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Behaviour of the extractant Me-TODGA upon gamma irradiation: quantification of the degradation compounds and individual influences on complexation and extraction

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Diglycolamides (DGAs), and in particular N,N',N",N"'-tetracetyl diglycolamide (TODGA), are well-known candidates for the co-extraction of trivalent actinides (An(III)) and lanthanides (Ln(III)) from highly acidic aqueous solutions of nuclear waste. A derivative of TODGA, the so-called Me-TODGA with the addition of a methyl-substituent on the central part of the TODGA molecule, has been proposed to improve its stability properties and extracting behaviour. This work describes the stability and viability of Me-TODGA by studying the properties of its degradation compounds formed upon gamma irradiation. The main degradation products have been synthesised and studied individually. Particular attention has been paid on their quantification, as well as complexing and extracting properties, for a better understanding of the degradation pathways and the behaviour of the solvents upon gamma irradiation. The extraction behaviour of the irradiated Me-TODGA solvents and its degradation compounds have been studied toward the fission products and lanthanides present in a highly active raffinate (HAR) solution. Binding properties of the parent molecules (TODGA and Me-TODGA) and their main degradation compounds with Ln(III) have also been determined in homogeneous phase. All the results obtained on degradation compounds are compared with those of the parent molecules in order to assess the effects of these compounds on the separation process. Among the radiolytic compounds, 2-hydroxoyctylamides are the most problematic compounds because of their high affinity to lanthanides but also to other fission products.

Introduction

For many years, efforts have been made to develop partitioning and recycling processes for used nuclear fuel in order to reduce the long-term radiotoxicity and heat load of nuclear waste. The current industrial Plutonium Uranium Reduction Extraction (PUREX) process, which allows the recovery of uranium and plutonium, could be followed by different processes (DIAMEX, SANEX, i-SANEX) proposed to separate long-lived trivalent minor actinides from the highly active raffinate. Among the molecules designed and tested, tridentate diglycolamides (DGAs) and in particular N,N',N",N"'-tetracetyl diglycolamide (TODGA) (Fig. 1) showed good extraction abilities for the first step which is a co-separation of trivalent actinides (An(III)) and lanthanides (Ln(III)) from highly concentrated nitric acid solutions. Recently, TODGA derivatives with additional methyl-substituents in the DGA backbone were studied and found to be interesting alternatives to TODGA, especially methyl-TODGA (Me-TODGA in Fig. 1). The objective of such a modification (introduction of a methyl group between the ether and an amide moiety) is the increase of its radiolytic stability and the improvement of the stripping behaviour.

Fig. 1 Chemical structures of TODGA and Me-TODGA.

To evaluate the applicability of new solvents for process development in the nuclear field, the important properties to check are their good extraction abilities, but also their hydrolytic and radiolytic stability since the extracting systems will be in contact with highly radioactive aqueous solutions and high nitric acid concentrations. The presence of degradation products may lead to undesirable effects such as decrease of performances (extraction efficiency and selectivity), or deterioration of physical properties.
(third phase formation). The addition of a regeneration process to avoid (or limit) such behaviour could increase the volume of the secondary waste and the process costs. Most often, the new species generated have extracting properties that markedly differ from those of the original ligands and can have an impact on the long-live radioactive waste management and safety.

A methodology for studying the stability of DGAs as selective extractants of Am(III) and Ln(III) was previously set up, involving a complete characterization by HPLC-MS of irradiated samples. This methodology allowed exploring the degradation process with an identification and quantification of the degradation products formed during the irradiation. It has been applied to TODGA solvents to get a complete set of data, to assess how and why the experimental conditions can affect the proportions and amounts of degradation products. Among others, these studies have shown a double protective role of nitric acid on the stability of diglycolamide-based ligands. The acid medium (H+) provides a protective effect on the O-C bond, which was found to be the weakest bond of the molecule and on the other hand, nitrate ions would act as scavengers of reactive species formed during gamma irradiation as described in related work. Recently, the radiolytic stability of TODGA, Me-TODGA and Me₂-TODGA has also been published pointing out the effect of the additional methyl group(s) in the diglycolamide structure. The addition of one methyl group seems to increase the degradation rate constant of DGAs, favoring the rupture of one of the O-C bonds over the other. Analytical methods based on LC-MS and especially Atmospheric Pressure Chemical Ionization (APCI), a generally weak ionization method, have been used to identify and quantify the degradation products formed during the irradiation process for TODGA and Me-TODGA degraded samples in TPH as diluent. Considering the main chromatographic peaks and assigned structures, Me-TODGA samples gave rise to ten degradation compounds due to radiation damage and hydrolytic degradation of amide groups. Based on the intensities of the peaks corresponding to compounds 1, 2, 3 and 4 (the main degradation compounds), the rupture of the ether linkage was proposed with paths ‘a’ and ‘b’ as shown in Fig. 2. The rupture path ‘a’ with the formation of 1 and 2 compounds was found to be preferred. Koubský et al. studied the radical degradation of TODGA and the methylated analogues using quantum chemistry. Although their findings for the degradation of Me-TODGA were ambiguous taking into account DFT energy levels, calculation at the Hartree-Fock level of theory gave a clear preference for degradation path ‘a’.

The present work, which should be noticed as a continuation of Galán et al., delves into a complete characterization of Me-TODGA degraded solvents, irradiated by an external Co source under different irradiation conditions. In the previous publication, only the parent molecule was well quantified, while the quantity of degradation products was only evaluated from the intensities observed in the LC-MS analysis. Therefore, in this study, a particular attention is paid on the quantification of the degradation products formed during the irradiation process. The second part of this paper is focused on the extraction properties of the irradiated Me-TODGA. To better understand the variation of extraction of Am(III), Ln(III) and some fission products (FPs), the synthesis of various identified radiolysis fragments was performed and the extraction behaviour of such individual degradation products solutions was followed. Microcalorimetric studies were also carried out to better describe the thermodynamic properties related to the extraction, but also the complexion of lanthanides with the parent molecules (TODGA and Me-TODGA) and some of their degradation compounds.

