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Separation of Americium by Liquid-Liquid Extraction using Diglycolamides Water-Soluble Complexing Agents

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Abstract

Recycling americium (Am) alone from spent nuclear fuels is an important option studied for the future nuclear cycle (Generation IV systems) since Am belongs to the main contributors of the long-term radiotoxicity and heat power of final waste. Since 2008, a liquid-liquid extraction process called EXAm has been developed by the CEA to allow the recovery of Am alone from a PUREX raffinate (a dissolution solution already cleared from U, Np and Pu). A mixture of DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-(hexyloxy)ethyl)-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) in TPH is used as the solvent and the Am/Cm selectivity is improved using TEDGA (*N,N,N',N'*-tetraethyldiglycolamide) as a selective complexing agent to maintain Cm and heavier lanthanides in the acidic aqueous phase (5M HNO_3). Americium is then stripped selectively from light lanthanides at low acidity (pH=3) with a polyaminocarboxylic acid. The feasibility of sole Am recovery was already demonstrated during hot tests in ATALANTE facility and the EXAm process was adapted to a concentrated raffinate to optimize the process compactness. The speciation of TEDGA complexes formed in the aqueous phase with Am, Cm and lanthanides was studied to better understand and model the behavior of TEDGA in the process. Some Ln-TEDGA species are extracted into the organic phase and this specific chemistry might play a role in the Am/Cm selectivity improvement. Hence the hydrophilicity-lipophilicity balance of the complexing agent is an important parameter. In this comprehensive study, new analogues of TEDGA were synthesized and tested in the EXAm process conditions to understand the relationship between their structure and selectivity. New derivatives of TEDGA with different N-alkyl chain lengths and ramifications were synthesized. The impact of lipophilicity on ligand partitioning and Am/Cm selectivity was investigated.

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: americium, curium, liquid-liquid extraction, diglycolamides

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1. Introduction

The French Act of June 28th 2006 has defined several strategies to totally or partially reprocess minor actinides from spent nuclear fuels in Generation IV systems. One of these strategies would involve the recovery of americium alone from a PUREX raffinate (already cleared from U, Np and Pu) and leave curium with vitrified wastes dedicated to a future deep geological repository. Separating americium alone from those final waste would allow the reduction of their long term radiotoxicity but also heat emissions, leading to a significant minimization of the surface needed for repository.[1, 2] Moreover, curium recycling would be difficult to implement due to its very significant neutron emissions which would require very thick shielding at any step of the fuel cycle. In order to recover americium from a PUREX raffinate, two main challenges have to be accomplished: the separation of Am from all the lanthanides AND curium. In order to prove the feasibility of this separation, the CEA has developed a hydrometallurgical process, called EXAm (Extraction of Americium),[3,4] using a mixture of two extractants: DMDOHEMA (*N,N*′-dimethyl-*N,N*′-dioctyl-2(2(hexyloxy)ethyl)-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) diluted in hydrogenated tetrapropylene (TPH) diluent.

The key step of this process is the first "extraction/scrubbing" section where the americium/curium separation is achieved using TEDGA (*N,N,N',N'*-tetraethyldiglycolamide) complexing agent in the acidic aqueous phase (4-5 M HNO_3). Americium is co-extracted in the organic phase with lighter lanthanides (Ln) and some fission products (Fe, Mo, Ru, Pd). Hence additional steps are necessary to separate Am from those elements. In this paper we will only focus on the chemistry of the first main "extraction-scrubbing" section where the Am/Cm separation takes place, focusing on the role of TEDGA in the separation between Am and Cm and evaluating the impact of structural modifications on the diglycolamide ligand (DGA).

Nomenclature

TEDGA	*N,N,N',N'*-tetraethyldiglycolamide
EXAm	Extraction of Americium Process
DMDOHEMA	*N,N*′-dimethyl-*N,N*′-dioctyl-2-(2-(hexyloxy)ethyl)-malonamide
HDEHP	di-2-ethylhexylphosphoric acid
TPH	hydrogenated tetrapropylene
DGA	diglycolamide
Ln	Lanthanides
An	Actinides
SF	Separation Factor

2. Highlights on the EXAm process chemistry with TEDGA

2.1. Previous work

The Am/Cm separation is very challenging since both elements have very close physico-chemical properties. The DMDOHEMA extractant has a low selectivity for Am versus Cm ($SF_{Am/Cm}$= 1.6). Hence, the water soluble complexing agent TEDGA was added into the feed solution and in the scrubbing aqueous phase to improve the Am/Cm selectivity ($SF_{Am/Cm}$= 2.5). TEDGA has a higher affinity for heavy lanthanides and curium, maintaining them preferentially in the aqueous phase, while light lanthanides and americium are extracted by the EXAm solvent in the organic phase.

