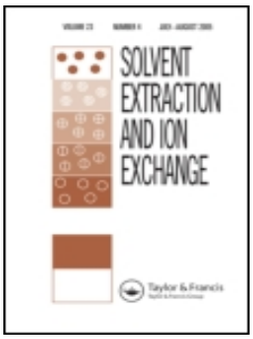

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NEW INSIGHT INTO THE AMERICIUM/CURIUM SEPARATION BY SOLVENT EXTRACTION USING DIGLYCOLAMIDES

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The liquid–liquid extraction process called EXAm was developed by the CEA to allow the recovery of Americium alone from a PUREX raffinate. Americium is extracted from a highly acidic feed solution (HNO_3 4–6 M) by a mixture of two extractants: DMDOHEMA and HDEHP. The Am/Cm selectivity is improved using a specific diglycolamide (TEDGA) as a selective aqueous complexing agent which retains preferentially Cm and heavier lanthanides in the aqueous phase. In this study, the impact of the lipophilicity and steric hindrance of several diglycolamides on the Am/Cm selectivity was investigated in order to understand the enhancement brought by TEDGA. For this purpose, liquid–liquid extraction and partitioning experiments were performed under various conditions.

Keywords: *americium, curium, lanthanides, solvent extraction, diglycolamides*

INTRODUCTION

In the future nuclear fuel cycle, one promising strategy considered by several countries for the management of high activity and long-lived final waste is a closed cycle supporting partitioning and transmutation. In the framework of the 2006 French Waste Management Act, several strategies were defined to totally or partially recycle minor actinides (An) from spent nuclear fuels in Generation IV systems.[1] After recycling U, Pu, and Np, the remaining long term radiotoxicity is mainly due to minor actinides, essentially americium and curium. It will take 10,000 years for wastes to reach the natural uranium radiotoxicity level instead of few centuries if americium and curium are removed.[2] Furthermore, after 100 years, americium is the main contributor to heat emissions in final spent fuel wastes. Hence, separating Am from the waste will decrease the heat source of the vitrified waste, optimizing the surface of the future deep geologic repository.[3,4] Moreover, Cm reprocessing would be difficult to implement due to very significant neutron emissions which would require very thick shielding at any step of the fuel cycle. Hence, one of the strategies considered is to recycle Am alone and leave Cm with vitrified fission

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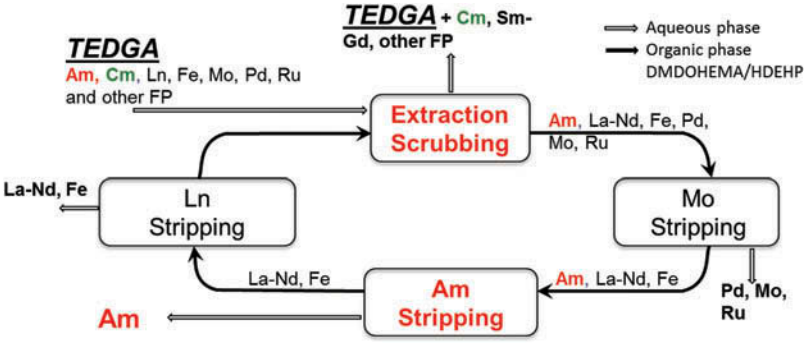


Scheme 1 Simplified scheme of the EXAm process.

products. A hydrometallurgical process, called EXAm (Extraction of Americium), was thus developed to separate Am alone from Cm and other fission products. Scheme 1 shows a simplified diagram of the EXAm liquid-liquid extraction process.[4]

The key step of this process is the extraction/scrubbing section where the americium/curium separation is achieved from a highly acidic aqueous phase (4-6 M HNO_3) with a mixture of a diamide (*N,N′*-dimethyl-*N,N′*-dioctyl-2((hexyloxy)ethyl)-malonamide, DMDOHEMA) and a dialkyl phosphoric acid (di-2-ethylhexylphosphoric acid, HDEHP) diluted in hydrogenated tetrapropylene (TPH).

Americium is extracted into the organic phase along with lighter lanthanides (Ln), some fission and activation products (Fe, Mo, Ru, Pd). After Mo stripping, Am is selectively back extracted from the solvent. Lanthanides are finally stripped and the solvent is recycled after specific acidic and basic washing treatment.

Separation between americium and curium is challenging because they have very close physico-chemical properties. To enhance the Am/Cm separation during the extraction/scrubbing section, the complexing agent *N,N,N',N'*-tetraethyl-diglycolamide (TEDGA) (Fig. 1) is added in the aqueous phase.[5]

The introduction of TEDGA raises the Am/Cm separation factor from 1.6 to 2.5 allowing a drastic reduction of the number of stages needed for the separation in a continuous process.[8] Cm is preferentially maintained in the aqueous phase with heavy lanthanides by complexation with TEDGA while Am is preferentially extracted in the organic phase with light lanthanides. An advantage is that diglycolamides (DGA) compounds are neutral donors, which can be used in acidic conditions and have demonstrated good radiolytic stability. For example, no degradation of TODGA was observed after gamma irradiation at 100 kGy.[6,7]

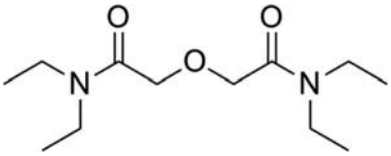


Figure 1 *N,N,N',N'*-tetraethyl-diglycolamide (TEDGA).

