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Solvent extraction of U(VI) from media containing competing anions and metal cations by a calix[6]arene bearing carboxy groups

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Abstract

The selective extraction of uranium by a macrocyclic molecule, 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-tri(carboxymethyl)-38,40,42-trimethoxy-calix[6]-arene has been studied in a two-phase solvent-extraction system. The first part of this study concerns the determination of extraction mechanism. The variation of the extraction parameters, performed for two different ionic strengths ($I=0.1$ and $I=3$), allows to propose an extraction scheme. The second part of this work concerns the selectivity of calix[6]arene towards uranium. Some competing metal cations present in urine have been taken into account. In the aqueous phase (spiked with ^{230}U), divalent metals such as Zn^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+} were added. The results show that the uranium extraction is independent of the cation concentration, whatever the pH and the ionic strength are. The competition between the chosen calix[6]arene and other complexing anions, such as phosphate or sulphate, has been investigated. The results indicate that the uranium–calixarene extraction constant is higher than the uranium–anion complexation constant.

Keywords: Uranium; Calixarene; Selectivity; Solvent extraction

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1. Introduction

Determination of uranium in urine is routinely used for individual monitoring of workers exposed to the risk of internal contamination in the nuclear industry [1]. Urine is a complex medium composed of numerous mineral and organic compounds [2]. In order to measure uranium at low level by α-spectrometry in such a medium, ligand macrocycles can be used to selectively separate uranyl ions from other components (actinides, metal ions, complexing anions, etc.) present in urine [3]. The unusual coordination structure of UO_2^{2+} complexes has provided the design of this ligand. X-ray crystallographic studies have established that UO_2^{2+} complexes adopt a pseudoplanar hexacoordinate structure [4–6], suggesting that a macrocyclic host having a nearly coplanar arrangement of the ligand group in C_3 symmetry would act as a specific ligand of UO_2^{2+}.

Calixarenes have several attractive features [7] as macrocycles of higher degree of preorganization. They are formed by *para*-phenolic units linked by methylene bridges *ortho* to the OH functions. Calixarene can be chemically modified by substitution of the phenolic hydrogens with various types of functions known for their affinity of the cation of interest. Furthermore, phenolic groups can be functionalized on the *para* position to make the calixarene either lipophobic or lipophilic. In this study the calixarene is composed of a ring of six phenolic units used as molecular substructures, on which preorganised ligands, such as the three carboxy groups in C_3 symmetry, are assembled to provide the required structure (Fig. 1).

In this paper, the application of a lipophilic calix[6]arene (1,3,5-trimethoxy-2,4,6-tricarboxy-*p*-*tert*-butyl-calix[6]arene) [8,9] is reported for the selective extraction of UO_2^{2+} from media containing competing anions and metal cations.

2. Experimental

2.1. Two-phase solvent extraction

An organic solution (Solvesso washed overnight with nitric acid 1 mol l^{-1}) containing 1,3,5-trimethoxy-2,4,6-tricarboxy-*p*-*tert*-butyl-calix[6]arene was mixed with an equal volume of aqueous solution containing

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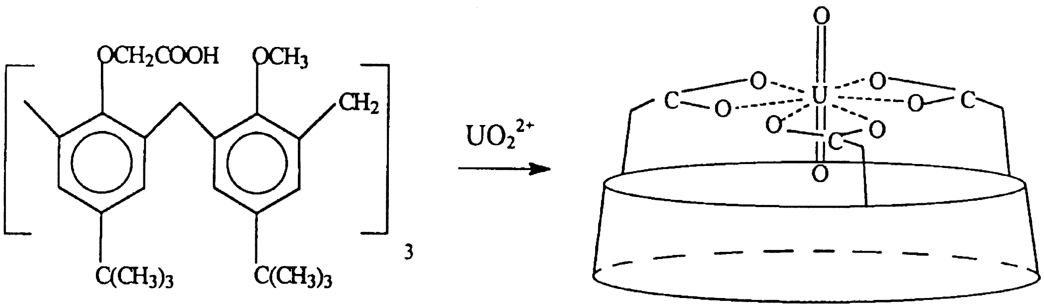

Fig. 1. Structure of the complex UO_2^{2+}/(1,3,5-trimethoxy-2,4,6-tricarboxy-*p*-*tert*-butyl-calix[6]arene).

10^{-10} mol l^{-1} ^{238}U (spiked with ^{230}U) and various concentrations of sodium nitrate in order to maintain the ionic strength ($I=0.1$ or $I=3$).

The mixture was carefully shaken for 3 h at room temperature. Extraction equilibria were reached within 2 h.