**Experimental**

**Reagents and chemicals**

Reagents and chemicals for the synthesis of compounds and intermediates were purchased from commercially available sources without further purification. Solvents were reference distilled and dried before use by standard methods. CH₃CN and HCOOH were of HPLC-MS quality grade. The diluent TPH (hydrogenated tetrapropene) was supplied by CEA, Marcoule. Nitric acid was purified by Quartz sub-boiling distillation system (MLS- Milestone), which solutions were prepared by diluting the concentrated nitric acid obtained with ultrapure water (18 MΩ-cm). Methanol, 1-octanol, n-dodecane used for microcalorimetry were bought from Sigma Aldrich and of 99.9% purity. The metal salts La(NO₃)₃·6H₂O, Eu(NO₃)₃·6H₂O and Yb(NO₃)₃·xH₂O (Alfa Aesar, 99.99%) were dried under vacuum before use, and the concentration of lanthanides in solutions was determined by spectrophotometric titrations with Titrplex III and Xylenol orange as indicator. Titrplex complexing agent was bought from Merck and color indicator Xylenol orange from Riedel-de-Haen.

The radionuclides ²⁶⁰Am and ¹⁵²Eu were supplied by Isotope Products Laboratories, California (USA) and by Isotopenlieferant M. Blaseg GmbH, Waldburg, Germany and Eckert and Ziegler Nuclitec GmbH, Braunschweig, Germany. For the selectivity study the aqueous solutions were prepared with a 10 vol% dilution of simulated HAR solution in 3 or 4 mol L⁻¹ HNO₃. The synthetic HAR solution used corresponds to a PUREX raffinate with a volume of 5000 L t⁻¹ UOX fuel with an initial 23⁵U enrichment of 3.5%, thermal burn-up of 40 GWd⁰t⁻¹ and 3 years cooling. The synthetic PUREX raffinate was prepared by a specific dissolving strategy, mainly based on the use of metal nitrate salts. Its composition was described in a previous work.
Gamma irradiation

Organic solutions of TODGA and Me-TODGA were prepared by dissolving the appropriate amount of each of them, up to 0.1 mol L⁻¹ in TPH at 23 ± 2 °C. Before use, the organic solutions were pre-equilibrated twice with nitric acid solutions by vigorous stirring for 5 min (600 µL of organic solution and the same volume of 3 mol L⁻¹ nitric acid). The phases were separated by centrifugation at 5000 rpm and sent to the Náyade, which is the gamma-irradiation facility at CIEMAT. It consists of a pool of 1.2 m³ by 4.5 m depth with ⁶⁰Co sources distributed in six lots with a total activity of 1.1 × 1⁰¹⁴ Bq. The irradiation container used provides a homogeneous irradiation flux. The samples were irradiated up to 250, 500, 750 and 1000 kGy at dose rates of 1.78 and 6.32 kGy h⁻¹. No volume decrease was observed during irradiation, hence evaporation of the solvent is assumed to be negligible. The glass bottles were then stored in a freezer while awaiting further analyses. Reference samples for aging control were kept in the laboratory during the irradiation process.

HPLC-DAD/MS measurements

The chemical composition of the irradiated samples was characterized by HPLC-DAD/MS (Agilent 1100, Quadrupole detector 6120A at CIEMAT). The measurements were performed by using a Prontosil C-8 column (50 x 2 mm, 5 µm) at 40 °C using a gradient of mobile phase ([A: 0.1% v/v CH₃CN/HCOOH], [B: 0.1% v/v H₂O/HCOOH]) in the APCl³ ionization mode (SCAN 100 a 1500 umas /SIM). The mass spectrometer conditions were: capillary voltage: 2000 V; Corona current: 5 µA; charging voltage: 2000 V; positive mode; dry temp.: 250 °C; vaporization temp 200 °C; nebulizer gas and dry gas were both N₂; nebulizer pressure: 1.4 bar; dry gas flow rate: 5 L/min. Samples were analyzed without pre-evaporation and diluted up to 0.5 and 1.0 mmol L⁻¹ in a 90:10 v/v MeOH/1-octanol mixture. All measurements were repeated twice.

Synthesis of the compounds and intermediates

¹H- and ¹³C-NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. ESI mass spectra were recorded on a WATERS LCT mass spectrometer.

N,N-Diocyl propionamide (3)

To a solution of sodium hydroxide (1.04 g, 26 mmol, 10 equiv) in water (25 mL) was added diocylamine (0.62 g, 2.6 mmol) at 0 °C under vigorous stirring. Subsequently, a solution of propionyl chloride (0.96 g, 10.4 mmol, 4 equiv) in ethyl acetate (30 mL) was added dropwise to the suspension at that temperature, whereupon it was reacted for 3 h at room temperature. After separation of the layers, the organic layer was washed with 5% NaHCO₃ solution (3 x 50 mL) and water (2 x 50 mL), dried with MgSO₄. Removal of the solvent gave the pure compound as an oil in 93% yield. 

¹H NMR (400 MHz, CDCl₃) δ 3.25–3.19 (m, 2H), 3.15–3.09 (m, 2H), 2.24 (q, J = 7.4 Hz, 2H), 1.51–1.39 (m, 4H), 1.28–1.13 (m, 20H), 1.07 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.3, 48.0, 46.0, 31.9 (2x), 29.5, 29.4 (2x), 29.3, 29.2, 27.9, 27.2, 27.0, 26.4, 22.7 (2x), 14.2 (2x), 9.8. ESI-MS: m/z 298.2 [M+H⁺]; ESI-HRMS: m/z 298.3046 [M+H⁺]; calculated 298.3110 for C₁₅H₃₂NO.

N-Octyl propionamide (7) was prepared in a similar way as compound 3 starting from sodium hydroxide (2.10 g, 52.6 mmol), octylamine (0.68 g, 5.3 mmol) and propionyl chloride (1.95 g, 21.0 mmol) as an oil in 96% yield. 

¹H NMR (400 MHz, CDCl₃) δ 5.40 (br s, 1H), 3.24 and 3.23 (t, J = 7.2 Hz, 2H), 2.19 (q, J = 7.6 Hz, 2H), 1.53–1.44 (m, 2H), 1.33–1.23 (m, 10H), 1.15 (t, J = 7.6 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 39.7, 31.9, 30.0, 29.8, 29.4, 29.3, 27.1, 22.8, 14.2, 10.1; ESI-MS: m/z 186.2 [M⁺H⁺]; ESI-HRMS: m/z 186.1869 [M⁺H⁺]; calculated 186.1858 for C₁₃H₂₃NO.

