Article

Improving Americium/Curium Separation Factors in the AmSel Process through Symmetry Lowering of the Diglycolamide Extractant

Filip Kolesar, Karen Van Hecke,* Ken Verguts, Cécile Marie, Laurence Berthon, Koen Binnemans, and Thomas Cardinaels

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ABSTRACT: Partitioning and transmutation are important strategies for closing the nuclear fuel cycle. The diglycolamide extractant TODGA has played a major role in the development of solvent extraction processes for nuclear fuel reprocessing due to its good extraction performance, its hydrolytic and radiolytic stability, and its compliance with the CHON principle. However, due to drawbacks such as the tendency to form a third phase during extraction if no phase modifiers are used, continued research on diglycolamide-type extractants has led to the development of diglycolamides with decreased symmetry. In this study, it is shown that the recently developed diglycolamide, N,N-diisopropyl-N',N'-didodecyldiglycolamide (iPDdDGA), is a potential alternative to TODGA with improved separation between Am and Cm or the Ln. Using the AmSel system as a reference, the extraction kinetics, influence of the acid concentration, influence of the iPDdDGA concentration, and influence of temperature were evaluated. Slope analysis indicates similar average stoichiometries for iPDdDGA and TODGA complexes, but the extraction efficiency of iPDdDGA is orders of magnitude higher. The feasibility of selective americium stripping in combination with the hydrophilic sulfonated bis-triazinyl bipyridine SO_3-Ph-BTBP complexant was demonstrated. Selective stripping of americium was found to be possible, and the use of iPDdDGA gave an unexpected improvement in Am/Cm separation, with $SF_{Cm/Am}$ values of up to 3.0. This represents a small but significant improvement compared to the 2.5 value typically found for TODGA, and it demonstrates the potential of this solvent extraction system to improve existing processes based on diglycolamide-type extractants.
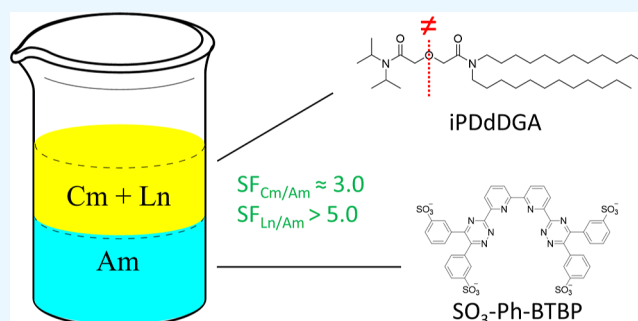
INTRODUCTION

Nuclear energy has become vital for world electricity supply, but dealing with the spent nuclear fuel is challenging. Particularly, the generation of long-lived minor actinides, which dominate long-term radiotoxicity and heat generation, poses a problem for the storage of spent nuclear fuel. In theory, implementation of a partitioning and transmutation (P&T) strategy could reduce the time necessary for spent nuclear fuel to reach the radiotoxicity level of uranium ore from 250,000 years to less than 300 years.[1] Additionally, the decrease in heat generation by performing full P&T of uranium, plutonium, and the minor actinides could significantly decrease the footprint and construction cost of deep geological repositories.[2] After removal of plutonium, uranium, and possibly neptunium from dissolved spent nuclear fuel, by the Plutonium Uranium Reduction EXtraction (PUREX) process, the leftover is a highly active raffinate comprising primarily the fission products and the minor actinides americium and curium.[3] Further partitioning steps for the remaining minor actinides are still under development, with a particular focus on ensuring that the process is compliant with the CHON principle. Molecules that consist exclusively of carbon, hydrogen, oxygen, and nitrogen are preferred as extractants as they are completely incinerable, which minimizes the amount of solid waste left at the end of the partitioning process.[4]

A class of extractants called diglycolamides (DGAs) has attracted strong interest due to their superior properties compared to the previously studied extractants. These DGAs were originally developed by Sasaki et al.,[5] who synthesized and tested a series of extractants. These DGAs had varying alkyl chains attached to the nitrogen atoms of the central molecular framework, ranging in length from n-propyl to n-decyl. Of the tested DGAs, N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) was found to be the most promising

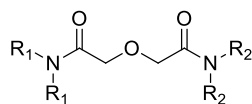**Table 1. Overview of DGAs with Varying Alkyl Chains**

R$_1$	R$_2$	abbreviation[a]	name	references
pyrrolidinyl	octyl	pyrODGA	N,N-pyrrolidinyl-N′,N′-dioctyldiglycolamide	Tokheim[28]
piperidinyl	octyl	pipODGA	N,N-piperidinyl-N′,N′-dioctyldiglycolamide	Tokheim[28]
morpholinyl	octyl	morODGA	N,N-morpholinyl-N′,N′-dioctyldiglycolamide	Tokheim[28]
methyl	octyl	MODGA	N,N-dimethyl-N′,N′-dioctyldiglycolamide	Stamberga,[29] Liu[30]
hexyl	octyl	HODGA	N,N-dihexyl-N′,N′-dioctyldiglycolamide	Ravi[24]
2-ethylhexyl	octyl	EHODGA	N,N-di-2-ethylhexyl-N′,N′-dioctyldiglycolamide	Ravi[22,28]
hexyl	decyl	HDDGA	N,N-dihexyl-N′,N′-didecyldiglycolamide	Ravi,[31] Mowafy[28,32]
octyl	decyl	ODDGA	N,N-dioctyl-N′,N′-didecyldiglycolamide	Ravi[24,28]
ethyl	dodecyl	EDdDGA	N,N-diethyl-N′,N′-didodecyldiglycolamide	Mossand[21,32]
isopropyl	dodecyl	iPDdDGA	N,N-diisopropyl-N′,N′-didodecyldiglycolamide	Mossand[21]
pyrrolidinyl	dodecyl	PyrrDdDGA	N,N-pyrrolidinyl-N′,N′-didodecyldiglycolamide	Mossand[21]
butyl	dodecyl	BDdDGA	N,N-dibutyl-N′,N′-didodecyldiglycolamide	Ravi[31,33]
hexyl	dodecyl	HDdDGA	N,N-dihexyl-N′,N′-didodecyldiglycolamide	Ravi[33]
2-ethylhexyl	dodecyl	EHDdDGA	N,N-di-2-ethylhexyl-N′,N′-didodecyldiglycolamide	Ravi[34]
octyl	dodecyl	ODdDGA	N,N-dioctyl-N′,N′-didodecyldiglycolamide	Ravi[24,33]
decyl	dodecyl	DDdDGA	N,N-didecyl-N′,N′-didodecldiglycolamide	Ravi[33]

[a]Different abbreviations for these molecules might be found in the referenced literature. To avoid confusion, a single, consistent naming system was used throughout this work, where the smaller/branched alkyl chain is mentioned first.

one, with good solubility in organic diluents while also yielding high distribution ratios for extraction of trivalent lanthanides and actinides.[6−8] Moreover, TODGA shows excellent hydrolytic and radiolytic stability.[9−14] Although TODGA has the tendency for third-phase formation, this third-phase formation can be prevented by adding N,N-dihexyl octanamide (DHOA), tributyl phosphate (TBP), or 1-octanol as a modifier.[7,15,16] However, a recurrent issue of TODGA is the coextraction of certain fission and corrosion products, among which are Zr, Mo, Pd, Sr, and Ru. To prevent this coextraction, the use of masking agents is required. A combination of oxalic acid and N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetic acid (HEDTA), to prevent coextraction of Zr and Pd, respectively, has been demonstrated for both the DIAMEX[17] and TODGA-TBP process.[10] Alternatively, trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CDTA) was also shown to be highly effective in suppressing both Zr and Pd coextraction for these two processes and was successfully demonstrated in combination with oxalic acid for the TODGA−octanol system.[18,19] The branched structural isomer N,N,N′,N′-tetra-2-ethylhexyldiglycolamide (TEHDGA) is also promising for minor actinide partitioning. Fission product coextraction is decreased compared to TODGA due to its lower basicity, but it also shows lower extraction efficiencies for the trivalent actinides and lanthanides and a greater tendency for third-phase formation.[20]

A subclass of DGAs, containing two different alkyl (R, R′) groups on the opposing amidic nitrogen atoms, has been called "unsymmetrical" diglycolamides (UDGAs), although it must be noted that, strictly speaking, these DGAs are not unsymmetrical since their central frame has one mirror plane. Two types of UDGAs can be discerned: Type 1 UDGAs contain two identical alkyl chains on each nitrogen atom, but the two nitrogen atoms bear different alkyl chains.[21] A general structure of this type is shown in Table 1. Type 2 UDGAs comprise two different alkyl chains on each nitrogen atom, but each of the two nitrogen atoms bears the same two

alkyl chains. In order to avoid confusion, the following introduction will mainly focus on the literature of the Type 1 UDGAs, as this is the type to which the extractant studied in this work belongs. An overview of these DGA extractants can be found in Table 1. These were first synthesized and tested by Ravi et al. by combining the alkyl groups of both TEHDGA (2-ethylhexyl) and TODGA (octyl) to obtain N,N-di-2-ethyl-hexyl-N′,N′-dioctyldiglycolamide (EHODGA), in an attempt to retain the beneficial properties of both DGAs.[22] The combined EHODGA DGA showed Am extraction and third-phase behavior that was improved compared to TEHDGA but poorer than what was found for TODGA. Similarly to TODGA, EHODGA was found to completely extract Zr(IV) and Y(III) alongside the Ln(III) and An(III), but the distribution ratios of other fission products such as Sr(II), Cr(IV), Mo(VI), Pd(II), Ru(III), Ba(II), and Cd(II) were found to be much lower when extracted with EHODGA.[23] Ln(III) and An(III) could be stripped from a loaded EHODGA organic with a 0.1 mol·L^{-1} HNO$_3$ solution, although a crud-type precipitate was formed when the organic phase was loaded from a simulated high-level liquid waste solution, possibly due to fission product costripping. This necessitated the use of complexing agents. A stripping solution containing DTPA and citric acid at pH 3 was able to strip the Ln(III) and An(III) without crud formation.[23]

In further studies, several DGAs with varying alkyl chains were synthesized and tested for minor actinide partitioning. One of these studies concerns the synthesis of N,N-dihexyl-N′,N′-dioctyldiglycolamide (HODGA), N,N-dioctyl-N′,N′-didecyldiglycolamide (ODDGA), and N,N-dioctyl-N′,N′-dido-decyldiglycolamide (ODdDGA) and their comparison with TODGA.[24] Longer alkyl chains gave lower distribution ratios, as already reported by Sasaki for DGAs with four identical alkyl chains, and this is likely due to increased steric hindrance.[5] Longer alkyl chain lengths also correlate with higher limiting organic concentrations (LOCs) for nitric acid, i.e., the maximum concentration of nitric acid that can be loaded in

the organic phase without third-phase formation. At 0.1 mol·L^{-1} DGA, HODGA was shown to form a third phase at trace levels of Nd(III) in 3 mol·L^{-1} HNO$_3$ solution, ODdDGA did not form a third phase until 105 mmol·L^{-1} of Nd(III) in 5 mol·L^{-1} HNO$_3$ was used.[24] Third-phase formation is caused by poor solubility of polar acid–extractant or metal–extractant complexes in apolar diluents, such as n-dodecane, and is influenced by the C/O ratio in the molecular structure, as well as by the alkyl chain length, branching, and position of the branching in the extractant molecule.[25−27] However, elongating the DGA alkyl chains increases steric hindrance and lowers extraction efficiencies.[35] Ravi et al. showed an alternative approach by decreasing the alkyl chain length on one side of the DGA and increasing the chain length on the other side to prevent third-phase formation while preserving a high extraction efficiency.[31] This was demonstrated by synthesizing a series of DGA extractants with fixed dodecyl groups on one side and varying alkyl groups on the other side.[33] Of these extractants, none showed third-phase formation when contacted with HNO$_3$ solutions up to 10 mol·L^{-1}, showing that attaching dodecyl chains on one side of the DGA is an effective approach to preventing third-phase formation. Due to its ability to efficiently extract lanthanides and actinides from nitric acid medium without forming a third phase, ODdDGA was further investigated as a potential candidate for a modifier-free extraction system. Tests of modifier-free ODdDGA (0.1 mol·L^{-1}) extractions from a simulated HLLW showed extraction behavior similar to that of TODGA-based solvents where N,N-dihexyl-octanamide was used as a phase modifier. These tests showed quantitative extraction of Am(III), Ln(III), Y(III), and Zr(IV); low extraction of Sr(II), Pd(II), and Ru(III); marginal extraction of Ba(II), Ni(II), Mo(IV), and Fe(III); and negligible extraction of Co(II), Sb(II), Mn(II), and Cs(I).[36] Based on ODdDGA, the "Single-cycle method for partitioning of Minor Actinide using completely incinerable ReagenTs" (SMART) system was developed.[37] This system is able to separate Am(III) from HLLW in a single processing cycle using a solvent of 0.05 mol·L^{-1} ODdDGA in n-dodecane, to which was added 0.2 mol·L^{-1} N,N-di-2-ethylhexyldiglycolamic acid (HDEHDGA) to improve the An–Ln separation. The stripping solution consisted of 0.001 mol·L^{-1} diethylenetriaminepentaacetic acid (DTPA) at pH 1.5.

