# Partitioning of Minor Actinides from High Active Raffinates using Bis-Diglycolamides (BisDGA) as new efficient Extractants

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**Abstract** *–Two new polyamide extractants has been selected, namely UAM-069 and UAM-081, both synthesized at the Universidad Autónoma de Madrid (UAM), to develop a new separation process. These two ligands are bis-diglycolamides, consisting of two diglycolamides moieties grafted on an aromatic platform (UAM-069) or on an aliphatic linker (UAM-081), respectively. The extraction of actinides and fission products was studied from synthetic PUREX raffinate. Actinides(III) and lanthanides(III) are highly extracted from acidities > 1 mol/L $HNO_3$. The extraction of Zr, Mo and Pd could be surpressed with complexing agents such as oxalic acid and HEDTA. In the present paper the results of the batch extraction results are presented which serve for the development of a new continuous counter current process to be tested in centrifugal contactors.*

## INTRODUCTION

Several processes have been developed for the co-extraction of americium and curium from the PUREX waste stream containing lanthanides and other fission products [1]. The European research over the last decade, i.e. in the NEWPART, PARTNEW and the recent EUROPART programs, has resulted in the development of the combination of DIAMEX and the SANEX processes [2-4]. These are based on the co-separation of trivalent actinides and lanthanides (DIAMEX) by a diamide followed by the subsequent selective separation of minor actinides (MA) in the SANEX process.

The DIAMEX process use malonamide extractants such as DMDOHEMA (N,N`-dimethyl-N,N`-dioctyl-2-hexylethoxy-malonamide) dissolved in an aliphatic diluent, e.g. kerosene. The DIAMEX extractant follows the CHON principle, i.e. the molecule is built from constituents that can be easily incinerated, thus minimizing generation of secondary waste. Recent research has shown that the tridentate diglycolamides (DGAs) [5], exhibit even higher affinity for trivalent actinides and lanthanides than the reference diamide and could therefore be an interesting alternative to the DIAMEX process. Amongst the DGAs N,N,N',N'-tetraoctyl diglycolamide (TODGA) has been identified as an promising extractant for the recovery of actinides from nuclear wastes [6,7]. Although TODGA already meets the requirements of process flow-sheet development (good extraction properties, good loading capacities, high stabilities etc.), it was assumed that pre-organizing two DGAs on a suitable platform or linker would enhance extraction efficiency and perhaps improve the decontamination to non lanthanide fission products.

It was recently demonstrated that the use of two malonamide moieties attached to a suitable linker in a more pre-organized chemical structure improves the extraction properties [8]. A similar strategy could be developed for the highly efficient extractant TODGA, based on a diglycolamide function [9].

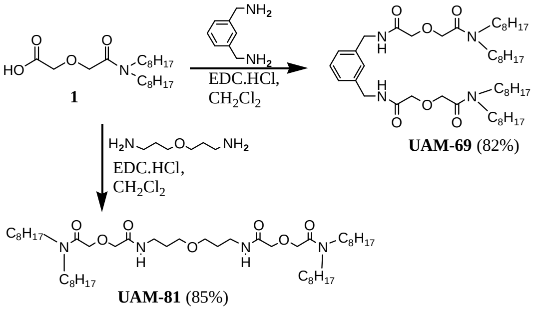
On the basis of the extraction data acquired at CIEMAT during the European EUROPART project [4], two new Bis-DGAs have been selected, namely UAM-069 and UAM-081, both synthesized at the Universidad Autónoma de Madrid to develop a new separation process.

Within the further course of the process orientated work at Forschungszentrum Jülich the extracting properties of the Bis-DGAs have been examined with different modifiers and complexants in order to control and optimize the separation process. Beside the extraction of actinides (Am, Cm, Cf) the extraction of fission products from synthetic PUREX raffinates was investigated. In the present paper the results of the batch extraction results are presented which serve for the development of a new continuous counter current process to be tested in centrifugal contactors.

## EXPERIMENTAL

### Synthesis of UAM-069 and UAM-081.

Compounds UAM-069 and UAM-081 were prepared with high yields by activation of carboxylic acid 1 and addition of the corresponding amines (Scheme 1) [9].



**Scheme 1.** *Synthesis of compounds UAM-069 and UAM-81.*

### Solutions and Isotopes

The composition of the synthetic PUREX raffinate used for the batch extraction studies is shown in Table 1. It was prepared by a specific dissolving strategy, mainly based on the use of metal nitrate salts. It corresponds to a PUREX raffinate with a volume of 5000L/t UOx fuel with an initial $^{235}U$ enrichment of 3.5 %, thermal burn-up of 33000 MWd/$t_{HM}$ and 3 years cooling. The feed was spiked with $^{241}Am$, $^{244}Cm$, $^{252}Cf$, and $^{152}Eu$, and mixed with variable concentrations of oxalic acid (Zr, Mo complexation) and 0.05 mol/L N-(2-hydroxyethyl)ethylenediamine-triacetic acid (HEDTA) for Pd complexation.

