



ELSEVIER

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Radiolytic degradation of a new diglycol-diamide ligand for actinide and lanthanide co-extraction from spent nuclear fuel



Annalisa Ossola^a, Elena Macerata^{a,*}, Dario A. Tinonin^b, Federica Faroldi^b, Marco Giola^a, Mario Mariani^a, Alessandro Casnati^b

^a Department of Energy, Nuclear Engineering Division, Politecnico di Milano, Piazza L. da Vinci, 32, 20133 Milano, Italy

^b Department of Chemistry, University of Parma, Parco Area delle Scienze 17/a, 43124 Parma, Italy

HIGHLIGHTS

- Ageing and radiolytic resistance of a new DGA-type ligand for An–Ln co-extraction.
- Extraction efficiency decreases with time due to ligand-diluent reactions.
- Extracting capability is almost completely impaired by a 100 kGy γ -radiation dose.
- Ligand selectivity for both An and Ln is not affected by ageing and radiolysis.
- The ligand extracting capability is strongly influenced by storing conditions.

ARTICLE INFO

Article history:

Received 15 October 2015

Received in revised form

10 December 2015

Accepted 14 December 2015

Available online 17 December 2015

Keywords:

Actinides

Lanthanides

Partitioning

DIAMEX

Radiolysis

Hydrolysis

ABSTRACT

Within the Partitioning and Transmutation strategies, great efforts have been devoted in the last decades to the development of lipophilic ligands able to co-extract trivalent Lanthanides (Ln) and Actinides (An) from spent nuclear fuel. Because of the harsh working conditions these ligands undergo, it is important to prove their chemical and radiolytic stability during the counter-current multi-stage extraction process. In the present work the hydrolytic and radiolytic resistance of the freshly prepared and aged organic solutions containing the new ligand (2,6-bis[(N-methyl-N-dodecyl)carboxamide]-4-methoxy-tetrahydro-pyran) were investigated in order to evaluate the impact on the safety and efficiency of the process. Liquid–liquid extraction tests with spiked solutions showed that the ligand extracting performances are strongly impaired by storing the samples at room temperature and in the light. Moreover, the extracting efficiency of the irradiated samples resulted to be influenced by gamma irradiation, while selectivity remains unchanged. Preliminary mass spectrometric data showed that degradation is mainly due to the acid-catalysed reaction of the ligand carboxamide and ether groups with the 1-octanol present in the diluent.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The partitioning of the long-lived α -emitters and high-yield fission products from spent nuclear fuel is a key point for the development of advanced processes conceived for the recycling of the still precious components of spent nuclear fuel as well as for reducing the long term radiotoxicity of the final waste, improving thus a sustainable growth of the nuclear energy in term of social acceptance and environmental impact (Bourg et al., 2012; González-Romero, 2011). In this context, in the last decades great

efforts have been devoted to develop efficient multi-cycle advanced separation processes based on the combined co-extraction of actinides (An) and lanthanides (Ln) from the PUREX (Plutonium and URanium EXtraction process) raffinate, followed by the subsequent An/Ln separation, necessary to successfully implement the An transmutation (Modolo et al., 2013; Malmbeck et al., 2011; Paiva and Malik, 2004). Such advanced separation processes are based on aqueous technologies and plan to use specific organic extractants (Hill, 2009; Serrano-Purroy et al., 2005) that should be able to work under harsh conditions, due to the acidity of the aqueous phases, the high intensity radiation field present in the system to be decontaminated and the long application time in the multi-stage counter-current centrifugal contactor battery (Berthon

* Corresponding author.

E-mail address: elena.macerata@polimi.it (E. Macerata).

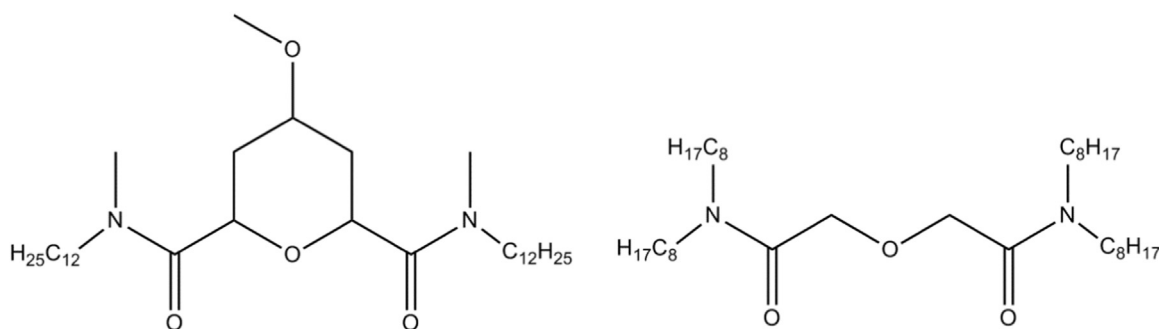


Fig. 1. Molecular structures of the ligand DMDCATHP under study (left) and of the reference molecule TODGA (right).

and Charbonnel, 2009). Therefore, it becomes crucial to investigate the impact of the radiolytic and hydrolytic phenomena, as well as the ageing, on the extracting performances of the system (Mincher et al., 2009; Sugo et al., 2002; Modolo et al., 2007). In fact, structural changes of ligands and diluents induced by degradation play a fundamental role in determining the extraction efficiency, selectivity, and solvent-recycling options (Mincher and Mezyk, 2009; Mincher et al., 2009).