Further indications that steric hindrance has a significant influence on extraction efficiencies were found in experiments with N,N-di-2-ethylhexyl-N′,N′-didodecyldiglycolamide (EHDdDGA).[34] The determined $D_{Am(III)}$ values were lower than those for EHODGA and TODGA but higher than those for TEHDGA, and this can be explained by the degree of steric hindrance. Distribution ratios for Sr(II) were also found to be lower than those for EHODGA and TODGA and even lower than those for TEHDGA. Both ODdDGA and EHDdDGA were tested for their radiolytic stability to determine the influence of radiation on their extraction properties.[38,39] The DGAs were irradiated under static conditions, neat, dissolved in n-dodecane, or dissolved in n-dodecane after contact with 4 mol·L^{-1} HNO$_3$. Both DGAs showed decreasing distribution ratios for Am(III) with an increase in absorbed doses, similarly to what was found for TODGA. For an absorbed dose of 500 kGy, ODdDGA in n-dodecane showed a $D_{Am(III)}$ of 97, TODGA showed a $D_{Am(III)}$ of 62, and EHDdDGA showed a $D_{Am(III)}$ of 55. Stripping of Am(III) with 0.1 mol·L^{-1} of HNO$_3$ was quantitative for both DGAs, showing that degradation products do not interfere with the stripping of Am. Overall,

assuming the implementation of an appropriate solvent management strategy, both extractants were shown to be robust enough to be used for Am extraction from HLLW.

Although many DGAs with varying alkyl chains have already been synthesized and tested for An(III) and Ln(III) extraction, only a few of these were tested for selective Am(III) separation. Chapron synthesized a series of short-chained DGAs and evaluated them for their applicability in Am/Cm separation processes.[40] Comparison of N,N,N′,N′-tetra-n-butyldiglycolamide (TnBDGA), N,N,N′,N′-tetra-iso-butyldiglycolamide (TiBDGA), and N,N,N′,N′-tetra-sec-butyldiglycolamide (TsBDGA) showed a decrease in Cm/Am selectivity when the branching and therefore steric hindrance increased. All of the extractants showed improved distribution ratios for the lanthanides when compared to TODGA, but while TnBDGA and TiBDGA showed some selectivity toward the heavier lanthanides, the selectivity of TsPDGA was poor.[41] The DGAs N,N′-dimethyl-N,N′-di-n-propyldiglycolamide (MPDGA) and N,N′-dimethyl-N,N′-di-iso-propyldiglycolamide (MiPDGA) showed a similar trend of lower selectivity with increasing steric hindrance, although both performed worse than TEDGA.[40] In a separate study, the DGAs N,N-diethyl-N′,N′-didodecyldiglycolamide (EDdDGA), N,N-diisopropyl-N′,N′-didodecyldiglycolamide (iPDdDGA), and N,N-pyrrolidinyl-N′,N′-didodecyldiglycolamide (PyrrDdDGA) (see Figure 1) were synthesized[21] and tested[42] for selective
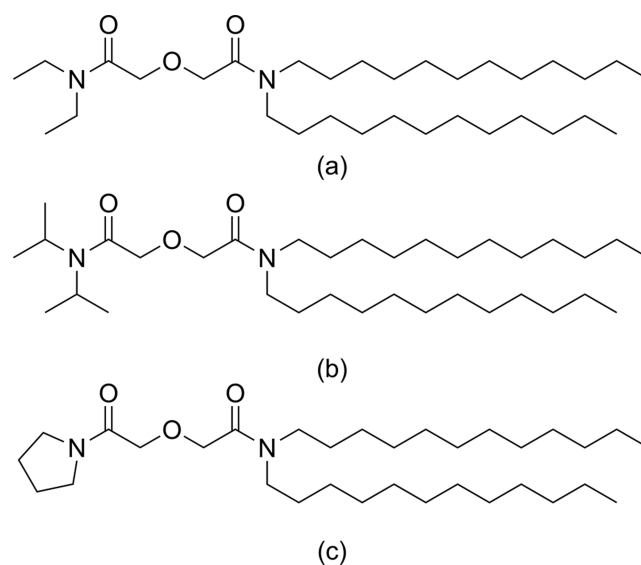

Figure 1. Structures of DGAs synthesized by Mossand: (a) EDdDGA, (b) iPDdDGA, and (c) PyrrDdDGA.[21]

americium partitioning. EDdDGA and iPDdDGA showed significantly higher distribution ratios for Ln(III) extraction than did TODGA, while PyrrDdDGA had poorer Ln(III) extraction. However, all three DGAs showed high distribution ratios for both Am(III) and Cm(III). Stripping from an organic phase containing 0.1 mol·L^{-1} DGA dissolved in TPH (tetrapropylene hydrogenated, an industrial apolar solvent which is a mixture of various alkanes) + 10%$_{Vol}$ 1-octanol with 2.5 mmol·L^{-1} N,N,N′N′-tetrakis[(6-carboxypyridin-2-yl)-methyl]ethylenediamine (TPAEN) in 0.1 mol·L^{-1} HNO$_3$ resulted in distribution ratios that were too high for efficient americium stripping from EDdDGA or PyrrDdDGA. iPDdDGA, on the other hand, showed promising results for
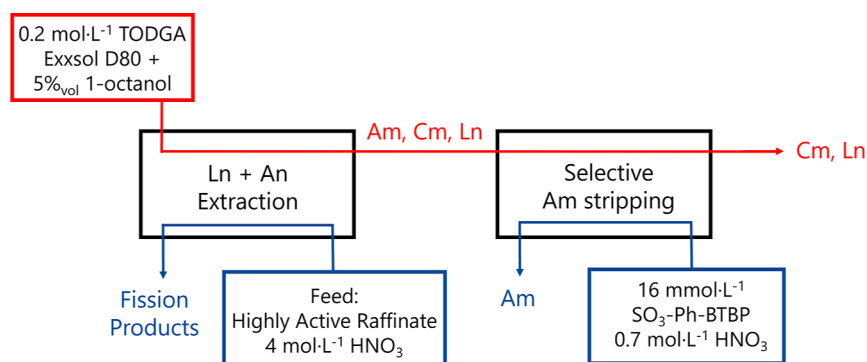
Figure 2. Simplified scheme of the AmSel process.

this system, with data suggesting an unexpected improvement in the Am/Cm separation factor. This improvement in the separation factor could make iPDdDGA an interesting alternative for TODGA, with the potential to improve Am selectivity in processes currently using TODGA as an extractant. However, experimental data on the extractant behavior are lacking at the moment.

In this work, the AmSel (Americium Selective extraction) process developed by Wagner et al. was chosen as a reference system.[43] This process consists of two stages: an initial extraction stage during which Am(III), Cm(III), and the Ln(III) are coextracted to the organic phase, followed by a stripping stage where Am(III) is selectively stripped. These two stages are schematically represented in Figure 2. During the extraction stage, TODGA is used to achieve the extraction, and the selective stripping of Am is achieved with the hydrophilic bis-triazinyl bipyridine 3,3′,3″,3‴-([2,2′-bipyridine]-6,6′-diylbis(1,2,4-triazine-3,5,6-triyl))-tetrabenzenesulfonate (SO$_3$-Ph-BTBP) ligand. The separation is achieved through reverse selectivity of the two complexing agents, as the hard O donor atoms of TODGA prefer to bind the trivalent lanthanide ions, whereas the softer N-donor atoms of BTBP prefer to bind to the trivalent actinide ions. Separation of Am(III) from Cm(III) is possible due to a slight difference in ionic radii. The main benefits of this process are its performance in acidic conditions and its capability of extracting Am(III) without the need of additional buffers, ligands, or salting out agents that might complicate the process. However, the process is hampered by a low, but still workable, Cm(III)/Am(III) separation factor of ca. 2.5, as well as the presence of sulfur that complicates waste treatment. This work aims to thoroughly examine iPDdDGA as a selective extractant for Am with regards to Cm and the lanthanides and evaluate its usability within the AmSel system. To assess the properties of iPDdDGA, it was used instead of TODGA in combination with SO$_3$-Ph-BTBP. The influence of various factors on both extraction and stripping steps was evaluated. The behavior of the fission products and a study of the third-phase formation are outside the scope of this study but remain important topics of research to ensure the viability of iPDdDGA as a replacement for TODGA.

■ EXPERIMENTAL SECTION

Chemicals. HNO$_3$ solutions were prepared by diluting 69% trace metal grade HNO$_3$, acquired from Fischer Chemicals (Seastar Chemicals Inc.), with Milli-Q grade water. Y(NO$_3$)$_3$·6H$_2$O (purity 99.9%), Ce(NO$_3$)$_3$·6H$_2$O (purity 99.9%), Pr(NO$_3$)$_3$·6H$_2$O (purity 99.9%), Nd(NO$_3$)$_3$·6H$_2$O (purity

99.9%), and Sm(NO$_3$)$_3$·6H$_2$O (purity 99.9%) were obtained from Strem Chemicals (Kehl, Germany). La(NO$_3$)$_3$·6H$_2$O (purity 99.0%) was procured from Fluka (Seelze, Germany). Eu(NO$_3$)$_3$·6H$_2$O (purity 99.99%) and Gd(NO$_3$)$_3$·6H$_2$O (purity 99.9%) were acquired from Alfa Aesar GmbH (Karlsruhe, Germany). Dy(NO$_3$)$_3$·6H$_2$O (purity 99.9%) and Yb(NO$_3$)$_3$·5H$_2$O (purity 99.9%) were obtained from Sigma-Aldrich (Steinheim, Germany). First, a solution containing 10^{-2} mol·L^{-1} Ln(III) was prepared by dissolving weighed amounts of each salt in 0.1 mol·L^{-1} HNO$_3$ solution. This solution was then diluted 1:100 to obtain a stock solution containing 10^{-4} mol·L^{-1} of each lanthanide (10^{-3} mol·L^{-1} total concentration) at the targeted HNO$_3$ concentration. The HNO$_3$ concentration was then verified by titration with 0.05 mol·L^{-1} NaOH in a MT Titrator Excellence T5 autotitrator. Yb(III) was added as a representative ion to study the behavior of heavier lanthanides.

The new DGA extractant, iPDdDGA (min 99% purity by HPLC), was synthesized by DIVERCHIM CDMO according to a previously described method.[21] ReagentPlus grade *n*-dodecane and ACS grade 1-octanol were obtained from Sigma-Aldrich (Steinheim, Germany). SO$_3$-Ph-BTBP in free acid form (min 98% purity by HPLC) and TODGA (min 99% purity by HPLC) were purchased from Technocomm Ltd. (Edinburgh, UK).

