WATER SOLUBLE PDCA DERIVATIVES FOR SELECTIVE Ln(III)/An(III) AND Am(III)/Cm(III) SEPARATION

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The synthesis and solvent extraction behavior of dipicolinic acid (pyridine-2,6-dicarboxylic acid, PDCA) and their derivatives have been studied for possible use in selective back-extraction of actinides, especially americium. The extraction was performed from an organic phase containing a mixture of trivalent actinides and lanthanides pre-extracted with N,N,N',N'-tetraoctyl diglycolamide (TODGA). The efficiency of the back-extraction was enhanced when the picolinate platform was used in a heterocyclic decadentate ligand called h₄tpaen. Beyond selective An/Ln extraction, the aqueous soluble h₄tpaen ligand seemed a potential reagent for an intra-group Am(III)/Cm(III) separation with a separation factor SF_Cm/Am of about 3.5.

Keywords: Solvent extraction, picolinic acid, PDCA, h₄tpaen, Actinides(III)/Lanthanides(III)

INTRODUCTION

Solvent extraction is widely applied in the nuclear fuel cycle for separating uranium and plutonium from irradiated nuclear fuel via the Plutonium URanium EXtraction (PUREX) process.¹ The residual high level liquid waste (HLLW) contains fission products along with the remaining minor actinides.

The intra-and intergroup separation of lanthanides and trivalent actinides (An(III)) is currently one of the main challenges in nuclear waste reprocessing, due to the chemical similarities between the two groups of elements (similar charge and chemical behavior).² Such an issue arises when considering Am and Cm, the most abundant minor actinide cations, which have almost the same radii and charge density as the common fission

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Color versions of one or more of the figures in the article are available online at www.tandfonline.com/lsei
product lanthanides.\textsuperscript{[13,4]} A great deal of effort has gone into the design of extractants and ligands for the separation of minor trivalent actinides from lanthanides\textsuperscript{[5,6,7,8]} and among them, \textit{N,N,N',N'\textsuperscript{-}-tetaoctyl diglycolamide (TODGA)} has emerged as one of the reference molecules due to its high distribution ratios for \textit{An} and \textit{Ln} in a nitric acid medium.\textsuperscript{[9,10]}

Selective back-extraction and the concept of selectively retaining ions in an aqueous phase during a solvent extraction process has been shown to hold great promise in processes for \textit{An(III)/Ln(III)}.\textsuperscript{[11,12]} The goal is to develop aqueous extraction agents or hold-back agents which can be used to improve the selectivity of solvent extraction systems.

Polyaminocarboxylic acids are well-known reagents used in combination with specific extractants to separate \textit{An(III)} from \textit{Ln(III)} because their complex formation constants with \textit{An(III)} are higher than those for light \textit{Ln(III)}.\textsuperscript{[13,14,15,16]} The Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Complexes (TALSPEAK) process has demonstrated the considerable usefulness of polyaminocarboxylic acids such as ethylenediamine-\textit{N,N,N',N'\textsuperscript{-}-tetraacetic acid (EDTA)} or diethylenetriamine-\textit{N,N,N',N''\textsuperscript{-}-pentaacetic acid (DTPA)} for the selective extraction of trivalent actinides from trivalent fission product lanthanides in solution.\textsuperscript{[3, 11, 17,18]}

The TALSPEAK process can be simplified to a combination of di-2-ethyl-hexyl-phosphoric acid (HDEHP), a cationic exchanger solvent, with DTPA, an aqueous soft nitrogen donor. HDEHP is able to selectively extract the lanthanides from the organic phase while DTPA, which interacts with \textit{An(III)} more strongly than with \textit{Ln(III)}, retains the actinides in the aqueous phase. In this process, the aqueous phase contains the aqueous-soluble aminopolycarboxylate complexant in a concentrated carboxylic acid buffer.

Beyond traditional TALSPEAK and the use of aqueous-soluble aminopolycarboxylate complexant, the study of other systems and likely candidates has been considered for the selective back extraction of \textit{Am(III)} from organic solutions containing \textit{Ln (III)} elements.

