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Status on the PyTri- Diol properties

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Summary

The stripping solvent based on PyTri-Diol (PTD) has been extensively studied in the previous SACSESS project, resulting to be very promising for the selective actinide stripping and, in the present GENIORS project, its applicability to the i-SANEX and EURO-GANEX processes was demonstrated. The present work, together with PTD complexation studies already performed, contributes to a better understanding of the selective complexation mechanism involved in the i-SANEX extracting system. To this purpose, detailed ESI-MS investigations were performed by POLIMI to go further in the understanding of metal ion to ligand complex formation and, in particular, of possible mixed complexes between PTD and TODGA. The results reported lead to the conclusion that the selectivity of the innovative PTD-based system can arise from the formation of intermediary mixed species during the extraction procedure. Relevant information can still be obtained from a better understanding of the fragmentation process of these species. In addition, further complexometric titration experiments were performed with PTD ligand by UV-Vis spectrophotometry, confirming the PTD selectivity for Actinides towards different Lanthanides.

Approval

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CONTENT

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ABSTRACT

The stripping solvent based on PyTri-Diol (PTD) has been extensively studied in the previous SACSESS project, resulting to be very promising for the selective actinide stripping. Further studies developed in the present GENIORS project enabled to demonstrate the applicability of PTD-based stripping solvent to the i-SANEX and EURO-GANEX processes. Details about loading experiments performed at CEA in collaboration with POLIMI and studies on the temperature dependence of stripping performances are reported in Deliverable 6.1. Further progresses in studying the PTD-based solvent stability are reported in Deliverable 2.2.

Furthermore, in the present GENIORS project, detailed ESI-MS investigations were performed by POLIMI to go further in the understanding of metal ion to ligand complex formation and, in particular, of possible mixed complexes between PTD and TODGA. In addition, further complexometric titration experiments were performed with PTD ligand by UV-Vis spectrophotometry, confirming the PTD selectivity for Actinides towards Lanthanides.

INTRODUCTION

In the i-SANEX process, PTD ligand (Figure 1) is intended to be used as hydrophilic stripping agent, selective for Actinides towards Lanthanides, with a metal loaded TODGA based organic solvent [1-2]. Thus, in order to better understand the extraction mechanism, focused experiments have been performed to study the possible formation of mixed TODGA-PTD complexes by ESI-MS analysis. To deepen the affinity towards different Lanthanides, complexometric titration experiments have been performed by using UV-Vis spectrophotometry.

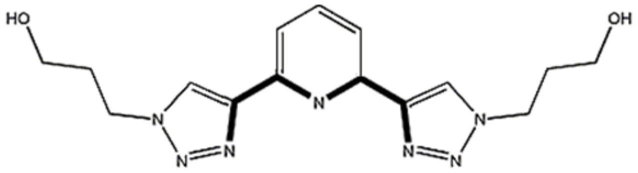

Figure 1 Molecular structure of PTD ligand.

FORMATION OF MIXED TODGA-PTD COMPLEXES

In order to go further in the understanding of metal ion to ligand complex formation, some ESI-MS measurements were performed on *ad hoc* solutions containing both the ligand and the metal ions (experiments in homogeneous phase), as well as on the aqueous and organic phases after the extraction [3-5].

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First, preliminary ESI-MS measurements were performed on ad hoc solutions containing PTD or TODGA and lanthanum as the metal ion, in order to optimize the experimental conditions. Figure 2 reports the positive ESI-MS spectrum of a solution containing lanthanum nitrate at 3x10^{-4} M and PTD at 4x10^{-4} M in methanol. Table 1 collects La complexes observed in such conditions, where no nitric acid is present, whose identifications were confirmed by means of MS^n.

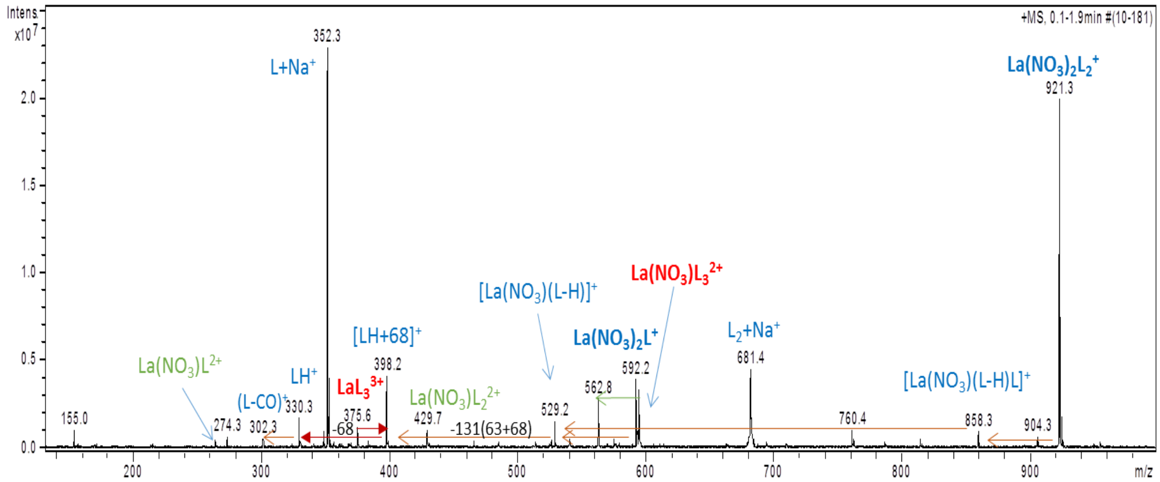

Figure 2 Positive ESI-MS spectrum of a solution containing lanthanide nitrate at 3x10^{-4}M and PTD at 4x10^{-4} M in methanol. L represents the ligand PTD. The arrows indicate the main products obtained from fragmentation of the parent peaks.

Table 1 La^{3+} complexes detected by ESI-MS analysis of an *ad hoc* solution containing the PTD ligand.