Organic phases were prepared by dissolving a weighed amount of DGA in a diluent consisting of 10%$_{Vol}$ 1-octanol in *n*-dodecane. 1-Octanol was added as a phase modifier to prevent third-phase formation, a known phenomenon for DGA extraction at elevated HNO$_3$ concentrations.[44] A higher modifier concentration was chosen to ensure no third-phase formation occurs during the experiment, as LOC data on iPDdDGA extractions was unknown. Stripping solutions were prepared by dissolving a weighed amount of SO$_3$-Ph-BTBP in HNO$_3$ solution.

^{152}Eu tracer (radionuclide purity >99%) and ^{244}Cm tracer (radionuclide purity >99.9%) dissolved in 1 mol·L^{-1} HNO$_3$ solution were obtained from Eckert and Ziegler Nuclitec GmbH (Braunschweig, Germany), and ^{241}Am radiotracer in 1 mol·L^{-1} HNO$_3$ solution (radionuclide purity >99%) was available from the legacy stocks of SCK CEN. Stock solutions were spiked with ca. 3 kBq/mL of radiotracer before extraction experiments. Due to the hazards associated with radioactivity, these tracers must be handled with care in facilities designed to safely handle such materials.

■ METHODS

Extractions were performed by combining equal parts of aqueous and organic phases (A/O = 1) in a 4 mL glass vial and shaking them in a TMS-200 Thermoshaker at 1900 rpm. Extractions were typically performed with an aqueous Ln(III) stock solution containing radiotracers in 3 mol·L^{-1} HNO$_3$ and an organic solution consisting of 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, which has been twice pre-equilibrated with the relevant concentration of HNO$_3$. When stripping was performed, a loaded organic phase was typically in contact with an aqueous solution of 2.5 mmol·L^{-1} SO$_3$-Ph-BTBP in 0.1 mol·L^{-1} HNO$_3$. Unless stated otherwise, the samples were shaken for 15 min at a fixed temperature of 20 °C controlled by an RC10 VWR digital chiller. Prior to shaking, the vial caps were wrapped in Parafilm laboratory film to prevent any leaks during shaking. After shaking, the phases were separated by centrifuging the samples for 3 min at 4000 rpm in a Medifuge centrifuge. When the two phases were fully separated, they were pipetted into separate vials with Eppendorf Research Plus pipettes.

A select number of extractions were performed twice: once with the addition of radiotracers and once without. Radioactive samples were analyzed by γ and α spectroscopy, and nonradioactive samples were analyzed with ICP–MS. γ spectroscopy was used to determine ^{241}Am and ^{152}Eu activities, and α spectroscopy was used to determine ^{241}Am and ^{244}Cm activities. ICP–MS was used to measure the concentrations of the Ln(III). HNO$_3$ concentrations were determined through potentiometric titration of inactive samples diluted in Milli-Q water with 0.05 mol·L^{-1} NaOH in a MT Titrator Excellence T5 autotitrator. Organic phases were titrated with the addition of an equal volume of a 10% Triton-X solution.

The distribution ratio (D) of an element was calculated as the ratio between its (activity) concentration in the organic phase and its (activity) concentration in the aqueous phase. Except for kinetic experiments, distribution ratios were calculated at equilibrium. The formula is represented in eq 1.

$$D = \frac{[M]_{org,eq}}{[M]_{aq,eq}} \tag{1}$$

For the stripping experiments, samples were analyzed with ICP–MS. As the strong extraction properties of iPDdDGA prevented back-extractions from the organic phase, leading to poor mass balances, only aqueous phases were measured. The organic concentrations were then calculated from the initial concentration ($[M]_{aq,init}$), the equilibrium concentration in the aqueous phase after extraction ($[M]_{aq,eq,extr}$) and the equilibrium concentration in the aqueous phase after stripping ($[M]_{aq,eq,strip}$). The formula for the distribution ratio for phases with equal volumes is shown in eq 2. As the loaded organic phase was always prepared by extraction from 3 mol·L^{-1} HNO$_3$, and extraction is quantitative for all of the measured elements at this concentration, $[M]_{aq,eq,extr}$ was below the limit of detection and was negligible.

$$D = \frac{([M]_{aq,init} - [M]_{aq,eq,extr}) - [M]_{aq,eq,strip}}{[M]_{aq,eq,strip}} \tag{2}$$

The separation factor between the two elements was calculated as the ratio of their distribution ratios. To obtain a value larger than 1, the higher distribution ratio was always taken as the numerator. The separation factor between Cm and Am was always calculated with α spectroscopy data, and the separation factor between Eu and Am was always calculated with γ spectroscopy data. The formula is represented in eq 3

$$SF = \frac{D_{M_1}}{D_{M_2}} \tag{3}$$

Inductively Coupled Plasma Mass Spectrometry. Nonradioactive aqueous samples were analyzed using ICP–MS. The samples were measured with a Thermo Fisher Scientific X2 series II instrument. Samples were diluted 1:100 with a 2% HNO$_3$ solution. The maximum uncertainty on the measurements is 6% (2σ).

γ Spectroscopy. Active samples were analyzed by using γ spectroscopy to determine the distribution of ^{241}Am and ^{152}Eu. Both aqueous and organic phases were analyzed. Equal volumes of sample solution were pipetted into preweighed vials and weighed afterward to determine the net mass of the samples. The samples were analyzed with a Canberra high-performance germanium detector (model: GC2520) equipped with a DSA-1000 multichannel analyzer. The data was interpreted with Genie2000 software. The samples were measured until the ^{241}Am peak (at 59.5 keV) and ^{152}Eu peak (at 121.8 keV) showed at least 10,000 counts. When this is the case, the relative counting uncertainty of the corrected net peak area is below 1%.[45] Samples that showed very low activity were measured overnight. The activities were used to confirm that the deviation on the activity balance was within 8%.

α Spectroscopy. Active samples were analyzed using α spectroscopy to determine the distribution of ^{241}Am and ^{244}Cm. Both aqueous and organic phases were analyzed. Thin-layer α samples were prepared on C-1S stainless steel planchets with a diameter of 20 mm acquired from GA-MA and Associates, Inc., Florida, USA. Samples with high activity or SO$_3$-Ph-BTBP concentration were diluted prior to sample preparation. Aqueous samples were diluted with a 1 mol·L^{-1} HNO$_3$ solution, and organic samples were diluted with n-dodecane. 10 μL of aqueous phase or 2 μL of organic phase was pipetted onto the planchets. The exact mass of the sample was determined by weighing the planchets before and after pipetting. For aqueous samples, after the sample was deposited on the planchet, 1 drop of 1 mol·L^{-1} HNO$_3$ solution and 1 drop of 25% NH$_4$NO$_3$ solution were added to obtain a more uniform spreading of the sample on the planchet. Afterward, the deposited liquid was evaporated under an infrared lamp and burned with a gas torch to fix the samples. The planchets were measured using a Canberra Alpha Analyst spectrometer equipped with passivated implanted planar silicon (PIPS) detectors. The data was interpreted with Canberra Apex Alpha software. The area under ^{241}Am peaks (at 5.485 MeV) and ^{244}Cm peaks (at 5.805 MeV) was measured and used to determine their activities in the samples.

■ RESULTS AND DISCUSSION

Kinetics of Extraction. To investigate the kinetics of An(III) and Ln(III) extraction with iPDdDGA, a number of identical samples were shaken for various periods of time. All samples contained an organic phase consisting of 0.1 or 0.005 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane and an aqueous phase consisting of Ln(III) stock solution + radiotracer in 3 mol·L^{-1} HNO$_3$. The samples were shaken for 5, 10, 30, or 60 min at 1900 rpm, after which the phases were separated and analyzed. A concentration of 0.1

mol·L^{-1} of iPDdDGA was initially chosen to enable comparison with literature data on extractions with DGAs. With an iPDdDGA concentration of 0.1 mol·L^{-1}, very fast extraction kinetics and very efficient extraction were observed. After only 2 min of shaking at 1900 rpm, activities in the aqueous phases fell below the limit of detection, indicating distribution ratios of at least 1000. Therefore, the experiment was repeated with a lower iPDdDGA concentration of 0.005 mol·L^{-1}, and the results are presented in Figure 3.
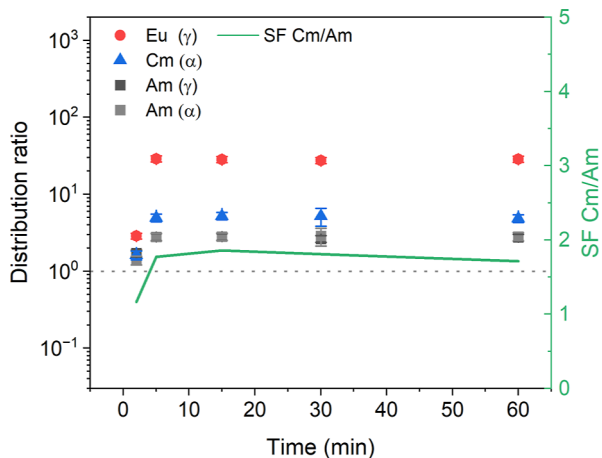

Figure 3. Distribution ratios as a function of mixing time with iPDdDGA. Aq: 10^{-3} mol·L^{-1} Ln + 3 kBq/mL ^{152}Eu, ^{241}Am, and ^{244}Cm radiotracers in 3 mol·L^{-1} HNO$_3$. Org: 0.005 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in *n*-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$. A/O: 1, 1900 rpm, 20 °C.

When the extraction was performed with 0.005 mol·L^{-1} of iPDdDGA, equilibrium is attained within 5 min of shaking for Am, Cm, and Eu. This is a shaking time similar to what was found sufficient to reach equilibrium with TODGA and TEHDGA, although these studies were performed with significantly higher concentrations (0.1 mol·L^{-1}) of DGA and no phase modifier.[46,47] The viscosity of the organic solvent, which increases with higher extractant and phase modifier concentrations, must also be taken into account as this can affect the extraction kinetics.[48] Separation factors show stable values in the 1.7–1.8 range after an initial increase, an improvement of the 1.6 factor reported for TODGA, despite the lower DGA concentration used in this extraction.[43,49,50] To ensure equilibrium was reached in subsequent experiments, a shaking time of 15 min was used. Nevertheless, extractions with 0.1 mol·L^{-1} showed kinetics sufficiently fast for the use of iPDdDGA in a continuous process.

Extraction of HNO$_3$ by iPDdDGA. DGAs are known to extract HNO$_3$, especially at higher nitric acid concentrations, and this is a result of the presence of the basic C=O groups.[51] The extraction of nitric acid by DGAs can be described as an equilibrium reaction, which is represented in Scheme 1. This shows that the amount of extracted HNO$_3$ depends on both the initial HNO$_3$ and DGA concentrations. As stripping is
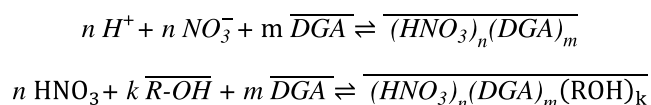
usually performed at lower HNO$_3$ concentrations than extraction, the equilibrium shifts toward the left of the equation, and part of the extracted HNO$_3$ is stripped alongside the metal species. This can alter stripping conditions and have an impact on the distribution ratio of stripped metals, usually requiring the addition of acid scrubbing steps prior to metal stripping when the process is scaled up. As separation of americium from curium is typically only feasible in a small window of carefully selected variables, it is very important to understand the behavior of nitric acid. By using slope analysis, both Ansari et al. and Mowafy et al. observed the presence of 1:1 HNO$_3$·TODGA adducts, although at higher nitric acid concentration, 2:1 adducts are observed.[6,7,51,52] The formation of 1:1 adducts was also found for the DGAs with varying alkyl chain lengths.[22,24,32] The influence of the phase modifier on the extraction of HNO$_3$ should also not be underestimated. To prevent third-phase formation in this study, a solvent is used that contains 10%$_{Vol}$ of 1-octanol in addition to *n*-dodecane. Higher alcohols (R−OH) such as 1-hexanol, 1-octanol, and 1-decanol were found to extract a significant amount of nitric acid, even without the addition of other extractants.[53] Most often, HNO$_3$ is not extracted as a pure DGA or 1-octanol adduct but as a mixed complex.[52] Synergistic effects may therefore cause a higher uptake of nitric acid than would be expected from the extraction behavior of DGAs or 1-octanol individually. The mechanism of acid extraction by DGAs was shown not to be molecular. Instead, DGAs like TODGA are organized into so-called reverse-phase micelles, whereby an aqueous core, with or without HNO$_3$, is surrounded by the basic C=O groups of the DGAs, while the hydrophobic alkyl chains are pointed outward.[44,54] This aggregation was found to be driven by the water and acid extraction. Particularly, the formation of tetrameric TODGA aggregates in aliphatic solvents at HNO$_3$ concentrations higher than 1 mol·L^{-1} was found to greatly promote extraction of trivalent metal ions, such as Ln^{3+} and An^{3+}.