The origin of the Am/Cm selectivity enhancement brought by TEDGA in this separation system is still poorly understood. Charbonnel et al. confirmed using different speciation techniques that TEDGA has a higher affinity for heavy lanthanides explaining their lower distribution ratios in the extraction section of the EXAm process.[9] Moreover, we have previously shown that TEDGA forms (An, Ln)-TEDGA$_n^{3+}$ aqueous species (n = 1 to 3) that are partially extracted into the organic phase (n = 1 and n = 2 species only).[10] The distribution of TEDGA complexes might influence the Am/Cm selectivity and it was interesting to study if other DGA (with different alkyl chains than ethyl) show a similar behavior in order to confirm or not this suggestion.

The main objective in the present study is to try to establish a relationship between physico-chemical properties (lipophilicity/partitioning, steric hindrance . . .) of the DGA complexing agents and Am/Cm selectivity, but also to obtain a better understanding on TEDGA behavior during the separation. If An(TEDGA)$_n^{3+}$ species partitioning plays a role on Am/Cm selectivity, it might be possible to optimize it by further tuning the lipophilicity of the molecule. For this purpose, TEDGA complexant and six other diglycolamides (Fig. 2) were considered: *N,N,N',N'*-tetramethyl-diglycolamide (TMDGA), *N,N,N',N'*-tetrapropyl-diglycolamide (T*n*PDGA), *N,N,N',N'*-tetrabutyl-diglycolamide (T*n*BDGA), *N,N,N',N'*-tetra-*iso*-propyldiglycolamide (T*i*PDGA), *N,N,N',N'*-tetra-*iso*-butyl-diglycolamide (T*iB*DGA), *N,N,N',N'*-tetra-*sec*-butyldiglycolamide (T*sB*DGA). The diglycolamide skeleton was kept constant and the effect of the side chains length (methyl, ethyl, propyl, and butyl) and branching (*iso*-propyl, *iso*-butyl and *sec*-butyl) was studied regarding An(III) and Ln(III) extraction and Am/Cm selectivity.

The objective was to first introduce these ligands with cations (Ln^{3+}, Y^{3+}, and An^{3+}) in nitric acid (5–6 M) like in the EXAm process. But these initial conditions could be reached only if the ligand is sufficiently soluble in aqueous medium. By increasing the length of alkyl chains, the risk of course is to obtain ligands with a higher affinity for the organic than the aqueous phase. As a consequence, the more lipophilic derivatives could not be kept in the aqueous medium and it appeared interesting to evaluate them also as extractants directly in the organic phase. Hence, a second set of experiments was run with propyl and butyl derivatives in an organic diluent and the results were compared to performances of TODGA. The objective of those additional results was to identify the impact of structural modifications and especially branching on extraction performances.

Sasaki et al. has already shown that TMDGA and TEDGA solubilities in water are high (> 1 M) while T*n*PDGA and T*n*BDGA are less soluble (57 mM and 2.3 mM,

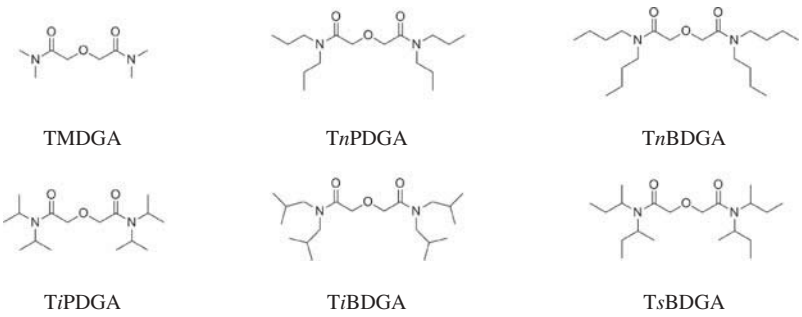


Figure 2 DGA synthesized and evaluated for Am/Cm separation.

respectively).[11] They have tested TMDGA and T*n*PDGA as water soluble complexing agents and distribution ratios of Am were determined with *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) in TPH as solvent.[12] On the other hand, T*n*PDGA, T*i*PDGA, and T*n*BDGA were tested as extracting molecules in an organic phase and extraction of Am was evaluated in different organic diluents such as chloroform, toluene, and benzene.[13] T*i*BDGA was also tested as Am extractant in a mixture of 1-octanol and kerosene (40/60 $\%_{vol.}$) by Tian et al.[14] The solubility and extraction properties of Am(III) by diglycolamides with different alkyl chains (ranging from *n*-propyl to *n*-dodecyl) attached to the amidic nitrogen atoms have already been studied by Sasaki and Mowafy[11,13,15] with branching chains, but to the best of our knowledge, no study has reported the influence of alkyl chains (side chain length and branching) of diglycolamides ligands on Am/Cm selectivity. The purpose of the current study is to evaluate the impact of side chain length and branching on diglycolamides performances and try to highlight some relationships between the structure and complexation/separation performances.

