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Performances and mechanistic investigations of triphosphine trioxide / ionic liquid system for rare earth extraction

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The extraction of rare earth elements (REEs) from nitric acid solution by a triphosphine trioxide (TPO) is presented. Performances of such ligand in ionic liquids *vs* classical solvent (dibenzylether) are compared. TPO shows to be 10 to 100 times more efficient when is dissolved in ionic media whatever the concentration of nitric acid involved. Mechanistic investigations reveal that cation exchange classically observed in ionic liquids is not consistent with the experimental data. Moreover, clear differences in TPO/Ln complexes between classical and ionic media are highlighted. A stable complex of 1 lanthanide for 3 TPO is formed in ionic liquid whereas a complex of 1 lanthanide for 6 to 9 TPO is formed in dibenzylether. Back extraction is also studied and good recovery of REEs could be obtained. TPO / ionic liquid system shows remarkable performances *i.e.* efficiency and selectivity towards lanthanides in a simulated leaching solution of Nd/Fe/B/Dy magnet.

1. Introduction

Rare earth elements (REEs) have become essential in our everyday life, and find applications in a wide range of domains such as new technologies (cell phones, LCD panels, disk drives), hybrid vehicles, renewable energy (wind turbines), etc... They are essentially extracted from bastnaesite or monazite ores and more than 90% of the world's production comes from China. Western nations (European Union or USA), considers them as critical metal due to their economic importance combined with their supply risk. With the increasing demand for REE in the international market and in order to limit the scarcity of these elements, Waste Electrical and Electronic Equipment (WEEE), were reconsidered as "urban mines" with high potential.[1]

Whatever the resources, REEs are generally extracted by hydrometallurgical methods involving dissolution and solvent extraction. This technic is among the most powerful to separate and purify REEs. However despite its efficiency, this methodology suffers from some drawbacks as the use of organic diluents which are environmentally questionable. They are often toxic, flammable and responsive of the emission of VOCs in the atmosphere. Due to the growing environmental awareness and the development of green chemistry, intense researches have been devoted to the development of alternative processes limiting the use of volatiles. Application of ionic liquids (ILs) appeared as one of the most promising process. ILs are today considered as greener alternative to common solvents mainly due to their very low vapor pressure, their non-flammability limiting thus the atmospheric pollution and increasing at the same time the safety for workers.

Since the pioneering work of Dai *et al.*[2] who pointed out that crown ethers were hundreds times more efficient for strontium extraction when dissolved in ionic liquids compared to classical solvents, numerous studies described the extraction of REEs in these media.[3,4] Most of the well-known extractants have thus been studied in ionic liquids, such as CMPO,[5] HDEHP,[6,7] phosphate or phosphonate,[8,9] TODGA,[10] Htta[11] or neutral phosphine oxides: cyanex 923[12] and TOPO.[13]

Except in few cases, ionic liquids are described as more efficient systems for the extraction of metal cations.[6] Nevertheless, the effect of classical solvents and ionic liquids are very difficult to compare since the extraction mechanisms are often different. Three main mechanisms are today admitted in ionic liquids: i) mechanisms based on cation exchange involving the organic cation of the ionic liquid,[10,14] and/or acidic proton extracted,[15] ii) similar mechanism than in classical systems[6] or iii) anion exchange in which an organic anion is exchanged in aqueous phase by a metal anion extracted in organic phase.[11]

Some models have been developed to predict the extraction in ionic liquids.[15,16] Taking into account the three proposed mechanisms and comparing experimental data with the model predictions, appears sometimes quite consistent. Nevertheless

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Electronic supplementary information (ESI) avalaible : Fig SI-1 - Fig SI-7.

these models do not take into account the structure of the cation which can play a crucial role in the extraction process.[17] Such influence in these media are very complex and are not easily predictable. As a consequence, better understanding of extraction mechanisms remains essential. The diversity of ligands and more generally, the increasing set of available data in these media may help the establishment of more accurate models.

In 1999, Cristau *et al.* have developed a series of new polyphosphine oxides for An/Ln separation.[18] Among them, the following TPO, triphosphine trioxide ligand, (Figure 1), exhibited remarkable efficiency for the extraction of europium but no further study has been reported on this system.

Despite that such ligand appears as a very attractive candidate for the liquid-liquid extraction of REEs, its insolubility in aliphatic solvents, usually used in liquid – liquid extraction, require the use of chlorinated solvents or dibenzylether, which raises environmental issues in regards to its use for such processes. For these reasons and according to the promising preliminary results in classical media, we investigate the possibility of using this ligand for the extraction of REEs in an unconventional medium such as ionic liquids which can represent an alternative to organic solvent. The extraction of a series of REEs from nitric acid with TPO dissolved in ionic liquid was studied and compare to dibenzylether. The selective extraction efficiency for REEs was compare in both solvents and the discrepancies in regards to the results were highlighted through a mechanistic study.

2. Experimental

2.1. Synthetic chemistry

The triphosphine trioxide TPO ligand (3-(1'-Dodecyl)-1,1,5,5-tetraphenyl-1,3,5-triphosphapentane-1,3,5 Trioxide),[19] and the ionic liquids N-butyl-N-ethylpiperidinium bis(trifluoromethylsulfonyl)imide [EBPip][NTf$_2$][20] and N-octyl-N-ethylpiperidinium bis(trifluoromethylsulfonyl)imide [EOPip][NTf$_2$][20] were synthetized according to literature.

2.2. Solvent extraction procedure

In order to illustrate the entire rare earth elements (REEs) series three light rare earth elements (LRREs): La, Nd and Eu and two heavy rare earth elements (HREEs): Dy, Yb, have been chosen for the extraction experiments.