Species (ratio) M:L	Species designation	*m/z*
1:1	$[La(NO_3)L]^{2+}$	265.2
1:3	$[LaL_3]^{3+}$	375.6
1:2	$[La(NO_3)L_2]^{2+}$	429.7
1:1	$[La(NO_3)(L-H)]^{+}$	529.2
1:1	$[La(NO_3)_2L]^{+}$	592.2
1:3	$[La(NO_3)L_3]^{2+}$	594.2
1:2	$[La(NO_3)(L-H)L]^{+}$	858.3
1:2	$[La(NO_3)_2L_2]^{+}$	921.3*

*represents the base peak of the parent spectrum.

Similarly, the ESI-MS analysis of an equimolar (4x10^{-5} M) solution containing lanthanum nitrate and TODGA in CH_3CN showed the formation of 1:2 and 1:3 M:L complexes as displayed in Figure 3 and Table 2.

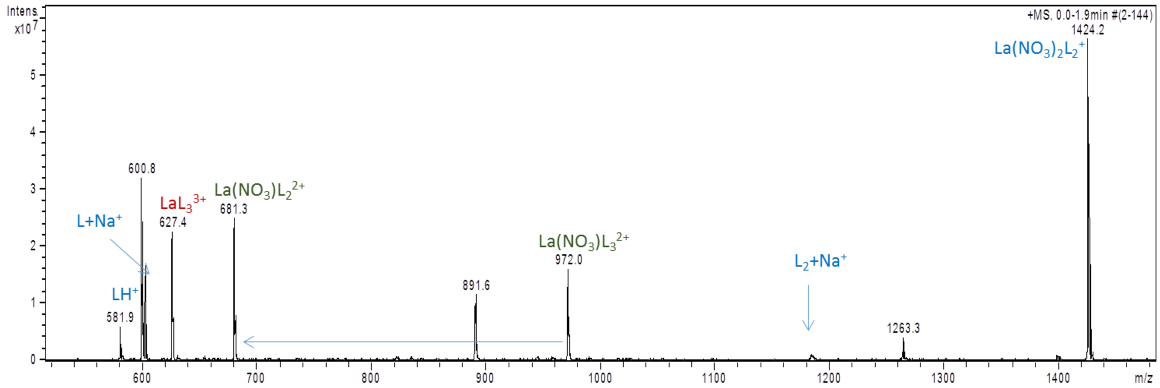

Figure 3 Positive ESI-MS spectrum of an equimolar solution containing lanthanum nitrate and TODGA in CH_3CN. L represents the ligand TODGA. The arrow indicates the main products obtained from fragmentation of the parent peak.

Table 2 La^{3+} complexes detected by ESI-MS analysis of an *ad hoc* solution containing TODGA ligand.

Species (ratio) M:L	Species designation	*m/z*
1:2	$[La(NO_3)L_2]^{2+}$	681.3
1:3	$[LaL_3]^{3+}$	627.4
1:3	$[La(NO_3)L_3]^{2+}$	972.2
1:2	$[La(NO_3)_2L_2]^{+}$	1424.2*

*represents the base peak of the parent spectrum.

The metal ion to ligand complex formation was checked on the aqueous and organic fractions coming from the extraction tests. For this purpose, the following extraction experiments were performed:

A. One-step extraction:

Aqueous phase: 0.04 M lanthanum nitrate and 0.08 M PTD in 0.44 M HNO_3

Organic phase: 0.2 M TODGA in kerosene/1-octanol 95/5 %v/v.

B. One-step extraction:

Aqueous phase: 0.04 M lanthanum nitrate and 0.08 M PTD in $1x10^{-3}$ M HNO_3

Organic phase: 0.2 M TODGA in kerosene/1-octanol 95/5 %v/v.

C. Full step extraction:

Extraction

Aqueous phase: 0.04 M lanthanum nitrate in 3M HNO_3

Organic phase: 0.2 M TODGA in kerosene/1-octanol 95/5 %v/v;

Scrubbing

Organic phase: loaded organic phase from the Extraction step;

Aqueous phase: 0.5M HNO_3

Stripping

Organic phase: loaded organic phase from the Scrubbing step;

Aqueous phase: 0.08 M PTD in 0.44 M HNO_3.

ESI-MS spectra of the aqueous and organic fractions before and after the extraction tests are reported in the following Figures.

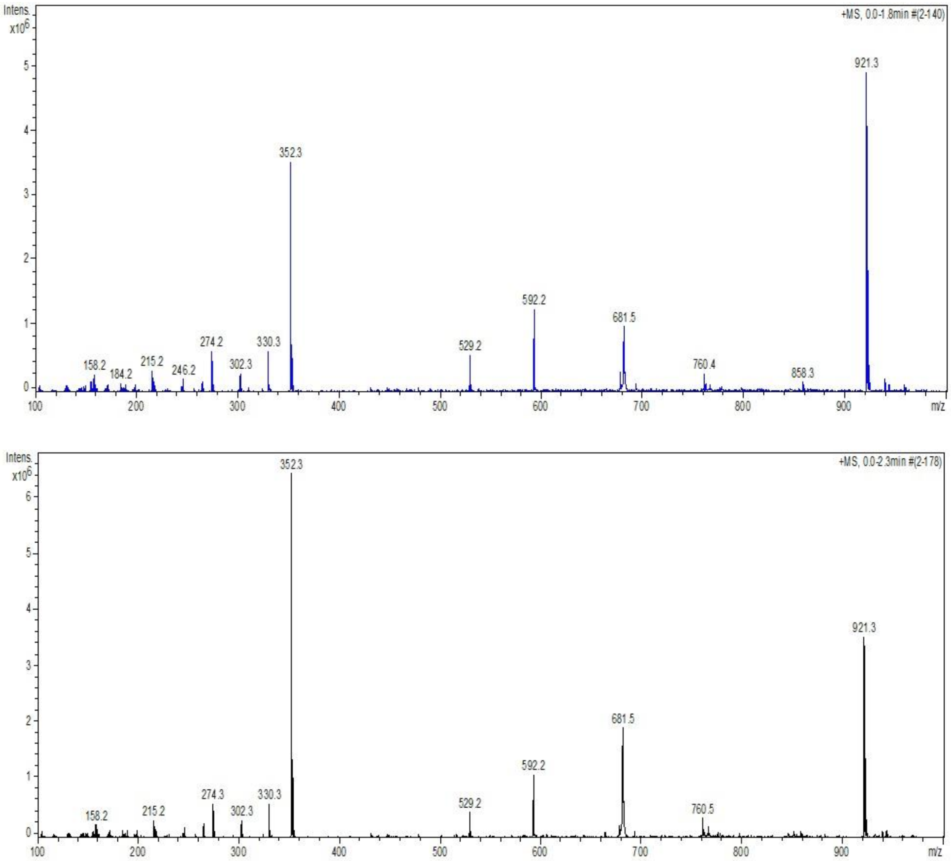

Figure 4 Aqueous phase A before (*top*) and after (*bottom*) extraction.