### Distribution Ratio Measurements

The extraction experiments were performed in 2 mL glass vials. 500 µL of organic and aqueous phases were equilibrated for 15 minutes, while being vigorous shaken by a vortex mixer. After phase separation by centrifugation, 200µL aliquots of each phase were sampled for analysis with the aid of a high-purity germanium spectrometer system (EG&G Ortec).

The nuclides $^{241}Am$, $^{244}Cm$ and $^{252}Cf$ were measured by means of alpha-spectrometry. Stable lanthanides were determined by ICP-MS on an Elan 6100 DRC from Perkin Elmer Sciex, Roggau-Jügesheim, Germany.

The distribution ratio D was measured as the ratio between the radioactivity or concentration of an isotope or element in the organic and the aqueous phase. Distribution ratios between 0.1 and 100 exhibit a maximum error of ± 5 %. The error may be up to ± 20 % for smaller and larger values.

**Table 1.** Composition of the synthetic HAR with an acidity of 3.2 mol/L $HNO_3$

| Element | mg/L | Element | mg/L |
|---|---|---|---|
| Ag | 12.6 | Na | 2034 |
| Al | 2 | Nd | 718 |
| Ba | 264 | Ni | 47 |
| Cd | 17 | Pd | 123 |
| Ce | 518 | Rb | 65 |
| Cr | 91 | Pr | 219 |
| Cu | 19 | Rh | 80 |
| Cs | 556 | Ru | 388 |
| Y | 102 | Sb | 4.4 |
| Eu | 33 | Se | 9 |
| Fe | 1900 | Sm | 146 |
| Gd | 35 | Sn | 11 |
| La | 218 | Sr | 167 |
| Mo | 672 | Zr | 1165 |
| Te | 481 | $HNO_3$ | 3.2 mol/L |

## RESULTS AND DISCUSSION

UAM-081 has an aliphatic (oxoalkyl) spacer instead of an aromatic spacer (as in UAM-069). Stability studies by CIEMAT show that both molecules are extremely stable during hydrolysis and radiolysis and are therefore suitable candidates for process development [9].

The extraction of americium(III), curium(III), californium(III) and some fission products (Eu, Cs, Fe, Mo, Pd, Rh, Ru, Sr and Zr) from $HNO_3$ [0.01 – 5 mol/L) was therefore investigated at Forschungszentrum Jülich. The extractions were carried out in solutions that contained $10^{-4}$ mol/L of the stable elements as well as trace amounts of $^{241}$Am, $^{244}$Cm, $^{252}$Cf and $^{152}$Eu. A solution of 0.1 mol/L UAM-069 or UAM-081 in 1-octanol/TPH $(10:90)_{vol\%}$ was used as the extractant. The influence of the complexing agents (oxalic acid and HEDTA) was also investigated. Since no significant difference was detected between the two ligands, Figures 1 present the extraction results of UAM-069. With an increasing concentration of $HNO_3$, the distribution ratios of the actinides increase significantly, where the order in the extraction is the following: $D_{Am} < D_{Cm} < D_{Cf.}$

Fe (moderate), Pd and Zr were also extracted without a complexing agent (Figure 1a). By adding oxalic acid and HEDTA, the extraction of Zr and Pd could be heavily suppressed (Figure 1b). However, it was surprising that the distribution ratio of zirconium between 3 and 5 mol/L $HNO_3$ also increased again in the presence of oxalic acid. It is assumed that the complex stability of the zirconium oxalate declines at high acidities.

The results in Table 2 show that UAM-069 and UAM-081 (0.1 mol/L) have extraction properties similar to those of TODGA (0.2 mol/L) [6]. The actinides Am(III), Cm(III) and Cf(III) as well as the trivalent lanthanides are extracted with high distributions ratios from HAR containing 3.2 mol/L $HNO_3$. Without oxalic acid and without HEDTA, Zr and Pd are co-extracted as in the TODGA process. With TODGA, however, we observed a third phase under these conditions. As expected, the co-extraction of zirconium, molybdenum and palladium is prevented using oxalic acid and HEDTA. These reagents have been proved in the DIAMEX and the TODGA/TBP process [7] as effective complexing agent.

A great difference between TODGA and UAM-069 (UAM-081) consists in the extraction of strontium, which so far has posed difficulties in the TODGA/TBP process. With UAM-069, distribution ratios of DBSrB < 0.13 are achieved, which is lower by a factor of 10, so that no special Sr scrubbing is necessary anymore in a possible continuous process; this would be a great advantage.