Rare earth elements (REEs) stock solutions were prepared at the desired acidity from lanthanum (III) nitrate hexahydrate (Sigma Aldrich, 99.99%), neodymium(III) nitrate hexahydrate (Alfa Aesar, 99.99%), europium(III) nitrate hexahydrate (Alfa Aesar, 99.9%), dysprosium (III) nitrate hexahydrate (Alfa Aesar, 99.9%), ytterbium (III) nitrate hexahydrate (Alfa Aesar, 99.9%).

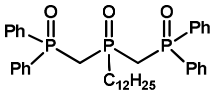

Fig. 1 TPO ligand for the extraction of Eu

A synthetic solution mimicking the leaching of NdFeB magnet was prepared from neodymium(III) nitrate hexahydrate (Alfa Aesar, 99.99%), iron(III) nitrate, (Riedel-de Haën, 99%) and boron (1000 mg.L^{-1} ICP standard, in 1% HNO$_3$). The salts were dissolved at the desired concentration using ultrapure water (MilliQ, Millipore, >18 MΩ cm^{-1}) and the acidity was adjusted with nitric acid.

Different organic solutions were prepared from TPO at the specific concentration in benzylether (Bn$_2$O) or in ionic liquids [EBPip][NTf$_2$], [EOPip][NTf$_2$].

Organic phases were pre-equilibrated with an aqueous phase at the same acidity as the extraction step without REEs cations. For this purpose, the organic phases were contacted volume to volume (1.5 mL) to an aqueous acid phase in plastic vial of 15 mL, in a thermostated shaker (Infor-ht® ecotron) at 25°C for one hour at 400 rpm. Phases were separated after centrifugation at 4000 rpm for 20 minutes (sigma 3-16 PK).

The pre-equilibrated organic phases were then contacted with an equal volume of an aqueous acidic stock solution of REEs in the same conditions as the pre-equilibrium step.

After centrifugation, the separated phases were subjected to analysis (ICP-AES, NMR, acid and water titration).

2.3. Quantification

NMR analyses were performed using a Bruker 400 ultrashield VS spectrometer. Chemical shifts are reported in ppm using the deuterated solvent as internal reference.

After extraction 100 µL of aqueous phase were placed in a NMR tube (5 mm) and completed with 100 µL of 50 mM of p-Toluenesulfonic acid in D$_2$O, 100 µL of CF$_3$CH$_2$OH in D$_2$O and 200 µL of D$_2$O. ^{1}H (400 MHz) and ^{19}F (376 MHz) NMR analyses were performed to follow respectively the presence of cation and the anion in the aqueous phase.

The ^{31}P (162 MHz) NMR analysis was implemented in the following manner: 300 µL of organic phase were placed in a NMR tube in which an inlet containing CDCl$_3$ and TBP as internal reference was added. This CDCl$_3$ and TBP cannot interact with the organic solution and modify the complexes formed after extraction.

Water extraction was evaluated by Karl Fisher titration of the organic phases using a Metrohm 809 Titrando with hydranal – composite 2 (Fluka analytical) and a methanol – rapid solution as reception phase (Fluka analytical).

Nitric acid concentration in the aqueous phases was analyzed using the same device by titration with NaOH 0.1 M (Fluka analytical).

Metal concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES, Spectro Arcos).

The distribution coefficients of the metals and the selectivity were computed from the ICP-AES results:

$$D_M = \frac{[M]_{initial} - [M]_{aq}}{[M]_{aq}} \quad and \quad S_{Ln/M} = \frac{D_{Ln}}{D_M} \qquad (1)$$

3. Results and discussion

3.1. Extraction properties

3.1.1. Extraction by ionic liquids alone

The first step was to investigate if the ILs alone are able to extract Ln. Indeed, Dai *et al.* showed that pure ILs (*i. e.* without extractant) could extract 10 % of strontium from low acidic aqueous phase due to cation exchange mechanism.[2]
In our case, no extraction of Ln from the aqueous to the IL phase was observed. Pure [EBPiP][NTf_2] is not able to extract Ln whatever the nitric acid concentration.

3.1.2. Comparison between the extraction efficiency of TPO in ionic liquid and benzyl-ether.

The extraction of REEs (La, Nd, Eu, Dy, Yb) with TPO in dibenzylether and [EBPip][NTf_2] was evaluated (Figure 2).

Extraction of REEs in dibenzylether increased with the concentration of nitric acid up to 1 M (Figure 2a), with higher selectivities for light rare earth elements (LREEs).
Interestingly the extraction performance seems to be related to the lanthanide contraction (La > Nd > Eu > Dy > Yb).
This can be also linked to the fact that for the REEs series the nitrate complexing increases, while hydration decreases, with increasing atomic number Z.

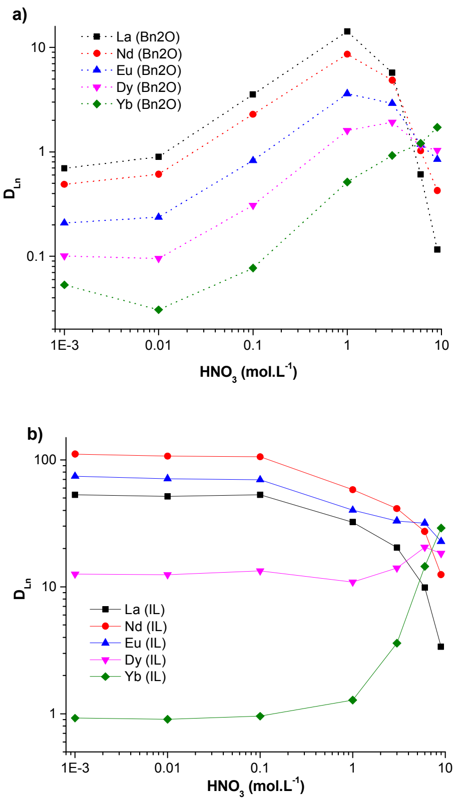

Fig. 2 Extraction of REEs (total amount: 14 mM) by TPO (35 mM) in: a) Bn_2O and b) [EBPip][NTf_2]