As clearly shown in Figure 4, after the one-step extraction (case A), there is a slight decrease (around 30%) in the intensity of the formed La-PTD complexes (m/z 529, 592 and 921), as part of the metal ions (La^{3+}) are extracted by TODGA to the organic phase, as demonstrated in Figure 5.

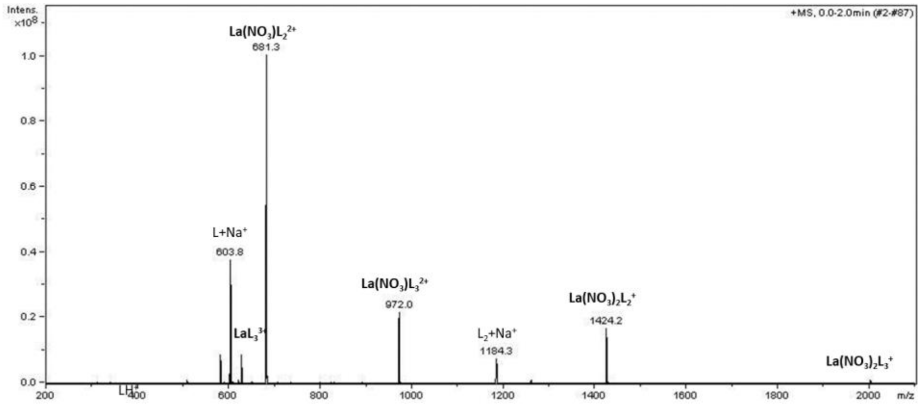

Figure 5 Organic phase A after the extraction.

As expected, in the one-step extraction in diluted nitric acid (case B), no significant decrease in the intensity of the La-PTD formed complexes (m/z 921) was observed (see Figure 6), since TODGA has low extraction efficiency in such conditions. The fact that the extraction was not successfully accomplished is confirmed also by the ESI spectrum of the organic phase after extraction. However, the presence of a less acidic medium in the aqueous phase leads to the formation of 1:3 La-PTD complex species, $[La(PTD)_3]^{3+}$ (m/z 375.5) and $[La(NO_3)(PTD)_3]^{2+}$ (m/z 594.2), that were not observed in more acidic conditions. This is in agreement with the results obtained from MS spectrum of the *ad hoc* methanol solution without HNO_3 addition (Figure 2) and with the observations from Wagner et al. on the complexation of Cm(III) and Eu(III) with PTD by time-resolved laser fluorescence spectroscopy (TRLFS) [6].

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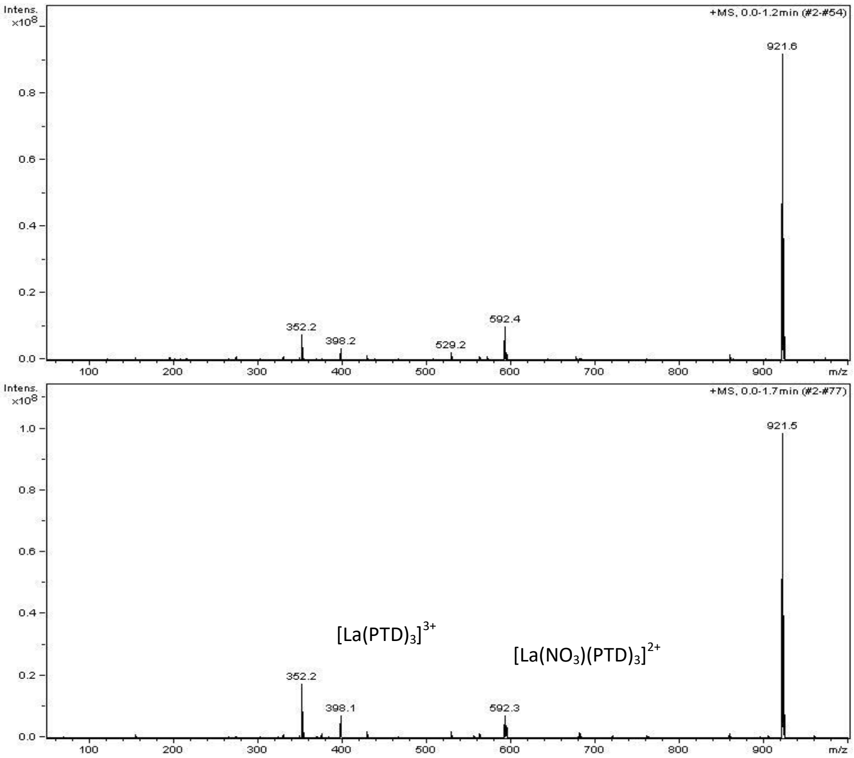

Figure 6 Aqueous phase B before (top) and after (bottom) extraction.

Concerning the full step extraction (case C), it is clearly observable that in the aqueous stripping phase after the test (Figure 7 in purple) occurs the formation of 1:1 and 1:2 La-PTD complexes (m/z 592.3 and 921.5 respectively) with significant ion intensity in the MS spectrum and, consequently, lower intensity of the free ligand (m/z 330). This confirms that, under these extraction conditions, PTD stripes back into the aqueous feed the metal ion (La^{3+}) out of the organic phase coordinating preferentially in the 1:2 ratio (m/z 921.5).