Some aqueous-soluble diglycolamides with alkyl\textsuperscript{[19,20]} or ethylene glycol\textsuperscript{[21]} chains on the amidic nitrogens have been studied, but in some cases water solubility is limited and selectivity remains low. Dipicolinic acid or pyridine-2,6-dicarboxylic acid (PDCA) is a highly useful tridentate ligand known to form moderately strong complexes with a variety of metal ions, including trivalent lanthanides, and an application as a potential substitute for DTPA in TALSPEAK-like separations has been explored.\textsuperscript{[22]} The preliminary assessment showed that PDCA is an effective holdback reagent in TALSPEAK-like systems, but it is limited by a lack of solubility in water.

TODGA shows a slightly higher affinity towards \textit{Ln(III)} compared to \textit{An(III)}, it appeared interesting to add a selective aqueous-soluble complexant able to form stronger complexes with \textit{An(III)} than \textit{Ln(III)}. The effects of DTPA on the extractions of actinides(III) and lanthanides(III) from a nitrate solution into TODGA/n-dodecane have been investigated.\textsuperscript{[23]}

In the study presented here, picolinic acid and its derivatives were studied as potential aqueous-soluble complexants in back-extraction applications for the separation of minor trivalent actinides from lanthanides using an organic TODGA phase. The focus was on the effects of pyridine-2,6-dicarboxylic acid modification (Fig. 1a) incorporating electron acceptor and donor groups. A structure-extraction relationship was examined to see if the type of substituent (alkyl, donor, or acceptor) was a parameter affecting the ligand’s extraction ability. Another objective was to evaluate the correlation between ligand architecture and extraction ability and/or selectivity. The picolinate platform was therefore inserted into a podand-type molecule \textit{N,N,N',N''\textsuperscript{-}-tetrakis(2-methylpyridyl)ethylenediamine (TPEN)}, which has six soft-donor site combination, demonstrated good selectivity for \textit{Am(III)} compared to \textit{Ln (III)} and was of particular interest in the partitioning of minor
Some drawbacks had to be taken into account, such as the enhanced solubility of protonated TPEN. Next, attempts were made to improve extraction performance. Furthermore, the existence of a strong correlation between ligand architecture and metal ion binding selectivity was demonstrated. It was clear that aqueous-soluble derivatives of this ligand and their applicability for selective back extraction could be considered. N,O-tetrapodal ligands derived from ethylenediamine have been developed, whose stripping efficiency is linked to a compromise between softness and affinity.

During this study, a picolinate platform in a heterocyclic decadentate ligand (Fig. 1b) called $N,N,N',N'$-tetrakis[(6-carboxypyridin-2-yl)methyl]ethylenediamine ($h_4$tpae) was used for the separation of lanthanide and actinide cations. It has been shown that such decadentate ligands yield lanthanide chelates that are highly soluble and stable at physiological pH values, suggesting a possible use as luminescent probes for biomedical applications.

The choices were based on the need to use aqueous-soluble ligands able to promote the separation of Am$^{3+}$/Ln$^{3+}$ and Am$^{3+}$/Cm$^{3+}$ when in a liquid-liquid extraction process with TODGA first used as a neutral extractant in the organic phase.

Attention focused specifically on the selective recovery of americium compared to rare earths (europium) and transuranian cations (curium) in an acidic aqueous phase after contact with a TODGA-containing organic phase.

The synthesis and solvent extraction properties of these ligands are described below.

**EXPERIMENTAL**

**Synthetic Chemistry**

The general procedures for ligand synthesis and characterizations are described in the supporting information.

**Solvent Extraction Experiments**

**Chemicals and Solutions.** The organic TODGA phase (0.1 M) was prepared by dissolving TODGA (1.452 g, 2.5 mmol) in 25 mL of hydrogenated tetrapropene (TPH). The solution was shaken vigorously for 5 min and left to homogenize for 30 min before use.