The two phases were separated after centrifugation, and uranium contents were measured in each phase. ^{230}U concentrations were measured by γ-spectrometry:

$$\left({}^{230}_{92}U \xrightarrow{\alpha} {}^{226}_{90}Th,\ T_{1/2} = 30.9\ \text{min},\ E\gamma = 111.12\ \text{keV}\right).$$

The pH of the aqueous solution was initially adjusted and measured after reaching equilibrium.

2.2. Distribution coefficient

Calix[6]arenes functionalized with carboxylic acid groups are potentially proton-ionizable macrocycles [10]. Therefore, the liquid–liquid extraction of metal ion (UO_2^{2+}) in the presence of the protonated complexing agent (LH_3) could be represented as a proton–cation exchange process:

$$a\text{LH}_{3\text{org}} + b\text{M}^{n+}_{\text{aq}} \leftrightarrow (\text{L}_a\text{M}_b\text{H}_{3a-bn})_{\text{org}} + bn\text{H}^+_{\text{aq}}$$

The corresponding thermodynamic extraction equilibrium constant K_M is given by:

$$K_M = \frac{[\text{L}_a\text{M}_b\text{H}_{3a-bn}]_{\text{org}}[H^+]^{bn}_{\text{aq}}}{[\text{LH}_3]^a_{\text{org}}[\text{M}^{n+}]^b_{\text{aq}}} \tag{1}$$

The distribution coefficient D_M is given by the ratio of metal concentration in the organic and in the aqueous phases:

$$D_M = \frac{[\text{M}_{\text{total}}]_{\text{org}}}{[\text{M}_{\text{total}}]_{\text{aq}}} \tag{2}$$

Combining Eq. (1) and Eq. (2), K_M can be rewritten:

$$K_M = \frac{D_M[\text{H}^+]^{bn}_{\text{aq}}}{[\text{LH}_3]^a_{\text{org}}} \tag{3}$$

Which gives:

$$\log D_M = \log K_M + a\log[\text{LH}_3] + bn\ \text{pH} \tag{4}$$

The slope of the curve $\log D_M$ versus pH gives the number of protons exchanged (parameter *bn* in Eq. (4)). The slope of the curve $\log D_M$ versus $\log[LH_3]$ gives the number of ligand molecules involved in the extraction (parameter *a* in Eq. (4)).

3. Results

3.1. Proposition of an extraction scheme

3.1.1. pH dependence

Figs. 2 and 3 illustrate the variation of $\log D_U$ versus pH for the two ionic strengths $I=0.1$, $I=3$. For pH ranging between 2.5 and 4, there is a constant increase of the extraction percentage with pH.

For the various ligand concentrations used, all plots lie on a straight line with a slope equal to 2, which is in good agreement with UO_2^{2+} extraction.

For such conditions, the results observed seem to be in good agreement with a selective extraction of UO_2^{2+}.

3.1.2. Stoichiometry of the extraction species

For the two ionic strengths, the curve $\log D_U$ versus $\log [LH_3]$ for pH 4 (Fig. 4) shows a slope of 1, implying

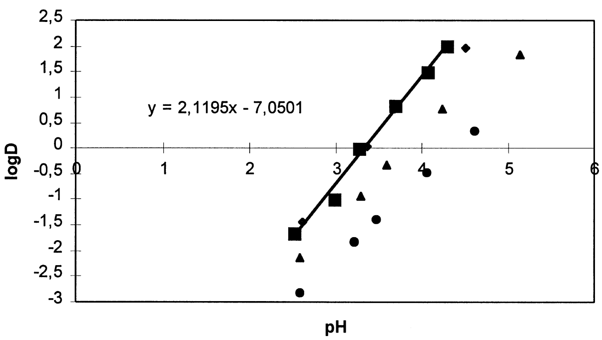

Fig. 2. Extraction of uranium by LH_3 in Solvesso at 293 K, $I=0.1$, as a function of pH for various LH_3 concentrations: (■) 10^{-3} mol l^{-1}, (♦) 5×10^{-4} mol l^{-1}, (▲) 10^{-4} mol l^{-1}, (●) 10^{-5} mol l^{-1} with ^{238}U 10^{-10} mol l^{-1}.