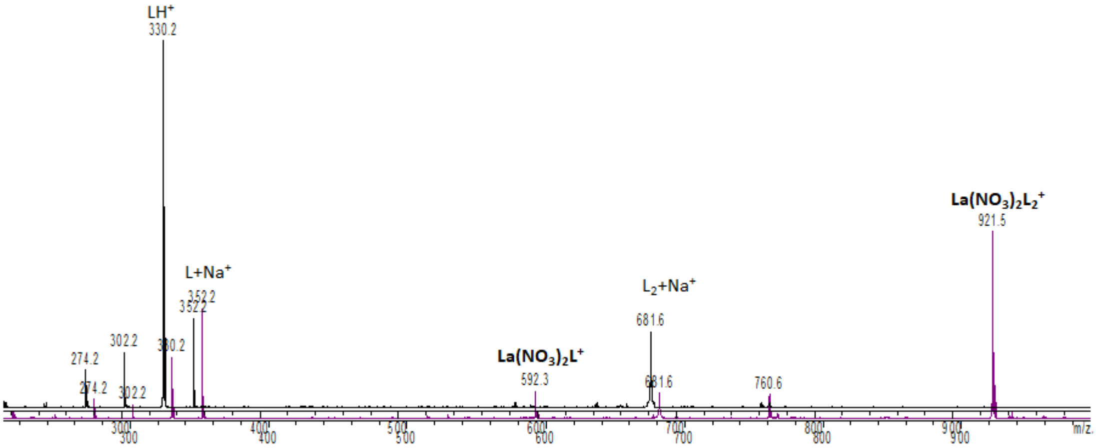

Figure 7 ESI-MS spectra of the stripping aqueous phase C before (in black) and after (in purple) the extraction. L represents the ligand PTD.

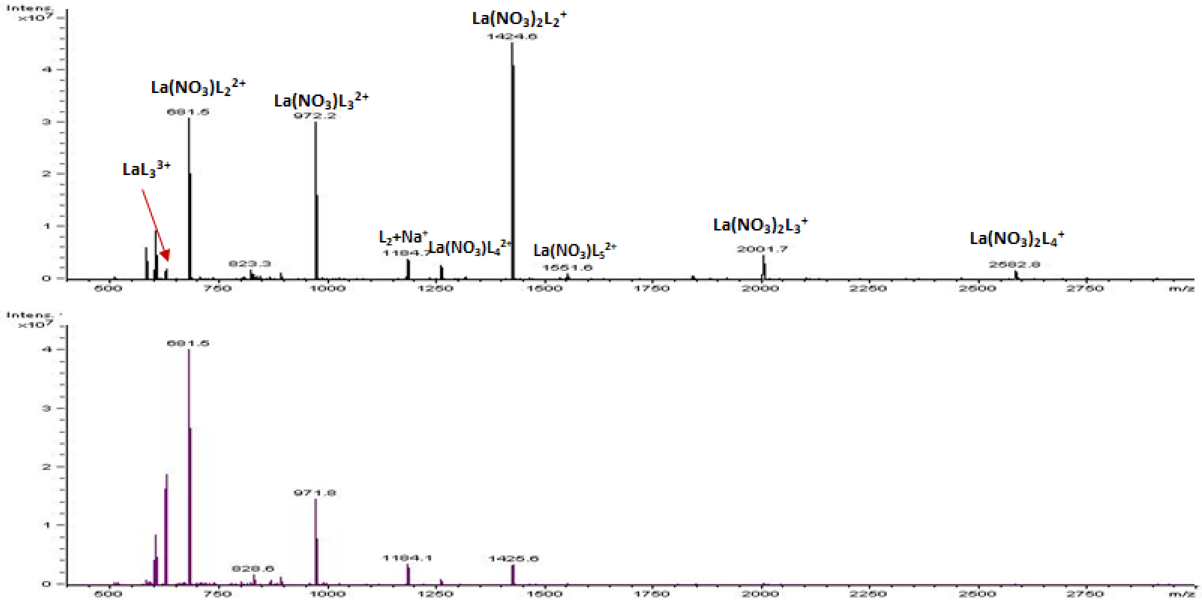

Figure 8 ESI-MS spectra of the organic phase C. Top spectrum: scrubbed organic phase before stripping; Bottom spectrum: organic phase after stripping. L corresponds to TODGA.

Regarding the MS spectra of the organic phase after stripping (Figure 8, bottom), there is also much lower ion intensity of the La-TODGA complexes formed (Figure 8, top), which indicates the migration of the metal ion back into the aq. feed, confirming the observations from the MS spectra of the aqueous fractions.

No mixed species were observed in any of the extraction fractions under the conditions used.

To go deepen, further ESI-MS analyses on mixed complexes formed from solutions containing both the extractants (PTD and TODGA) was used aiming at understanding the role of each extractant in metal ion complexes and to gain insights on the coordination sphere of the metal ion complexes by one extractant and the changes induced by addition of the other extractant to an *ad hoc* solution.

Ligand concentration effect

The concentration ratio between the two ligands and lanthanum nitrate was optimized aiming at obtaining mixed complexes of La^{3+} with desirable stoichiometries of 1:1:1 or 1:1:2 (M^{3+}:TODGA:PTD). The sample preparation for these mixtures was also optimized in terms of solubility of both ligands in solution prior to the ESI analysis. CH_3CN/MeOH 50/50 v/v was selected as the solution remained clear, unlike the CH_3CN/H_2O 50/50 v/v previously tested that immediately became cloudy after adding TODGA. Figure 9 represents the parent spectra of a solution prepared at the varying concentration ratios between metal ion: TODGA: PTD, namely 1:2:2 (black), 1:1:2 (blue) and 1:1:10 (red).