EXPERIMENTAL

Organic Synthesis

DGA derivatives were synthesized by nucleophile substitution of diglycolic acid chloride with the corresponding amine with overall yields ranging from 34 to 80% (Fig. 3). Compounds were purified by silica-gel chromatography using a mixture of cyclohexane and ethyl acetate. The purity of ligands (> 95%) was determined by NMR and GC-HRMS. The general procedure for the ligand synthesis and their characterizations are reported in supporting information. TMDGA, TEDGA and DMDOHEMA were purchased from Pharmasynthese, HDEHP from Sigma Aldrich, and TPH from NOVASEP. Other chemicals (analytically pure) were used without further purification.

Solvent Extraction

The aqueous solutions containing the DGA derivatives (30 mM) were prepared in nitric acid 6 M with 0.1 mM of La, Nd, Sm, Eu, and Y each (starting from the nitrate salts $Ln(NO_3)_3$, xH_2O). For Am/Cm separation studies, the aqueous solutions were spiked with ^{241}Am and ^{244}Cm (8,000–10,000 Bq/mL). The solvent was prepared by dissolving DMDOHEMA (0.6 M) and HDEHP (0.45 M) in TPH. For the second set of experiments with more lipophilic derivatives, the DGA extractants were dissolved at 20 mM in a mixture of 1-octanol/TPH 40/60$\%_{vol.}$ and the aqueous phase was the same but in HNO_3 1 M.

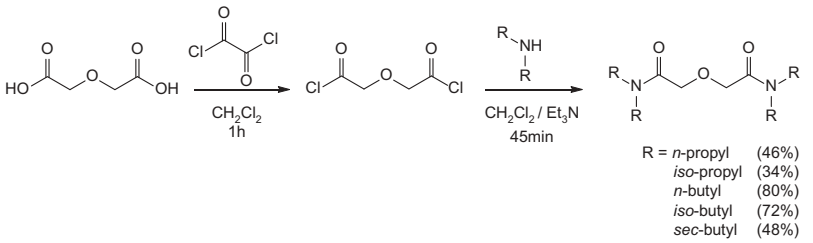


Figure 3 General synthesis of diglycolamide analogues.

Aqueous solutions were contacted until equilibrium was reached at 25 ± 1°C with equal volumes of organic phase ($V_{aq} = V_{org}$) by means of an automatic vortex shaker equipped with a thermostated cell. After phase separation by centrifugation, the aqueous phase was analyzed by ICP-OES. Cations in the organic phase were stripped by using a solution of TEDGA (0.2 M), oxalic acid (0.5 M), and HEDTA (0.07 M) in nitric acid (1 M) for 30 minutes at 25 ± 1°C and the aqueous solution was then analyzed by ICP-OES. The activities of ^{241}Am and ^{244}Cm in the aqueous and organic phases were analyzed using a gamma counting spectrometer (Hyper pure Ge detector, CANBERRA) to quantify ^{241}Am, and an alpha counting spectrometer (silicon detector, CANBERRA) to measure ^{244}Cm and ^{241}Am activities.

From the results obtained by ICP and radiometry, the distribution ratios ($D_M = [M^{n+}]_{org}/[M^{n+}]_{aq}$) and separation factors ($SF_{(M1/M2)} = D_{M1}/D_{M2}$) were determined at equilibrium. Extraction tests were performed in duplicate and errors reported in figures and tables were calculated from the standard deviation. It is assumed that performing only duplicates does not provide ideal statistics. Therefore, it should be considered that D-values between 0.1 and 10 exhibit a maximum error of about 5% while the error may be up to 10% for lower (0.01–0.1) and higher (10–100) values.

The concentration of complexing agent was quantified by HPLC using a non-polar stationary phase (ACCLAIM 120 C18 3 μM 4.6×150 mm) eluted at 1 mL/min by a mixture of water and acetonitrile (70/30) at 35°C. In aqueous samples, the concentration was determined after treatment with a solution of sodium oxalate (0.2 M) allowing the precipitation of cations, centrifugation, and dilution. For organic phases, the concentration was determined after back extraction with a solution of sodium oxalate (0.2 M) followed by centrifugation.

RESULTS AND DISCUSSION

Different diglycolamides with side chains length from methyl to butyl were evaluated for An(III) and Ln(III) extraction and Am/Cm selectivity. The influence of a symmetrical introduction of CH_3 substituents in the alpha (iso-propyl and sec-butyl) or beta (iso-butyl) positions of amide groups was also investigated in order to evaluate the influence of alkyl chains ramification on the extraction performances.