2-Bromo-N,N-dioctylpropanamide (11)

A solution of Et₂N (3.3 g, 33 mmol, 1.3 equiv) and diocylamine (5.9 g, 24.5 mmol, 0.98 equiv) in Et₂O (150 mL) was added dropwise to a solution of 2-bromopropionyl bromide (10; 5.4 g, 25 mmol, 1 equiv) and Et₂N (0.5 g, 4.9 mmol, 0.2 equiv) in dry Et₂O (200 mL) at 0 °C. After stirring for 2 h at room temperature, the solid was filtered off and the liquid phase evaporated. The residue was dissolved in Et₂O (100 mL) and washed with 10% HCl (3 x 100 mL). After filtration, the solution was dried with MgSO₄ and the solvent evaporated under reduced pressure to give the product (1.82 g, 99%) as an oil. 

¹H NMR (400 MHz, CDCl₃) δ 5.42 (q, J = 6.6 Hz, 1H), 3.61–3.39 (m, 2H), 3.17–3.01 (m, 2H), 1.81 (d, J = 6.6 Hz, 3H), 1.74–1.61 (m, 1H), 1.61–1.45 (m, 3H), 1.36–1.17 (m, 20H), 0.88 (q, J = 6.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 77.2, 48.2, 46.6, 38.7, 31.8, 31.75, 29.6, 29.4, 29.3, 29.2 (2x), 27.2, 26.9, 22.7, 22.6, 21.8, 14.1 (2x); ESI-MS: m/z 376.3 [M⁺H⁺]; ESI-HRMS: m/z 376.2627 [M⁺H⁺]; calculated 376.2137 for C₂₃H₄₃BrNO.

2-Acetoxy-N,N-dioctylpropanamide (12)

A suspension of 2-bromo-N,N-dioctylpropanamide (11; 0.48 g, 1.26 mmol, 1.4 equiv), potassium acetate (0.5 g, 0.55 mmol, 4 equiv) and 18-crown-6 (10 mg, 0.04 mmol, 0.03 equiv) in dry acetonitrile (10 mL) was refluxed for 5 h. The reaction mixture was filtered through celite and the solvent evaporated. The solid residue was dissolved in Et₂O (30 mL) and washed with water (3 x 20 mL). The organic solution was dried with MgSO₄ and the solvent evaporated to afford pure 12 (0.47 g, 94%) as an oil. 

¹H NMR (400 MHz, CDCl₃) δ 5.30 (q, J = 6.7 Hz, 1H), 3.48–3.38 (m, 1H), 3.32–3.12 (m, 3H), 2.11 (s, 3H), 1.76–1.62 (m, 1H), 1.63–1.46 (m, 1H), 1.43 (d, J = 6.7 Hz, 3H), 1.38–1.19 (m, 20H), 0.94–0.82 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 169.9, 77.2, 67.0, 47.6, 46.3, 31.8 (2x), 29.3 (2x), 29.25, 29.2, 29.0, 27.5, 26.9 (2x), 22.7, 22.6, 20.9, 17.3, 14.1. ESI-MS: m/z 356.3 [M⁺H⁺]; ESI-HRMS: m/z 356.3131 [M⁺H⁺]; calculated 356.3086 for C₂₃H₄₂NO₃.

2-Methoxy-N,N-dioctylpropanamide (13)

A solution of 2-hydroxy-N,N-dioctylpropanamide (1; 500 mg, 1.6 mmol, 1 equiv) in dry THF (15 mL) was added dropwise to a suspension of NaH (96 mg, 2.4 mmol, 1.5 equiv) in dry THF (20 mL) at 0 °C, whereupon the suspension was stirred at room temperature for 1 h. Subsequently, MeI (150 µL, 335 mg, 2.4 mmol,
1.5 equiv) was added and the mixture was stirred overnight. After evaporation of the solvent, the residue was dissolved in Et₂O (30 mL), and the resulting solution was washed with saturated NH₄Cl (3 x 30 mL), dried with MgSO₄, and the solvent was evaporated under reduced pressure. The residue was passed through a short pluck of silica (hexane : ethyl acetate = 3:1) to afford the product (420 mg, 80%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ 4.14 (q, J = 6.6 Hz, 1H), 3.42–3.20 (m, 4H), 3.31 (s, 3H), 1.64–1.47 (m, 4H), 1.36 (d, J = 6.6 Hz, 3H), 1.34–1.20 (m, 20H), 0.96–0.80 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 171.4, 77.2, 75.1, 56.4, 45.95, 31.8 (2x), 29.4, 29.3 (3x), 29.2, 27.5, 27.1, 26.9, 22.6, 17.8, 14.1. ESI-MS: m/z 328.3 [M+H⁺]; ESI-HRMS: m/z 328.3190 [M+H⁺]; calculated: 328.3137 for C₁₀H₂₈NO₂.

Solvent extraction studies
Organic solutions of degradation compounds were prepared by dissolving the appropriate amount of each of them, up to 0.1 mol L⁻¹ in TPH. The extraction experiments were performed by mixing 500 μL of both, the organic and the aqueous phase at room temperature (22 ± 2 °C) for 15 or 60 min, respectively. After centrifugation (2,500 or 5,000 rpm), the phases were separated and aliquots of each phase (300 μL) were taken for analysis. Used HPGe detectors were supplied by Canberra electronics or EG&G Ortec, equipped with the Genie-2000 or Gamma Vision software, respectively. The gamma lines at 59.5 keV (35.9%) and 121.8 keV (28.4%) were analyzed for radioactive elements present in the samples. Changes in enthalpies also include the heat of dilutions. Hence, a blank experiment with the addition of metal solution into 2.5 mL of pure solvent (methanol in this case) was done in order to obtain the enthalpy values related to the complexation reaction. The overall stability constants (β) and the enthalpies of complexation (ΔH°C) were refined simultaneously from the recorded data using the ligand binding analysis program DIGITAM version 4.1. The corresponding overall entropies of complexation (ΔS°C) were calculated from the expression ΔG°C = ΔH°C − TΔS°C, knowing that ΔG°C = −RT ln β. Chemical calibration was made by determination of the complexation enthalpy of Ba²⁺ with 18C6 in water or of Rb⁺ with 18C6 in methanol, as recommended.

Microcalorimetry and van’t Hoff studies
Microcalorimetric titrations were performed at 25.00 ± 0.05 °C using a 2277 thermal activity monitor microcalorimeter (TA instruments).

