



A new solvent system containing N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline in 1-(trifluoromethyl)-3-nitrobenzene for highly selective UO_2^{2+} extraction



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ABSTRACT

A novel tetradentate ligand combining hard O-donor and soft N-donors in the same molecule, N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen), was developed in our laboratory aiming at the group separation of actinides from lanthanides. Herein, the solvent extraction of UO_2^{2+} by Et-Tol-DAPhen in 1-(trifluoromethyl)-3-nitrobenzene diluent was investigated in detail. The effects of contact time, Et-Tol-DAPhen concentration, acidity, and competing ions on the extraction were discussed, the extracted UO_2^{2+} speciation was analysed, and the stripping of UO_2^{2+} from organic phase was performed. The results clearly show that Et-Tol-DAPhen/1-(trifluoromethyl)-3-nitrobenzene provides a highly efficient extraction of UO_2^{2+} from HNO_3 media with a fast extraction kinetics of less than 5 min and a large distribution ratio of more than 300. Moreover, the system shows excellent selectivity toward UO_2^{2+} over Ln^{3+} in a wide acidity range. Stripping experiments indicate that almost a complete back extraction of UO_2^{2+} could be achieved via only one stage operation using 5% Na_2CO_3 solution. Findings of the present work provide new data for assessing the feasibility of Et-Tol-DAPhen, as well as other new ligand with hard-soft donors combined in the same molecule, applied in the group separation of actinides over lanthanides.

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1. Introduction

In response to the rising trend of energy requirement from the world, nuclear power has been developed as a powerful tool for electricity generation without polluting the atmosphere. As a consequence, the already large number of nuclear power reactors will continue to expand, along with the nuclear waste depositories [1]. The required management of spent nuclear fuel (SNF) becomes more severe. Moreover, as the radioactive elements are largely included in SNF, reprocessing of SNF is of great indispensability and significance for environmental protection and organism health consideration.

Uranium and plutonium, the major radionuclide of spent nuclear fuel, prone to be separated by the PUREX (plutonium and uranium extraction) process and transferred into MOX fuel [2]. The traditional PUREX process is implemented by the O-donor extractant Tri-n-Butyl Phosphate (TBP) in n-dodecane and has been modified into various versions [3]. However, the waste

stream (high level liquid waste, HLLW) from PUREX process still contains quantities of short-lived fission products along with a slight of long-lived minor actinides (e.g. americium, curium, neptunium), which exhibit a long lasting radiotoxicity and thus bring difficulties in geological repository management [4]. Currently, these minor actinides can be reduced in a partitioning and transmutation (P&T) process [5]. However, the existing lanthanides render transmutation process towards actinides weaken significantly [6]. Consequently, the separation (partitioning) of actinides from lanthanides is a vital step in this radioactive-waste management (see Fig. 1).

Recently, a conceptual GANEX (Group ActiNide EXtraction) process was proposed for the hydrometallurgical reprocessing of Generation IV, aiming to recover all the actinides from SNF [7]. The process consists of two cycles. During the first cycle, O-donor extractants, such as N,N-dialkylamide and N,N-di-2-ethylhexylisobutyramide (DEHiBA), were applied for the good extracting feature towards UO_2^{2+} as well as high selectivity versus fission products [8]. The second cycle usually follows the Diamex-Sanex process, which is relatively complicated and three steps were involved: (1) Using a mixture of a malonamide (DMDOHEMA)

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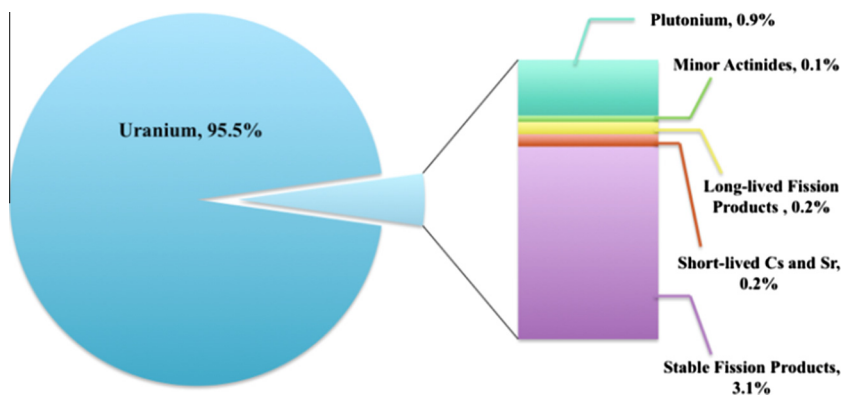


Fig. 1. The composition of spent nuclear fuel.

