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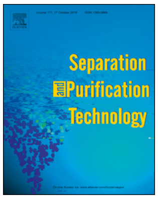

Insights in uranium extraction from spent nuclear fuels using dicyclohexano-18-crown-6 – Fate of rhenium as technetium homolog

Alain Favre-Réguillon[a,*], Micheline Draye[b,*], Gérard Cote[c], Kenneth R. Czerwinsky[d]

[a] Chimie Générale, Conservatoire National des Arts et Métiers, 2 Rue Conté, Paris 75003, France
[b] Univ. Savoie Mont Blanc, LCME, Chambéry F-73000, France
[c] PSL Research University, Chimie ParisTech–CNRS, Institut de Recherche de Chimie Paris, 11 Rue Pierre et Marie Curie, Paris 75005, France
[d] Department of Chemistry and Biochemistry, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas, NV 89154, USA

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ABSTRACT

The single extraction of rhenium(VII) and uranium(VI) from nitric acid solution by dicyclohexano-18-crown-6 (DCH) solutions was investigated. The extraction of Re(VII), in the form of perrhenate (ReO_4^-) anion, was optimum for a nitric acid concentration of 3 M and was explained by the ion-pair extraction of perrhenate anions by the hydroxonium DCH complex. The stoichiometry of the Re(VII) complex was obtained from the distribution data by slope analysis and the extracted specie was identified as $\{ReO_4^-(DCH\text{-}H_3O)^+\}$. The uranyl extraction by DCH solutions was evaluated under the same conditions and the extracted specie was identified as $\{(NO_3^-)_2(DCH\text{-}UO_2^{2+})\}$ for a nitric acid concentration above 5 M. The extraction of rhenium(VII) from nitric acid solution by DCH solutions in the presence of large excess of uranium(VI) was then investigated. For a nitric acid concentration of 3 mol/L, the extraction efficiency of perrhenate was found to be almost independent of uranium concentration. Based on the chemical similarities between Re(VII) and Tc(VII), this suggests that DCH could be considered for the separation of technetium (VII)/uranium(VI) from nitric acid solution.

1. Introduction

Selective extraction of uranium from spent nuclear fuel is a prerequisite for its reuse or storage. One problem during the uranium extraction from spent nuclear fuel, *e.g.* in the PUREX process, is its rather poor separation from the radioelement technetium [1,2]. Under the oxidizing conditions, both elements are present in the oxidized forms of uranium (VI), *i.e.* uranyl (UO_2^{2+}) and technetium (VII), *i.e.* pertechnetate (TcO_4^-) [3]. It has been shown that the pertechnetate anion binds U(VI) in aqueous solution [4–7] and is co-extracted with U(VI) during PUREX process,[8–10] thus contaminating produced streams. Furthermore, pertechnetate is known to catalyse unwanted side reactions through its redox chemistry [6,11,12]. The ability to selectively control Tc behaviour during separations can markedly improve advanced reprocessing schemes [11].

The PUREX process, that is currently the most effective separation process, has several disadvantages, primarily the degradation of the extractant tributylphosphate (TBP) by radiolysis and hydrolysis. Research of more effective extractants has been performed [13,14]. The importance of crown ether in hydrometallurgy and, in particular, dicyclohexano-18-crown-6 (DCH) for the reprocessing of spent nuclear fuel has been demonstrated [15,16]. Furthermore, DCH has been previously shown to be highly stable towards radiolysis and hydrolysis [17,18].

The extraction of pertechnetate anion from radioactive waste using liquid/liquid extraction has been studied by numerous researchers. Crown ethers have proven their efficiency for TcO_4^- or ReO_4^- extraction at low ionic strength [19–21] or in ionic liquids [22]. These extractions involve ion-pair binding between alkaline ions sitting in the crown ether and the perrhenate anion, through one O atom. Furthermore, X-ray structure of crown ether [23] and calix[4]arene bis crown-6 [24] sodium perrhenate complexes have been described in the literature.