Therefore, this hydration has a corresponding effect on the complex formation and more favourable extractable nitrate complex are obtained for LREEs in comparison to HREEs.[21]
However, the performances decreased for higher nitric concentrations, except for Yb. For [HNO_3] > 6 M a complete inversion of selectivity is observed (Yb > Dy > Eu > Nd > La).

As seen in Figure 2b, TPO is 10 to 100 times more efficient for REEs extraction, when it is diluted in ionic liquid than in benzylether. Two different behaviors have been highlighted with a selective extraction of LREEs in regards to the HREEs: the different behavior may reflect a change in the electrostatic interaction between the cation and the extractant, or in the steric factors of the extracted complexes, or both, as the radius of the cation decreases.[22] The behavior of TPO is different in the ionic liquid media when the concentration of nitric acid increases. In fact, extraction is continuously decreasing with the increase in nitric acid concentration except for Dy which seems to have a constant extraction and Yb which is, as observed in Bn_2O, more extracted at high concentration of nitric acid. Moreover selectivity between lanthanide is affected by concentration of nitric acid. From 0.001 to 3 M [HNO_3] the order is as follows: Nd > Eu > La > Dy > Yb and the selectivity is also inverted at HNO_3 9 M and follows the series Yb ≥ Eu ≥ Dy > Nd > La.
The composition of the aqueous solution can have a significant effect on separation efficiency; the increase of salting-out agents which dehydrate lanthanide ions play a role in the separation selectivity.[23] The inversion of selectivity has already been observed in the literature when using tetraphenylmethylenediphosphine dioxide dissolved in 1,2-dichloroethylene.[24] It was attributed to a difference in hydration energy which increases from La to Lu. Therefore, by increasing the nitric acid concentration, and thus decreasing the activity of water, the effect of hydration decreases and the extraction undergoes an inversion.

3.1.3. Equilibration time

The time required to reach the equilibrium was studied in order to have informations on the kinetic of mass transfer. The extraction of Ln was determined as a function of time in 6 M HNO_3 (Figure SI-1).
These experiments show that the equilibrium is obtained in less than 5 minutes with the classical system. The ionic liquid medium needs at least 10 minutes to reach the equilibrium.

3.1.4. Temperature effect

As usually observed, increasing the temperature leads to a decrease in extraction efficiency (Figure SI-2). This is the case for La, Nd and Eu indicating an exothermic extraction with TPO due to a predominant enthalpic term.
On the contrary, Yb is more extracted at high temperature showing again a distinctive behavior of the extraction of this heavy rare earth in contrast to the light ones. Entropy seems thus to be the main driving force for the ytterbium extraction.
As already mentioned the difference can be related the size and hydration of the complex are significantly different with the increase of atomic number Z in the REEs serie.

3.1.5. Water and nitric acid extraction

Figure 3a shows the amount of water uptake in the organic phase after the pre-equilibration step, as a function of initial nitric acid concentration. There is no significant change in the amount of extracted water between 10^{-3} and 1 M of nitric acid. From 3 M [HNO_3] a rapid increase of the water content is observed in the IL phase.

These observations are in agreement with those reported in literature.[15,25] The more acidic the aqueous phase, the more hydrated the organic phase, with values reaching 2.7 M and 0.6 M for $EBPipNTf_2$ and Bn_2O respectively at 9 M HNO_3.

No significant differences are observed between the pre-equilibrated and the extracted phase confirming that the thermodynamic equilibrium was reached.

Following the same strategy, the extraction of nitric acid was studied, after equilibration and after extraction (Figure SI-3).

By extrapolation of these linear laws, the difference of nitric acid extracted in organic phase between extraction and pre-equilibrium steps can be illustrated in the following way (Figure 3b). Unlike water extraction, no significant differences between the IL and the organic solvent were observed for nitric acid extraction. Again, nitric acid extraction cannot explain the efficiency of ionic liquid in extraction.

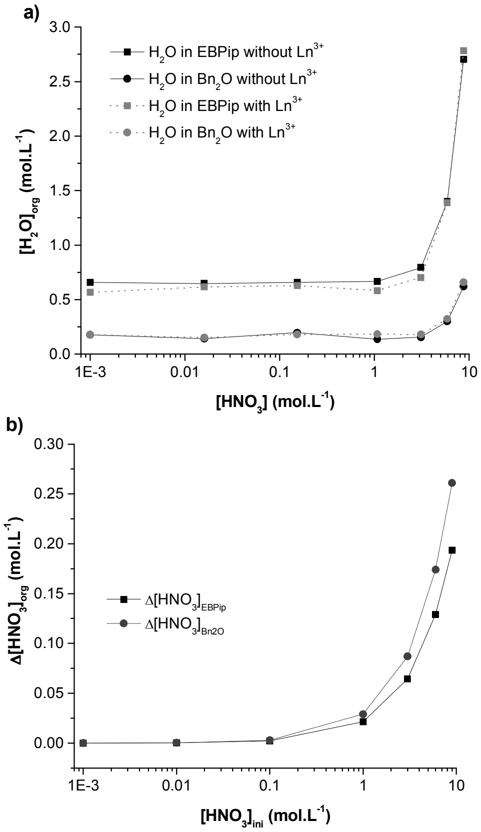

Fig. 3 a) Comparison of water extraction with different solvents *vs* [HNO_3]; b) Extrapolation of the nitric acid extracted in organic phase vs [HNO_3]

3.2. Parametric study of extraction

3.2.1. Effect of ligand concentration

In order to predict the stoichiometry of the complex(es) involved in the IL-based extraction, single-metal ion extractions were conducted at different concentrations of TPO.