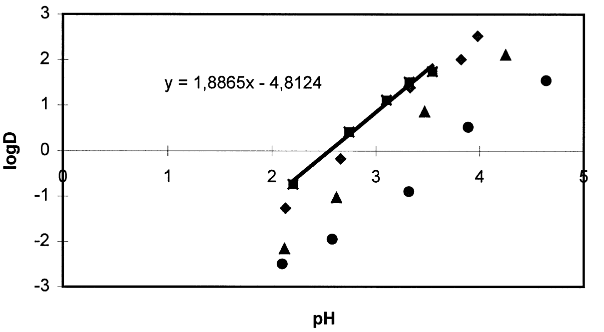

Fig. 3. Extraction of uranium by LH_3 in Solvesso at 293 K, $I=3$, as a function of pH for various LH_3 concentrations: (■) 10^{-3} mol l^{-1}, (♦) 5×10^{-4} mol l^{-1}, (▲) 10^{-4} mol l^{-1}, (●) 10^{-5} mol l^{-1} with ^{238}U 10^{-10} mol l^{-1}.

that a single ligand molecule is involved. In this pH range, and for such uranium concentrations, the thermodynamic data on uranium hydrolysis [11] allow us to consider UO_2^{2+} as the main species in the aqueous solution.

As two protons are exchanged and one molecule of ligand is involved, the results support the following extraction scheme, including the formation of the 1:1 calix[6]arene/UO_2^{2+} complex:

$$LH_{3org} + UO^{2+}_{2aq} \leftrightarrow LHUO_{2org} + 2H^{+}_{aq}$$

3.2. Influence of divalent cations on uranium extraction

Selectivity of calix[6]arene for uranium has been studied towards some divalent cations added in the aqueous phase: Zn and Cu, for two different concentrations (10^{-4} and 10^{-3} mol l^{-1}), Ca and Mg for two different concentrations (10^{-2} and 10^{-1} mol l^{-1}).

Uranium repartition was measured when experiments were carried out for both ionic strengths, $I=0.1$ and $I=3$, in the aqueous phase. Results are compared with those obtained when experiments were carried out without metal added for both ionic strengths, $I=0.1$ and $I=3$, in the aqueous phase. Figs. 5 and 6 show that the uranium extraction is independent of the cation concentration, whatever the pH and the ionic strength are.

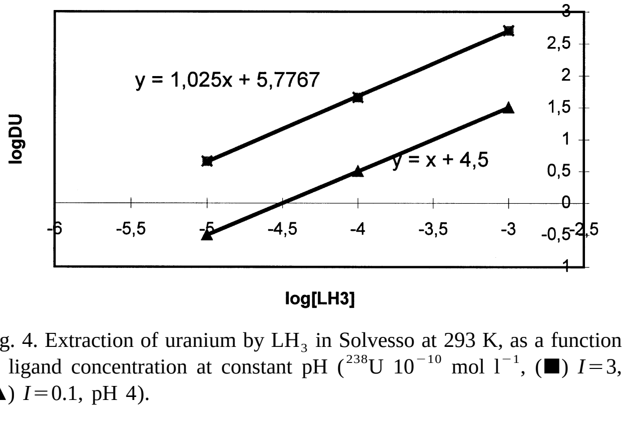

Fig. 4. Extraction of uranium by LH_3 in Solvesso at 293 K, as a function of ligand concentration at constant pH (^{238}U 10^{-10} mol l^{-1}, (■) $I=3$, (▲) $I=0.1$, pH 4).

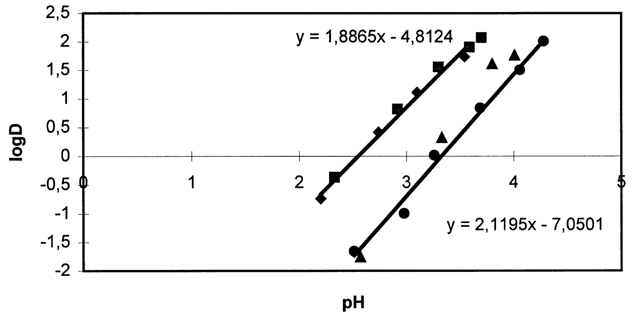

Fig. 5. Comparison of uranium extraction in presence of calcium (■) $Ca(NO_3)_2$ 10^{-1} mol l^{-1}, $I=3$, (▲) $Ca(NO_3)_2$ 10^{-1} mol l^{-1}, $I=0.1$, and without calcium (♦) $I=3$, (●) $I=0.1$.

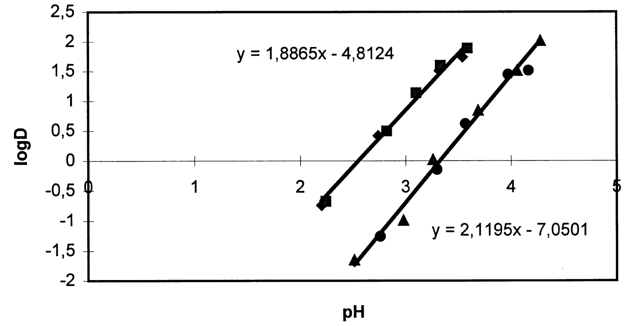

Fig. 6. Comparison of uranium extraction in presence of zinc (■) $Zn(NO_3)_2$ 10^{-3} mol l^{-1}, $I=3$, (▲) $Zn(NO_3)_2$ 10^{-3} mol l^{-1}, $I=0.1$, and without zinc (♦) $I=3$, (●) $I=0.1$.