Tetrabutyl analogues are only slightly soluble in acidic medium, so they could not be evaluated as holdback reagent in the aqueous phase like methyl and propyl analogues. In regards to the hydrophilicity/lipophilicity balance of these ligands, two different sets of experiments were performed:

- The water soluble ligands (TMDGA, T*n*PDGA, and T*i*PDGA) were evaluated in aqueous phase with the EXAm solvent (DMDOHEMA/HDEHP in TPH) as the organic phase.
- Tetrabutyl analogues, poorly soluble in water, were evaluated as extractants in a mixture of 1-octanol/TPH.

Water Soluble Analogues

To enhance the precision on distribution ratios measurement and separation factors, experimental conditions were carefully chosen in order to reach D_M-values close to 1. To avoid precipitations, low concentrations of elements (La, Nd, Sm, Eu, and Y) were selected (about 0.1 mM for each cation) with 30 mM for the ligand concentration. With

low concentrations of cations, D_M decrease due to a high complexation effect of the ligands. As a consequence, the HNO_3 concentration was increased to 6 M to maintain D_M close to 1. Under these acidic conditions, it was observed that T*i*PDGA is quickly hydrolyzed. This phenomenon was highlighted by comparing HPLC chromatograms of T*i*PDGA solutions (30 mM) in pure water and 6 M HNO_3. Contrary to TMDGA, TEDGA, and T*n*PDGA, no UV signal corresponding to amide groups was detected in nitric acid solution of T*i*PDGA indicating a degradation of the ligand. The di-*iso*-propyl amine group is a better leaving group than di-*n*-propyl amine because of steric hindrance. The addition of *a* ramification on the N-alkyl chains might accelerate the hydrolysis by a steric effect. The other ligands were found stable in nitric acid even after 12 hours in 6 M HNO_3 and could be evaluated in these conditions.

Figure 4 shows D_M values for Am and Cm and $SF_{Am/Cm}$ obtained for TMDGA, TEDGA and T*n*PDGA as aqueous complexing agents in EXAm conditions (DMDOHEMA 0.6 M and HDEHP 0.45 M in TPH, HNO_3 6 M). The results were compared to the intrinsic properties of the EXAm solvent when the initial aqueous phase did not contain any ligand.

The results depicted in Fig. 4 show that the three ligands partially complex Am and Cm in the aqueous phase at 6M HNO_3 as D-values are lower than with the reference system without any ligand. The lowest distribution ratios are found with TEDGA, showing that TMDGA and T*n*PDGA must have a lower affinity for those cations. Both TMDGA and TEDGA improve the Am/Cm separation with a $SF_{Am/Cm}$ value higher than 1.4.[8] However, TMDGA is slightly less selective than TEDGA ($SF_{Am/Cm} = 1.8$ and 2.3, respectively). T*n*PDGA shows a $SF_{Am/Cm}$ close to 1 which is not only below tetramethyl and tetraethyl analogues but also under the SF obtained without complexing agent (1.4).

These results show that two carbons for the symmetrical alkyl chains attached to the amidic nitrogen atoms of the diglycolamide skeleton seems to allow an optimal Am/Cm separation in those conditions.

The selectivity of these ligands was also evaluated for several Ln and Y (Fig. 5). The data without complexing agent clearly show a strong extraction of rare earth cations by the EXAm solvent with D_M-values up to 10, but the solvent brings no selectivity between the different rare earth elements (REE) (no intragroup separation). In the presence of TMDGA

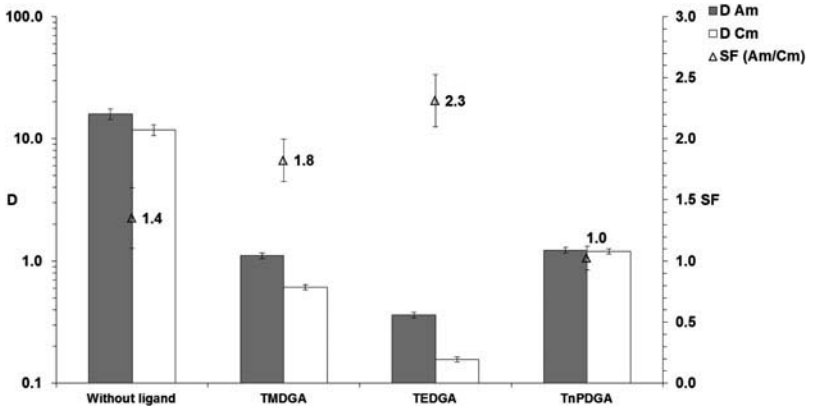


Figure 4 Distribution ratios and Am/Cm separation factors for some complexing agents. Organic phase: 0.6 M DMDOHEMA, 0.45 M HDEHP in TPH; Aqueous phase: 30 mM of ligand, 6 M nitric acid, 0.1 mM of each cation (La, Nd, Sm, Eu, Y) spiked with radiotracers (^{241}Am, ^{244}Cm).