In order to evaluate the extraction of nitric acid by iPDdDGA, a series of extractions were performed with aqueous phases containing between 1 and 6 mol·L^{-1} of nitric acid. Organic phases consisted of 0.1 mol·L^{-1} of iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in *n*-dodecane. As no data was found in the literature for extraction of nitric acid with TODGA at these conditions, the experiment was also repeated with TODGA. After equilibration, the nitric acid concentrations in both aqueous and organic phases were measured by potentiometric titration. The equilibrium concentrations of nitric acid in the organic phase as a function of the equilibrium concentration in the aqueous phase are presented in Figure 4.

iPDdDGA extracts a significant amount of HNO$_3$ to the organic phase. At a starting concentration of 6 mol·L^{-1} of nitric acid, the highest acidity tested, more than 0.33 mol·L^{-1} of HNO$_3$ is extracted to the organic phase. Between initial aqueous concentrations of 2 and 6 mol·L^{-1}, the extracted concentration follows a linear trend, with ca. 5% of the initial concentration of nitric acid being extracted into the organic phase. A similar acid uptake is observed when extractions are performed with 0.1 mol·L^{-1} TODGA instead of 0.1 mol·L^{-1} iPDdDGA, and the concentration of 1-octanol is kept the same.

As observed in Figure 4, the increase in 1-octanol concentration induces an increase in nitric acid extraction, confirming a trend already observed in literature.[52,53,55] Nitric acid in the organic phase can significantly impact subsequent
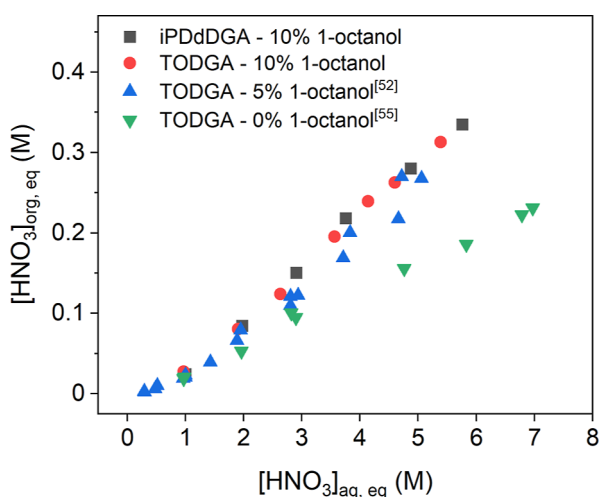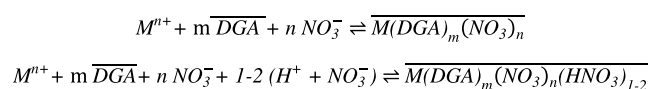
Scheme 1. Chemical Equilibria of DGA−HNO$_3$ Complexes

$$n\,H^+ + n\,NO_3^- + m\,\overline{DGA} \rightleftharpoons \overline{(HNO_3)_n(DGA)_m}$$

$$n\,HNO_3 + k\,\overline{R\text{-}OH} + m\,\overline{DGA} \rightleftharpoons \overline{(HNO_3)_n(DGA)_m(ROH)_k}$$

Figure 4. HNO_3 extraction by iPDdDGA and TODGA. Aq: 10^{-4} mol·L^{-1} Ln in x mol·L^{-1} HNO_3. Org: 0.1 mol·L^{-1} iPDdDGA or TODGA dissolved in 0, 5, or 10%$_{Vol}$ 1-octanol in n-dodecane. A/O: 1, 1900 rpm, T: 20 °C, shaking time: 15 min.

extraction steps and should therefore be limited as much as possible. Although some amount of phase modifier is required with most DGAs to prevent third-phase formation, this concentration should be optimized and kept as low as is practicably achievable. An optimization of the organic phase was, however, outside the scope of this study, and 10%$_{Vol}$ was chosen to ensure no third phase formation would occur at any point during the extraction experiments.

The acid uptake has not yet been tested for many DGAs with varying alkyl chains. Ravi et al. have evaluated the nitric acid extraction properties of EHODGA dissolved in n-dodecane.[22] They found an extraction of nitric acid similar to that found for TODGA for an initial HNO_3 concentration up to 4 mol·L^{-1}. Higher concentrations resulted in third-phase formation, a phenomenon also observed for TODGA at similar concentrations. TEHDGA shows a nitric acid uptake similar to that of EHODGA and TODGA at these conditions.[56] This observation, combined with the findings for iPDdDGA, seems to imply that as long as the total number of carbons in the alkyl chains remains more or less constant, the structure or length of the individual alkyl chains attached to the DGA skeleton does not have a significant influence on the uptake of nitric acid during solvent extractions. Rather, it appears the extraction is mainly ruled by the basicity of the carbonyl functions and is increased by the addition of phase modifier when alcohols are used for this purpose.

Influence of HNO_3 Concentration on Extraction. The HNO_3 concentration is an important factor that influences the distribution ratios of extracted metal ions.[5] This is explained by the solvation mechanism which describes the complex formation of metal ions with DGAs, as shown in Scheme 2.[47] Furthermore, complexes with one or two additional HNO_3 molecules can be formed.[57] Higher nitrate concentrations were shown to increase the extraction efficiency of DGA-type extractants.[5] Both TODGA and TEHDGA were shown to

Scheme 2. Chemical Equilibria of M−DGA Complexes

$$M^{n+} + m\,\overline{DGA} + n\,NO_3^- \rightleftharpoons \overline{M(DGA)_m(NO_3)_n}$$

$$M^{n+} + m\,\overline{DGA} + n\,NO_3^- + 1\text{-}2\,(H^+ + NO_3^-) \rightleftharpoons \overline{M(DGA)_m(NO_3)_n(HNO_3)_{1\text{-}2}}$$

yield higher distribution ratios for Am(III) when extractions were performed at higher HNO_3 concentrations.[20,47] Similar behavior was observed for DGAs with varying alkyl chain lengths.[22,31] This was explained by the promotion of the formation of tetrameric TODGA aggregates at higher acid concentrations, which show high affinity for complexation with trivalent lanthanide and actinide ions.[44,54]

The influence of the nitric acid concentration on the extraction efficiency of iPDdDGA was investigated by extracting from a series of spiked solutions with [241]Am, [244]Cm, and [152]Eu and with nitric acid concentrations between 0.25 and 3 mol·L^{-1}. Initially, an iPDdDGA concentration of 0.1 mol·L^{-1} was used, with the results presented in Figure 5
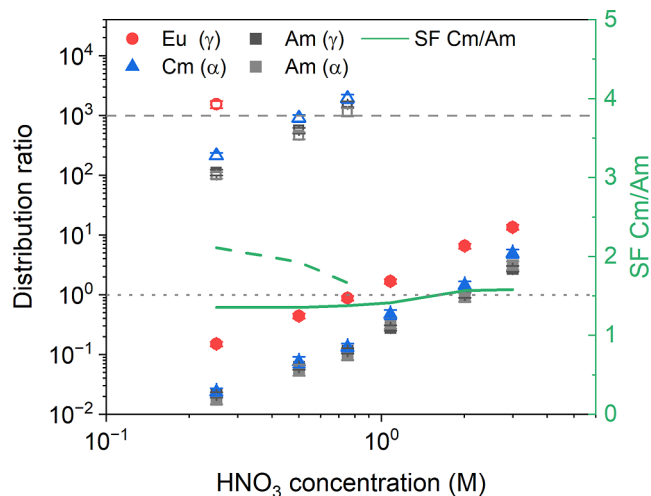

Figure 5. Influence of HNO_3 on iPDdDGA extraction. Aq: 10^{-3} mol·L^{-1} Ln(III) + 3 kBq/mL [152]Eu, [241]Am, and [244]Cm radiotracers in x mol·L^{-1} HNO_3. Org: 0.1 mol·L^{-1} (open symbols, dashed line) or 0.005 mol·L^{-1} (closed symbols, full line) iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, 2× pre-equilibrated with x mol·L^{-1} HNO_3. A/O: 1, 1900 rpm, T: 20 °C, shaking time: 15 min.

(open symbols, dashed line) showing very high distribution ratios ($D > 100$), even at the lowest tested HNO_3 concentration. The extraction was repeated with an iPDdDGA concentration of 0.005 mol·L^{-1}, with the results also presented in Figure 5 (closed symbols, full line).

When extractions are performed with 0.1 mol·L^{-1} iPDdDGA, Eu(III) shows distribution ratios higher than 1000 all along the acidity range. Distribution ratios of Am(III) and Cm(III) can be measured up to a nitric acid concentration of 0.75 mol·L^{-1}, and then they become too high to be measured ($D > 1000$). When the data is compared with extractions with TODGA in similar conditions, distribution ratios for Am(III), Cm(III), and Eu(III) obtained for iPDdDGA are at least 1 order of magnitude higher.[57] For 0.1 mol·L^{-1} iPDdDGA, $SF_{Cm/Am}$ values of around 1.9 were observed, a significant increase to the 1.6 value reported for TODGA.

For extractions performed with 0.005 mol·L^{-1} of iPDdDGA, measurements were within the detection limits all along the nitric acid concentration range (between 0.25 and 3 mol·L^{-1}). Even at such a low DGA concentration, distribution ratios higher than 1 can be observed (at HNO_3 concentrations of 1 mol·L^{-1} or higher for Eu and HNO_3 concentrations of 2 mol·L^{-1} or higher for Am and Cm). At a lower iPDdDGA concentration, lower separation factors for Cm/Am separation

are observed, with values varying between 1.4 and 1.6. In the literature, it has already been observed that increasing the branching or chain length of the alkyl groups attached to the nitrogen atoms of DGA extractants resulted in lower distribution ratios. This observation can be explained by the increase in steric hindrance favorable to coordination of trivalent lanthanides or actinides.[58] This behavior was also observed for other DGAs with varying alkyl chains. Ravi et al. found decreasing distribution ratios for both Am(III) and Eu(III) when the length of the two alkyl chains on one side of the DGA is increased while maintaining two octyl groups on the other side (ODdDGA < ODDGA < TODGA ≈ HODGA).[24] This trend is similar to what was observed for DGAs with four identical alkyl chains. By comparing isomeric DGAs with the same carbon-to-oxygen ratio, Ravi also found that the extraction behavior was predominantly controlled by the longer alkyl chains, resulting in a decrease in distribution ratios when the alkyl chains were shortened on one side and elongated on the other side.[31] In contrast to their findings, the extraction behavior of iPDdDGA does not seem to be determined by the dodecyl chains, as distribution ratios are orders of magnitude higher than those measured for TODGA. Very high distribution ratios were likewise observed for EDdDGA and PDdDGA, DGAs that are similar in structure to iPDdDGA and also contain dodecyl chains.[42] This behavior corresponds more to DGA extractants with short alkyl chains and seems to imply that if the alkyl chains on one side of the DGA are shortened sufficiently, then these will determine the extraction strength rather than the longer alkyl chains on the other side of the DGA. A possible reason for the different behavior of these DGAs with shorter alkyl chains and the ones tested by Ravi et al. is the difference in carbon-to-oxygen ratio, as iPDdDGA, PDdDGA, and EDdDGA contain fewer carbon atoms than the DGAs tested previously. Changing the C/O ratio affects the aggregation behavior of the DGAs and, with it, the metal extraction behavior. New DGAs that bridge the alkyl chain gap between the extractants tested in this study and the study by Ravi et al. would have to be investigated to provide a conclusive answer to this divergence of extraction properties.