The single-metal extractions were performed at their optimal nitric acid concentration *i.e.* 1 M, 6 M and 9 M [HNO_3] for La, Eu and Yb respectively.

Two different kinds of exploitation were done by a) plotting the extraction yield as a function of the ligand's concentration over the initial concentration of lanthanum for the determination of the optimal ratio able to quantitatively extract the metal and b) plotting the concentration of ligand as a function of the amount of lanthanum in organic phase for the determination of the stoichiometry of the complex(es) involved in the extraction.

3.2.1.1. Lanthanum extraction:

As seen in Figure 4a, lanthanum is completely extracted in the IL when an excess of 3 ligands per metal are involved with a clear break in slope at this excess.

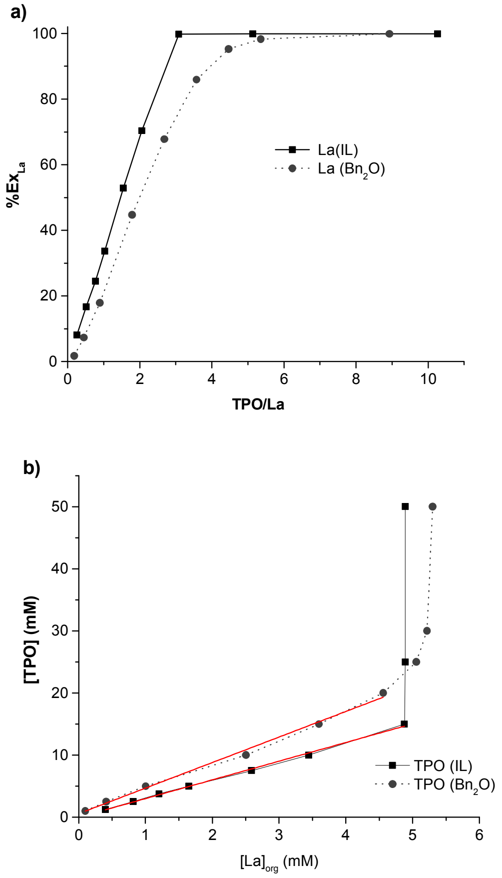

Fig. 4 a) variation of La extraction vs ratio ligand/La ; b) variation of the ligand concentration vs La extracted in organic phase. [TPO]-(IL) =f ($[La]_{org}$): y = 3.01x + 0.02, R^2 = 0.997; [TPO]-(Bn_2O) =f ($[La]_{org}$): y = 4.11x + 0.57, R^2 = 0.993.

The slope analysis method (Figure 4b) was used to confirm the ratio of the extractant to the metal for this IL-based extraction system, a slope of 3 was found which is consistent with the previous results.

In dibenzylether, interestingly from 0.25 to 4 equivalents of ligands over La, extraction is linear with a slope of 4, which would imply a 4:1 complex. However, the slope method result should be taken with caution given that in Bn_2O the extraction is weak and the break in slope is smoother. Therefore the complete extraction seems to be obtained when 6 to 9 equivalents of ligands were added which is not consistent with the fact that 4 ligands per metal are involved. In order to estimate the stoichiometry of the different complexes in organic phases ^{31}P NMR experiments at different concentrations of ligand have been performed (Figure 5).

Up to 3 equivalents of ligands in [EBPip][NTf_2], only the complexed phosphorus derivative is observed at 32 and 49 ppm according to the presence of two different types of phosphorous atom. Beyond this ratio, the signals at 29 and 46 ppm corresponding to the free ligand reappear indicating that only a strong complex lanthanum/ligands (1/3) is formed in the ionic liquid medium.

A completely different behavior is observed in benzylether. Indeed for less than 6 equivalents of ligand, only complexed phosphorus derivative are seen. Beyond this ratio, the free ligand is not detected and coalescence of phosphorus signals is observed showing that all the ligands are involved in the extraction mechanism without the formation of a stable complex in solution. Since in the case of TPO/Bn_2O system the extraction is weak, the NMR measurement suggests a possible ligand exchange in the organic phase. Due to free ligands available for the ligand exchange, a very fast exchange rate results in an averaged signal from the bonded and free extractant molecules.

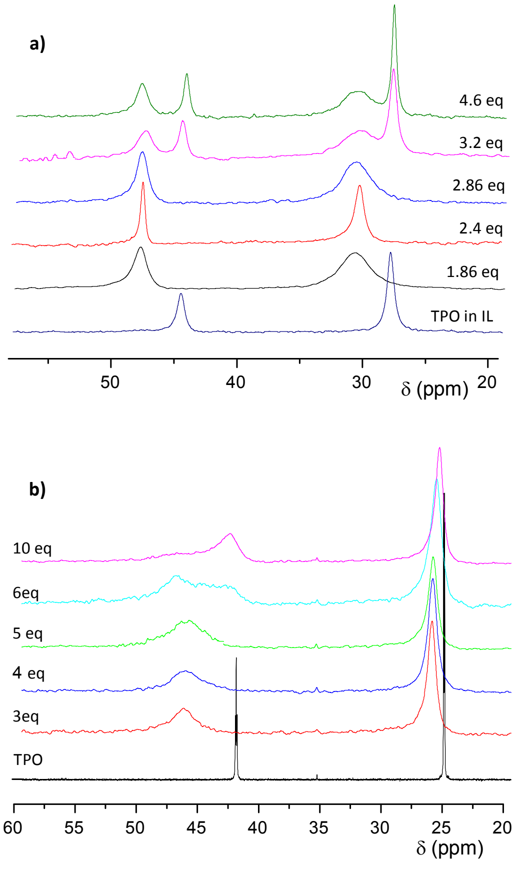

Fig. 5 ^{31}P NMR of the complexes formed in a) [EBPip][NTf_2] and b) Bn_2O

It is thus very important to note that for a same TPO ligand, the complexation can be very different following the solvent used.

