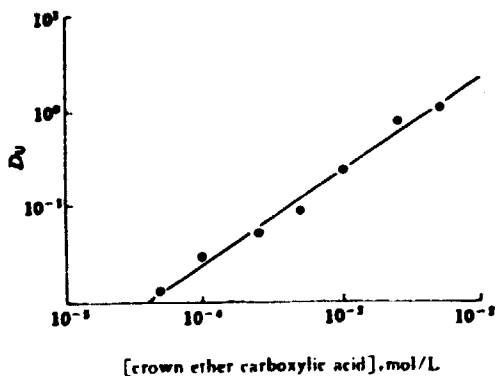


Fig. 3 Dependence of the distribution ratio of uranium on the E concentration at pH=5

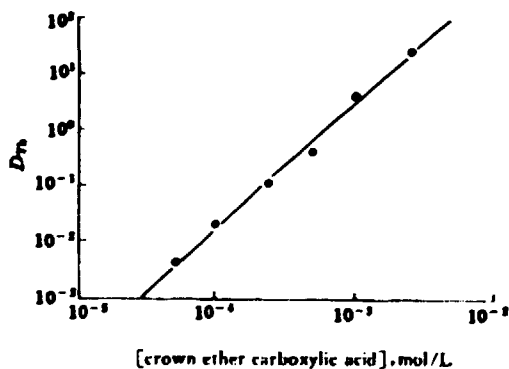


Fig. 4 Dependence of the distribution ratio of thorium on the E concentration at pH=5

3.3 Separation of uranium and thorium

In view of the results shown in Fig. 2, the separation of uranium and thorium should be feasible using solvent extraction with E. The experiments to check this were performed as follows. A 5.0 ml sample of 0.25 mol/L NaOAc solution was added to a 20.0 ml of a sample solution containing UO_2^{2+} and Th^{4+} . This was extracted with 100 ml of 5.0×10^{-3} mol/L E in chloroform at pH

3-4. The extraction was repeated twice with a fresh solution of E in chloroform being used each time. The combined organic phases were washed twice with 20.0 ml of a 5×10^{-2} mol/L NaOAc solution (pH 3.4) and then shaken for 10 min with 3.0 ml of 1.0 mol/L HNO₃ solution to back-extract all the thorium into the aqueous phase. Then 1.0 ml of the aqueous phase was pipetted into a 2.5 dram polyethylene vial and heat-sealed for neutron activation analysis. The analytical results showed that no detectable thorium was observed in the aqueous phase after twice successive extraction. Similarly, no detectable uranium was observed in the organic phase. The purity of uranium and thorium obtained were estimated to be about 99.9%. This new extraction method which is simple, fast and convenient should be very suitable for the separation and preliminary concentration of uranium and thorium.

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