and an organophosphorous acid (HDEHP) to co-extract both of the actinide and the lanthanide; (2) selectively stripping of the actinides with a mixture of HEDTA and citric acid and (3) stripping of the lanthanides and other fission products [9]. The GANEX may be effective for the group separation of actinides over lanthanides using several kinds of extractants in one progress, however, complicates the extraction system, thus leads to difficulties in controlling and handling. Therefore, it is necessary to develop a new kind of extractant, with which the grouped actinides can be extracted into the organic phase, while lanthanides as well as other fission products remain in the aqueous phase. In our previous work, a novel tetradentate ligand *N,N'*-diethyl-*N,N'*-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen, as shown in Fig. 2) had been developed for the aim of the group separation of actinides over lanthanides [10]. Et-Tol-DAPhen consists of a phenanthroline moiety with soft nitrogen atoms showing selectivity for actinides(III) over lanthanides(III) and two amide moieties with hard oxygen atoms in favor of light actinides, such as Th, U, Np, and Pu. The preliminary solvent extraction experiments show that the ligand in cyclohexanone extracts both uranium, thorium and minor actinides efficiently but do not favor lanthanides. The crystallography results confirm that one Et-Tol-DAPhen ligand binds to one UO_2^{2+} or Th^{4+} through two nitrogen atoms of the phenanthroline moiety together with two oxygen atoms of the amide moieties, forming a very stable actinides complex. To further elucidate the feasibility of such a ligand applied in group separation of actinides, herein, we investigated in detail the extraction behaviors of Et-Tol-DAPhen towards UO_2^{2+} and Ln^{3+} by using 1-(trifluoromethyl)-3-nitrobenzene (Fig. 2) as a diluent. The effects of contact time, extractant concentration, acidity, and competing ions on the extraction were discussed, the extracted UO_2^{2+} speciation as well as the extraction mechanism was analysed, and the selective extraction behavior of the Et-Tol-DAPhen towards UO_2^{2+} over lanthanides was elucidated. Moreover, stripping of extracted UO_2^{2+} from the organic phase was also performed to probe the possibility of cyclic utilization of the extraction system.

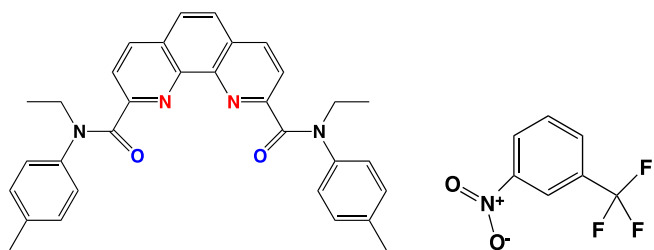


Fig. 2. The structure of Et-Tol-DAPhen (left) and 1-(trifluoromethyl)-3-nitrobenzene (right).

2. Experimental

2.1. Materials and instruments

A stock solution of UO_2^{2+} was prepared by dissolving U_3O_8 powder in 65% HNO_3 . Lanthanide nitrate stock solutions were obtained by dissolving $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ solid with ultrapure water in volumetric flasks. All Lanthanide nitrates were purchased from Aladdin Company with purity of 99.9%. Et-Tol-DAPhen has been synthesized as previously described [10]. 1-(trifluoromethyl)-3-nitrobenzene was purchased from J&K Scientific with purity of 96% and used as received. Other reagents were analytical pure and used without further purification.

The residual concentration of tested ion(s) in supernatants in the selectivity test experiments were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Horiba JY2000-2), while the quantitative determination of UO_2^{2+} in single component extraction experiments was made by measuring the UV absorbance of Arsenazo III- UO_2^{2+} complex at 656 nm on HITACHI UV-3900 spectrophotometer.

2.2. Extraction experiments

The Extraction experiments were processed in 10 mL polypropylene centrifuge tubes at 1:2 organic: aqueous phase volume ratio (from point of the view of both reducing usage of organic diluent and achieving higher extraction capacity). Organic phase were solutions of Et-Tol-DAPhen in 1-(trifluoromethyl)-3-nitrobenzene at different concentrations, which has been investigated with no complication to the metals. Aqueous phases were uranyl/lanthanides nitrate (0.5 mol/L) in nitric acid at different concentrations. Prior to extraction, the organic solutions were pre-equilibrated with the aqueous phase of the same composition as the extraction experiment except for being void of metal ions. Then 1 mL of the organic phase and 2 mL of aqueous phase were mixed in a stoppered test tube and vigorously shaken by a vortex mixer for 30 min at room temperature (25 ± 1 °C). After 2 min' centrifugation and separation, the concentration of metal ions in the aqueous phase was determined by the Arsenazo III spectrophotometric method or ICP-OES. For Arsenazo III spectrophotometric method (the detection limit is below 0.1 ppm), the supernatant was diluted 2.5–100 times to make sure that the U(VI) concentration in the dilution is 0.1–5 $\mu\text{g}/\text{mL}$, corresponding to the UV absorbance of 0.05–1.0 at 656 nm. For ICP-OES method (the detection limit is below 0.01 ppm), the supernatant was diluted 25–100 times to make sure that the Ln(III) concentration in the dilution is 1–5 $\mu\text{g}/\text{mL}$. The distribution coefficient (D) and the extraction efficient (E) were calculated as follows:

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