Liquid-liquid extraction of metal (Nd³⁺ and Yb³⁺) from an aqueous phase to an organic phase containing the ligand was performed as follows: 500 μL of an aqueous phase (0.06 mol L⁻¹ of metal nitrate in a solution containing 0.1 mol L⁻¹ HNO₃ and 0.9 mol L⁻¹ LiNO₃ (1 = 1 mol L⁻¹)) and 300 μL of an organic phase (0.1 mol L⁻¹ TODGA or Me-TODGA in a mixture of n-dodecane/1-octanol (95/5)) were introduced in a calorimetric cell. Each titration experiment consisted of 10 injections of 15 μL of the organic phase containing 0.1 mol L⁻¹ of ligand. Prior to microcalorimetry titration, organic phases were pre-equilibrated with an identical aqueous phase without the metal cation. In order to respect the equilibrium kinetics, the time of the measurement was set to 90 minutes between each addition. The aqueous phase was sampled after the calorimetric run and analyzed by ICP-AES to determine the amount of metal cation transferred into the organic phase. The global heat of reaction has to take into account the multiple reactions that occur in the cell during the extraction process, and especially the dilution of both phases during the extraction process. These additional heats have to be identified, measured, and subtracted from the titration heat thermogram in order to assess the extraction heat. The measurement of the heat released during the extraction led to the determination of the enthalpy change ΔH°C. Knowing the ΔG°C value, it is possible to calculate the entropy change ΔS°C.

Results and discussion
To study the Me-TODGA degradation products, irradiation experiments as described in ref. 20 were deepened and were carried out at the Náyade facility at 23 ± 2 °C, with an integrated dose up to 250, 500, 750 and 1000 kGy, at 1.78 and 6.32 kGy h⁻¹ dose rates. After irradiation, no precipitate was observed, but the samples got a slightly yellow color when the integrated dose increased. This effect was especially observed for samples irradiated at low dose rate, since more time was necessary to get an integrated dose of 1000 kGy.

Fig. 3 shows the qualitative HPLC-DAD analysis of Me-TODGA samples irradiated with 6.32 kGy h⁻¹. At 250 kGy the chromatogram shows the presence of at least ten new peaks corresponding to the degradation compounds formed. The intensity of these new signals increased with the integrated dose (marked as circles in Fig. 3), while the Me-TODGA signal decreases, a result in agreement with previous work on m-xylene bis-diglycolamide. However, it is important to mention that the minor degradation compounds

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observed at 250 kGy, marked as stars in Fig. 3, disappear as the integrated dose increases. This behaviour indicates that the initial compounds are sensitive to irradiation, which was not observed with irradiated TODGA samples. These results are in good agreement with our previous work.\textsuperscript{20}

![HPLC-DAD chromatograms of aging and irradiated Me-TODGA samples](image)

Fig. 3 HPLC-DAD chromatograms of aging and irradiated Me-TODGA samples, irradiated at 6.32 kGy h\textsuperscript{-1} in 100% TPH pre-equilibrated with 3 mol L\textsuperscript{-1} HNO\textsubscript{3} (circles indicates compounds with increasing intensity, stars indicate compounds with decreasing intensity).

**Synthesis of the studied compounds**

Among all the Me-TODGA degradation compounds identified, nine molecules (1 to 9 Fig. 4) were synthesized to verify their structures, quantify them in the irradiated solutions and to study their influence in a liquid-liquid extraction process. The extraction properties, third phase formation and behaviour during the stripping step were followed. To compare the TODGA and Me-TODGA radiolytic behaviour, the degradation compound I (TODGA degradation product obtained by the loss of one octyl group) was also synthetized. A similar degradation was identified with Me-TODGA,\textsuperscript{20} however, the related chromatographic peaks (at 14.9 and 15.7 min in Fig. 3) disappear as integrated dose increases. The structures of the synthesized and individually studied degradation products are summarized in Fig. 4.

![Structures of the degradation products of Me-TODGA (1 to 9) and TODGA (I)](image)

Fig. 4 Structures of the degradation products of Me-TODGA (1 to 9) and TODGA (I).

TODGA was synthesized with a modified route compared to the published one, working under air atmosphere and without drying solvents and glassware.\textsuperscript{17,20} Me-TODGA was synthesized following the methodology described before.\textsuperscript{14} Compounds 1, 2, 4, 5, 6, 8 and 9 were prepared according to the procedure described in previous works.

\(\text{N,N-dioctyl-(3)}\) and \(\text{N-octyl propionamide (7)}\) were prepared by reaction of propionyl chloride and the proper amine using Schotten-Baumann conditions in 93 and 96% yield, respectively.

To better study the possible influence of the hydroxyl group in propanamide 1, 2-acetoxy (12) and 2-methoxy-N,N-dioctylpropanamide (13) were also prepared as summarized in Scheme 1. 2-Bromopropionyl bromide 10 was reacted with dioctylamine to give propanamide 11 in 99% yield. Subsequent reaction of 11 with potassium acetate in the presence of 18-crown-6 gave the target compound 12 in 94% yield. In its \(^1\text{H}\) NMR spectrum the CH\textsubscript{2}Cl(O) peak is at \(\delta 2.11\), while the CHC(O) signal shifted from \(\delta 4.52\) (q) in 11 to \(\delta 5.30\) (q) in 12 and the CHCH\textsubscript{3} methyl absorption shifted from \(\delta 1.81\) (d) to \(\delta 1.43\) (d). Saponification of the ester moiety in 12 with sodium methoxide afforded 1 in 93% yield, which was reacted with methyl iodide in the presence of NaH as a base to afford 13 in 80% yield. The \(^1\text{H}\) NMR spectrum exhibits a characteristic singlet for the methoxy group at \(\delta 3.31\), while in this case the CHCH\textsubscript{3} resonates at \(\delta 4.14\) (q) and \(\delta 1.36\) (d).

![Synthesis of 2-acetoxy- (12) and 2-methoxy-N,N-dioctylpropanamide (13)](image)

Scheme 1 Synthesis of 2-acetoxy- (12) and 2-methoxy-N,N-dioctylpropanamide (13).
Quantification of Me-TODGA degradation products

The new results obtained with these synthesized degradation compounds confirmed the main bond ruptures (Fig. 2) as well as the structure of the identified compounds due to both degradation pathways, hydrolytic degradation of amide groups and radiolysis damage.20

Fig. 5 shows the results obtained from quantitative HPLC-MS analysis of a 0.1 mol L⁻¹ solution of Me-TODGA in TPH after 1000 kGy irradiation with two different dose-rates (1.78 and 6.32 kGy h⁻¹). The concentration of the degradation compounds confirms the preference of degradation path ‘a’ in Fig. 2, since the amounts of 1 and 2 are higher than those of 3 and 4. These findings support the assumption that the introduction of an additional methyl group in the diglycolamide backbone increases the radiolytic resistance of the substituted C-O linkage.