Technetium fate in the spent nuclear fuel reprocessing is of importance [12,25]. The aim of the present work is to extend the knowledge of technetium extraction by DCH solution at high nitric acid concentration. In this publication, a mixture of DCH isomers supplied by Fluka was used. It has been shown that Pu extraction was influenced by the stereochemical configuration of DCH [15]. However, for oxy anions like TcO_4^- or ReO_4^- or uranyl ions *i.e.* UO_2^{2+}, the influence of stereochemical configuration of DCH could be overlooked because of structure of the extracted species (*vide supra*) [17,18].

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[*] Corresponding authors.
E-mail addresses: afr@lgpc.cpe.fr (A. Favre-Réguillon), micheline.draye@univ-smb.fr (M. Draye).

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The influence of the U(VI) in such systems is also studied. The close relationship between TcO_4^- and the isoelectric perrhenate ion ReO_4^- makes the latter a convenient and widely used homolog [26,27]. Based on the results of this study experiments with pertechnetate will be performed in the near term.

Furthermore, with the ever-increasing demands of rhenium and its compounds in the petrochemical industry, aerospace industry and nuclear medicine, the extraction of rhenium from non-traditional sources needs to be studied [28]. Among them, solutions obtained during underground leaching of uranium ore could be a new source for commercial production of rhenium despite their low metal concentration [29]. As such new separation methods like those discussed here are in high demand and will benefit from expanding the knowledge of rhenium solvent extraction chemistry.

2. Experimental section

2.1. Chemicals

All chemicals were of analytical grade and used without further purification. Stock solutions of uranyl nitrate (Prolabo) or sodium perrhenate (Alfa Aesar, 99.95% based on Re) were prepared by dissolving the proper amount of the salt in analytical grade concentrated nitric acid diluted with ultrapure water (Millipore Alpha-Q). The mixture of DCH isomers was supplied by Fluka and analytical grade $CHCl_3$ was supplied by Aldrich.

2.2. Analytical

Uranium and rhenium concentrations in aqueous solutions were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Liberty II, Varian) with a standard deviation of ± 2%.

2.3. Extraction experiments

Extractions were performed at various concentrations of nitric acid. Initial concentration of rhenium was 186.2 mg/L (*i.e.* 1.00×10^{-3} M). The DCH concentration in $CHCl_3$ was 0.10 M. The extractions of metal ions were determined by equilibrating equal volumes of aqueous and organic phase at 25 °C. Though 10 min were required to obtain an equilibrium extraction value, a 30 min phase contact time was maintained throughout this work. Suitable aliquots from the aqueous phase were withdrawn for analysis. Each data point was at least duplicated under identical conditions. The reproducibility of the measurements was within 6% for the lowest metal ion concentrations and mostly 3% for the most of the conditions. In blank experiments, no extraction was found in the absence of DCH.

The extraction efficiency (E) and distribution ratio (D) were calculated by using the Eqs. (1) and (2) respectively, where C refers to the metal concentration in the aqueous phase and the subscripts i and f refer to initial and final conditions.

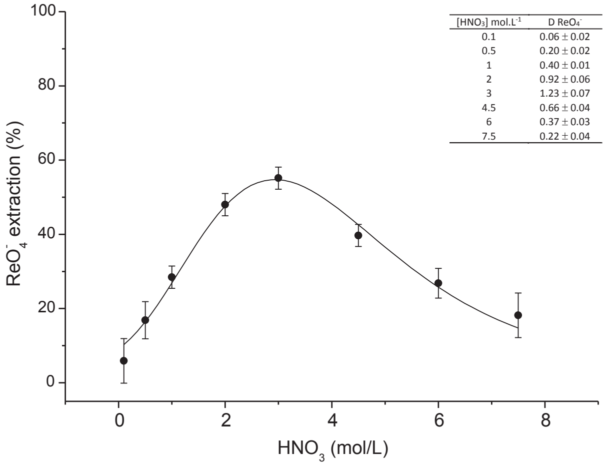
$$E = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

$$D = \frac{(C_i - C_f)}{C_f} \times 100 \tag{2}$$

3. Results and discussion

3.1. Perrhenate extraction by dicyclohexano-18-crown-6 solution

A plot of the extraction efficiency of ReO_4^- by DCH solutions as function of the nitric acid concentration is shown in Fig. 1. The extraction efficiency increases with increasing acidity until a maximum is reached at 3 M nitric acid. Above 3 M nitric acid the ReO_4^- extraction continually decreases under the examined conditions.