A lanthanide-actinide stock solution was prepared with Eu(NO$_3$)$_3$, 5H$_2$O (1.3 x $10^{-3}$ M) and trace amounts of $^{152}$Eu (1.1 x $10^{-8}$ M), $^{241}$Am (4.5 x $10^{-7}$ M) and if required $^{244}$Cm (1.92 x $10^{-8}$ M). $^{152}$Eu tracer was purchased from CERCA-LEA and used without further purification. $^{241}$Am(III) stock solution was obtained by dissolution of AmO$_2$ in HNO$_3$.
followed by Am(III) purification on a DOWEX-50 cation exchange resin. $^{244}$Cm(III) stock solution was obtained from the raffinate of an Am/Cm separation process carried out in the Atalante facility. All radioactive solutions were handled in glove boxes.

The aqueous solutions containing the ligands were prepared from PDCA derivatives ($1.3 \times 10^{-3}$ M) or h$_4$tpaen ($6.55 \times 10^{-4}$ M) in NaNO$_3$ aqueous solution (1 M or 3 M). The solution concentrations were checked by TOC analyzer. Aqueous solution acidity was maintained with an aqueous solution of nitric acid (3 M), with the nitric acid concentration in the aqueous phase at equilibrium ($[\text{HNO}_3]_{\text{eq}}$) determined by automatic titration with NaOH 0.1 M.

Pre-equilibrium

In a centrifuge tube, TODGA solution (0.1 M) was contacted with an equal volume of an appropriate sodium nitrate aqueous solution (1 M) at the set pH for 15 min at 25 ± 0.5°C in a vibrating shaker (2000 min$^{-1}$). No third-phase formation was observed in any of the experiments. After the pre-equilibrium of pH, the resulting mixture was centrifuged at 4000 rpm for 5 min and the organic phase was completely separated from the aqueous phase.

Extraction

The organic phase was then contacted with an equal volume of the aqueous lanthanide-actinide stock solution (containing Am, Cm, and Eu) for 15 min before centrifugation (5 min at 4000 rpm). Next, a sample aliquot was taken from each phase to evaluate the lanthanide and actinide concentrations. Emission spectroscopy (ICP-AES) was used to assess the Eu concentration in the aqueous phase. The activities of $^{152}$Eu, $^{241}$Am, and $^{244}$Cm in the aqueous and organic phases were analyzed by an alpha and/or gamma spectrometer system (Canberra), with gamma measurements for $^{152}$Eu, alpha for $^{244}$Cm, and both alpha and gamma for $^{241}$Am.

Back-extraction

A preliminary study on the phase transfer kinetics indicated that equilibrium was reached quickly. As the equilibrium values after 5 minutes changed no further during up to 60 minutes of shaking, a 15 min shaking-time was therefore used in the experiments to ensure thermodynamic equilibrium. The previously-described organic phase spiked with cations was contacted with an equal volume of aqueous solution containing the ligands for 15 min in a vibrating shaker (2000 min$^{-1}$). The resulting mixture was centrifuged at 4000 rpm for 5 min to completely separate the organic phase from the aqueous phase. The aqueous phase pH was monitored by a pH meter, while the europium concentration was measured by ICP-AES. The activities of $^{152}$Eu, $^{241}$Am, and $^{244}$Cm in the aqueous and organic phases were analyzed by an alpha and/or gamma-spectrometer system.

Distribution coefficients ($D_M = [\text{M}]_{\text{org}}/[\text{M}]_{\text{aq}}$) and separation factors ($SF_{M1/M2} = D_{M1}/D_{M2}$) were determined in order to evaluate the efficiency and selectivity of the extractant and the ligand combination, compared to the other cations. The extractions were run at least in duplicate, and the D values between 0.1 and 10 had a maximum error of about 5%. The error could be up to 10% for smaller (0.01-0.1) and larger (10-100) values.
RESULTS AND DISCUSSION

Preliminary screening tests were performed with pyridine-2,6-dicarboxylic acid (PDCA) as an aqueous soluble ligand for the selective back-extraction of americium as compared to europium from an organic TODGA phase into an aqueous phase. The suitability of the ligand is associated with a distribution ratio $D_{Am}$ value which is as low as possible and with the highest possible separation factor $SF_{Eu/Am}$.