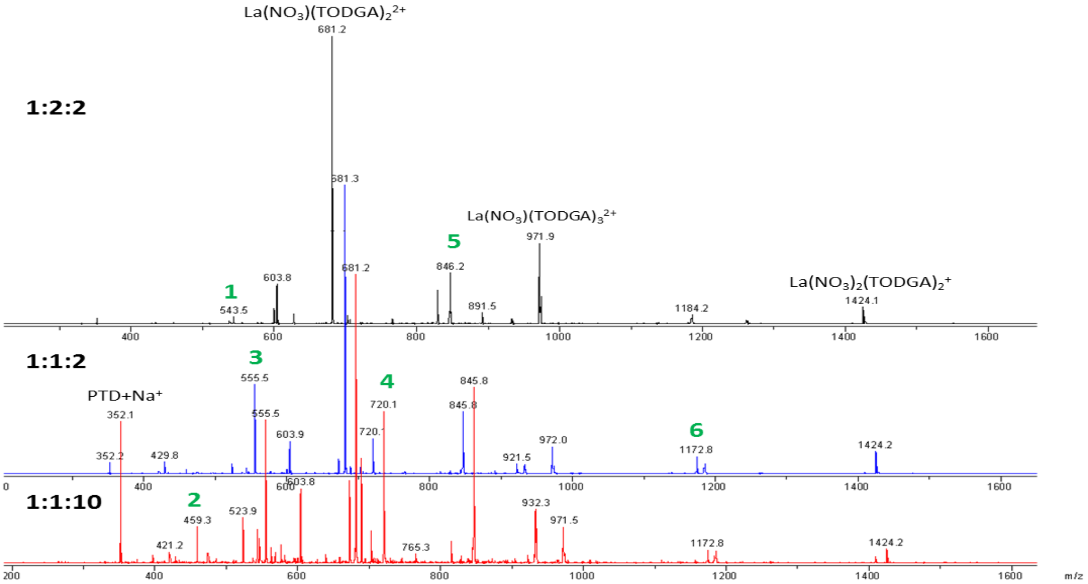

Figure 9. ESI mass spectra of a solution containing Lanthanum nitrate, TODGA and PTD at varying concentration ratios (with an order of magnitude of 10^{-4} M) in CH_3CN/CH_3OH 50/50 v/v. Top: 1:2:2, middle: 1:1:1 and bottom 1:1:10. Peaks identification: 1. $La(PTD)(TODGA)_2^{3+}$, 2. $La(PTD)_2(TODGA)^{3+}$, 3. $La(NO_3)(PTD)(TODGA)^{2+}$, 4. $La(NO_3)(PTD)_2(TODGA)^{2+}$, 5.$La(NO_3)(PTD)(TODGA)_2^{2+}$, 6. $La(NO_3)_2(PTD)(TODGA)^{+}$.

The ion intensity of the PTD mixed complexes formed upon ESI increases with the increase of the PTD concentration in solution, especially the mixed complexes of $La(PTD)_2(TODGA)^{3+}$ (m/z = 459.3, 2), $La(NO_3)(PTD)(TODGA)^{2+}$ (m/z = 555.5, 3), $La(NO_3)(PTD)_2(TODGA)^{2+}$ (m/z = 720.1, 4), $La(NO_3)(PTD)(TODGA)_2^{2+}$ (m/z = 846.2, 5) and $La(NO_3)_2(PTD)(TODGA)^{+}$ (m/z = 1172.8, 6). Nevertheless, it seems that $La(NO_3)(TODGA)_2^{2+}$ remains being the most abundant species in all 3 concentration ratios tested, indicating great affinity and stability of the complex in solution.

Influence of the metal center on the formed mixed species

In order to study the affinity of the extractants TODGA and PTD across the lanthanide series, solutions containing a metal nitrate and both ligands were prepared under equal experimental conditions and analyzed by ESI-MS. Spectra are reported in Figure 10.

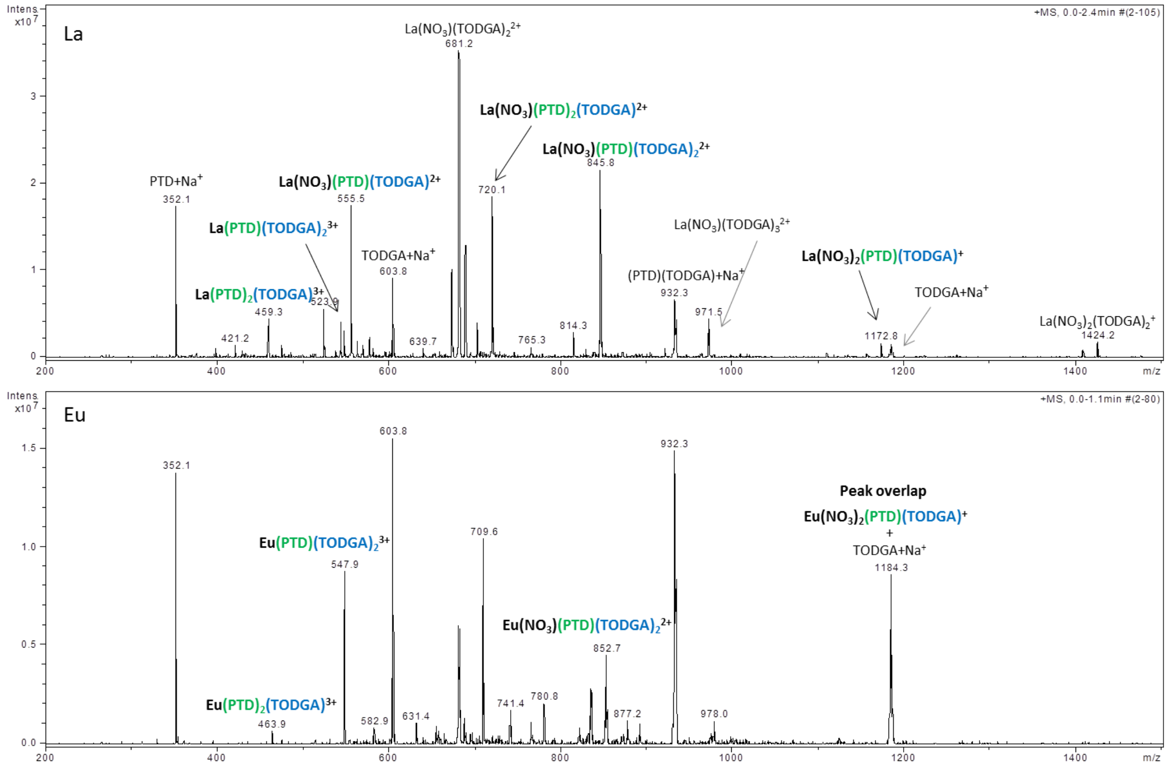

Figure 10. ESI-MS parent spectra of a solution containing 0.5×10^{-4} M $Ln(NO_3)_3$ + 0.5×10^{-4} M TODGA + 5 M x 10^{-4} M PTD in CH_3CN/CH_3OH 50/50 v/v (1:1:10 Ln:TODGA:PTD concentration ratio).