Influence of iPDdDGA Concentration on Extraction. The solvation mechanism with DGAs is a complexation reaction that can be represented with Scheme 2.[47] This is a simplified formula that ignores the presence of phase modifier and the aggregation properties of DGAs but illustrates the influence of the acid and ligand concentration. The reaction shows that apart from the nitrate concentration, the concentration of the extractant molecule is an important factor influencing the extraction process. For such an extraction mechanism, the equilibrium constant, K_{ex}, and the distribution ratio for M^{3+}, D_M, can be expressed by eqs 4 and 5, respectively. The combination of both equations and their conversion to the logarithmic form then yields eq 6. According to this equation, the stoichiometry of the formed complex can be determined by plotting the logarithm of the distribution ratio ($\log(D_M)$) as a function of the logarithm of the free ligand concentration ($\log([DGA]_{org,free})$), and the resulting slope gives the stoichiometric number m. For this equation to be valid, the nitrate concentration in the aqueous phase must remain constant, and the free ligand concentration instead of the initial ligand concentration in the organic phase must be used. The nitrate concentration was kept constant by pre-equilibrating the organic phase twice to limit coextraction during the extraction experiment. The free ligand concen-

tration was estimated by calculating the concentration of extracted metal and assuming a 1:3 M−DGA stoichiometry that is typical for DGAs.[46] The stoichiometry was confirmed afterward (see Figure 6). It is important to note here that
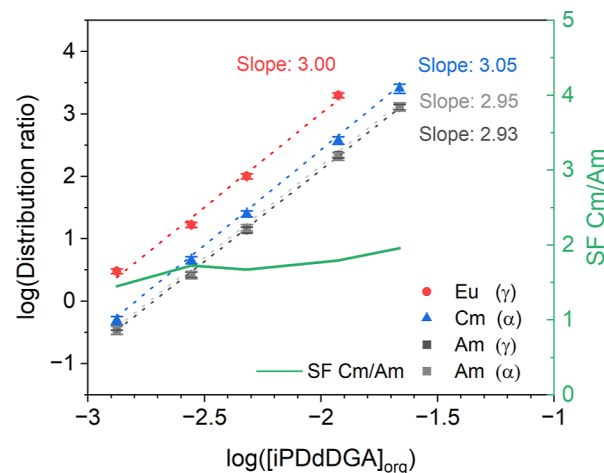

Figure 6. Slope analysis of iPDdDGA extraction. Aq: 10^{-3} mol·L^{-1} Ln + 3 kBq/mL ^{152}Eu, ^{241}Am, and ^{244}Cm radiotracers in 3 mol·L^{-1} HNO$_3$. Org: x mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$. A/O: 1, 1900 rpm, T: 20 °C, shaking time: 15 min.

complexes formed between iPDdDGA and 1-octanol or nitric acid were not taken into account, as the formation of mixed species makes it difficult to estimate their influence on the free ligand concentration. This means that the calculated free ligand concentrations are higher than the actual concentrations. However, as it was found previously that extracted acid varies linearly with the DGA concentration, the impact on the slopes should be limited, allowing for the slope analysis to be used as an estimation of the stoichiometry.[52] Nevertheless, the slope will only be an approximation of the true stoichiometry and cannot be a replacement for more accurate speciation techniques.

$$K_{ex} = \frac{[M(DGA)_m(NO_3)_n]_{org}}{[M^{3+}]_{aq} \times [DGA]_{org}^m \times [NO_3^-]_{aq}^n} \quad (4)$$

$$D_M = \frac{[M(DGA)_m(NO_3)_n]_{org}}{[M^{3+}]_{t,aq}} \quad (5)$$

$$\log(D_M) = \log(K_{ex}) + n\log([NO_3^-]_{aq}) + m$$
$$\log([DGA]_{org}) \quad (6)$$

Extractions were performed with 0.003, 0.005, 0.0075, 0.015, 0.025, and 0.05 mol·L^{-1} iPDdDGA in the organic phase and 3 mol·L^{-1} HNO$_3$ in the aqueous phase. The logarithms of the distribution ratios, $\log(D_M)$, were plotted against the logarithms of the estimated free DGA concentration, log-($[DGA]_{org}$), and the slopes were determined by linear regression. The results are listed in Figure 6.

Slopes of around 3 were obtained for Am(III) (γ: 2.93; α: 2.95), Cm(III) (α: 3.05), and Eu(III) (γ: 3.00). Good correspondence was observed between γ and α results for Am(III). Separation factors for Cm/Am show a continuous increase, going from 1.4 for 0.003 mol·L^{-1} iPDdDGA to 2.0 for

0.05 mol·L^{-1} iPDdDGA. This implies even higher separation factors might be observed for 0.2 mol·L^{-1} DGA, the concentration for which SF$_{Cm/Am}$ 1.6 is reported for TODGA, but this could not be confirmed experimentally due to the high distribution ratios.[43,49,50] An overview of the literature is presented in the Supporting Information (Table S1), where the results of slope analyses with various DGAs are summarized. Previous studies have shown slopes of 3.75 and 3.72 for extraction of Am(III) with TODGA dissolved in aliphatic diluents from 1 mol·L^{-1} nitric acid solutions.[5,47] Wilden et al., however, obtained a slope of 2.73 for Am(III) and a slope of 2.68 for Eu(III) for extraction from 3 mol·L^{-1} and confirmed through TRLFS that TODGA forms 1:3 complexes with Eu(III), Am(III), and Cm(III).[46] Slope analysis of TEHDGA, a more strongly branched DGA molecule, has shown slopes of 3.02 and 2.95 for extraction of Am(III) from 2 and 1 mol·L^{-1} HNO$_3$, respectively.[47,59] Panja et al. found slopes of around 2 for extraction of Am(III) and Eu(III) from nitric acid solutions with TDDGA, THDGA, and TPnDGA, differing from what is typically observed for DGAs such as TODGA.[60,61] However, these results are not confirmed by Sasaki et al., who obtained a slope of 3 for extractions of Am with TDDGA, as well as with TDdDGA, at similar extraction conditions.[62] Slope analyses were also performed for a number of DGAs with varying alkyl chains. Ravi et al. investigated the stoichiometry of the extracted species of Am(III) with EHDdDGA, EHODGA, ODdDGA, and ODDGA, showing the formation of 1:3 complexes for all of them.[22,24,34] HODGA, on the other hand, was found to form 1:4 complexes with Am(III), a finding that has also been reported by Sasaki for both *N,N′*-dihexyl-*N,N′*-dioctyldiglycolamide and *N,N′*-diheptyl-*N,N′*-dioctyldiglycolamide.[62] Liu et al. showed a slope of 2.94 for the extraction of Am(III) with *N,N′*-dimethyl-*N,N′*-dioctyldiglycolamide (MODGA), a DGA with two short methyl chains and two octyl chains, from 1 mol·L^{-1} of HNO$_3$.[63] It is evident that DGAs primarily form 1:3 complexes with Am(III) and Eu(III) during extractions from nitric acid solutions. This behavior has been observed for both branched and unbranched DGAs, as well as for DGAs with varying alkyl chains. The slopes observed in Figure 6 are in agreement with this behavior and confirm the formation of 1:3 complexes of Am(III), Cm(III), and Eu(III) with iPDdDGA. Even so, as noted previously, these results should be confirmed through speciation studies due to the assumptions made in the calculation of the free ligand concentration.

Influence of Temperature on Extraction. Due to the presence of *α*- and *β*-emitting radionuclides in the highly active raffinate, a temperature increase may occur during extraction processes. The process equipment can also significantly raise the temperature. Furthermore, the temperature is a useful variable to enhance performance during the stripping step, as TODGA extraction is exothermic and increasing the temperature will lead to improved stripping. Hence, it is interesting to study the extraction thermodynamics of various extractants meant for actinide partitioning. Such studies have already been performed for a number of extractants, such as CMPO, TODGA, and TEHDGA.[47,64,65] Exothermic behavior was observed for all three ligands with decreased extraction efficiency at higher temperatures. To evaluate the thermodynamics of iPDdDGA, extraction experiments were performed at different temperatures (from 15 to 40 °C) with organic phases containing 0.005 mol·L^{-1} of iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in *n*-dodecane (Figure 7).
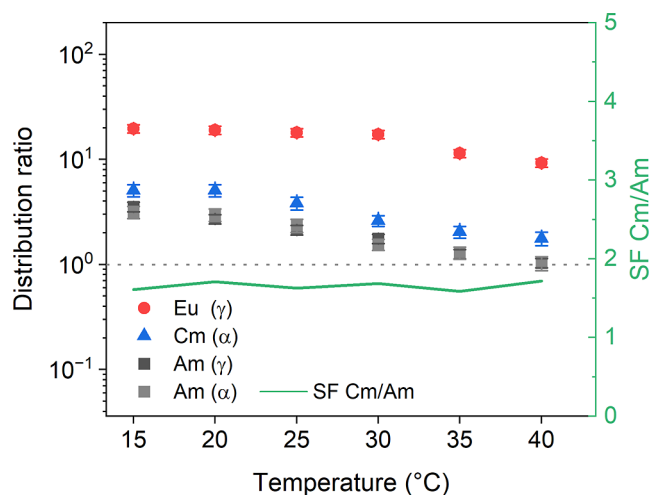

Figure 7. Influence of temperature on iPDdDGA extraction. Aq: 10^{-3} mol·L^{-1} Ln + 3 kBq/mL ^{152}Eu, ^{241}Am, and ^{244}Cm radiotracers in 3 mol·L^{-1} HNO$_3$. Org: 0.005 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in *n*-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$. A/O: 1, 1900 rpm, *T*: *x* °C, shaking time: 15 min.

When the distribution ratios are plotted as a function of the temperature during extractions, a decrease in values was observed with an increase in temperature. This is indicative of an exothermic complexation reaction, something that has already been observed for several DGAs.[47,65] Between 15 and 40 °C, a 2- to 3-fold decrease in distribution ratios is observed for Eu, Cm, and Am. The separation factor remains constant throughout the temperature range and shows values in the 1.6—1.7 range. It would be interesting to calculate values for the changes in enthalpy and free energy, as this would allow for an easy comparison with other DGAs such as TODGA. For this, an in-depth thermodynamic study of iPDdDGA would be required to accurately calculate its thermodynamic parameters, but this is outside the scope of this work.

Stripping Kinetics. The AmSel process consists of the initial coextraction of Am(III), Cm(III), and the Ln(III) with TODGA, followed by selective stripping of Am(III) with the hydrophilic bis-triazinyl bipyridine SO$_3$-Ph-BTBP ligand.[43] At optimum conditions, a separation factor SF$_{Cm(III)/Am(III)}$ of ca. 2.5 can be obtained as well as efficient separation of Am(III) from the Ln(III).

The stripping kinetics of the iPDdDGA AmSel system were investigated by shaking several identical samples for various periods of time. Organic phases consisting of 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in *n*-dodecane were first contacted with 10^{-3} mol·L^{-1} Ln(III) and radiotracers in 3 mol·L^{-1} HNO$_3$. In a second step, this loaded organic phase was contacted with an aqueous phase containing 2.5 mmol·L^{-1} SO$_3$-Ph-BTBP in 0.5 mol·L^{-1} HNO$_3$. The composition of the stripping aqueous phase was chosen based on optimized conditions described for the TODGA-based AmSel system.[43] The samples were shaken (A/O = 1, 20 °C) for 5, 15, 30, or 60 min at 1900 rpm, after which the phases were separated and analyzed. The aqueous phases were also titrated to determine the equilibrium HNO$_3$ concentrations. The results are plotted in Figure 8 for actinides and Figure 9 for lanthanides.