The back-extraction experiments with Am(III) and Eu(III) were studied as a function of PDCA, HNO$_3$, and NaNO$_3$ concentrations, and the results are summarized in Table 1. The Am(III) and Eu(III) extraction properties of PDCA were examined in the light of the results obtained with or without ligand. The low $D_{Am}$ values indicate that a larger amount of Am(III) was transferred from the organic to the aqueous phase when the aqueous-soluble PDCA was present. Increasing the concentration of PDCA led to a decrease in the distribution ratio, resulting in a better ability to strip Am(III) from the TODGA organic phase. The separation factor $SF_{Eu/Am}$ seems to be constant, close to 9.5 for a $[PDCA]/[Eu(III)]+\cdot[Am(III)]$ concentration ratio between 0.5 and 3.

Stability constants have been evaluated by Heathman and Nash as $\log \beta_{101} = 8.90$, $\log \beta_{102} = 15.64$, and $\log \beta_{103} = 21.64$, for the 1:1, 1:2, and 1:3 Eu$^{3+}$ complexes and $\log \beta_{101} = 8.90$, $\log \beta_{102} = 15.87$, and $\log \beta_{103} = 21.88$ for Am$^{3+}$ complexes.\cite{122} In the ligand concentration and acidic conditions of this study, the formation of 1:1 and 1:2 complexes can be expected. A combination of these effects, including the slight differences in the stability constants for Am$^{3+}$ and Eu$^{3+}$ in the dipicolinic system and the intrinsic separation factor of TODGA (close to 4.5), can explain the significant $SF_{Eu/Am}$ value. This behavior contributes to the effective holdback potential of a dipicolinic system for Am/Eu separation in a TODGA-organic phase.

In a second set of experiments, the ligand concentration was set at 1.3 mM, in order to maintain the concentration ratio for ligand to metal constant and equal to 1. The efficiency of the PDCA ligand was studied for HNO$_3$ and NaNO$_3$ dependency by measuring the distribution coefficients for different HNO$_3$ and NaNO$_3$ concentrations.

| Aqueous Phase | [PDCA] (mM) | HNO$_3$ (M) | NaNO$_3$ (M) | $D_{Am}$ | $D_{Eu}$ | $SF_{Eu/Am}$ |
|---------------|-------------|------------|-------------|----------|----------|---------------|
| 0             | 0.1         | 1          | 3.34        | 15.92    | 4.77     |
| 0.1           | 0.1         | 1          | 2.00        | 13.07    | 6.54     |
| 0.5           | 0.1         | 1          | 0.70        | 5.85     | 8.36     |
| 1             | 0.1         | 1          | 0.37        | 3.29     | 8.89     |
| 1.31          | 0.1         | 1          | 0.30        | 2.85     | 9.50     |
| 3.93          | 0.1         | 1          | 0.09        | 0.97     | 10.78    |
| 1.31          | 0.063       | 1          | 0.14        | 1.19     | 8.50     |
| 1.31          | 0.103       | 1          | 0.30        | 2.76     | 9.20     |
| 1.31          | 0.035       | 3          | 0.84        | 9.76     | 11.62    |
| 1.31          | 0.039       | 3          | 1.27        | 12.94    | 10.19    |
| 1.31          | 0.048       | 3          | 2.22        | 24.54    | 11.05    |
| 1.31          | 0.059       | 3          | 3.86        | 42.2     | 10.93    |

$^a$ Back-extraction from an organic phase [TODGA]: 0.1 M in TPH, [Eu(NO$_3$)$_3$], 5H$_2$O]: 1.3 x $10^{-3}$ M, [$^{152}$Eu]: 1.1 x $10^{-8}$ M, [$^{241}$Am]: 4.5 x $10^{-7}$ M.
As expected, there was a slight decrease in the distribution coefficient with lower acidity. When acidity decreases, cations are more easily complexed by the carboxylic acid functionalities, which can be linked to the relationship between the proton concentration and the behavior of the carboxylic acid group in cation complexation. When the concentration of NaNO$_3$ was set at 3 M instead of 1 M, the same behavior was observed. The separation factor SF$_{Eu/Am}$ remained constant, close to 11, which is slightly higher than the value measured for the 1 M ionic strength.