Although TEDGA is a water-soluble complexing agent, its partial transfer to the solvent during the extraction process has to be taken into account. According to a recent complexation study,[5] TEDGA would form preferentially 1:1 and 1:2 complexes with lighter lanthanides in the aqueous phase, and such complexes are extractable into the organic phase, while heavier lanthanides and Cm should mainly form non-extractable 1:3 species. In order to better characterize the impact of this specific TEDGA chemistry on Am/Cm separation, a new series of batch extraction experiments was performed and modelled.

2.2. Experimental data

The objective of this experiment was to vary the total concentration of lanthanides in the initial aqueous phase and to study the impact of free TEDGA concentration on Am/Cm selectivity. A single lanthanide (neodymium) was selected to simulate the cation loading in order to simplify the interpretation of data (modelling). ^{241}Am and ^{244}Cm were introduced in the aqueous phase in traces amounts (10^{-7} M) while Nd was in macro-concentration (0 to 70 mM) with a constant amount of TEDGA (70 mM) in 5 M HNO_3. The organic phase (0.6 M DMDOHEMA and 0.45M HDEHP in TPH) was contacted to an equal volume of aqueous solution during 30 minutes by means of a vortex shaker. After centrifugation and separation of phases, the concentrations of Nd, Am, Cm and TEDGA were measured in both phases by ICP-OES, gamma, alpha spectrometry and HPLC respectively. Distribution coefficients and Am/Cm separation factors are reported in Fig.1. When the concentration of Nd increases, distribution coefficients of Am and Cm get higher, which can be explained by a lower concentration of free TEDGA due to neodymium complexation in the aqueous phase. But meanwhile, the distribution ratio of TEDGA increases, confirming its tendency to partition into the organic phase, especially in the presence of cations. The Am/Cm separation factor presents a maximum at around 20 mM of Nd, which corresponds to a [TEDGA]/[Nd] ratio close to 3 (total concentrations).

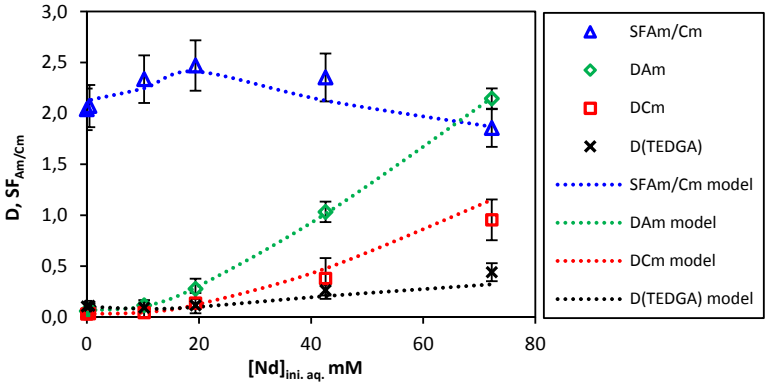

Fig. 1: Effect of the initial Nd concentration in the aqueous phase on distribution ratios of Am, Cm, TEDGA and $SF_{Am/Cm}$ using 0.6 M DMDOHEMA and 0.45 M HDEHP diluted in TPH and 5 M HNO_3 (mixing 30 minutes, 25°C).

2.3. Modelling

In order to give a more precise interpretation, those extraction data were fitted using the model proposed in an earlier study.[6] The proposed thermodynamical model takes into account the formation of three different $An(TEDGA)_x^{3+}$ complexes in the aqueous phase with one to three molecules of TEDGA surrounding the cation (as already characterized experimentally for lanthanides and americium).[5] Two kinds of extraction mechanisms were considered:

- extraction of the free actinide An^{3+} cation by DMDOHEMA (At this high acidity, the participation of HDEHP to the complexes formed in the organic phase is negligible but it may form adducts with DMDOHEMA);[7]
- extraction of $An(TEDGA)_x^{3+}$ species by DMDOHEMA (with x=1 or 2).