The extraction experiments showed that iPDdDGA follows the same trends as described for other DGAs in the literature with regard to changes in various extraction parameters. iPDdDGA was, however, also repeatedly shown to be a very
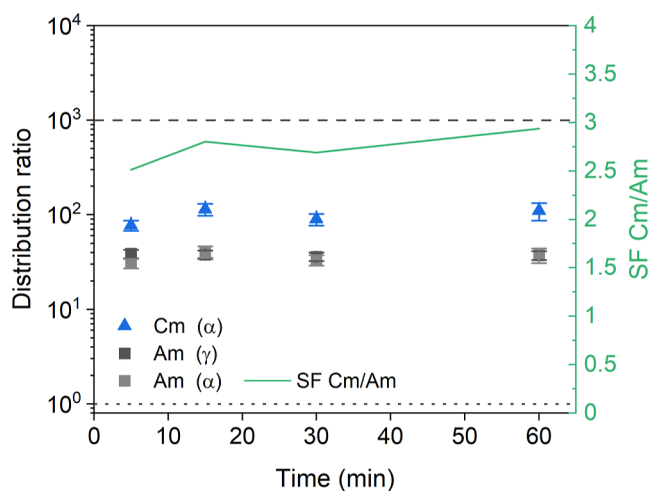
Figure 8. Kinetics of actinide stripping with SO_3-Ph-BTBP from iPDdDGA organic phase. Org: 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$, loaded from 10^{-3} mol·L^{-1} Ln + 3 kBq/mL ^{152}Eu, ^{241}Am, and ^{244}Cm radiotracers in 3 mol·L^{-1} HNO$_3$. Aq: 0.0025 mol·L^{-1} SO$_3$-Ph-BTBP with initial HNO$_3$ concentration of 0.5 mol·L^{-1}. A/O = 1, 1900 rpm, T = 20 °C.

Figure 9. Kinetics of lanthanide stripping with SO_3-Ph-BTBP from iPDdDGA organic phase. Org: 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$, loaded from 10^{-3} mol·L^{-1} Ln in 3 mol·L^{-1} HNO$_3$. Aq: 0.0025 mol·L^{-1} SO$_3$-Ph-BTBP with initial HNO$_3$ concentration of 0.5 mol·L^{-1}. A/O = 1, 1900 rpm, T = 20 °C.

strong extractant. Such strong complexation influences the subsequent stripping step, which is based on competition between the extractant molecule in the organic phase and a selective ligand in the aqueous phase. The use of soft-donor ligands showing a reverse selectivity compared to the hard-donor DGAs, in this case, preferring complexation with Am(III) over complexation with Cm(III) or Ln(III), allows for a selective stripping step. This type of system is sometimes referred to as a "push–pull" system.[66] For this stripping to take place, a ligand in the aqueous phase is required that complexes more strongly to Am(III) than iPDdDGA (in the organic phase) does. In this experiment, Am stripping is not observed at the chosen conditions, with D_{Am} values of about 40 measured. For stripping to take place, the SO_3-Ph-BTBP concentration will have to be increased and/or the HNO$_3$ concentration decreased. Although ^{152}Eu radiotracer was added to the active experiment, the distribution ratios were

too high (>1000) to be measured. Equilibrium appears to have been reached in a short amount of time, as all measured actinides and lanthanides achieve equilibrium in less than 5 min of shaking, the shortest time tested. Short equilibration times were also observed by Wagner et al. in the TODGA-based AmSel process.[43] $SF_{Cm/Am}$ values around 2.8 are observed throughout the series, slightly higher than what is typically observed for TODGA (2.5).[43] However, these values must be confirmed for conditions that do allow for Am stripping.

The distribution ratios observed in this experiment are higher than those observed for the original AmSel system, where TODGA was used as extractant.[43] This is first and foremost a result of the higher extraction strength of iPDdDGA compared to that of TODGA, a property that has already been discussed previously. An additional contributing factor is the equilibrium nitric acid concentration. In this study, the organic phase was saturated with nitric acid prior to the stripping step, raising the equilibrium nitric acid concentration from 0.50 mol·L^{-1} to an average of 0.59 mol·L^{-1}, leading to higher distribution ratios. It was shown in Figure 4 that both TODGA and iPDdDGA can extract significant amounts of nitric acid in the loading step, highlighting the need for an acid-scrubbing step before and careful control of the equilibrium acid concentration during the stripping step to achieve stripping of americium. As the introduction of such a step requires a careful optimization of both the organic phase and the aqueous phase, the stripping experiments in this study were performed without acid scrubbing after the loading step. Instead, the equilibrium acid concentrations are reported in the Supporting Information to provide the basic data needed for such an optimization.

Influence of the SO_3-Ph-BTBP Concentration on Stripping. In addition to the stripping kinetics, the influence of the SO_3-Ph-BTBP concentration on stripping was also investigated. The stripping kinetics experiment showed that a stripping solution of 2.5 mmol·L^{-1} of SO_3-Ph-BTBP in 0.5 mol·L^{-1} of HNO$_3$ does not allow for Am stripping. For this purpose, the SO_3-Ph-BTBP and HNO$_3$ concentrations were varied to find a region where selective Am stripping is possible. Stripping was performed from a loaded organic phase, comprising 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane. These were contacted with aqueous phases containing between 2.5 and 100 mmol·L^{-1} of SO_3-Ph-BTBP dissolved in HNO$_3$. Initially, an HNO$_3$ concentration of 0.5 mol·L^{-1} was combined with higher SO_3-Ph-BTBP concentrations to achieve stripping. However, for concentrations up to 100 mmol·L^{-1}, D_{Am} values higher than 1 were measured (see Figures S1 and S2); therefore, the experiment was repeated with aqueous phases of which the initial HNO$_3$ concentration was 0.1 mol·L^{-1}. The samples were shaken for 60 min at 1900 rpm, after which the phases were separated and analyzed. Both series were performed twice: once with and once without the addition of ^{241}Am, ^{244}Cm, and ^{152}Eu radiotracers. The former was analyzed by γ and α spectroscopy to observe the behavior of the tracers, with the results plotted in Figure 10. The latter series was analyzed with ICP–MS to observe the behavior of the other lanthanides, and the results are plotted in Figure 11.

For both series, a decrease of distribution ratios is observed for all elements as the SO_3-Ph-BTBP concentration is increased, but at higher concentrations, a deviation of the linear trend was found. The most likely reason for this

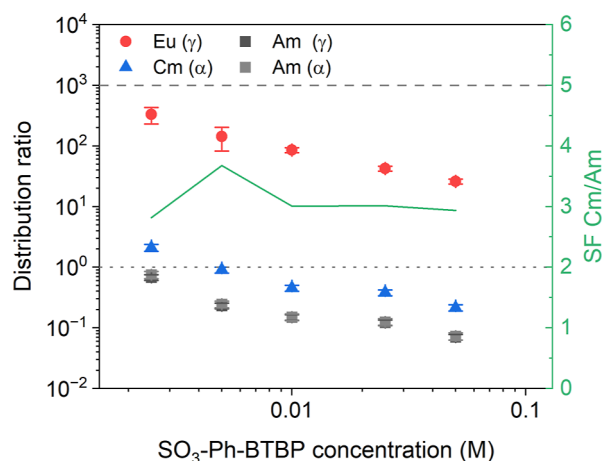**Figure 10.** Influence of SO$_3$-Ph-BTBP concentration on the stripping of Am, Cm, and Eu from an iPDdDGA organic phase. Org: 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$, loaded from 10^{-3} mol·L^{-1} Ln + 3 kBq/mL ^{152}Eu, ^{241}Am, and ^{244}Cm radiotracers in 3 mol·L^{-1} HNO$_3$. Aq: x mol·L^{-1} SO$_3$-Ph-BTBP with initial HNO$_3$ concentration of 0.1 mol·L^{-1}. A/O: 1, 1900 rpm, T: 20 °C, shaking time: 60 min.

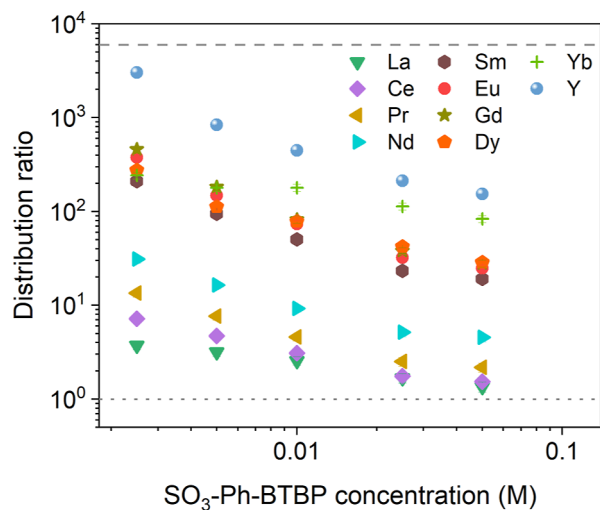**Figure 11.** Influence of SO$_3$-Ph-BTBP concentration on the stripping of lanthanides from an iPDdDGA organic phase. Org: 0.1 mol·L^{-1} iPDdDGA dissolved in 10%$_{Vol}$ 1-octanol in n-dodecane, 2× pre-equilibrated with 3 mol·L^{-1} HNO$_3$, loaded from 10^{-3} mol·L^{-1} Ln in 3 mol·L^{-1} HNO$_3$. Aq: x mol·L^{-1} SO$_3$-Ph-BTBP with initial HNO$_3$ concentration of 0.1 mol·L^{-1}. A/O: 1, 1900 rpm, T: 20 °C, shaking time: 60 min.

deviation is the introduction of the BTBP ligand itself, which was used in a free acid form. To confirm this, the acid concentrations were measured by titration of the aqueous phases at equilibrium (in the second stripping step). This showed a significant increase of the total proton concentration (Table S2) for all of the measured samples, with larger increases observed for samples with a higher BTBP concentration. Although this increase can be partially explained by a back-extraction of the acid extracted in the loading step, an insufficient amount of nitric acid was present in the loaded organic phase to account for the whole increase (See Figure 4). Furthermore, the amount of back-extracted nitric acid should remain constant throughout the series as this amount is determined by the initial HNO$_3$ concentration and not the

BTBP concentration. H$^+$ is known to have a synergistic effect on extractions of Ln^{3+} with DGA extractants.[67]

Lowering the initial HNO$_3$ concentration from 0.5 to 0.1 mol·L^{-1} decreases the distribution ratios by ca. 2 orders of magnitude. Hence, selective Am stripping (D_{Am} < 1) can already be observed for SO$_3$-Ph-BTBP concentrations between 2.5 and 5 mmol·L^{-1}. SF$_{Cm/Am}$ values of ca. 3.0 were measured, with a slightly lower value (2.8) for 2.5 mmol·L^{-1} of SO$_3$-Ph-BTBP. A higher value (3.6) was measured for 5 mmol·L^{-1} SO$_3$-Ph-BTBP but additional extractions would be necessary to confirm this value. At higher SO$_3$-Ph-BTBP concentrations, separation factors of 3.0 are readily obtained. These values show an overall improvement on the separation values obtained with TODGA (ca. 2.5).[43] Taking into account the selectivity of SO$_3$-Ph-BTBP (SF$_{Cm/Am}$: 1.6), we can calculate a separation factor of ca. 1.9 for iPDdDGA without the addition of complexant. This corresponds to the values found in Figure 5 for extractions with 0.1 mol·L^{-1} of iPDdDGA, the same concentration used in the stripping experiments.

Distribution ratios of lanthanides are higher than 1 at all tested concentrations of nitric acid and BTBP ligand. At 2.5 mmol·L^{-1} of SO$_3$-Ph-BTBP in 0.1 mol·L^{-1} of HNO$_3$, a condition where Am is effectively stripped (as observed in Figure 10), a workable SF$_{La/Am}$ value of 5 is obtained. However, this separation factor increases with higher SO$_3$-Ph-BTBP concentrations, going up to 19. This indicates that the separation factor can be improved by optimizing both the SO$_3$-Ph-BTBP and HNO$_3$ concentrations of the stripping solution.