A major difference in the ion abundance between the mass spectra of La nitrate mixed solution (Figure 10, top) and the Eu nitrate mixed solution (Figure 10, bottom) could be seen. Less mixed species are formed with Eu than with the La nitrate mixed solution. While for La^{3+} the major mixed species formed is the dipositive $La(NO_3)(PTD)(TODGA)_2^{2+}$, for Eu^{3+} the $Eu(PTD)(TODGA)_2^{3+}$ is formed with higher ion abundance. It is clear that, in the Eu solution, the tripositive species play an important role indicating a preference for species without nitrate ions in the coordination sphere. Also, out of the 4 mixed species formed, the two species with highest ion abundance comprise 2 TODGA molecules and only one PTD molecule attached to the metal center. This could be indicative of the reported preference of Eu^{3+} to the organic phase (TODGA based) and less affinity to the acidic aqueous phase (PTD based). On the contrary, La^{3+} species with 2 PTD molecules attached are formed with significant ion intensity as is the case of La(NO$_3$)(PTD)$_2$(TODGA)$^{2+}$ (m/z 720). Interestingly, regarding the tripositive species only Eu(PTD)$_2$(TODGA)$^{3+}$ (m/z 464) is formed, while with La^{3+} the La(PTD)(TODGA)$_2$$^{3+}$ (m/z 543) is also observed but with decreased ion intensity in comparison with La(PTD)$_2$(TODGA)$^{3+}$ (m/z 459).

To have a better overview of the importance of the mixed species possibly formed as intermediaries during the extraction procedure, it would be very helpful to perform this studies also with americium.

Kinetic stability of mixed complexes in gas phase

The kinetic stability of the observed La^{3+} and Eu^{3+} mixed species was studied by measuring the influence of the cone voltage variation (in-source CID) on the ion abundance. Results are shown in Figure 11.

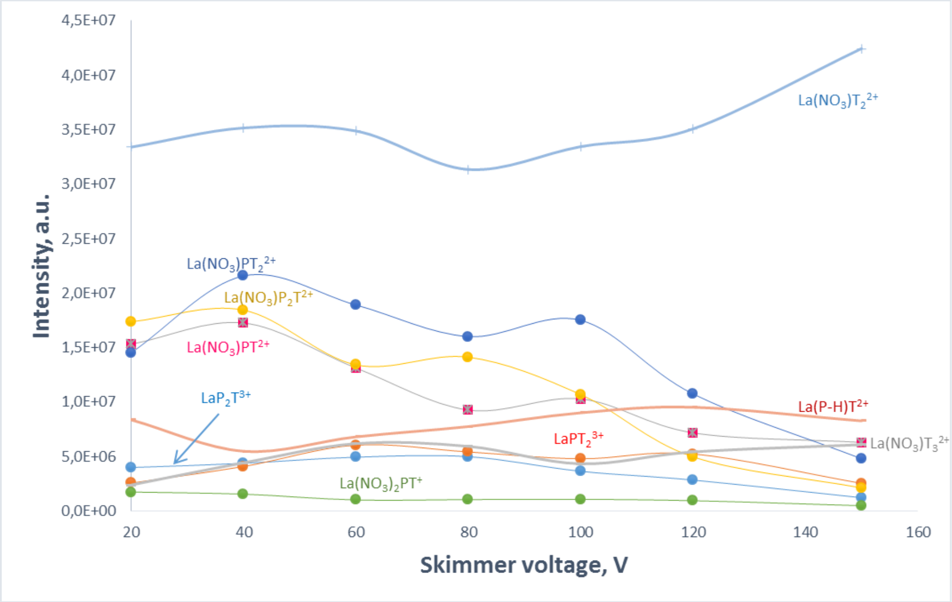

Figura 11. Intensity of the La species as a function of the cone voltage variation (V) for 0.5x10^{-4} M La(NO$_3$)$_3$ + 0.5x10^{-4} M TODGA + 5 M x 10^{-4} M PTD in CH$_3$CN/CH$_3$OH 50/50 v/v. P = PTD, T = TODGA.

According to the plot from the variation of the ion abundance with the increasing skimmer voltage, some conclusions can be made:

i) Increasing the cone voltage induces fragmentation of some of the species formed, confirmed from the CID with He gas in the ion trap;

ii) La(NO$_3$)T$_2$$^{2+}$ is a predominant species in the parent spectrum and reaches higher intensity at higher cone voltage due to the fragmentation of both La(NO$_3$)PT$_2$$^{2+}$ and La(NO$_3$)T$_3$$^{2+}$;

iii) Decreased ion intensity with the increase of the cone voltage of La(NO$_3$)PT^{2+} is observed after 40 V due to dissociation leading to the formation of a stable species, La(P-H)T^{2+} as confirmed in the CID experiments;

iv) Decreased ion intensity after 40 V is also observed for $La(NO_3)P_2T^{2+}$ and $La(NO_3)PT^{2+}$, also due to dissociation.

No significant change in the ion abundance was observed until 120 V for the triply charged mixed species LaP_2T^{3+} and $LaPT_2^{3+}$ nor for $La(NO_3)_2PT^+$, revealing that these are stable in the gas-phase and are possible intermediaries in solution.

The analysis of the MS^n of the doubly and triply charged species formed from the solution at a concentration ratio of 1:1:10 (M:TODGA:PTD) enabled to extract information regarding possible structure and affinity of the two ligands towards the metal center.