$[HNO_3]$ mol.L^{-1}	D ReO_4^-
0.1	0.06 ± 0.02
0.5	0.20 ± 0.02
1	0.40 ± 0.01
2	0.92 ± 0.06
3	1.23 ± 0.07
4.5	0.66 ± 0.04
6	0.37 ± 0.03
7.5	0.22 ± 0.04

Fig. 1. Effect of nitric acid concentration on the extraction efficiency of ReO_4^- by DCH, insert distribution ratio (D) (organic phase $CHCl_3$, 0.1 M DCH; aqueous phase 1.00×10^{-3} M ReO_4^-; phase volume ratio 1; T = 298 K).

Macrocyclic polyether and especially DCH can behave as electron-donating compound, forming adducts with oxonium ions (*i.e.* H_3O^+) [30]. X-ray diffraction study of the structure of DCH and hydroxonium perchlorate complex showed that hydroxonium ion is located inside the macrocyclic cavity [31]. Kudo et al. [21] have shown a 1:1 complex and in the conditions of the present study, $CHCl_3$ as diluent and a 3 M HNO_3 aqueous phase, the same stoichiometry was assumed as shown in Eq. (3):

$$NO_{3aq}^- + H_3O_{aq}^+ + DCH_{org} \rightleftarrows \{NO_3^-(DCH\text{-}H_3O^+)\} \tag{3}$$

The corresponding extraction equilibrium constant, $K_{ex}^{NO_3^-}$, can be defined as in Eq. (4):

$$K_{ex}^{NO_3^-} = \frac{[\{NO_3^-(DCH\text{ - }H_3O^+)\}]_{org}}{[NO_3^-]_{aq}\,[H_3O^+]_{aq}\,[DCH]_{org}} \tag{4}$$

Due to their anionic nature, the extraction of perrhenate ions by DCH may be explained by a mechanism of anion exchange involving the protonated form of DCH. The overall reaction for the extraction of aqueous ReO_4^- with DCH-H_3O^+ can be described by Eq. (5) where the subscripts "aq" and "org" denotes "aqueous" and "organic" phases respectively.

$$ReO_{4aq}^- + \{NO_3^-(DCH\text{-}H_3O^+)\} \rightleftarrows \{ReO_4^-(DCH\text{-}H_3O^+)\}_{org} + NO_{3aq}^- \tag{5}$$

The corresponding extraction equilibrium constant, $K_{ex}^{ReO_4^-}$, can be defined as in Eq. (6):

$$K_{ex}^{ReO_4^-} = \frac{[\{ReO_4^-(DCH\text{ - }H_3O^+)\}]_{org}\,[NO_3^-]_{aq}}{[ReO_4^-]_{aq}\,[\{NO_3^-(DCH\text{ - }H_3O^+)\}]_{org}} \tag{6}$$

Taking into account of the expression of the distribution ratio of ReO_4^- Eq. (7), the logarithmic expression of Eq. (6) can be expressed as Eq. (8):

$$D_{ReO_4^-} = \frac{[\{ReO_4^-(DCH\text{ - }H_3O^+)\}]_{org}}{[ReO_4^-]_{aq}} \tag{7}$$

$$Log D_{ReO_4^-} = Log K_{ex}^{ReO_4^-} + Log\,[\{NO_3^-(DCH\text{ - }H_3O^+)\}]_{org} - Log\,[NO_3^-]_{aq} \tag{8}$$

By considering the total of free concentration of DCH in organic phase (*i.e.* not engaged in ReO_4^- complexes):

$$[DCH]_{org,total,free} = [DCH]_{org} + [\{NO_3^-(DCH\text{ - }H_3O^+)\}]_{org} \tag{9}$$

Eq. (8) can be rewritten as Eq. (10):