The calculated speciation of americium and curium in organic and aqueous phases as a function of the total neodymium concentration are reported in

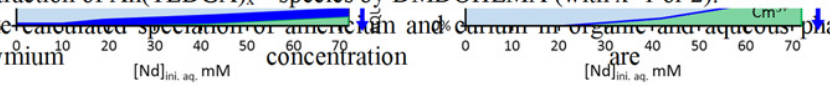

Fig. 2. According to this model, the major species in the aqueous phase at equilibrium is $An(TEDGA)_3^{3+}$ for both Am and Cm. When increasing the concentration of Nd, its proportion decreases and some 1:2 complex appear in the aqueous phase with Am only.

In the organic phase, the formation of $An(NO_3)_3(TEDGA)_2D$ is observed for both Am and Cm cations and must result from the extraction of the 1:2 An-TEDGA aqueous complex. But the main difference between Am and Cm would be the formation of $Am(NO_3)_3(TEDGA)D$ organic compound, which would result from the extraction of 1:1 Am-TEDGA aqueous complex. This 1:1 stoichiometry is not considered at all for curium in the fitting.

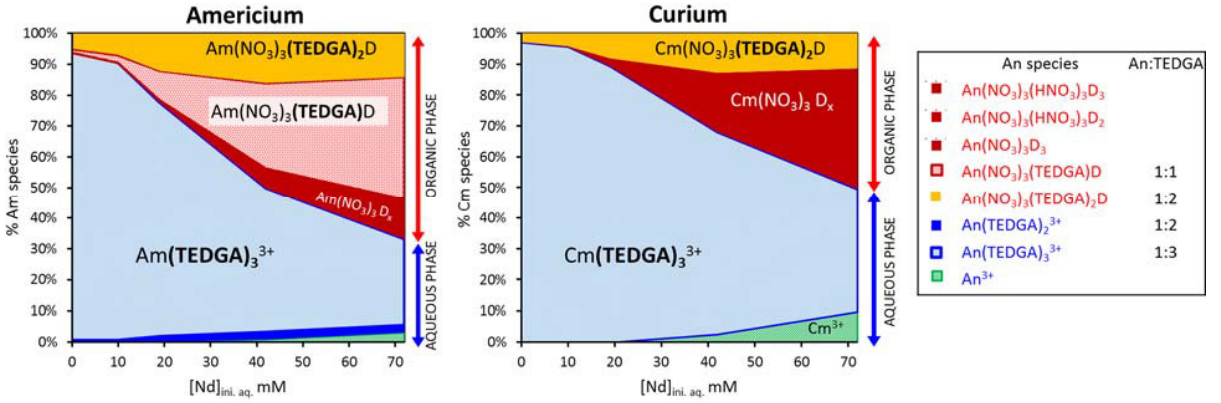

Fig. 2: Calculated speciation of Am and Cm in organic and aqueous phases at equilibrium (% of An species is related to the total amount of An in the batch extraction test)

To summarize, all extraction mechanisms that should be taken into account to describe the extraction of An(III) cations in the EXAm process (at high acidity) are depicted in Fig. 3. The distribution of TEDGA is a key point of the process as it impacts the extraction properties, the Am/Cm selectivity and the solvent loading capacity. But its extraction mechanism is complex and must be linked to the cation loading and An-TEDGA speciation. These new results were used to refine the existing thermodynamical model implemented in the PAREX code for process modeling.[6]