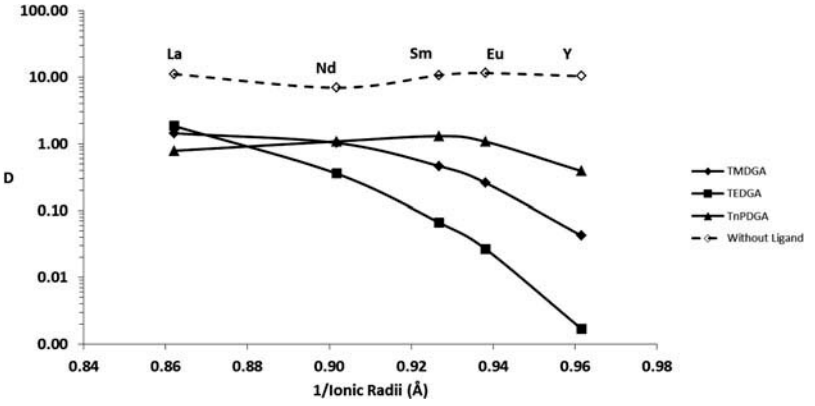


Figure 5 Distribution ratios of Ln(III) and Y(III) for some complexing agents. Organic phase: 0.6 M DMDOHEMA, 0.45 M HDEHP in TPH; Aqueous phase: 30 mM of ligand, 6 M nitric acid, 0.1 mM of each cation (La, Nd, Sm, Eu, Y) Ionic radii values were taken from Shannon (Acta Crystallogr. Sect. A 1976, 32, 751–767) and correspond to a coordination number of 8.

and TEDGA, distribution ratios of REE decrease with the decrease of ionic radius showing a higher affinity towards heavy lanthanides in agreement with the literature.[15,16] TEDGA exhibits the strongest masking effect on heavy lanthanides (lowest distribution ratios), while TMDGA behaves similarly but with a lower selectivity all along the lanthanide series. TnPDGA induces a lower extraction for all cations (compared to the reference without complexing agent) indicating a certain affinity but a very low selectivity.

In order to determine more precisely the ligand partitioning, the concentration of each DGA was evaluated by HPLC in both aqueous and organic phases at equilibrium. The corresponding distribution ratios ($D = [DGA]_{org}/[DGA]_{aq}$) are reported in Fig. 6. The objective of those additional analyses was to better understand the relationship between the hydrophilicity/lipophilicity balance of the complexing agent and the separation performances.

In attempts to find a logical interpretation of ligand partitioning, the results were related to partition coefficients values (log P). The partition coefficient P is a ratio of concentrations of compound between octanol and water. The log P value is known as a measure of lipophilicity ($\log P = \log([ligand]_{octanol}/[ligand]_{water})$) and could be predicted with ACD/Labs (PhysChem Suite 2014) for each ligand considered: TMDGA (−0.73),

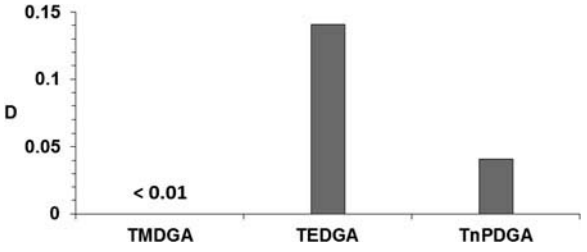


Figure 6 Partitioning of ligands analyzed by HPLC. Organic phase: 0.6 M DMDOHEMA, 0.45 M HDEHP in TPH; Aqueous phase: 30 mM of ligand, 6 M nitric acid, 0.1 mM of each cation (La, Nd, Sm, Eu, Y).

TEDGA (1.31), T*n*PDGA (3.35). According to those calculated values, the longer the alkyl chains are, the higher the affinity of the ligand for the organic phase should be.

Regarding our experimental results, TMDGA is poorly extracted in the EXAm solvent, which may be correlated to its higher polarity and hydrophilicity (log P = −0.73). The tetrapropyl analog shows higher D-values than TMDGA, which is also consistent with a lower hydrophilicity. But surprisingly, the highest partitioning value was found for TEDGA ($D_{TEDGA} = 0.14$). Since TEDGA partitioning does not simply follow a trend depending on its intrinsic lipophilicity, it is obvious here that additional mechanisms are involved which should be better understood.