Solvent extraction behaviour

Extraction of Ln and fission products by degradation products.

The extraction of Am(III) and Eu(III) using irradiated Me-TODGA solvent was assayed by contacting the solvent with ²⁴¹Am and ¹⁵²Eu spiked tracer solutions. The distribution ratios obtained with reference, aging and irradiated Me-TODGA samples are represented in Fig. 6. The low influence of dose rate could be explained by the low hydrolytic degradation in an apolar diluent such as TPH, where hydrolysis reaction is not favored. The radiolytic degradation effect can be observed from 250 kGy where the D₄₃ values decrease progressively for Am(III) and Eu(III) at both dose rates (1.78 and 6.32 kGy h⁻¹). Previous studies estimated that after around 1-2 years of operation of the DIAMEX process (which is also a first step after PUREX), the organic phases will be exposed to around 800 kGy.13 Me-TODGA (as TODGA) systems show a sufficient extraction capability (1 < D < 10) for Am(III) and Eu(III) even after 750 kGy of absorbed dose. When both systems are compared under the same experimental conditions (Fig. 6), the TODGA system looks more resistant. Even if the initial extraction is higher with TODGA, the sensitivity of Me-TODGA upon irradiation is more important as indicated by the reduction of the concentration by 50% after 250 kGy.20 Moreover, the extraction behaviour of degradation compounds may be different. As described previously, only compounds 1 and 4 showed extraction properties for Ln(III), specially compound 1, which still has a diglycolamide structure and may play a role keeping the original performance of TODGA samples.17 A similar degradation compound as 1 was also identified for Me-TODGA, however, as we mentioned before this compound disappears as dose increases, being eligible after 750 kGy (Fig. 3, 14.9-15.7 min. Therefore compound 1 seems to be more sensitive to irradiation.

Fig. 5 Quantitative determination of the remaining Me-TODGA concentration and the most relevant degradation products present in an irradiated Me-TODGA sample by HPLC-MS (APCI) (initial Me-TODGA concentration: 0.1 mol L⁻¹ in TPH pre-equilibrated with 3 mol L⁻¹ HNO₃, 1000 kGy).

Fig. 6 Am(III) and Eu(III) distribution ratios obtained by extraction with reference, aging and irradiated Me-TODGA and TODGA samples at different integrated doses and dose rates. Organic phase: 0.1 mol L⁻¹ TODGA or Me-TODGA in TPH. Aqueous phase: ²⁴¹Am and ¹⁵²Eu in 3 mol L⁻¹ HNO₃. TODGA data are taken from ref. 17.

To better evaluate the performance of irradiated Me-TODGA solvents, for example as substitute for TODGA in a GANEX (Grouped Actinide Extraction) process,34,35 Ln and FPs extraction by Me-TODGA and the main degradation compounds was assessed. In order to compare the affinity of degradation compounds toward Ln and FPs, similar compositions were selected, although the concentrations of each degradation compound differ in irradiated solvents as presented in Fig. 5: a concentration of each molecule of 0.1 mol L⁻¹ in TPH or kerosene and 3 and 4 mol L⁻¹ HNO₃. The D values obtained previously showed that from compounds 2, 4, 6 and 8, only 4 is able to extract Ln(III) as well as ²⁴¹Am(III) with a D value around 1 (D₁₅₂ = 1.5; D₁₆⁴ = 1.6) from an aqueous solution at 3 mol L⁻¹ HNO₃.17 The extraction studies of Me-TODGA and the fragments 1, 3, 5 and 7 were carried out simultaneously at Jülich and CIEMAT and the data are in good agreement. It turned out that none of the tested compounds showed comparable distribution ratios as Me-TODGA under these conditions. Distribution ratios measured at lower nitric acid concentrations (not shown) were even lower, in line with literature data.13 These data explain why upon degradation of Me-TODGA a significant decrease of Am(III) and Eu(III) extraction is observed, its degradation products not being able to keep the extraction ability in contrast to bis-DGAs16 and TODGA degradation compounds 17,26 (in particular 1 (Fig.4)) which showed significant D values (D₁₅₂ = 3.5; D₁₆⁴ = 30).13

To check the presence of possible higher distribution ratios under the conditions used in the GANEX process, the extraction of Ln(III), Am and FPs from the synthetic HAR solution26 by Me-TODGA...
and its degradation compounds was assessed at higher nitric acid concentration (4 mol L\(^{-1}\) HNO\(_3\)). The D values presented in Fig. 7 showed that under these conditions, compounds 1 and 4 are able to extract Ln(III) and \(^{241}\)Am effectively (especially compound 4 which shows \(D_{\text{eq}}\) values >1).

ratios of all other FPs are <0.1 except for Cu (D around 0.3 - 6.2).

Regarding the FPs and the rest of the Ln elements, metals such as Zr, Mo and Pd were co-extracted mainly due to the presence of compounds 1, 2, 4 and 5, which have also shown solubility problems in apolar diluents as TPH or kerosene at a concentration of 0.1 mol L\(^{-1}\). At high nitric acid concentrations, the distribution

To study the possible influence of the hydroxyl group in the extraction ability of compounds 1 and 4, the hydroxyl group of 1 was protected as methoxy and acetoxy groups, i.e. the compounds 12 and 13 (Scheme 1). These compounds were tested with a similar concentration (0.1 mol L\(^{-1}\) in TPH) and with different nitric acid concentration (from 0.01 to 4.1 mol L\(^{-1}\)). Distribution ratios for both nuclides, \(^{241}\)Am as well as \(^{152}\)Eu, were very low (\(D < 0.002\)) and therefore not shown here. These results indicate that the presence of the -OH functional group in compounds 1 and 4 contributes to the extraction.

Since 2-hydroxypropionamide (1) is one of the major degradation compounds and one of the few compounds able to extract Ln(III), further experiments were conducted using higher nitric acid concentrations. Experiments up to 6.8 mol L\(^{-1}\) HNO\(_3\) provided distribution ratios of \(D_{\text{Am}} = 1.7\), and \(D_{\text{Eu}} = 1.9\) (Fig. 8).

Hence, the concentration of degradation product 1 was varied and a slope analysis was conducted from the log-log plot shown in Fig. 9 to get information about the complex stoichiometry. Therefore, the concentration of 1 was increased, while the nitric acid concentration was kept constant at 6.8 mol L\(^{-1}\). The slope of the linear fit of the logarithmic distribution ratio as function of the logarithmic ligand concentration provides a slope of 4.04 and 4.10 for \(^{152}\)Eu and \(^{241}\)Am, respectively. Therefore, it is concluded that degradation product 1 forms 1:4 complexes with americium(III) as well as europium(III), assuming that 2-hydroxypropionamide is not consumed by co-extraction of nitric acid and is monomer in TPH.