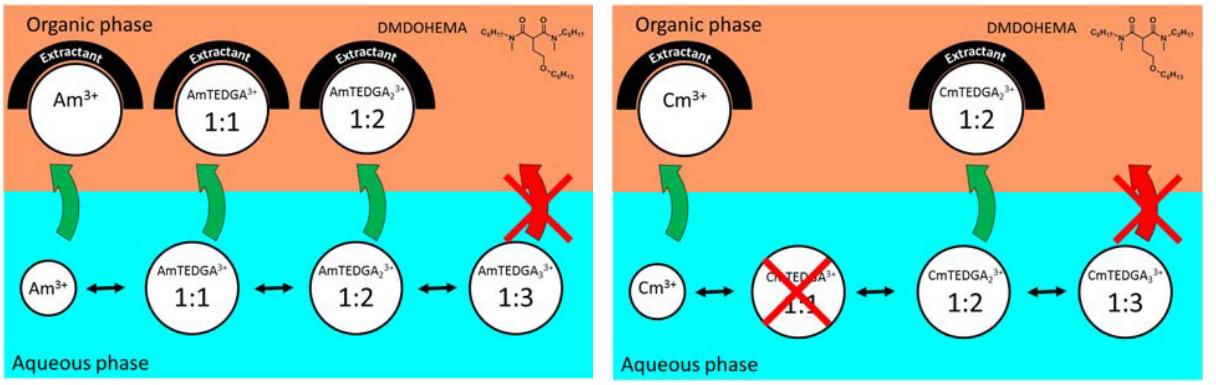

Fig. 3: Schematic view of complexation equilibria and extraction mechanisms involving Am and Cm in the biphasic system {DMDOHEMA (D), HDEHP (HP) / 5M HNO_3, TEDGA, Am (*left*) and Cm (*right*)}.

3. Impact of the complexing agent lipophilicity on Am/Cm selectivity

Speciation studies investigated on the EXAm process with TEDGA as a water complexing agent have highlighted the importance of the M^{3+}-TEDGA speciation in both phases. As a consequence, it was interesting to vary the lipophilicity of the diglycolamide ligand, in order to better understand the relationship between physico-chemical properties of the ligand and Am/Cm selectivity. As already reported before, when increasing the alkyl chains length with more than two carbon atoms (ethyl), the molecule will have a higher affinity for the organic phase. The butyl analog TBDGA is not soluble anymore in the aqueous phase while TPDGA has a very low solubility.[8-10] In order to complete the series of ligands (Cf. Fig. 4), two new analogues where synthesized with two different alkyl chains on each amide function: *N,N'*-diethyl-*N,N'*-dimethyldiglycolamide (DEDMDGA) and *N,N'*-diethyl-*N,N'*-dipropyldiglycolamide (DEDPDGA).

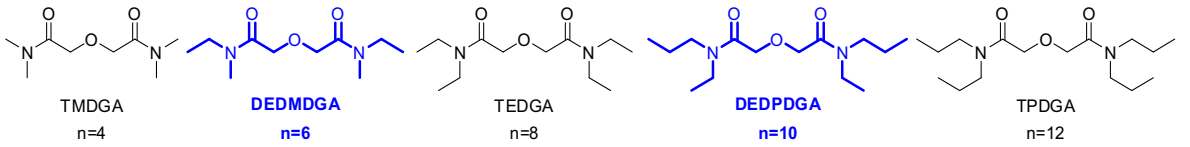

Fig. 4: Structures of diglycolamide derivatives (n = total number of carbon atoms on amide functions)

These molecules were tested at a concentration of 30 mM in 6 M HNO_3 with 0.1 mM of each following cation: La, Nd, Sm, Eu and Y and traces amounts (10^{-7} M) of ^{241}Am and ^{244}Cm. The organic phase (0.6 M DMDOHEMA and 0.45 M HDEHP in TPH) was pre-equilibrated with 6 M nitric acid and then contacted to an equal volume of this aqueous solution during 30 minutes. Distribution coefficients and Am/Cm separation factors (measured as reported in paragraph 2.2.) are reported in Fig. 5. The first observation is that americium and curium complexation in the aqueous phase is more efficient with TEDGA and follows this order: TEDGA > DEDMDGA > TMDGA > DEDPDGA. Partitioning of the ligand is logically increased as lipophilicity gets higher (from TMDGA to DEDPDGA). In general, all diglycolamide derivatives still show higher affinity for heavy lanthanides. Concerning the Am/Cm selectivity, the separation factor between both elements increases from TMDGA to TEDGA (from 1.9 to 2.3 in those conditions), but decreases for DEDPDGA. For lanthanides, the intra-group selectivity is optimal for TEDGA and lower for TMDGA. For the La/Eu separation factor for example, the selectivity is as follows: TEDGA (56) > DEDPDGA (25) > DEDMDGA (16) > TMDGA (5.6).