Recently, experiments have shown that TEDGA can be extracted by the diamide DMDOHEMA and that its extraction is enhanced by the presence of Ln cations. The formation of mixed solvated $Ln(NO_3)_3$-$TEDGA_n$-DMDOHEMA (n = 1 or 2) in the organic phase was considered in order to model those extraction data. This proposed speciation in the organic phase is not a direct characterization of those mixed solvates but a possible interpretation of experimental data. Taking into account their formation was necessary to develop a phenomenological model allowing the prediction of Ln cations concentration profiles in the EXAm process.[10]

In order to better characterize extraction mechanisms involved in TEDGA transfer to the organic phase, additional sets of experiments were performed in various conditions where the distribution of TEDGA was determined using HPLC. The aqueous solution was made of 70 mM of TEDGA, either in pure water, HNO_3 (5–6 M) or with cations and was contacted with an equal volume of organic phase. The composition of the solvent was also varied to identify the role of each extractant (TPH, HDEHP/TPH, DMDOHEMA/TPH, or HDEHP/DMDOHEMA/TPH). After equilibrium was reached at 25°C, the aqueous phase was analyzed by HPLC in order to determine the remaining concentration of TEDGA in the aqueous phase (Table 1).

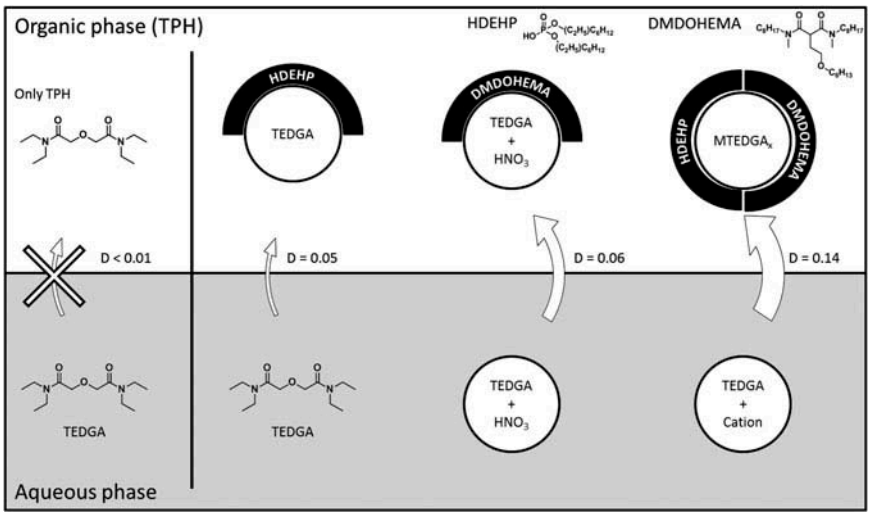
Without any extractant (experiment with TPH diluent alone) and any cations, TEDGA is not transferred to the organic phase ($D < 0.01$), even in the presence of nitric acid. As TPH is an aliphatic diluent, the absence of partitioning confirms that TEDGA has a relatively low lipophilicity according to the calculated logP.

From pure water, when DMDOHEMA was added as an extractant (0.6 M), the D_{TEDGA} was about 0.02 while with HDEHP alone (diluted at 0.45 M in TPH), the distribution ratio rose to 0.05. In pure water conditions, HDEHP extracts slightly more TEDGA than DMDOHEMA. With the EXAm solvent (HDEHP/DMDOHEMA/TPH), D_{TEDGA} is close to the value obtained with HDEHP alone, suggesting that starting from pure water, TEDGA would be mostly extracted by HDEHP. However, given the low D-values obtained and measurement uncertainties, this hypothesis should be taken with caution.

Starting from nitric acid only, TEDGA was not extracted by HDEHP, but slightly extracted by DMDOHEMA showing that in the EXAm solvent, TEDGA is extracted by the malonamide preferentially. A certain synergism might be induced by HDEHP when included in the solvent mixture with a distribution ratio of TEDGA increasing from 0.03 to 0.06. The partitioning of HNO_3 ($D_{HNO3} = 0.13$) was evaluated by potentiometric titration in another study and it was suggested that HNO_3 is also co-extracted by DMDOHEMA as an adduct with TEDGA {TEDGA-HNO_3}.[10] With cations, the D value of TEDGA increases (last entry of Table 1), probably due to the formation and co-extraction of Ln $(TEDGA)_n^{3+}$ species with DMDOHEMA and HDEHP, which is consistent with the literature.[10] Scheme 2 illustrates and summarizes the partitioning of TEDGA depending on the conditions.

Table 1 TEDGA partitioning depending on the presence of nitric acid and cations.

Aqueous phase	Solvent	D_{TEDGA}
Water without cations	DMDOHEMA (0.6M) + HDEHP (0.45M) in TPH	0.04
	TPH	< 0.01
	DMDOHEMA (0.6M) in TPH	0.02
	HDEHP (0.45M) in TPH	0.05
HNO_3 (5M) without cations	DMDOHEMA (0.6M) + HDEHP (0.45M) in TPH	0.06
	TPH	< 0.01
	DMDOHEMA (0.6M) in TPH	0.03
	HDEHP (0.45M) in TPH	< 0.01
HNO_3 (6M) La, Nd, Sm, Eu, Y (0.1mM of each cation)	DMDOHEMA (0.6M) + HDEHP (0.45M) in TPH	0.14



Scheme 2 Scheme of the TEDGA partitioning depending on the aqueous phase composition.