![Fig. 8 Distribution ratios of Am and Eu by 2-hydroxypropionamide (1) for different nitric acid concentrations. Organic phase: 0.1 mol L\(^{-1}\) of 1 in TPH. Aqueous phase: HNO\(_3\) with \(^{241}\)Am/\(^{152}\)Eu tracers. Contact time 60 minutes at 22 °C.](image_url)

![Fig. 9 Slope analysis for 2-hydroxypropionamide (1). Organic phase: varying concentrations of 1 in TPH. Aqueous phase: constant nitric acid concentration of 6.8 mol L\(^{-1}\), containing \(^{241}\)Am/\(^{152}\)Eu tracer. Extraction for 60 minutes at 22 °C.](image_url)
ARTICLE

Thermodynamic properties related to the extraction of lanthanides. To better understand the driving force of extraction, thermodynamic properties related to lanthanides extraction by TODGA and Me-TODGA were measured mainly with microcalorimetry. Even if a few studies are available, microcalorimetry remains the reference method to obtain enthalpic extraction data. Two lanthanides in the series were selected: Yb$^{3+}$ and Nd$^{3+}$ (comprehensive information are given in the Experimental section).

The extraction equilibrium considered in this study corresponds to the formation of $[M(NO_3)_3L_3]$ (L = TODGA or Me-TODGA and M = Yb$^{3+}$ or Nd$^{3+}$) as previously described for lanthanides. $^{15,39,40}$

$$M_{aq}^{3+} + 3NO_{aq}^3 + 3L_{org} \Leftrightarrow [M(NO_3)_3L_3]_{org}$$

with $K'_{ext}$ the extraction constant, defined as:

$$K'_{ext} = \frac{[M(NO_3)_3L_3]_{org}}{[M_{aq}^{3+}][NO_{aq}^3][L_{org}]}$$

The different concentrations were calculated as follows: $[M(NO_3)_3L_3]_{org} = C_{org}^{3L_3} M [M^{3+}] = C_{org}^{3L_3} L$ (the complexation by nitrate is negligible under these conditions), $[NO_{aq}^3] = C_{aq}^{NO_3} \text{init} \cdot 3C_{org}^{L} \text{init} [L] = C_{aq}^{NO_3} \text{ext} - 3C_{aq}^{L} \text{ext}$. The activity coefficients were not considered since the ionic force in the aqueous phase was similar and constant in all experiments. The Gibbs energy modification and the entropy modification, $\Delta_{ex}G'$ and $\Delta_{ex}S'$, respectively, were calculated from the following equations:

$$\Delta_{ex}G' = -RT\ln K'_{ext}$$

$$\Delta_{ex}G' = \Delta_{ex}H' - T\Delta_{ex}S'$$

with $R$, the gas constant and $T$ the temperature in Kelvin.

Thermograms obtained of the extraction of Yb$^{3+}$ and Nd$^{3+}$ by TODGA are shown in Fig. 10. Among all dilution experiments performed, only the dilution of the organic phase showed significant heat effects. These experimental data allowed the determination of $\Delta_{ex}H'$, the enthalpy change during the extraction process. The heat released during the extraction of Yb$^{3+}$ and Nd$^{3+}$ by Me-TODGA was very low and no reliable results were obtained.

![Thermograms of the extraction by TODGA of Yb$^{3+}$ (a) and of Nd$^{3+}$ (b); T = 25 °C. (initial conditions: 500 µL of aqueous phase, $C_{org}$ or Yb = 0.06 mol L$^{-1}$ in 0.1 mol L$^{-1}$ HNO$_3$ = 0.9 mol L$^{-1}$ LiNO$_3$ and 300 µL of organic phase, 0.1 mol L$^{-1}$ TODGA in n-dodecane/1-octanol (95/5) pre-equilibrated. Addition of 10x15 µL organic phase, stirring with gold propeller (120 rpm).)

In order to compare the extraction data obtained with TODGA and Me-TODGA, the Nd extraction enthalpies were also determined using the van’t Hoff method under similar chemical conditions. The variation of the distribution ratio with temperature was measured and the variation of $K'_{ext}$ is presented in Fig. 11.

![Variation of the extraction constant of Nd(NO$_3$)$_3$ by 0.1 mol L$^{-1}$ TODGA and 0.1 mol L$^{-1}$ Me-TODGA in n-dodecane/1-octanol (95/5) as a function of the reverse of the temperature (conditions: $C_{org}$ = 0.06 mol L$^{-1}$ in 0.1 mol L$^{-1}$ HNO$_3$ = 0.9 mol L$^{-1}$ LiNO$_3$ - Organic phase: 0.1 mol L$^{-1}$ C$_{ligand}$ in n-dodecane/1-octanol (95/5) pre-equilibrated).]

According to this approach, the enthalpy variation for the investigated extraction reaction ($\Delta_{ex}H'$) can be deduced from the temperature dependence of the extraction equilibrium constant:

$$\ln(K'_{ext}) = \frac{\Delta_{ext}H'}{RT} + \frac{\Delta_{ext}S'}{R}$$
Thermodynamic parameters related to the extraction of Yb³⁺ and Nd³⁺ by TODGA and Me-TODGA using microcalorimetry and the van’t Hoff method are reported in Table 1.

In the case of TODGA the enthalpy variations obtained both with the van’t Hoff method and with microcalorimetry are in very good agreement. The Gibbs energy modifications (ΔG) are similar for both cations Nd³⁺ and Yb³⁺ and are consistent with the values obtained with Eu³⁺ studied by Arisaka and Kimura.³⁹ The thermodynamic data reported in Table 1 indicate that the reaction is exothermic (ΔH < 0) and enthalpy-driven, as often observed with extraction by solvolysis. This feature could be explained by a strong interaction between the ligand and the cation.

The extraction of Nd³⁺ and Yb³⁺ by Me-TODGA led to less important values than in case of TODGA (ΔAG¹⁰⁻¹²═⁻⁸ kJ.mol⁻¹ and -19 kJ.mol⁻¹ for Nd³⁺ and Yb³⁺, respectively), which is consistent with the D values obtained for both ligands with lanthanides.