These observations have already been pointed out by some research groups by using the slope method[10,13] but, to the best of our knowledge, this is the first time that it is directly observed at the molecular level.

Extraction data were compared to the theoretical extraction yields calculated by the following equation:

$$\%Ex_{théo} = 100 - \frac{[M]_{ini} - \frac{[L]}{n}}{[M]_{ini}} x100 \qquad (2)$$

Where $[M]_{ini}$ is the initial concentration of the metal in the aqueous phase, [L] is the initial concentration of the ligand in the organic phase and *n* is the number of ligands involved in the complex.

The calculated extraction profile for *n* = 3 is in good agreement with the experimental results and confirms the formation of a 3:1 complex (Figure SI-4).

In benzyl ether, whatever the values of n, no correlation could be obtained to fit the experimental data. This is in agreement with the NMR data and confirms a more complex system.

The mechanisms of europium and ytterbium extractions have been studied following a similar approach.

3.2.1.2. Europium and Ytterbium extraction

Europium extraction in the ionic liquid follows the same trends than lanthanum with a complete extraction for 3 equivalents of ligand (Figure 6a) which is in agreement with the slope obtained in figure SI-5a. Considering now the benzyl ether system, very different results were obtained compared to lanthanum. Quantitative extraction of europium was never reached even with 10 equivalents of ligand (Figure 6a).

Plotting the ligand concentration as a function of europium extracted, slope of approximatively 9 is obtained (Figure SI-5a), indicating that at least 9 ligands per metallic cations are involved in the extraction mechanism. As for La, there is a good fit between theoretical and experimental data for 3 ligands per metallic cation in the case of the IL-based extraction (Figure SI-5b).

Concerning the ytterbium profile (Figure 6b), quantitative extraction of Yb in Bn_2O was not reached, even when 10 equivalents of ligands were used. Contrary to La and Eu, there is no marked break in slope in [EBPip][NTf_2] and a smooth decrease is observed from 3 equivalents of TPO/Yb.

Quantitative extraction was obtained with an excess of 4 in TPO. Moreover, in the case of ytterbium, experimental data involving 3 ligands per metallic cation in the case of the IL-based extraction (Figure SI-6) are totally incompatible with theoretical extraction whatever the value of *n*, showing a more complex extraction mechanism.

Solvation of the ligands and/or the complexes is thus very different in both systems and could explain why ligands are more efficient in ionic liquids. As already reported, the formation of aggregates can explain the performance of some extractive systems.[26] Thus supramolecular studies have to be envisaged to confirm that a different organization of the ligands, such as aggregates formation could be the driving force of extraction or on the contrary, aggregation could decreases the efficiency of the ligand.

3.3. Stripping

Beyond the green aspect and the efficiency of IL in metal extraction, one major aspect lies in the recovery of the metal from the IL phase for recycling them. To date, still few studies reported the back extraction of metal from these media.[5,27-29]

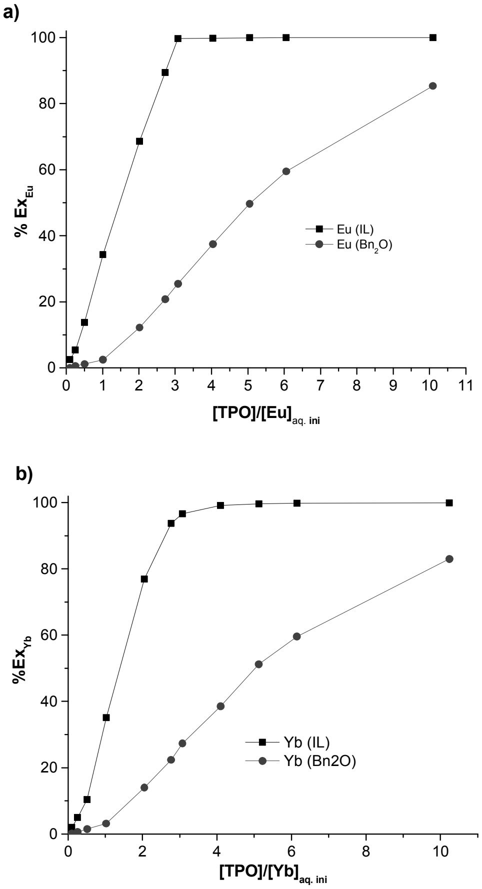

Fig. 6 a) variation of Eu extraction vs ratio ligand/Eu ; b) variation of Yb extraction vs ratio ligand/Yb

The main reason is related to the difficulty to strip the metal cation from IL and only two approaches have been already developed:

a) The use of an acidic aqueous phase in which ionic liquid does not extract the targeted ions (low or high concentration)

b) The use of water soluble extractants able to extract the ions from the IL diluent.

Considering the results obtained in the IL diluent the first opportunity is not an option because D values >> 1 are obtained from 10^{-3} to 9 M of [HNO_3].