The purpose of this research work is to study the ageing and the radiolytic resistance of a new promising carboxamide ligand, named DMDCATHP (Fig. 1), in order to find an extractant for An-Ln co-extraction even more effective than TODGA, the current reference molecule in the European context. Recent studies performed by Macerata et al. (Macerata et al., in preparation) demonstrated as solutions containing DMDCATHP, a ligand belonging to the class of diglycol-diamides (DGA) but having a more rigid and preorganised structure, show an extraction efficiency in different kerosene/1-octanol mixtures comparable to that of TODGA (Hérès et al., 2009; Sasaki et al., 2007; Zhu et al., 2004) and a selectivity ($SF_{Eu/Am}$) equal to about half of that of TODGA, feature that represents a significant improvement in term of decontamination of the aqueous feed for the same number of extraction stages. These experimental evidences justify the interest in further investigations to fully characterize the ligand behaviour. For this purpose, several liquid–liquid extraction tests were performed on irradiated and/or aged solutions, taking into account all those parameters that could play a crucial role in the ageing and radiolytic resistance of the extracting system under study.

2. Experimental

2.1. Chemicals

The synthesis of 2,6-bis[(N-dodecyl-N-methyl)carboxamide]-4-methoxy-tetrahydro-pyran (DMDCATHP) will be reported elsewhere (Macerata et al., in preparation).

All the reagents and chemicals used in the extraction experiment were of analytical reagent grade and they were used without any further purification. The organic solutions were prepared by dissolving weighted amounts of extractant in mixtures of kerosene and 1-octanol (from SIGMA-ALDRICH) in different proportion. Nitric acid solutions were prepared by diluting concentrated nitric acid (from FLUKA, purity $\geq 65\%$) with distilled water. The radioactive reference materials, $^{241}\text{Am}(\text{NO}_3)_3$ in 1 M HNO_3 (carrier 20 mg/L $\text{Sm}(\text{NO}_3)_3$) and $^{152}\text{EuCl}_3$ in 1 M HCl (carrier 10 $\mu\text{g/g}$ EuCl_3) solutions, were supplied by Eurostandard CZ (Czech Republic) and CERCA-LEA (France), respectively.

2.2. Ageing experiments

For ageing experiments several organic phases were prepared by dissolving DMDCATHP ligand (0.025 M) in kerosene/1-octanol 70/30% (v/v), previously pre-equilibrated with an equal volume of 3 M nitric acid solution. The pre-equilibration step is intended to saturate the 1-octanol capability to extract nitric acid from the aqueous phase leading to changes in acidity during the tests. The obtained organic solutions were stored for 14 and 30 days in different conditions. In particular, they were stored at low temperature in the refrigerator and at room temperature both in the light (exposed to day-light in summertime at Milano and laboratory lighting) and in the dark. Another series of 0.025 M DMDCATHP organic phases was prepared in kerosene/1-octanol 95/5% (v/v), to compare the ageing into different mixtures and assess the influence of the 1-octanol percentage on the ageing by-products. The ageing effect on the extracting performances was checked by liquid–liquid extraction tests carried out following a standard protocol. The pre-equilibrated and aged organic phases were contacted in closed single-use Eppendorf microtubes with an equal volume of 3 M aqueous phase spiked with about 8000 Bq of ^{241}Am and ^{152}Eu . Such aqueous phase simulates the feed coming from a PUREX process, containing the cations to be extracted. The phases were then vigorously shaken with a mixer for 1 h at room temperature and after centrifugation an aliquot of 200 μL of each phase was extracted for radiometric measurements. The activity of the radiotracers in each phase was measured by γ -spectrometry ($2'' \times 2''$ NaI(Tl), Silena SNIP N MCA) exploiting the γ -lines at 59.5 Kev and 121.8 Kev for ^{241}Am and ^{152}Eu , respectively. Distribution coefficients, D_M , were then calculated as the ratio between the activity of the radiotracer in the organic phase and that in the aqueous phase. The selectivity is expressed by the Separation Factor, $SF_{Eu/Am}$, which is the ratio of the distribution coefficients for Eu over Am. Only the extraction tests in which no third phase formation was observed and the activity balance was within 5% were considered reliable. For each series of tests, reference values on a freshly prepared organic phase were also acquired. The aged solutions were afterwards analysed by electrospray ionization-mass spectrometry (ESI-MS) in order to identify the degradation products. Mass spectra were recorded on a single quadrupole instrument SQ Detector, Waters (capillary voltage 3.8 kV, cone voltage 30–160 eV, extractor voltage 3 eV, source block temperature 80 $^\circ\text{C}$, desolvation temperature 150 $^\circ\text{C}$, cone and desolvation gas (N_2) flow rates 1.6 and 8 L/min, respectively) using methanol as solvent.

2.3. Radiolysis experiments

0.025 M DMDCATHP solutions in kerosene/1-octanol 70/30% (v/v) were prepared as described above and irradiated in step of 25 kGy from 25 kGy to 100 kGy by using two different dose rates

Download English Version:

<https://daneshyari.com/en/article/1891052>

Download Persian Version:

<https://daneshyari.com/article/1891052>

[Daneshyari.com](https://daneshyari.com)