From the mass dissociation scheme it is possible to denote several key aspects:

i) CID of the nitrate species $La(NO_3)(PTD)(TODGA)_2^{2+}$ and $La(NO_3)(PTD)_2(TODGA)^{2+}$ shows preference for loss of HNO_3 over PTD yielding predominantly the fragments $La(NO_3)(PTD)_n(TODGA)_m\text{-}H^{2+}$, n, m= 1,2;

ii) In the absence of nitrate ions, the dissociation of the species $La(PTD)(TODGA)_2\text{-}H^{2+}$ leads to the primary production of La(TODGA)(TODGA-269)-H^{2+} via loss of neutral PTD and subsequent $C\text{-}C_{carbonyl}$ bond cleavage of one TODGA molecule;

iii) Dissociation of the triply charged species $La(PTD)(TODGA)_2^{3+}$ and $La(PTD)_2(TODGA)^{3+}$ leads to charge reduction of the complex but the oxidation state of the metal is retained. This often occurs due to the lack of stabilizing solvent molecules and was also observed previously in the CID of $La(PTD)_3^{3+}$ and $La(TODGA)_3^{3+}$;

iv) CID of $La(PTD)(TODGA)_2^{3+}$ yields preferentially $La(TODGA)(TODGA\text{-}269)^{2+}$ via loss of the protonated PTD followed by cleavage of the $C\text{-}C_{carbonyl}$ bond of TODGA resulting in the formation of a neutral N,N-dioctyl-formamide ($C_{17}H_{36}NO$). CID of $La(PTD)_2(TODGA)^{3+}$ results in preferential loss of only $HPTD^+$ resulting in the formation of La(PTD)(TODGA)-H^{2+};

The formation of singly charged mixed species was also observed but only for the 1:1:1 M:L:L stoichiometry - $La(NO_3)_2(PTD)(TODGA)^+$, from which CID yielded preferentially La(PTD)(TODGA)-H^+ through 2 consecutive primary losses of neutral HNO_3 molecules. CID of the latter species corresponded to a MS^4 with reduced ion abundance but in any case it was possible to assign loss of neutral 269 mass unit from TODGA instead of loss of PTD.

From these preliminary stability studies it can be assumed that probably the synergic extraction observed results from the formation of intermediary mixed complexes containing both extractants, PTD and TODGA. The mechanisms of formation of the mixed species may differ in function of the initial conditions adopted for the extraction experiment and certainly depend on the acidity of the medium. The competition between water adducts, nitrate molecules and the extractants was not evaluated so far but it is an important missing component that would also contribute for the fundamental understanding of the reaction mechanisms occurring during extraction.

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PTD SELECTIVITY

In order to further study PTD selectivity for Actinides towards Lanthanides, complexometric titration experiments were performed with PTD ligand and Nd by UV-Vis spectrophotometry. The complexation of Nd(III) with PTD has been investigated in pH 3 $HClO_4$ since ClO_4^- is a non coordinating anion and has a negligible influence on complexation. The H^+ concentration has been set to 10^{-3} mol L^{-1} in order to limit the effect of ligand protonation. The titration experiments have been performed by UV-Vis technique following the cation signal at 575 nm. Samples were prepared by dissolving the $Nd(NO_3)_3$ stock solution so as to obtain 10^{-2} mol L^{-1} of Nd(III) initial concentration. Aliquots of PTD stock solution were subsequently added to the cation sample up to 0.26 mol L^{-1} ligand concentration. After each titration step, samples were allowed to equilibrate for 5 minutes before UV-Vis analysis. The normalized spectra are reported in Figure 12 as a function of PTD concentration.

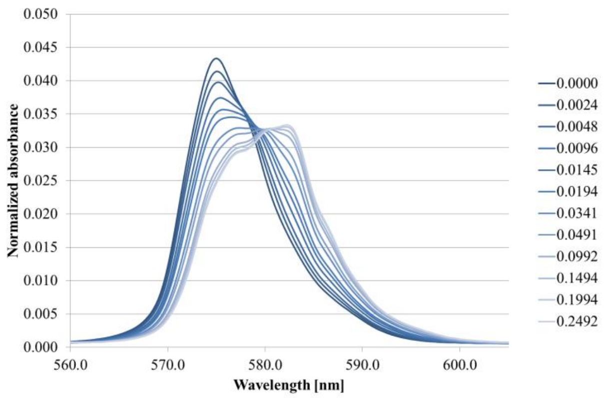

Figure 12. Normalized spectra of Nd(III) at increasing PTD concentration in 10^{-3} mol L^{-1} $HClO_4$.

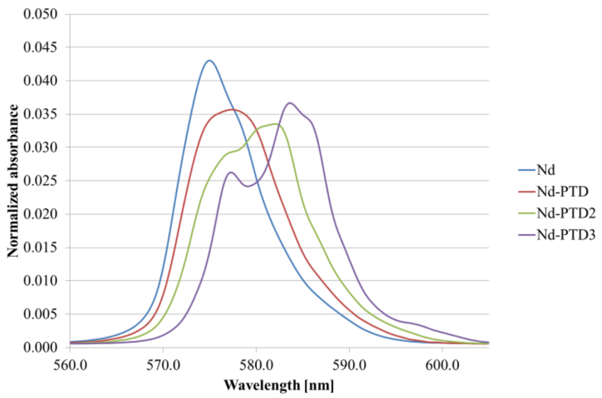

Figure 13. Normalized spectra of the $[Nd(PTD)_n]^{3+}$ (n = 0, 1, 2, 3) complexes in 10^{-3} mol L^{-1} $HClO_4$.

In absence of ligand, the pure Nd(III) aqua ion is observed, with emission band at 575 nm. At increasing ligand concentrations additional bands are observed at higher wavelengths, consistent with the stepwise complexation of Nd(III) with PTD. HypSpec2014 software has been used to determine the pure component spectra (see Figure 13) and deconvolute the experimental data, thus obtaining the conditional stability constants of Nd-PTD and Nd-PTD_2 complexes. As it could be inferred from Table 3, PTD selectivity for Actinides towards Lanthanides, already outlined by previous solvent extraction data and complexometric titration campaigns performed at KIT [6] and CEA, is confirmed. In agreement with extraction experiments, PTD forms more stable complexes with Cm(III) and Am(III) than with Eu(III) and Nd(III). In fact, the conditional stability constants obtained differ by orders of magnitude. These differences are consistent with the separation factors obtained in the extraction experiments.