Researchers have studied a variety of water soluble extractants for the back extraction of Ln and showed that the system 0.1 M citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate[30] allowed the total recovery of these metals.[5,27]

After quantitative extraction of Ln from an aqueous solution of 3 M HNO_3 into the [EBPip][NTf_2] phase, the stripping was carried out using various back extracting phases (Table 2).

Ammonium carbonate and ammonium oxalate lead to the precipitation (pr.) of REEs (conditions 1 and 2).

The most powerful system described by Nakashima *et al.* is totally inefficient in our case since less than 1% of Ln is released except for Yb with 40% of recovery (condition 3). The use of 0.5 M of DTPA with 2% of NH_4OH, leads to the recovery of 10% of La, Nd, Eu, 50% for Dy, and near 90% of Yb (condition 4). Complete back extraction of heavy REEs into the aqueous phase was possible in comparison to light REEs.

Table 2: Comparison of stripping behavior of Ln from EBPip]NTf_2 using various back extracting phase. Organic phase: 35 mM TPO in EBPip]NTf_2. $V_{aq/org}$ = 2. Aqueous phase: 1: ammonium carbonate 0,5M ; 2: ammonium oxalate 0.2M with NH_4OH 2%, 3: Citric acid 0.2M - Formic acid 0.8 M - hydrazine 0.8M; 4: DTPA 0.5M/NH_4OH 2%; 5: DTPA 0.5M/NH_4OH 2% at 60°C.

conditions	La	Nd	Eu	Dy	Yb
1	pr.	pr.	pr.	pr.	pr.
2	pr.	pr.	pr.	pr.	pr.
3	0,6 %	0,1 %	0,1 %	5 %	39,5 %
4	18 %	10 %	15 %	35 %	88 %
5	59 %	33 %	49 %	72 %	99 %

This is essentially due to the fact that Yb is poorly extracted for a low concentration of acid and thus is easily recovered in the same acidic conditions. The recovery of REE can be increased by a factor 3 by increasing the temperature (condition 5).

Considering that the mixture 0.5 M of DTPA with 2% of NH_4OH as the most efficient back extracting system, a comparison study of the stripping in the different diluents has been investigated (Table 3).

The results indicate that the REEs were totally recovered from Bn_2O phase, which is not the case for IL medium except for Yb.

Table 3: Comparison of stripping behavior of Ln. Organic phase: 35 mM TPO in diluent (ionic liquid phase or Bn_2O). Aqueous phase: 0.5 M of DTPA with 2% of NH_4OH

Solvent	La	Nd	Eu	Dy	Yb
[EBPip]NTf_2	59 %	33 %	49 %	72 %	99 %
Bn_2O	97 %	97 %	98 %	> 99%	> 99 %

3.4. Extraction mechanism

As shown from the slope analysis method and from the ^{31}P NMR experiments for a same TPO ligand, the complexation is very different following the solvent used. This point can explain the TPO efficiency differences between ILs and dibenzylether.

In order to better understand the extraction mechanism involved in the IL media the structure of the IL cation (influence of the alkyl chain lenghts from butyl C4 to octyl C8) and the possibility of cation or anion exchange in the aqueous phase have been studied.

3.4.1. Cation and/or anion exchange mechanism

3.4.1.1. Comparison of cation alkyl chain length:

As reported in literature, the length of the alkyl chain in the organic cation deeply affects the efficiency of extraction.[14, 31-33] For example, UO_2^{2+} is less than 100 times extracted by tributylphosphate (TBP) dissolved in decylmethylimidazolium than in butylmethylimidazolium.[32]

The extraction efficiency decreases as the hydrophobicity of the IL cation is increasing and accordingly less IL partitions in the aqueous phase, which limits the metal ion partitioning.

To highlight if such behavior is applicable in our conditions, we compared the extraction efficiency of TPO dissolved in N-butyl or N-octyl-N-ethylpiperidinium bis(trifluoromethylsulfonyl) imide ([EBPip][NTf_2] or [EOPip][NTf_2]).

Similar trends are observed when considering the water and nitric acid extraction from both EBPipNTf_2 and EOPipNTf_2 (Figure SI-7). As expected, the amount of extracted water depends on the hydrophilicity of the IL cation; indeed a lower concentration of water was measured in EOPipNTf_2 after the contact with water (Figure SI-7a). The increase of the alkyl chain of the piperidinium for the nitric acid extraction has no influence on the nitric acid extraction behaviour (Figure SI-7b).

The results summarized in Figure 7 show very similar trends and efficiencies for both carbon chain lengths. By contrast with the previously reported IL-based extraction systems, these results suggest that the extraction efficiencies are not dependent on the hydrophobicity of IL cations contrarily to traditional IL-based extraction systems.

This unusual behavior was once observed by X. Sun *et al.*[34] with ionic extractants in [C_nMIm][NTf_2], suggesting that the mechanism is not consistent with a cation exchange mechanism. Indeed, the only way to explain a cation exchange mechanism would be that EOPip cation with an octyl chain has the same aqueous solubility than the butyl derivative.

In order to confirm this hypothesis, aqueous phases were analyzed to quantify the solubility of each cation for various nitric acid amounts, with and without REEs metals.

3.4.1.2. Analysis of the aqueous phase:

The solubility of the ionic liquid/TPO system for various nitric acid concentrations was first studied by NMR analysis of the aqueous phase following the ^{19}F nucleus for the NTf_2 anion and ^{1}H for the IL cation.