3.3. Influence of complexing anions on uranium extraction

The competition between calix[6]arene and other complexing anions has been studied when various concentrations, ranging from 10^{-3} to 10^{-2} mol l^{-1}, of phosphate or sulphate ions are added in the aqueous phase.

Uranium repartition was measured when experiments were carried out for both ionic strengths, $I=0.1$ and $I=3$, in the aqueous phase. Results are compared with those obtained when experiments were carried out without anion added for both ionic strengths, $I=0.1$ and $I=3$, in the aqueous phase. Figs. 7 and 8 show that the uranium

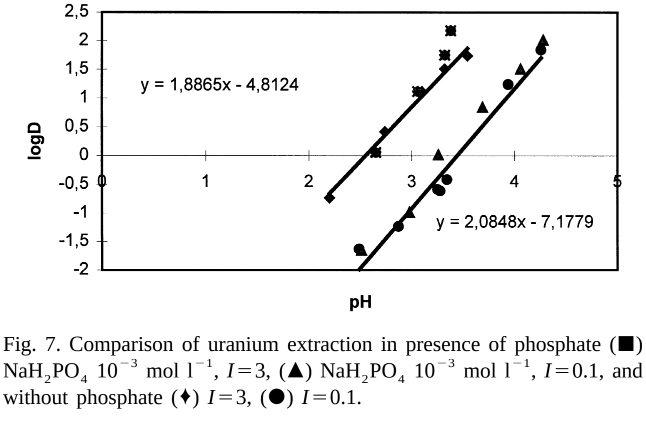

Fig. 7. Comparison of uranium extraction in presence of phosphate (■) NaH_2PO_4 10^{-3} mol l^{-1}, $I=3$, (▲) NaH_2PO_4 10^{-3} mol l^{-1}, $I=0.1$, and without phosphate (♦) $I=3$, (●) $I=0.1$.

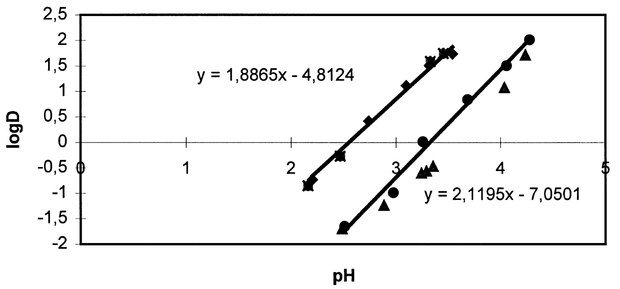

Fig. 8. Comparison of uranium extraction in presence of sulphate (■) Na_2SO_4 10^{-3} mol l^{-1} $I=3$, (▲) Na_2SO_4 10^{-3} mol l^{-1}, $I=0.1$, and without sulphate (♦) $I=3$, (●) $I=0.1$.

extraction is independent of the anion concentration, whatever the pH and the ionic strength are. These results indicate that the uranium–calixarene extraction constant is higher than the uranium–anion complexation constant.

4. Conclusion

It has been demonstrated that 1,3,5-trimethoxy-2,4,6-tricarboxy-*p*-*tert*-butyl-calix[6]arene (denoted LH_3), with its structure adequate for the coordination of uranyl ion, has an important affinity for uranium.

When studied alone for both ionic strengths, $I=0.1$ and $I=3$, the uranyl ion is extracted by LH_3 in the form of the $LH(UO_2)$ species.

Selectivity of LH_3 towards UO_2^{2+} has been studied by adding the aqueous phase metal ions, Cu^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, at various concentrations. The uranium repartition measurements show that the uranium extraction is not dependent on the cation concentration, whatever the pH and the ionic strength are. A great excess of divalent metal does not hamper the uranium extraction and does not affect the extraction mechanism.

The competition between the chosen calix[6]arene and other complexing anions, like phosphate and sulphate, has been investigated when the concentration of anion is equal to that of ligand, and when the concentration of anion is 10 times higher than the ligand concentration. The results indicate that the uranium–calixarene extraction constant is higher than the uranium–anion complexation constant. In order to complete these observations, further experiments taking into account other actinides, which can also be present in contaminated urine samples, and trivalent cations are in progress.

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