The reason for this increased selectivity between Am and Cm using the iPDdDGA derivative with branched alkyl chains is not yet fully understood. Comparison of N,N,N',N'-tetrabutyldiglycolamide (TnBDGA), N,N,N',N'-tetra-isobutyl-diglycolamide (TiBDGA), and N,N,N',N'-tetra-secbutyldigly-colamide (TsBDGA) with TODGA has shown improved SF$_{Cm/Am}$ for TnBDGA and decreased factors for TiBDGA and TsBDGA.[41] Branching in the β position decreases both D_{An} and SF$_{Cm/Am}$, while steric hindrance at the α position increased D_{An} 10-fold compared to the linear molecule but also decreased SF$_{Cm/Am}$. A study of the extraction of lanthanides by DGAs has indicated that introducing the branching point further away from the metal-ion binding site improves the extraction strength and selectivity, with branching in the β position giving the poorest selectivity.[29] Branching at the α position was, however, not tested, and of all the tested DGAs the best lanthanide separation properties were found for DMDODGA. The Cm/Am selectivity of these DGAs was not tested. Previous research suggested that EDdDGA likely has poorer selectivity than iPDdDGA, as well as higher extraction strength that would make stripping more difficult.[42] However, it is evident that steric hindrance is an important factor contributing to the Cm/Am selectivity of DGA-type extractants, with both chain length and branching influencing the separation factors. The synthesis and testing of new DGA analogues with small changes to the alkyl chains, as well as acquisition of thermodynamic data and the study of the complexes formed in the organic phase through spectroscopic methods, could give more insight into the influence of steric hindrance on the Cm/Am selectivity.

■ CONCLUSIONS

A new DGA extractant containing both isopropyl and dodecyl alkyl chains, iPDdDGA, was investigated for its extraction properties with the AmSel system, employing TODGA, as a

reference. It was observed that iPDdDGA was similar to TODGA and other DGAs in kinetics and complex stoichiometry, but the distribution ratios are at least 1 order of magnitude larger than those observed for TODGA. Despite stronger extraction of trivalent actinides and lanthanides, selective stripping of Am is feasible with an aqueous phase containing 2.5 mmol·L^{-1} of SO$_3$-Ph-BTBP in 0.1 mol·L^{-1} of HNO$_3$, resulting in a SF$_{Cm/Am}$ of 2.8 and a SF$_{La/Am}$ of 5. These values can be further optimized as separation factors between Cm and Am of 3.0 were readily obtained, and separation factors between La and Am as high as 19 were achieved. The SF$_{Cm/Am}$ in the iPDdDGA-based AmSel was on average higher than the original TODGA-based AmSel process by a value of 0.5, a 20% improvement in separation factor. This improvement in separation factor is a result of an optimized steric hindrance, although the reason for this influence is not yet fully understood and requires more research of the effect of alkyl chains on extractions of Am and Cm. Furthermore, key data necessary for the development of an iPDdDGA-based AmSel process are still missing. This includes insight into properties such as the hydrolytic and radiolytic stability, influence of degradation compounds, and loading capacity, which must be investigated to determine whether iPDdDGA is a viable alternative for TODGA. Such data would also allow for an optimization of both the organic and the stripping phase. Most critically, the behavior of fission products, some of which are known to be coextracted by DGA extractants, during the loading and stripping steps should also still be investigated to ensure a full separation of Am from the HAR can be achieved. Nevertheless, these first extraction results are promising and demonstrate the potential of novel DGA structures to improve current separation processes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c06426.

> Additional data of stripping experiments at higher nitric acid concentrations and equilibrium nitric acid concentrations after stripping experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Karen Van Hecke − *Institute for Nuclear Energy Technology, Belgian Nuclear Research Center (SCK CEN), 2400 Mol, Belgium;* ⓞ orcid.org/0000-0002-7100-192X; Email: karen.van.hecke@sckcen.be

Authors

Filip Kolesar − *Institute for Nuclear Energy Technology, Belgian Nuclear Research Center (SCK CEN), 2400 Mol, Belgium; Department of Chemistry, KU Leuven, 3001 Leuven, Belgium;* ⓞ orcid.org/0000-0002-7842-1409

Ken Verguts − *Institute for Nuclear Energy Technology, Belgian Nuclear Research Center (SCK CEN), 2400 Mol, Belgium*

Cécile Marie − *CEA, DES, ISEC, DMRC, University of Montpellier, F-30207 Bagnols-sur-Cèze, France;* ⓞ orcid.org/0000-0002-4373-0228

Laurence Berthon − *CEA, DES, ISEC, DMRC, University of Montpellier, F-30207 Bagnols-sur-Cèze, France;* ⓞ orcid.org/0000-0003-3474-8474

Koen Binnemans − *Department of Chemistry, KU Leuven, 3001 Leuven, Belgium;* ⓞ orcid.org/0000-0003-4768-3606

Thomas Cardinaels − *Institute for Nuclear Energy Technology, Belgian Nuclear Research Center (SCK CEN), 2400 Mol, Belgium; Department of Chemistry, KU Leuven, 3001 Leuven, Belgium;* ⓞ orcid.org/0000-0002-2695-1002

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.4c06426

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) *Implications of Partitioning and Transmutation in Radioactive Waste Management*; International Atomic Energy Agency: Vienna, 2004. https://www.iaea.org/publications/7112/implications-of-partitioning-and-transmutation-in-radioactive-waste-management.

(2) Lensa, W. v.; Nabbi, R. *RED-IMPACT Impact of Partitioning, Transmutation and Waste Reduction Technologies on the Final Nuclear Waste Disposal Synthesis Report*; INIS-DE--0496, Germany, 2008. http://inis.iaea.org/search/search.aspx?orig_q=RN:39117966.

(3) Herbst, R. S.; Baron, P.; Nilsson, M. Standard and advanced separation: PUREX processes for nuclear fuel reprocessing. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing, 2011; pp 141−175.

(4) European Commission; Directorate-General for Research and Innovation; Hudson, M.; Madic, C. *High-Level Liquid Waste Partitioning by Means of Completely Incinerable Extractants*; Publications Office of the EU, 1998.

(5) Sasaki, Y.; Sugo, Y.; Suzuki, S.; Tachimori, S. The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO$_3$-n-dodecane system. *Solvent Extr. Ion Exch.* **2001**, *19* (1), 91−103.

(6) Ansari, S. A.; Pathak, P. N.; Manchanda, V. K.; Husain, M.; Prasad, A. K.; Parmar, V. S. N. N,N',N'-Tetraoctyl diglycolamide (TODGA): a promising extractant for actinide-partitioning from high-level waste (HLW). *Solvent Extr. Ion Exch.* **2005**, *23* (4), 463−479.

(7) Modolo, G.; Asp, H.; Schreinemachers, C.; Vijgen, H. Development of a TODGA based Process for Partitioning of Actinides from a PUREX Raffinate Part I: Batch Extraction Optimization Studies and Stability Tests. *Solvent Extr. Ion Exch.* **2007**, *25* (6), 703−721.

(8) Whittaker, D.; Geist, A.; Modolo, G.; Taylor, R.; Sarsfield, M.; Wilden, A. Applications of Diglycolamide Based Solvent Extraction Processes in Spent Nuclear Fuel Reprocessing, Part 1: TODGA. *Solvent Extr. Ion Exch.* **2018**, *36* (3), 223−256.

(9) Sugo, Y.; Sasaki, Y.; Tachimori, S. Studies on hydrolysis and radiolysis of N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide. *Radiochim. Acta* **2002**, *90* (3), 161−165.

(10) Modolo, G.; Asp, H.; Vijgen, H.; Malmbeck, R.; Magnusson, D.; Sorel, C. Demonstration of a TODGA-Based Continuous Counter-Current Extraction Process for the Partitioning of Actinides from a Simulated PUREX Raffinate, Part II: Centrifugal Contactor Runs. *Solvent Extr. Ion Exch.* **2008**, *26* (1), 62−76.

(11) Mincher, B. J.; Modolo, G.; Mezyk, S. P. Review Article: The Effects of Radiation Chemistry on Solvent Extraction 3: A Review of

Actinide and Lanthanide Extraction. *Solvent Extr. Ion Exch.* **2009**, *27* (5−6), 579−606.

(12) Kimberlin, A.; Guillaumont, D.; Arpigny, S.; Camès, B.; Guilbaud, P.; Saint-Louis, G.; Galán, H.; Berthon, L. An experimental and computational look at the radiolytic degradation of TODGA and the effect on metal complexation. *New J. Chem.* **2021**, *45* (28), 12479−12493.

(13) Kimberlin, A.; Saint-Louis, G.; Guillaumont, D.; Camès, B.; Guilbaud, P.; Berthon, L. Effect of metal complexation on diglycolamide radiolysis: a comparison between ex situ gamma and in situ alpha irradiation. *Phys. Chem. Chem. Phys.* **2022**, *24* (16), 9213−9228.

(14) Galán, H.; Núñez, A.; Espartero, A. G.; Sedano, R.; Durana, A.; de Mendoza, J. Radiolytic Stability of TODGA: Characterization of Degraded Samples under Different Experimental Conditions. *Procedia Chem.* **2012**, *7*, 195−201.

(15) Tachimori, S.; Sasaki, Y.; Suzuki, S.-i. Modification of TODGA-n-dodecane solvent with a monoamide for high loading of lanthanides(III) and actinides(III). *Solvent Extr. Ion Exch.* **2002**, *20* (6), 687−699.

(16) Magnusson, D.; Christiansen, B.; Glatz, J. P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C. Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate. *Solvent Extr. Ion Exch.* **2009**, *27* (1), 26−35.

(17) Serrano-Purroy, D.; Baron, P.; Christiansen, B.; Malmbeck, R.; Sorel, C.; Glatz, J.-P. Recovery of minor actinides from HLLW using the DIAMEX process. *Radiochim. Acta* **2005**, *93*, 351−355.

(18) Sypula, M.; Wilden, A.; Schreinemachers, C.; Malmbeck, R.; Geist, A.; Taylor, R.; Modolo, G. Use of Polyaminocarboxylic Acids as Hydrophilic Masking Agents for Fission Products in Actinide Partitioning Processes. *Solvent Extr. Ion Exch.* **2012**, *30* (7), 748−764.

(19) Modolo, G.; Wilden, A.; Kaufholz, P.; Bosbach, D.; Geist, A. Development and demonstration of innovative partitioning processes (i-SANEX and 1-cycle SANEX) for actinide partitioning. *Prog. Nucl. Energy* **2014**, *72*, 107−114.

(20) Deepika, P.; Sabharwal, K. N.; Srinivasan, T. G.; Vasudeva Rao, P. R. Studies on the Use of *N,N,N′,N′*-Tetra(2-ethylhexyl) Diglycolamide (TEHDGA) for Actinide Partitioning. I: Investigation on Third-Phase Formation and Extraction Behavior. *Solvent Extr. Ion Exch.* **2010**, *28* (2), 184−201.

(21) Mossand, G. Recherche de nouveaux ligands pour l'extraction sélective de l'uranium et des terres rares. Ph.D. Dissertation, Université Grenoble Alpes, Grenoble, 2017. https://tel.archives-ouvertes.fr/tel-03086901.

(22) Ravi, J.; Suneesh, A. S.; Prathibha, T.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Extraction Behavior of Some Actinides and Fission Products from Nitric Acid Medium by a New Unsymmetrical Diglycolamide. *Solvent Extr. Ion Exch.* **2011**, *29* (1), 86−105.

(23) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Co-extraction and stripping behavior of trivalent actinides and fission products in *N,N*-di-2-ethylhexyl-*N′,N′*-dioctyl-diglycolamide. *Radiochim. Acta* **2013**, *101* (5), 301−306.

(24) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Tuning the diglycolamides for modifier-free minor actinide partitioning. *J. Radioanal. Nucl. Chem.* **2013**, *295* (2), 1283−1292.

(25) Vasudeva Rao, P. R.; Kolarik, Z. A review of third phase formation in extraction of actinides by neutral organophosphorus extractants. *Solvent Extr. Ion Exch.* **1996**, *14* (6), 955−993.

(26) Bauduin, P.; Testard, F.; Berthon, L.; Zemb, T. Relation between the hydrophile/hydrophobe ratio of malonamide extractants and the stability of the organic phase: investigation at high extractant concentrations. *Phys. Chem. Chem. Phys.* **2007**, *9* (28), 3776−3785.