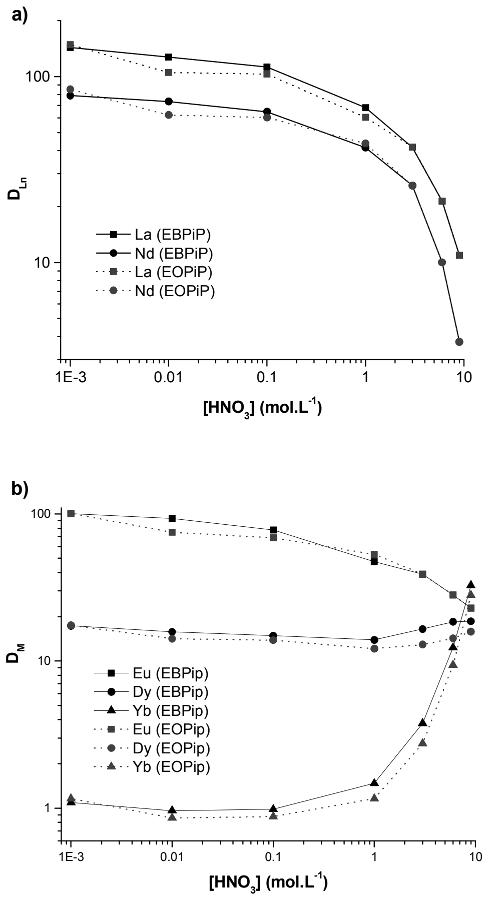

Fig. 7 Comparison of Ln extraction between [EBPip]NTf_2 and [EOPip]NTf_2; a) La and Nd ; b) Eu, Dy, Yb

Blank solutions were obtained after a pre-equilibrium step by contacting [EBPip][NTf_2] or [EOPip][NTf_2] with an aqueous solutions for various nitric acid concentrations (10^{-3} to 9M) without metal and then the pre-equilibrated organic phases were contacted with various aqueous phases containing lanthanide cations. Anion quantification in the aqueous phase is presented in Figure SI-7.

Similar extraction behaviour of [EBPip][NTf_2]/TPO or [EOPip][NTf_2]/TPO with and without Ln in the primary aqueous phase indicates that no anion exchange was involved in the mechanism of this ILs-based extraction.

The solubility of the anion is not affected by [HNO_3] from 10^{-3} to 1 M. Above 1 M concentration, dramatic increase in the anion solubility is observed with solubilities reaching 85 mM for [EBPip][NTf_2] and 42 mM for [EOPip][NTf_2] at 9 M [HNO_3]. This phenomenon can be attributed to an anion exchange with nitrate anion according to the equation:

$$\mathrm{EBPiP^+;\ NTf_2 + HNO_3\ \ <=>\ \ EBPiP^+;\ NO_3^- + HNTf_2} \quad (3)$$

Another set of extraction experiments using similar conditions was realized in order to quantify the IL cation dissolution in aqueous phase. Concentrations of EBPip in different aqueous phases are summarized in Table 1.

Table 1 EBPip quantification in aqueous phase.

Initial $[Ln]_{aq}$ = 13 mM; [TPO] = 34 mM

$[HNO_3]$ (M)	$[EBPip]_{aq}^{0}$ (blank) (mM)	$[EBPip]_{aq}^{Ln}$ after extr. (mM)	$[EBPip]_{aq}^{Ln} - [EBPip]_{aq}^{0}$ (mM)	$[Ln]_{org}$ (mM)	Ratio $\Delta[EBPip]_{aq}/[Ln]_{org}$
0.001	7.35	30.5	23.15	12.0	1.9
0.01	9.35	30	20.65	11.6	1.8
0.1	14.05	30.5	16.45	11.5	1.4
1	27.45	34.5	7.05	11.8	0.6
3	41.95	47	5.05	12.1	0.4
6	57.4	61.5	4.1	12.4	0.3
9	62.4	64	1.6	12.0	0.1

The amount of [EBPip] transferred in aqueous phase gradually increases as a function of the nitric acid concentration. This behavior is observed for both aqueous phase with or without lanthanides. Similar amount of IL cation is transferred at higher nitric acid concentration. Ln loading in the ionic liquid phase remains constant (≈ 12 mM) with the increase in nitric acid concentration of the initial aqueous feed solution.

Nevertheless, at low nitric acid concentration (from 0.001 to 0.1 M) the amount of IL cation transferred $[EBPip]_{aq}^{Ln}$ is more important in the aqueous phase initially loaded with lanthanides compared to the blank $[EBPip]_{aq}^{0}$. The ratio of the Δ[EBPip] transferred in aqueous phase over the lanthanides extracted in organic phase varies from 2 to 1.4 at these concentrations indicating that the Ln extracted are exchanged by around 2 $[EBPip]^+$.

As usually described, when a M^{n+} metallic cation is extracted by a neutral extractant at low acid concentration, an exchange of "n" organic cation in order to extract the metallic cation is observed. In our case, the Ln^{3+} is supposed to be extracted by 3 IL cations, however a ratio varying from 2 to 1.5 is observed for the IL cation transferred in aqueous phase over the lanthanides extracted in organic phase.

The extraction can thus be attributed to a cation exchange mechanism implying 2 or less EBPip and at least 1 proton coming from the acid initially extracted by the ionic liquid as described by Billard *et al.*[15] The equation can thus be written as follow:

$$Ln^{3+} + n\,\overline{TPO} + 2\,\overline{EBPip^{+}} + \overline{H^{+}} <=> \overline{LnTPO_n^{3+}} + 2\,EBPip^{+} + H^{+} \quad (4)$$

Nevertheless some aspects can refute this mechanism:

a) At 10^{-3} M HNO_3 only 1 mM of proton can be extracted by the ionic liquid. But, considering the equation and the total amount of Ln extracted by TPO in $[EBPip]NTf_2$ (12.0 mM), 12.0 mM of H^+ have to be involved in the mechanism.

b) Because $[EOPip]NTf_2$/TPO extracts in the same order of magnitude the lanthanides than $[EBPip]NTf_2$, the same amount of EOPip should be found in water. Nevertheless no EOPip was detected in the aqueous phase after extraction.