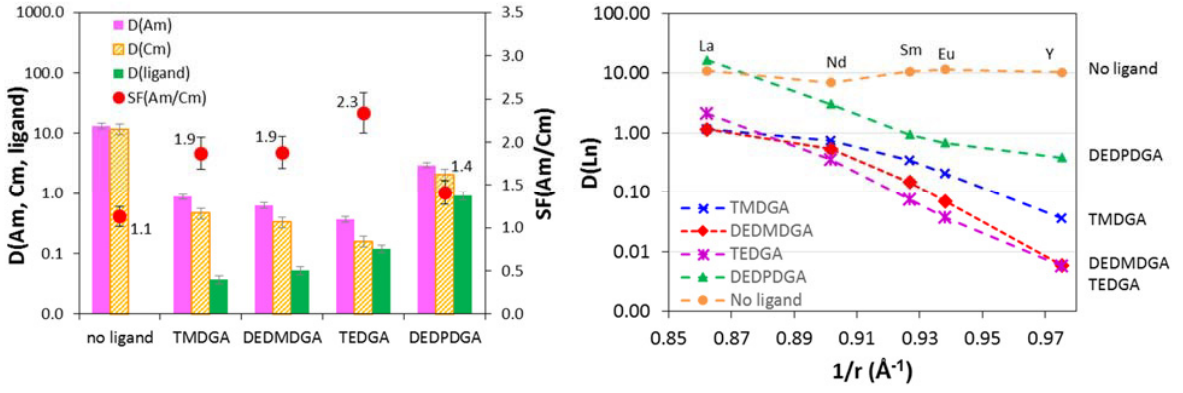

Fig. 5: Distribution ratios of lanthanides, Am, Cm, TEDGA and $SF_{Am/Cm}$ using 0.6 M DMDOHEMA and 0.45 M HDEHP diluted in TPH and 6 M HNO_3 (mixing 30 minutes, 25°C).

With this series of molecules, it may be observed that even slight changes on the ligand lipophilicity (addition or removal of two carbon atoms) changes significantly the intra-group selectivity. DEDPDGA with two additional carbon atoms shows higher affinity for the organic phase and lower Am/Cm selectivity. Compared to TEDGA speciation described in the first part, it could be assumed that complexes formed initially in the aqueous phase should be more extracted by the solvent. But in this case it does not allow to improve the selectivity, showing that among these ligands the properties of TEDGA are optimal to provide a favourable speciation of actinides (III) cations between the organic and aqueous phases.

4. Conclusion

In the EXAm process designed for selective recovery of americium from a PUREX raffinate, the use of TEDGA as a complexing agent allows to improve the americium / curium selectivity. This ligand has a higher affinity for the aqueous phase but has a tendency to partition into the solvent. According to speciation studies in the aqueous phase, TEDGA forms M^{3+}-TEDGA species with trivalent lanthanide and actinides cations involving one, two or three molecules of TEDGA surrounding the metal center. While 1:3 species are not extracted to the organic phase, 1:2 and 1:1 complexes can be extracted and form mixed species with the extractant DMDOHEMA. Using modelling of batch extraction data, it was possible to highlight that TEDGA forms more 1:3 complexes with curium compared to americium in the aqueous phase, and 1:1 complexes with americium (not taken into account at all for curium) leading to a higher extractability of Am-TEDGA species compared to curium. We believe that this difference in americium and curium speciation with TEDGA might be responsible for the improvement of selectivity observed by introducing TEDGA in the extraction system. The lipophilicity of the diglycolamide complexing agent was varied by changing the number of carbon atoms (n) on amide functions (lipophilicity). Especially, two new derivatives with two different alkyl chains on each amide function were synthesized and tested: *N,N'*-diethyl-*N,N'*-dimethyldiglycolamide (DEDMDGA) and *N,N'*-diethyl-*N,N'*-dipropyldiglycolamide (DEDPDGA). When increasing the lipophilicity as follows: TMDGA (n=4) < DEDMDGA (n=6) < TEDGA (n=8) < DEDPDGA (n=10), the ligand partitioning and americium/curium selectivity increase until n=8. With two additional carbon atoms, affinity for the organic phase is logically higher but selectivity drops slightly down. As a consequence, the diglycolamide TEDGA should remain the best compromise for the EXAm process as it provides the highest Am/Cm selectivity.

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