Overall, europium was less complexed by the PDCA ligand and stayed in the organic phase longer. PDCA has been demonstrated to be an effective ligand for Am(III)/Eu(III) separation from an organic TODGA phase with a selective recovery of Am(III) into the acidic aqueous phase.

To better understand this behavior, the chemical modification of PDCA was investigated in order to find out if its structural features may influence both the Am(III) extraction efficiency and the separation factor SF$_{Eu/Am}$. In the case of actinides (III), the 5f orbitals interact with ligands whereas in the case of lanthanides (III) the 4f orbitals are involved. The 5f orbitals are larger and more diffuse, which could explain why softer bases enable the separation.

The influences of relative inductive and electromeric strengths of various molecular groups were studied with the addition of electron-withdrawing or -donor substituents to pyridine-2,6-dicarboxylic acid, i.e., ketone, carboxylic acid, methoxy, halogen, alkyl, and hydroxymethyl groups were introduced on the para position of the nitrogen group. The synthesis and characterization details of the PDCA derivatives are described in the experimental section.

4-(hydroxymethyl) pyridine-2,6-dicarboxylic acid (−CH$_2$OH 3), 4-(ethyl)pyridine-2,6-carboxylic acid (C$_2$H$_5$ 5) and 4-(propionyl)pyridine-2,6-carboxylic acid (C(O)Et 7) were selectively introduced, starting from the dimethylated PDCA derivative (1) through free-radical reactions following the procedure described in the literature.$^{[33]}$ Pyridine-2,4,6-tricarboxylic acid (CO$_2$H 10) was synthesized by the oxidation of 2,4,6-trimethylpyridine with potassium permanganate.$^{[34]}$ Hydrolysis of the methyl ester groups was performed to obtain the corresponding acid derivatives. 4-methoxy-pyridine-2,6-dicarboxylic acid (OMe 13) and 4-chloro-pyridine-2,6-dicarboxylic acid (Cl 14) were synthesized after the modification of chelidamic acid (12).

The extraction properties of these derivatives were evaluated and compared with those of PDCA in the same conditions (Fig. 2). The experimental results show that the derivatives with electron-withdrawing groups have a behavior very close to that of PDCA. The distribution ratios increased for both Am and Eu when the substituents were an electron-donor group or a chlorine atom. Whatever the PDCA derivatives with substituents introduced in the para position of the pyridine, the steric hindrance should not have any effect on the cation complexation. It seems more likely that a factor such as the basicity of the ligand has a stronger effect on the Am and Eu distribution ratio. However, the basicity affects both cations in the same way, which results in similar separation factors SF$_{Eu/Am}$.

The back-extraction experiments showed that the modification of PDCA with an electron-withdrawing or donor group does not impact the selectivity to any significant degree. Similar behavior has been observed in the case of terpyridine framework modification. The basicity of the ligand played a role in the Am and Eu distribution ratio but had no effect on the Am/Eu selectivity.$^{[35]}$

Beyond the use of PDCA (dipicolinic acid) or para substituted PDCA derivatives, the use of picolinate in a podand type molecule was considered. Bearing in mind
the results obtained by Chatterton et al.\textsuperscript{[30]} where $N,N',N''N'''$-tetrakis[(6-carboxypyridin-2-yl)methyl]ethylenediamine (h$_4$tpaen) was used to form luminescent water-stable lanthanide complexes for medicinal purposes, the possibility of using such a picolinate platform for the separation of lanthanide and actinide cations was investigated. The h$_4$tpaen pattern can be considered as a picolinate platform in a heterocyclic decadentate ligand. The ligand (18) was synthesized in a four step procedure adapted from the literature,\textsuperscript{[30]} starting from the dimethylated PDCA derivative (1). In order to highlight the importance of the carboxylic acid group position in such a structure, a h$_5$tpaen ligand (23) was also synthesized starting from the dimethyl 2,5-pyridinedicarboxylate (19).