According to the low partitioning observed for T*n*PDGA even in the presence of cations, it can be assumed that co-extraction of the ligand together with cations does not occur with longer alkyl chains. Propyl chains might induce too much steric hindrance to allow the formation of adducts or mixed complexes with extractants in the organic phase. Since T*n*PDGA and TMDGA mostly remain in the aqueous phase, higher distribution ratios of cations obtained in the presence of those ligands should also indicate a weaker complexation of heaviest lanthanides and especially actinides in aqueous phase compared to TEDGA. In the EXAm process conditions, these results confirm that TEDGA seems to have the optimal amidic chains length on DGA skeleton to ensure optimized Am/Cm separation.

Tetrabutyl Analogues

Tetrabutyl analogues (T*n*BDGA, T*i*BDGA, T*s*BDGA) are only slightly soluble in water, even in presence of high concentrations of nitric acid, so they were evaluated as

extractants in the organic phase instead of aqueous ligands. The impact of steric hindrance in α (T*s*BDGA) or β (TiBDGA) position relatively to the nitrogen atoms was investigated in comparison to the analog with linear alkyl chains (T*n*BDGA) and also to tetraoctyl diglycolamide (TODGA) which is commonly used in many minor actinide separation processes.[11,15,17,18,19]

The organic solutions were composed of 20 mM of each extractant diluted in a mixture of 1-octanol/TPH 40/60 $\%_{vol.}$. The aqueous phase was prepared in 1 M nitric acid with 0.1 mM of each cation (La, Nd, Sm, Eu, and Y) and spiked with radiotracers (^{241}Am, ^{244}Cm). Distribution ratios and Cm(III)/Am(III) separation factors are reported in Fig. 7.

TODGA shows a $SF_{Cm/Am}$ of 1.2 with distribution ratios for Am and Cm close to 1. T*n*BDGA is a better extractant for Am and Cm due to its shorter alkyl chains, in agreement with the literature.[11] It also exhibits a slightly higher selectivity for Cm with a $SF_{Cm/Am}$ close to 1.5. The addition of steric hindrance in β positions of nitrogens with T*i*BDGA decreases the extraction of An and slightly the Cm/Am selectivity. In contrast, the introduction of steric hindrance in α positions of the nitrogens in the case of T*s*BDGA induces a drastic increase of Am and Cm distribution ratios (10 times higher than with linear butyl groups) but a loss of selectivity.

Extraction of Ln and Y was also assessed in the same conditions (Fig. 8). Extraction of lanthanides was higher for all the extractant molecules tested compared to TODGA. TODGA, T*n*BDGA and T*i*BDGA show selectivity towards heavier Ln, whereas T*s*BDGA has a different behavior: a flat bell shape was observed for distribution ratios along the 4f series with a poor selectivity between lanthanides (like between Cm and Am). It seems that the addition of branched alkyl chains with α ramifications involves a loss of selectivity towards the Ln. T*n*BDGA shows the same trend as TODGA with higher D-values for all cations, while the introduction of branched alkyl chains in β position (T*i*BDGA) decreases distribution ratios to values close to those obtained with TODGA. The extraction efficiency

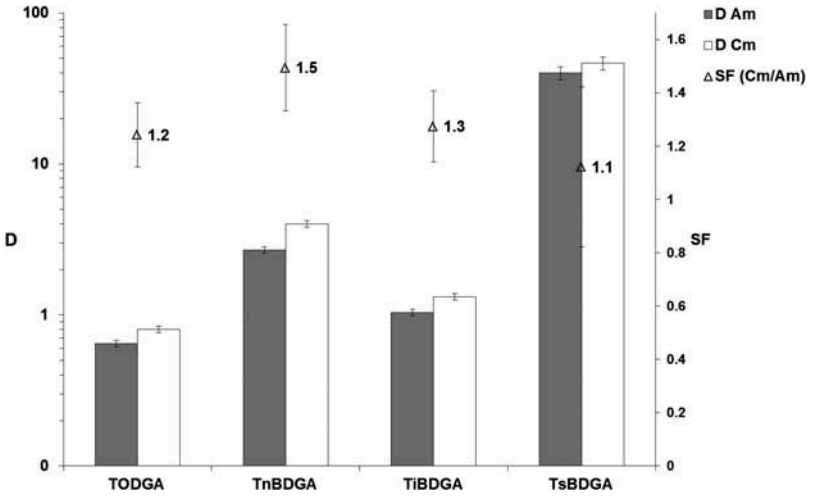


Figure 7 Distribution ratios and Cm/Am separation factors for different DGAs. Organic phase: 20 mM of extractant in 1-octanol/TPH 40/60 $\%_{vol.}$; Aqueous phase: 1 M HNO_3, 0.1 mM of each cation (La, Nd, Sm, Eu, Y) spiked with radiotracers (^{241}Am, ^{244}Cm).