(27) Testard, F.; Zemb, T.; Bauduin, P.; Berthon, L. Third-phase Formation in Liquid/Liquid Extraction: A Colloidal Approach. In *Ion Exchange and Solvent Extraction, A Series of Advances*, 19th ed.; Moyer, B. A., Ed.; CRC Press, 2009; Vol. *19*.

(28) Tokheim, B. G.; Kelly, S. S.; Ronald, R. C.; Nash, K. L. Synthesis and characterization of new unsymmetrical diglycolamide extractants for lanthanide ion partitioning: part one—straight-chain alkyl derivatives. *J. Radioanal. Nucl. Chem.* **2020**, *326* (1), 789−800.

(29) Stamberga, D.; Healy, M. R.; Bryantsev, V. S.; Albisser, C.; Karslyan, Y.; Reinhart, B.; Paulenova, A.; Foster, M.; Popovs, I.; Lyon, K.; et al. Structure Activity Relationship Approach toward the Improved Separation of Rare-Earth Elements Using Diglycolamides. *Inorg. Chem.* **2020**, *59* (23), 17620−17630.

(30) Liu, Y.; Zhao, C.; Liu, Z.; Liu, S.; Zhou, Y.; Jiao, C.; Zhang, M.; Gao, Y.; He, H.; Zhang, S. Study on the extraction of lanthanides by isomeric diglycolamide extractants: an experimental and theoretical study. *RSC Adv.* **2022**, *12* (2), 790−797.

(31) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Solvent extraction behavior of trivalent metal ions in diglycolamides having same carbon to oxygen ratio. *Sep. Sci. Technol.* **2016**, *51* (1), 32−40.

(32) Mowafy, E. A.; Mohamed, D. Extraction of rare earth elements from nitrate solution using novel unsymmetrical diglycolamide. *Sep. Sci. Technol.* **2017**, *52* (6), 1006−1014.

(33) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. New unsymmetrical digycolamide ligands for trivalent actinide separation. *Radiochim. Acta* **2014**, *102* (7), 609−617.

(34) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Unsymmetrical diglycolamide for the safe management of nuclear waste. *J. Environ. Chem. Eng.* **2013**, *1* (4), 690−695.

(35) Swami, K. R.; Venkatesan, K. A.; Sahu, P.; Ali, S. M. The effect of alkyl chain length attached to the diglycolamide and n-paraffin on the aggregation behaviour of diglycolamide and MD simulation of aggregates. *J. Mol. Struct.* **2020**, *1221*, 128795.

(36) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Feasibility of Using Di-Dodecyl-Di-Octyl Diglycolamide for Partitioning of Minor Actinides from Fast Reactor High-Level Liquid Waste. *Solvent Extr. Ion Exch.* **2014**, *32* (4), 424−436.

(37) Ravi, J.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Single-cycle method for partitioning of trivalent actinides using completely incinerable reagents from nitric acid medium. *Radiochim. Acta* **2014**, *102* (7), 599−607.

(38) Ravi, J.; Robert Selvan, B.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Evaluation of radiation stability of N,N-didodecyl N′,N′-di-octyl diglycolamide: a promising reagent for actinide partitioning. *J. Radioanal. Nucl. Chem.* **2014**, *299* (1), 879−885.

(39) Ravi, J.; Selvan, B. R.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Vasudeva Rao, P. R. Radiolytic stability of di-2-ethylhexyl-dioctyl diglycolamide. *Radiochim. Acta* **2014**, *102* (5), 451−457.

(40) Chapron, S. Synthesis and evaluation of aqueous complexing agents for the americium/curium separation. Synthèse et évaluation de complexants aqueux pour la séparation américium/curium. Ph.D. Dissertation, Université Montpellier II—Sciences et Techniques du Languedoc, 2014. https://tel.archives-ouvertes.fr/tel-01347107.

(41) Chapron, S.; Marie, C.; Arrachart, G.; Miguirditchian, M.; Pellet-Rostaing, S. New Insight into the Americium/Curium Separation by Solvent Extraction using Diglycolamides. *Solvent Extr. Ion Exch.* **2015**, *33* (3), 236−248.

(42) Bourg, S.; Marie, C. GENIORS project report: WPSAR 5; D11.5; CEA. 2020. https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5d21b4245&appId=PPGMS.

(43) Wagner, C.; Müllich, U.; Geist, A.; Panak, P. J. Selective Extraction of Am(III) from PUREX Raffinate: The AmSel System. *Solvent Extr. Ion Exch.* **2016**, *34* (2), 103−113.

(44) Nave, S.; Modolo, G.; Madic, C.; Testard, F. Aggregation Properties of N,N,N′,N′-Tetraoctyl-3-oxapentanediamide (TODGA) in n-Dodecane. *Solvent Extr. Ion Exch.* **2004**, *22* (4), 527−551.

(45) Dovlete, C.; Povinec, P. P. Quantification of uncertainty in gamma-spectrometric analysis of environmental samples. In *Quantifying Uncertainty in Nuclear Analytical Measurements*; International Atomic Energy Agency, 2004; pp 103−126.

(46) Wilden, A.; Modolo, G.; Lange, S.; Sadowski, F.; Beele, B. B.; Skerencak-Frech, A.; Panak, P. J.; Iqbal, M.; Verboom, W.; Geist, A.; Bosbach, D. Modified Diglycolamides for the An(III) + Ln(III) Co-separation: Evaluation by Solvent Extraction and Time-Resolved Laser Fluorescence Spectroscopy. *Solvent Extr. Ion Exch.* 2014, 32 (2), 119−137.

(47) Gujar, R. B.; Ansari, S. A.; Murali, M. S.; Mohapatra, P. K.; Manchanda, V. K. Comparative evaluation of two substituted diglycolamide extractants for 'actinide partitioning. *J. Radioanal. Nucl. Chem.* 2010, 284 (2), 377−385.

(48) Sastry, N. V.; Valand, M. K. Viscosities and Densities for Heptane + 1-Pentanol, +1-Hexanol, +1-Heptanol, +1-Octanol, +1-Decanol, and +1-Dodecanol at 298.15 K and 308.15 K. *J. Chem. Eng. Data* 1996, 41 (6), 1426−1428.

(49) Kaufholz, P.; Modolo, G.; Wilden, A.; Sadowski, F.; Bosbach, D.; Wagner, C.; Geist, A.; Panak, P. J.; Lewis, F. W.; Harwood, L. M. Solvent Extraction and Fluorescence Spectroscopic Investigation of the Selective Am(III) Complexation with TS-BTPhen. *Solvent Extr. Ion Exch.* 2016, 34 (2), 126−140.

(50) Boubals, N.; Wagner, C.; Dumas, T.; Chanèac, L.; Manie, G.; Kaufholz, P.; Marie, C.; Panak, P. J.; Modolo, G.; Geist, A.; Guilbaud, P. Complexation of Actinide(III) and Lanthanide(III) with H4TPAEN for a Separation of Americium from Curium and Lanthanides. *Inorg. Chem.* 2017, 56 (14), 7861−7869.

(51) Mowafy, E. A.; Aly, H. F. Synthesis of some N,N,N′,N′-Tetraalkyl-3-Oxa-Pentane-1,5-Diamide and their Applications in Solvent Extraction. *Solvent Extr. Ion Exch.* 2007, 25 (2), 205−224.

(52) Woodhead, D.; McLachlan, F.; Taylor, R.; Müllich, U.; Geist, A.; Wilden, A.; Modolo, G. Nitric Acid Extraction into a TODGA Solvent Modified with 1-Octanol. *Solvent Extr. Ion Exch.* 2019, 37 (2), 173−190.

(53) Geist, A. Extraction of Nitric Acid into Alcohol: Kerosene Mixtures. *Solvent Extr. Ion Exch.* 2010, 28 (5), 596−607.

(54) Jensen, M. P.; Yaita, T.; Chiarizia, R. Reverse-Micelle Formation in the Partitioning of Trivalent f-Element Cations by Biphasic Systems Containing a Tetraalkyldiglycolamide. *Langmuir* 2007, 23 (9), 4765−4774.

(55) Bell, K.; Geist, A.; McLachlan, F.; Modolo, G.; Taylor, R.; Wilden, A. Nitric acid extraction into TODGA. In *Atalante 2012 International Conference on Nuclear Chemistry for Sustainable Fuel Cycles*, 2012; Vol. 7, pp 152−159.

(56) Campbell, E. L.; Holfeltz, V. E.; Hall, G. B.; Nash, K. L.; Lumetta, G. J.; Levitskaia, T. G. Nitric Acid and Water Extraction by T2EHDGA in n-Dodecane. *Solvent Extr. Ion Exch.* 2017, 35 (7), 586−603.

(57) Sasaki, Y.; Rapold, P.; Arisaka, M.; Hirata, M.; Kimura, T.; Hill, C.; Cote, G. An additional insight into the correlation between the distribution ratios and the aqueous acidity of the TODGA system. *Solvent Extr. Ion Exch.* 2007, 25 (2), 187−204.

(58) Mowafy, E. A.; Alshammari, A.; Mohamed, D. Extraction Behaviors of Critical Rare Earth Elements with Novel Structurally Tailored Unsymmetrical Diglycolamides from Acidic Media. *Solvent Extr. Ion Exch.* 2021, 40, 387−411.

(59) Picayo, G. A.; Etz, B. D.; Vyas, S.; Jensen, M. P. Characterization of the ALSEP Process at Equilibrium: Speciation and Stoichiometry of the Extracted Complex. *ACS Omega* 2020, 5 (14), 8076−8089.

(60) Panja, S.; Mohapatra, P. K.; Tripathi, S. C.; Dhekane, G. D.; Gandhi, P. M.; Janardan, P. Liquid−liquid extraction and pertraction behavior of Am(III) and Sr(II) with diglycolamide carrier extractants. *J. Membr. Sci.* 2012, 399−400, 28−36.

(61) Panja, S.; Mohapatra, P. K.; Tripathi, S. C.; Dhekane, G. D.; Gandhi, P. M.; Janardan, P. Liquid − Liquid Extraction and Pertraction of Eu(III) from Nitric Acid Medium Using Several

Substituted Diglycolamide Extractants. *Sep. Sci. Technol.* 2013, 48 (14), 2179−2187.

(62) Sasaki, Y.; Sugo, Y.; Suzuki, S.; Kimura, T. A method for the determination of extraction capacity and its application to N,N,N′,N′-tetraalkylderivatives of diglycolamide-monoamide/n-dodecane media. *Anal. Chim. Acta* 2005, 543 (1−2), 31−37.

(63) Liu, Q.; Zhou, J.; Zhu, L.; Zhang, Y.; Li, D.; Yang, S.; Tian, G. Extraction of Actinides Including Neptunyl (V) by Asymmetrical N,N′-Dimethyl-N,N′-Dioctyl-Diglycolamide in Comparison with Symmetrical N,N,N′,N′-Tetraoctyl-Diglycolamide—Sterically Structural Insight into Actinide Separations. *Solvent Extr. Ion Exch.* 2020, 38 (5), 485−495.

(64) Mathur, J. N.; Nash, K. L. Thermodynamics of extraction of Am(III) and Eu(III) from nitrate and thiocyanate media with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide. *Solvent Extr. Ion Exch.* 1998, 16 (6), 1341−1356.

(65) Ansari, S. A.; Pathak, P. N.; Husain, M.; Prasad, A. K.; Parmar, V. S.; Manchanda, V. K. Extraction of actinides using N, N, N′, N′-tetraoctyl diglycolamide (TODGA): a thermodynamic study. *Radiochim. Acta* 2006, 94 (6−7), 307−312.

(66) Geist, A.; Adnet, J. M.; Bourg, S.; Ekberg, C.; Galan, H.; Guilbaud, P.; Miguirditchian, M.; Modolo, G.; Rhodes, C.; Taylor, R. An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, part 1-heterogeneous recycling. *Sep. Sci. Technol.* 2021, 56, 1866−1881.

(67) Peroutka, A. A.; Galley, S. S.; Shafer, J. C. Elucidating the speciation of extracted lanthanides by diglycolamides. *Coord. Chem. Rev.* 2023, 482, 215071.