Due to these low values and considering the even lower values expected for degradation products of Me-TODGA, it was decided to obtain information on the affinity between some lanthanides and a selection of degradation compounds by dedicated complexation studies in homogeneous phases. This methodology is logical if we consider that binding is often the principal contribution, compared with transfer contributions and by modification of the solvation.

Thermodynamic properties related to the complexation with lanthanides. The complexation of three representative lanthanides (La³⁺, Eu³⁺ and Yb³⁺) with the extractants (TODGA and Me-TODGA) and six of their main degradation compounds (I, an exclusive TODGA degradation product, 1, 3, 4, 5 and 7 presented in Fig. 4) was studied in methanol using microcalorimetric titrations.

TODGA and Me-TODGA exhibited a similar behaviour in the presence of the three lanthanides. In all cases, thermograms obtained during complexation showed more important heat effects than those related to dilution of the salts. With La³⁺ and Eu³⁺, exothermic signals were observed and after a ratio C₅/C₄ of 0.5, the intensity of the peaks decreased and overlapped with that of dilution, indicating the end of complexation (Fig. 12). With Yb³⁺, at least two phenomena were observed: the first one is strongly exothermic, while the second one is weakly endothermic, showing clearly the formation of more than one species. At the end of the experiments, the intensity of the peaks resembled that of dilution after a ratio C₅/C₄ > 1.

![Fig. 12 Microcalorimetric titration of TODGA with La³⁺ in methanol (T = 25 °C). Left: thermogram corresponding to the heat evolved during each addition of 17 × 15 μL of La(NO₃)₃ in 2.5 mL of TODGA solution (C(TODGA) = 10⁻³ mol L⁻¹) - 0 ≤ R ≤ 1 - The lower thermogram corresponds to the dilution of the metal salt into the solvent. Right: experimental and calculated values for the derivative curve dQ/d(amount) vs. C₅/C₄.](image)

The results were fitted with the complexation reactions: Ln³⁺ + nTODGA ⇌ Ln(TODGA)ₙ. The weak complexation with NO₃⁻ in methanol was neglected. Then, the related calculated values are apparent stability constants βₘ. With La³⁺ and Eu³⁺, the derivative curve dQ/d(amount) vs. C₅/C₄ obtained with the two ligands exhibited an inflexion point for C₅/C₄ = 0.5 (Fig. 12 right for TODGA) corresponding to the formation of a ML₂ species in methanol with these cations. In contrast with Me-TODGA, this inflexion appeared at C₅/C₄ = 0.3 corresponding to the formation of a ML₃ complex. For
both ligands, the best interpretation of these data was obtained considering two species: ML₂ and ML₃. These results are consistent with those determined in a mixture of water and ethanol (40/60%) by luminescence for TODGA. The complexation of TODGA, Me-TODGA and Me₂-TODGA (addition of two methyl groups to the central methylene carbon atoms of the TODGA) studied comparatively by solvent extraction and TRLFS showed the formation of ML and ML₂ complexes in ethanol solution for CM³⁺ and Eu³⁺ and the conditional stability constants have been calculated. In other studies, it was shown that the extraction of europium involves 1:2 and 1:2 and 1:3 (metal:TODGA) species, in polar and non-polar solvents, respectively.

With Yb³⁺, the derivative curve showed an inflexion near C₉/C₆ = 0.3, corresponding to the formation of a ML₂ complex. Taking into account a second ML species, deduced from the heat effects, the fit is slightly improved.

The speciation deduced from the thermograms is similar for the two ligands (Table 2); the presence of the methyl group does not influence the nature of the complexes. Thermodynamic parameters (log β', ΔH' and ΔS') related to the formation of these species also revealed a similar behaviour for the two ligands, but with lower values for Me-TODGA, a trend which was observed previously with Eu³⁺. The stabilization of these complexes is mainly enthalpy-driven, the entropy contribution being slightly favorable or near zero. Therefore, the strength of the interaction between cations and ligands is the main factor governing the stability of the complexes. Nevertheless, differences appear for the entropic contribution in ML₂ species formation in the case of Eu³⁺ and Yb³⁺.

For Me-TODGA, the entropy is near zero, whereas for TODGA, negative values were found, suggesting a possible higher order, assumed by the molecule in the final complex.

The complexation properties of six degradation products of TODGA and Me-TODGA (I, 1, 3, 4, 5 and 7) towards the same three lanthanides were studied using the same experimental conditions as those used for the parent molecules. The stability constants and the thermodynamic parameters are presented in Table 2.

With TODGA degradation compound I, significant exothermic peaks were observed during the titration of La³⁺ and Eu³⁺ at the beginning of the experiment and the intensity gradually decreased to reach the values of peaks related to dilution for a ratio R = C₀/Cₑ near to 1. On the other hand, the δQ/δ(amount) vs. C₀/Cₑ curve showed an inflexion at the ratio R = 0.5, as the TODGA parent molecule. These observations are in agreement with the formation of both ML and ML₂ species, a model which perfectly fits the experimental data (line in Fig. 13). With Yb³⁺, the thermogram presented similar phenomena as for TODGA: the first part is classical for a strongly exothermic reaction, while the second one, after a ratio of about 0.5, indicates weakly endothermic phenomena. At a ratio R = 1, the intensity of the peaks indicates an exothermic reaction. The derivative curve showed an inflexion near 0.3 corresponding to the formation of a ML₂ complex. Taking into account a second ML species the fit improved. In the presence of La³⁺, two species were determined with I (ML and ML₂), whereas the formation of only one ML₂ species was observed with TODGA. The ML₂ species is less stable with I than with TODGA. The interaction seems to be weaker regarding the lower value of the enthalpy (-ΔH = 34 kJ·mol⁻¹ for I and -ΔH = 48 kJ·mol⁻¹ for TODGA). The entropy is near zero as for TODGA.

In the case of Eu³⁺ and Yb³⁺, the experimental data were interpreted with the same complexes as for TODGA (ML₂ and ML₃ for Eu³⁺ and ML and ML₂ for Yb³⁺), but with lower stability constants and with less negative enthalpies suggesting lower interactions. Differences appear for the entropic contribution to the formation of the ML₂ species in the case of Eu³⁺: near to zero value for I, whereas for TODGA, negative values were found. Regarding the thermodynamic parameters for the ML complex in the Yb³⁺/I system, the near to zero value of the enthalpy is compensated by a high value of the entropic term. For the ML₃ species, enthalpy and entropy follow the same trends as for TODGA. They are characterized by a favourable enthalpic contribution and an unfavorable entropic term.