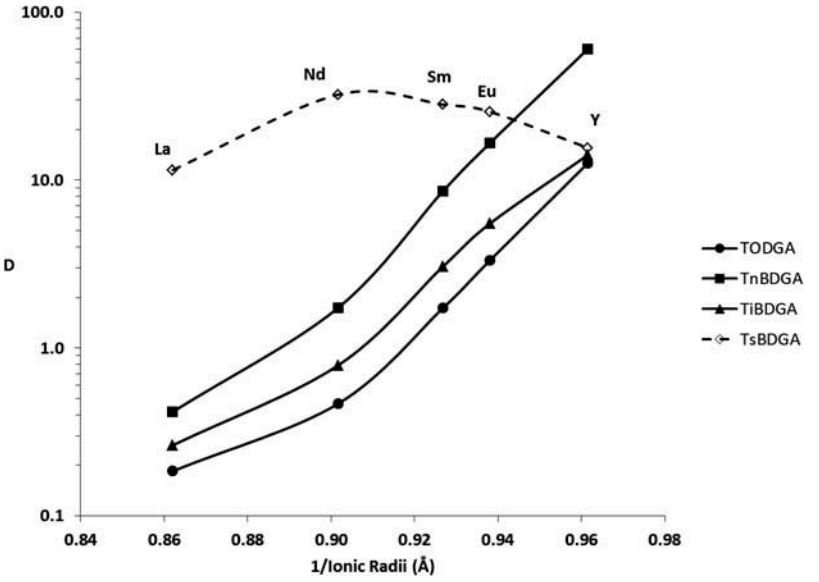


Figure 8 Distribution ratios of Ln(III) and Y(III). Organic phase: 20 mM of extractants in 1-octanol/TPH 40/60 $\%_{vol.}$; Aqueous phase; 1 M HNO_3, 0.1 mM of each cation (La, Nd, Sm, Eu, Y) Ionic radii values were taken from Shannon (Acta Crystallogr. Sect. A 1976, 32, 751–767) and correspond to a coordination number of 8.

is decreased by the introduction of β ramifications probably because of the steric hindrance but it does not impact significantly the selectivity.

CONCLUSIONS

TEDGA is the complexing molecule used in the EXAm process to selectively maintain Cm in the acidic aqueous phase while Am is extracted in the solvent. In this study, various derivatives of DGA were evaluated in order to study the influence of the side chains length and branching on Am, Cm and lanthanides extraction and selectivity. Understanding the relationship between the structure and the affinity/selectivity of a ligand is a very challenging task. The objective here was to study a series of molecules with simple structural changes to better identify its impact on Am/Cm selectivity.

The DGA series with short linear chains (TMDGA, TEDGA, T*n*PDGA) were tested as hydrophilic complexing agents in HNO_3 6 M with the EXAm solvent (DMDOHEMA 0.6M and HDEHP 0.45 M in TPH). In EXAm process conditions, all the aqueous complexing agents show a high chelating ability towards Am and Cm. The experiments demonstrate that 2 carbons (ethyl groups) are the optimum symmetrical alkyl chains length to reach interesting Am/Cm selectivity in EXAm process conditions. If shorter alkyl chains are introduced (TMDGA) the selectivity is lower, while with longer chains the selectivity is almost totally lost (T*n*PDGA).

This study has also confirmed the complexity of TEDGA partitioning. Indeed, TEDGA must be co-extracted with Ln/An cations forming mixed solvates of different stoichiometries in the organic phase with DMDOHEMA. The partitioning of T*n*PDGA was less important than with TEDGA despite its higher lipophilicity. Hence, it can be assumed

that T*n*PDGA is probably not co-extracted with cations and does not form any mixed solvate with DMDOHEMA in the organic phase. In contrast, the complex speciation described for TEDGA (partitioning of $Ln(Ligand)_n^{3+}$ species) probably plays an important role on the TEDGA partitioning and likely on Am/Cm selectivity.

The linear and branched tetrabutyl derivatives (T*n*BDGA, T*i*BDGA, and T*s*BDGA) were evaluated as extractants in the organic phase (1-octanol/TPH 40/60 $\%_{vol.}$) due to their higher lipophilicity. It was shown that β ramifications (T*i*BDGA) decrease Am and Cm extraction instead of α ramifications (T*s*BDGA) which improve distribution ratios but lead to a loss of selectivity between Am and Cm as well as on the Ln series. Considering the results obtained, it would be interesting to perform specific speciation studies with TsBDGA and other alpha branched DGA.

Further studies are in progress to determine more precisely the TEDGA chemistry in this process, especially by acquiring additional liquid/liquid batch extraction data and improving the thermodynamic model. Complexation and speciation studies will also be continued in order to characterize more precisely this complex chemical system and be able to predict the behavior of Ln and An cations, but also TEDGA in the process.

SUPPLEMENTAL MATERIALS

Supplemental data for this article can be accessed on the publisher's website.

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