As for PDCA, back-extraction experiments from an organic TODGA phase were tested as a function of h$_4$tpaen, HNO$_3$, and NaNO$_3$ concentrations. However, unlike the tests conducted with PDCA, curium was introduced as an additional cation. Going further than the inter-group separation ability studied by the selective back-extraction of Am(III) compared to Eu(III), the evaluation of back-extraction properties was also conducted under an intra-group separation of Am(III) from Cm(III).

The results of the back-extraction experiments for Am(III), Eu(III), and Cm(III) with h$_4$tpaen are summarized in Table 2. For the h$_4$tpaen Am(III) and Eu(III) extraction behavior, the general trend was similar to that observed with PDCA. It can be noted that the efficiency of the Am(III) back-extraction, which is related to small $D_{Am}$ values, was improved with an increased ligand concentration and at a lower nitric acid concentration. However, the $D_M$ values are higher for europium, while those for americium are fairly similar to those obtained with the PDCA ligand under the same conditions. This gives a greater separation factor $SF_{Eu/Am}$ and emphasizes the fact that the h$_4$tpaen ligand is more efficient and selective for Am(III) than PDCA, with values of up to 30 compared to 10 obtained with the latter.
Unlike PDCA, where the modification in the 4-position seems to have minimal impact on the selectivity, in the h4tpaen ligand the modification of the pyridine ring in the 2-position and the steric hindrance result in a significant increase of the separation factors SF$_{\text{Eu/Am}}$. The difference can be supported by the fact that the terminal complexes in the PDCA and h4tpaen system are different with respectively a terminal complex with 3 tridentate ligands bound to a metal center resulting in coordination of 3 nitrogen’s and 6 carboxylates for the dipicolinate system and with a metal ten-coordinate with 4 oxygen atoms and 6 nitrogens of the h4tpaen.\[30\] The presence of more soft donor atoms coordinating to the metal center and the steric hindrance help to explain why h4tpaen is more selective than the dipicolinate complexes.

The results demonstrated that it is possible to consider h4tpaen as an efficient ligand for Am(III)/Cm(III) separation. The D$_{\text{Cm}}$ variation depending on the ligand or HNO$_3$ concentration was similar to that previously observed. In a 0.1 M HNO$_3$ concentration with a ligand to metal ratio ([h4tpaen]/([Eu(III)]+[Am(III)]+[Cm(III)]) of 0.5, the back-extraction results give a separation factor SF$_{\text{Cm/Am}}$ of about 3.2 which represents a significant value compared to other systems used for americium/curium separation.

Special molecules have been used to obtain a maximum separation efficiency, and the synergistic mixture of $N,N',N''$-dimethyl-$N,N'$-dioctylhexylethoxymalonamide (DMDOHHEMA) and di-2-ethylhexyl phosphoric acid (HDEHP) can give a SF$_{\text{Am/Cm}}$ value of about 1.6.\[36\]

The use of an aqueous-soluble complexing agent such as $N,N,N',N''$-tetraethylidiglycolamide (TEDGA) leads to an increase from 1.6 to 2.5 in the separation factor SF$_{\text{Am/Cm}}$.\[36,37\] The EXAm process (EXtraction of Americium) is based on the overall efficiency of this system.\[38\]

In a different context, it has been shown that Am(III)/Cm(III) separation from an aqueous solution using a synergistic mixture of bis(aryl)dithiophosphinic acid ((ClPh)$_2$PSSH) and tris(ethylhexyl)phosphate (TEHP) in a complex organic phase (mixture
of iso-octane + tertiary butylbenzene or hexane + toluene) is possible with a separation factor $SF_{\text{Am/Cm}}$ of between 3 and 10 depending on the HNO$_3$ concentration.$^{[39]}$

In comparison, similar efficiency can be obtained for Am(III)/Cm(III) separation with the water soluble h$_4$tpaen ligand in the back-extraction of Am from an organic phase of 0.1 M TODGA in TPH.