Table 3. Summary of conditional stability constants of $[M(PTD)_n]^{3+}$ (n = 1, 2, 3) complexes, log β_1, log β_2 and log β_3. With the exception of Am(III) that was investigated in methanol + 25 vol% water (in pH 3 by TMA^+OH^-), all experiments were performed in 10^{-3} mol/L $HClO_4$.

Cation	log β_1	log β_2	log β_3
Am(III)	3.9 ± 0.2	7.4 ± 0.2	10.7 ± 0.2
Cm(III)	3.2 ± 0.2	6.6 ± 0.2	9.7 ± 0.2
Eu(III)	2.3 ± 0.1	4.8 ± 0.2	7.4 ± 0.3
Nd(III)	2.7 ± 0.3	4.5 ± 0.3	-

Since the formation of Nd-PTD_3 complexes has not been observed at the above-described conditions, a further experiment was performed by stepwisely adding $NaClO_4$ up to 2.49 mol L^{-1} in order to increase the ionic strength (I) and enhance the formation of higher stoichiometry complexes. In particular, the experiment was performed by maintaining the concentrations of $Nd(NO_3)_3$ and $HClO_4$ at 0.091 and 10^{-3} mol L^{-1}, respectively. Consequently, the ionic strength was increased from 0.056 (39% of Nd-PTD_1 and 61% of Nd-PTD_2 species) to 2.54 mol L^{-1}, until the formation of Nd-PTD_3 complex alone. At the last condition, the conditional stability constants of Nd-PTD_1, Nd-PTD_2 and Nd-PTD_3 complexes (log β_1, log β_2 and log β_3) are 2.70 ± 0.3; 5.91 ± 0.3; 8.50 ± 0.3, respectively. The normalized spectra are reported in Figure 14 as a function of ionic strength.

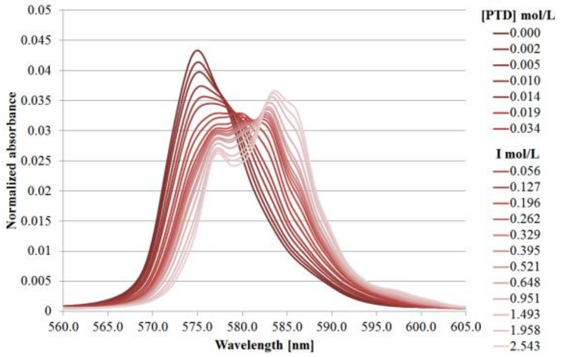

Figure 14. Normalized spectra of Nd(III) at increasing PTD concentration and ionic strength (I) in 10^{-3} mol L^{-1} $HClO_4$.

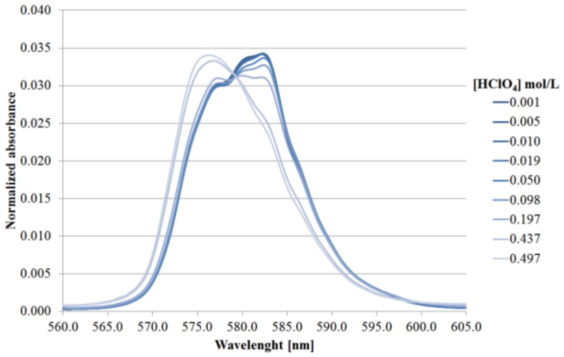

Figure 15. Normalized spectra of Nd(III) at increasing $HClO_4$ concentration.

Finally, since the Actinides stripping step is foreseen to be performed at 0.44 mol L^{-1} HNO_3, PTD protonation effect on Nd(III) complexation was investigated by increasing the $HClO_4$ concentration from 10^{-3} to 0.497 mol L^{-1} and maintaining the concentrations of $Nd(NO_3)_3$ and PTD at 0.0067 and 0.1663 mol L^{-1} respectively. As it could be inferred from Figure 15, the Nd(III) spectra display an evident decrease of the complexed Nd(III) species by increasing $HClO_4$ concentration.

Additional complexometric titration experiments are foreseen in order to obtain the conditional stability constants of Nd(III) complexation with PTD at extraction conditions, i.e. at 0.44 mol L^{-1} HNO_3 and compare them to the results previously obtained. Furthermore, the complexation of other light lanthanides with PTD will be investigated by UV-Vis technique. Since the absorption of the most relevant cations (La^{3+} and Ce^{3+}) is in the UV range as for PTD, they will be investigated following the ligand signal.

CONCLUSIONS

Together with PTD complexation studies already performed, the present work contributes to a better understanding of the selective complexation mechanism involved in the i-SANEX extracting system.

Concerning speciation studies of trivalent lanthanides with PTD and TODGA, ESI-MS was used for the characterization of Ln(III) complexes with N- and O-donor ligands, PTD and TODGA respectively. It was shown that after the optimization of the experimental conditions, the gas-phase products are representative of the solution. ESI-MS of the La(III)-PTD and La(III)-TODGA solutions confirmed the preferred stoichiometry of the 1:2 in both systems revealing the strong nature of the Ln-N and Ln-O in bonding. Formation of 1:1 and 1:3 complexes were also observed, but with decreased ion intensity indicating a lower preference for these stoichiometries. The dissociation of the singly charged 1:2 complexes of La-PTD and La-TODGA ($La(NO_3)_2L_2^+$) were performed, revealing a preferential loss of HNO_3 for L = PTD, while for L= TODGA: ligand loss is the major fragmentation pathway observed. It seems that in the gas-phase, when nitrate ions are bound to the complex and participate in the coordination sphere, TODGA has lower binding affinity to La than PTD, which is in agreement with the previous observations in solution where the complex is solvated by nitric acid. In addition, the preliminary gas-phase CID studies of mixed complexes containing both extractants (TODGA-PTD), lead to the conclusion that the selectivity of the innovative PTD-based system can arise from the formation of intermediary mixed species during the extraction procedure. As so, it would be helpful in the future to get a better insight on the fragmentation process of these species.

Finally, UV-Vis experiments enabled to derive conditional stability constants for Nd-PTD complexes, coherent with those already determined for Eu(III) and An(III) and the same will be done for La(III) and Ce(III).

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