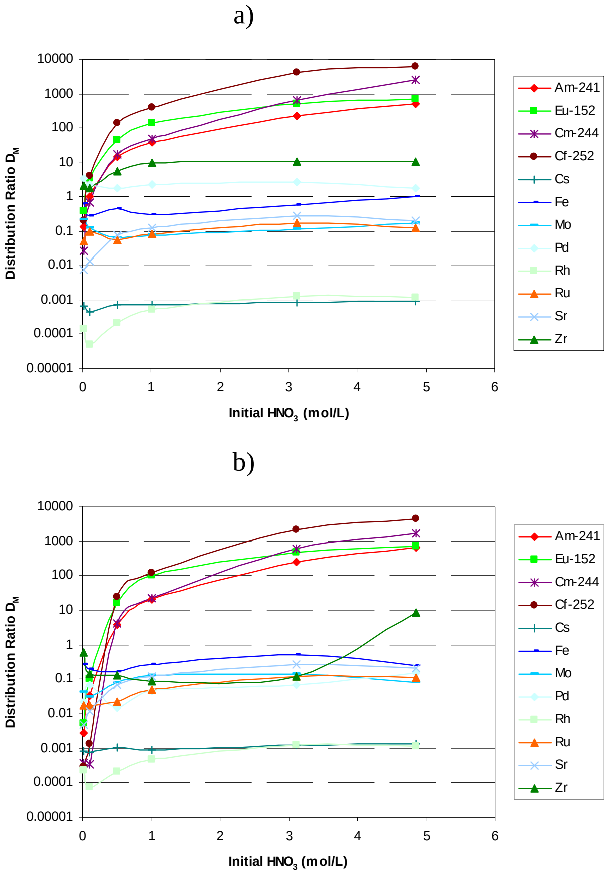


**Figure 1.** Extraction of actinides(III) and selected fission products with UAM-069 from nitric acid. Organic phase: 0.1 mol/L UAM-069 in 10% 1-octanol/90% TPH (not pre-equilibrated with $HNO_3$). Aqueous phase: variable nitric acid, $10^{-4}$ mol/L Ru, Pd, Mo, Sr, Fe, Zr, Rh, Cs without (**a**, upper figure) or with + 0.2 mol/L oxalic acid + 0.05 mol/l HEDTA (**b**, lower figure), traces of $^{241}$Am,$^{244}$Cm, $^{252}$Cf, $^{152}$Eu.

**Table 2.** Extraction of actinides(III) and HAR elements with UAM-069 in 10% 1-octanol / 90% TPH from a synthetic HAR solution. Organic phase: 0.1 mol/L UAM-069 or UAM-081 in 10% 1-octanol/90% TPH. Aqueous phase: synthetic Feed (see Table 1), without or with + 0.2 mol/L oxalic acid + 0.05 mol/l HEDTA. Traces of $^{241}$Am, $^{244}$Cm, $^{252}$Cf and $^{152}$Eu

| UAM | 069 | 081 | 069 | 081 |
|---|---|---|---|---|
| | Concentrations mol/L | | | |
| [$H_2C_2O_4$] | no | no | 0.2 | 0.2 |
| [HEDTA] | no | no | 0.05 | 0.05 |
| Element | Distribution ratios | | | |
| Am | 99 | 96 | 131 | 100 |
| Cm | 191 | 165 | 262 | 85 |
| Cf | 2079 | 1352 | 2057 | 511 |
| Eu | 685 | 267 | 764 | 341 |
| Ce | 23 | 17 | 36 | 24 |
| Gd | 166 | 160 | 239 | 197 |
| La | 13 | 10 | 21 | 12 |
| Nd | 94 | 74 | 142 | 101 |
| Pr | 39 | 32 | 59 | 44 |
| Sm | 615 | 266 | 690 | 432 |
| Y | 1753 | 574 | 1766 | 618 |
| Zr | 133 | 9.1 | 0.096 | 0,51 |
| Mo | 0.069 | 0.09 | 0.087 | 0.21 |
| Pd | 2.5 | 1.7 | 0.073 | 0,1 |
| Ru | 0.25 | 0.24 | 0.29 | 0.21 |
| Sr | 0.071 | 0.033 | 0.110 | 0.043 |
| Rest FP | < 0.03 | < 0.03 | < 0.03 | < 0.03 |

## CONCLUSIONS

In this work we have shown that the extraction behaviour of a new family of bis-diglycolamides with an aromatic linker (UAM-069) or an aliphatic linker (UAM-081) very much resembles that of the mono-diglycolamide TODGA. The first results indicate however, that the decontamination to some fission products e.g. strontium is much better as with TODGA. Preliminary results show also a higher loading capacity, thus reducing the formation of a third phase. For further assessment, in particular, the limits of the third phase formation, stability studies and the back-extraction behavior remain to be studied.

## ACKNOWLEDGEMENT

Financial support for this research was provided by the European Commission (project EUROPART, contract FI6W-CT-2003-508854) and ENRESA.

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