Concerning the complexation of 2-hydroxyacetamide I with lanthanides, studies conducted with similar ligand concentrations as performed with TODGA and Me-TODGA gave thermograms with slightly higher peaks for titration than for dilution. The increase in ligand concentration (8 times) in order to force the complexation, led to significant heat effects, but no enthalpy value could be deduced because of non-reproducible data. Nevertheless, these results reveal interaction of I with Ln(III) as also shown from the extraction results (Fig. 7).

The experiments performed with N,N-dioctylpropionamide (3) and N-octylpropionamide (7) with the three lanthanides, led to identical titration and dilution thermograms, even at high metal to ligand concentration ratios (R = C₀/Cₑ near 20) suggesting no complexation. These results are in agreement with the extraction studies (Fig. 7).

With compounds 1 and 5, bearing one hydroxyl group, the profiles of the thermograms with the three lanthanides were very similar, showing exothermic peaks being significantly higher than those obtained for dilution, suggesting the occurrence of
complexation with these cations. For both ligands, the best interpretation for the three lanthanides was obtained considering only one ML species with low stability (log β between 2.4 and 3.2). This can be explained by the small size of these molecules containing less donor atoms compared to TODGA and Me-TODGA. The stability constants determined for 1 and 5 (Table 2) are in the same order of magnitude for each cation and no selectivity is observed along the lanthanides series. This stoichiometry is not consistent with that determined with slope analysis (Fig. 9) and this feature should be deepened. In the case of 1, the stabilization is enthalpy-driven (ΔH around -17.5 kJ mol⁻¹ with the three lanthanides), suggesting a strong interaction which could provide from the formation of a 6-membered chelate. A major enthalpic contribution was also observed during solvent extraction, the entropic contribution remains low or negative.

Table 2 Stoichiometries (M:L), overall stability constants (log β) and thermodynamic parameters (in kJ mol⁻¹) for lanthanide complexes with TODGA, Me-TODGA and degradation products 1, 1 and 5 in methanol (T = 25 °C).a

<table>
<thead>
<tr>
<th>Chemical system</th>
<th>1:1 complexes</th>
<th>1:2 complexes</th>
<th>1:3 complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log β</td>
<td>-ΔG'</td>
<td>-ΔH'</td>
</tr>
<tr>
<td>La-TODGA</td>
<td>8.5 (3)</td>
<td>48 (2)</td>
<td>48 (2)</td>
</tr>
<tr>
<td>La-1</td>
<td>3.20 (4)</td>
<td>18.2 (2)</td>
<td>9 (2)</td>
</tr>
<tr>
<td>La-Me-TODGA</td>
<td>8.1 (1)</td>
<td>46.1 (2)</td>
<td>41 ± (1)</td>
</tr>
<tr>
<td>Eu-TODGA</td>
<td>8.58 (4)</td>
<td>48.9 (2)</td>
<td>48 (3)</td>
</tr>
<tr>
<td>Eu-I</td>
<td>7 (1)</td>
<td>40 (6)</td>
<td>33.7 (1)</td>
</tr>
<tr>
<td>Eu-Me-TODGA</td>
<td>7.7 (3)</td>
<td>44 (2)</td>
<td>42 (5)</td>
</tr>
<tr>
<td>Eu-1</td>
<td>2.64 (5)</td>
<td>15.1 (3)</td>
<td>17.4 (9)</td>
</tr>
<tr>
<td>Eu-5</td>
<td>2.4 (2)</td>
<td>14 (1)</td>
<td>6 (1)</td>
</tr>
<tr>
<td>Yb-TODGA</td>
<td>4.4 (3)</td>
<td>25 (2)</td>
<td>16 (1)</td>
</tr>
<tr>
<td>Yb-I</td>
<td>3.0 (2)</td>
<td>17 (1)</td>
<td>-2 (6)</td>
</tr>
<tr>
<td>Yb-Me-TODGA</td>
<td>4.00 (7)</td>
<td>22.8 (4)</td>
<td>15 (4)</td>
</tr>
<tr>
<td>Yb-1</td>
<td>3.2 (4)</td>
<td>18 (2)</td>
<td>18 (5)</td>
</tr>
<tr>
<td>Yb-5</td>
<td>3.2 (4)</td>
<td>18 (2)</td>
<td>8 (3)</td>
</tr>
</tbody>
</table>

aValues in parentheses are standard deviations (σ, log) in the last significant digit.

Conclusions

We investigated the effect of ⁶⁰Co γ-irradiation on the extraction behaviour of Me-TODGA. Upon irradiation ten degradation compounds were identified. Among them the products originating from rupture of the ether linkage are most abundant. 2-Hydroxypropionamide (1) and N,N-diacyclacetamide (2) are formed by preferred rupture on the non-substituted side of the molecule. Despite previous results revealed that the degradation rate constant of ligand Me-TODGA is higher than TODGA, the introduction of a methyl group in the diglycolamide backbone increases the radiolytic resistance of the substituted C-O linkage over the unsubstituted C-O bond. At high acidity, the main degradation products which impact the overall extraction of lanthanides, ²⁴²⁴Am but also fission products are 2-hydroxyalkylamides. Dedicated extraction studies performed with degradation products 1 and 4 alone support their affinity towards Zr, Mo and Pd. When the hydroxyl group is replaced by a methoxy or acetoxy group, the extraction of Eu(III) and Am(III) decreases. During the process, the compounds that should be monitored are 2-hydroxyalkylamides.

To better understand the driving force of lanthanide extraction and to study the interactions between lanthanides and ligands, thermodynamic studies were performed not only in biphasic systems, but also in homogeneous solution (methanol). The extraction and complexation with TODGA and Me-TODGA are always enthalpy driven. Among the TODGA and Me-TODGA degradation products studied by microcalorimetry, the compounds 1, 4 and 5 showed significant heat effects, which were related to a strong interaction with the three lanthanides. Unlike the initial diglycolamides TODGA and Me-TODGA, which give 1:1, 1:2 and 1:3 (metal:ligand) complexes with lanthanides, the 2-hydroxyalkylamides produced upon radiolysis, only form 1:1 complexes, consistent with the formation of chelates. This study shows the importance of a detailed analysis of complexation in solution to understand extraction processes.
Acknowledgements

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Notes and references


Table of contents entry

Behaviour of the extractant Me-TODGA upon gamma irradiation: quantification of the degradation compounds and individual influences on complexation and extraction


The understanding of the interaction ligands/metal is of great importance to develop new processes for nuclear wastes treatment.