These significant results were confirmed when the ionic strength was modified from 1 M to a 3 M NaNO$_3$ concentration. The trends observed remained consistent. The $D_{\text{Am}}$ values are very close to those obtained with 1 M NaNO$_3$, whereas those for the $D_{\text{Eu}}$ are considerably higher.

The slight difference in the results obtained at 1 compared to 3 M in NaNO$_3$ could probably be explained by the differences in Am and Eu complexation strengths with nitrate ions: stronger nitrate complexes are formed with Am than with Eu. The stability constants of nitrate complexes with Am and Eu can be found in the literature.$^{[40,41]}$ As the concentration of sodium nitrate is stronger, extraction by TODGA is favored and therefore the $D_{\text{Eu}}$ increases. Separation factors $SF_{\text{Eu/Am}}$ of up to 200 were obtained in such conditions. The Am(III)/Cm(III) separation was slightly improved with ionic strength modification as a function of the acidity, and separation factors $SF_{\text{Cm/Am}}$ from 3.5 up to 4.3 can be obtained.

In order to study the structural effect on such ligands, the modification of the position of the carboxylate group was considered and back-extraction experiments with the h$_5$tpaen ligand were performed. The experiment results were similar to those obtained without the ligand, and are due to the intrinsic selectivity of TODGA rather than being related to the h$_5$tpaen ligand. This indicates that the position of the carboxylic acid groups is critical. The behavior observed is due to the substituent position of the pyridine nitrogen and not to steric hindrance. The presence of electron-withdrawing groups at the $meta$ position of pyridine nitrogen reduces the electron density of the nitrogen to a point where complexation is no longer possible.

Thus, it is possible to consider selectively separating Am into an aqueous phase while retaining the other cations in the organic phase. The properties of the h$_4$tpaen ligand mean it can be considered as a good complexing agent in the EXAm process Am stripping step.$^{[38]}$ As part of an industrial process, it should be possible to recover more than 99% of Am(III) selectively from the other elements with less than 30 stages of liquid-liquid extraction.$^{[42]}$

**CONCLUSIONS**

This study demonstrated the efficiency of water soluble ligands such as dipicolinic acid (pyridine-2,6-dicarboxylic acid-PDCA) and their derivatives in the selective separation of Am(III) from Eu(III). Am is complexed by the chelating agent in the aqueous phase, while Eu is retained in the organic TODGA phase. The selectivity seems to be not impacted by the addition of different substituents to the PDCA. The dipicolinic acid modification appears to have a minimal impact on selectivity, opening the possibility to enhance solubility without affecting the complex stability.

In a heterocyclic decadentate such as h$_4$tpaen, where an ethylene diamine backbone is functionalized with picolinic acid, the selectivity was enhanced and the possibility of considering h$_4$tpaen for Am(III)/Cm(III) separation became clear. Very promising results were obtained for the inter- and intra-group separation of Am, which has been considered a challenging task in the nuclear fuel cycle due to its charge and chemical behavior being similar to those of other cations.
One limitation arises from the low solubility of the h₄tpaen ligand in an acidic aqueous solution. The ligand concentration must not exceed 5 mM in general, and cannot exceed values higher than 1 mM in 3 M NaNO₃.

In the future, it would be interesting to modify the h₄tpaen ligand structure in order to improve its solubility without changing its ability to selectively separate Am from other cations. This seems possible, since this study demonstrated that the modification of picolinate with various groups in the 4-position did not seem to impact extraction performances.

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