The main hypothesis to explain these results is that Ln are extracted under their neutral form. Considering the Bn_2O system, in which no cation exchange is possible, 25 % of La and Nd, and 15 % of Eu were extracted, which is far from negligible. Speciation of lanthanides would be of great interest but, unfortunately, it is not well described. It is known that they can be hydrolyzed and form neutral species $Ln(OH)_3$. But according to the literature,[35] and under the pH conditions studied here, Ln are essentially in the form of Ln^{3+}.

In regards to the different statements and behaviors observed by studying the IL cation exchange it appears that the cation exchange mechanism cannot be the driving force of the extraction and cannot explain the difference between the classical solvents and ionic liquids. This is in agreement with the fact that the hydrophobicity of IL cation does not impact the extraction efficiency.

The mechanism extraction pathway appears not consistent with both anion and cation exchange mechanism.

Therefore, it corroborates the fact that the extraction mechanism of this TPO/IL-based extraction is more likely to be solvation.

In the case of the solvation mechanism, the composition of the aqueous solution can have a significant effect on separation efficiency. The role of the nitrate from the nitric acid medium is classically to salt out the neutral species into the organic phase where it is solvated by the extractant. Interestingly in the TPO/IL system the extraction efficiency is obtained for weak nitric acid concentration. It means that in the IL diluent the TPO did not need the help of nitrate in order to extract the REEs, as it is classically observed for solvation mechanism in organic solvent.[36] Indeed, in the TPO/Bn_2O system the extractability property increases with the concentration of nitric acid. Again this highlights the different behavior between the classical organic diluent and the ionic liquid media.

3.5. Application to feed simulant solution from sintered Nd/Fe/B magnets

Taking into account the performances and the potential of TPO extractant in IL diluent for the extraction of REEs, we then studied the efficiency and the selectivity of this system for lanthanides (Nd, Dy) towards Fe and B contained in a simulated leaching solution of permanent magnets. A new set of experiments was performed by using the TPO in $[EBPip][NTf_2]$ (Figure 8).

As already observed in the previous results, an inversion of selectivity occurs between light and heavy REEs at high acidity. Indeed, the selectivity of Nd over Dy around 4 at 1-3 M $[HNO_3]$ switches to value lower than 1 at higher concentration from 6 to 9 M $[HNO_3]$. Interestingly, Fe(III) shows the same behavior than Yb, *i.e.* it is more extracted when the aqueous phase is more acidic.

An interesting point in favor with a selective extraction of REEs is that the D_{Fe} remains lower than 1 over the full range of HNO_3 concentrations studied. Finally, whatever the acidity, boron is not extracted at all by the system TPO/IL.

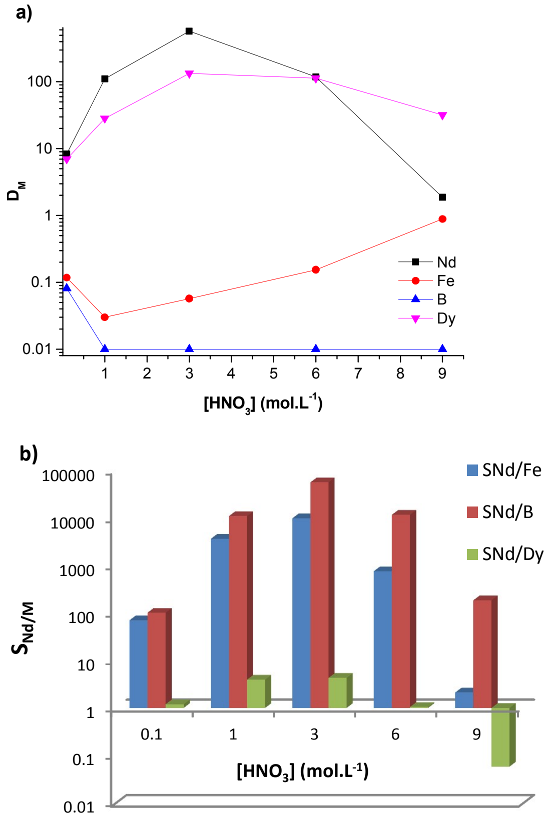

Fig. 8: a) Extraction of a simulated Nd/Fe/B magnet by TPO in [EBPip][NTf_2] vs [HNO_3]. Conditions: TPO = 50 mM; Nd = 4.9 mM; Fe = 5.1 mM; B = 1 mM; Dy = 1.85 mM b) Selectivity of Nd/M

The highest selectivity towards Ln against B and Fe was obtained in the range 1 to 6 M [HNO_3] with values reaching 10^4. These encouraging results demonstrate the potential of extracting systems constituted by TPO/IL for the selective extraction of Ln in regards to other competitive ions that may be present in a nitric acid leaching solution of permanent magnets and especially the iron which is the main competitive ion in Nd/Fe/B/Dy magnets.

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4. CONCLUSION

A comparative study of the efficiency of a lipophilic triphosphine trioxide (TPO) ligand dissolved in dibenzyl ether (Bn_2O) or in ionic liquids (ILs) as diluent established that the ILs-based extracting systems are largely more performant.

The classical cation exchange mechanism which is generally proposed in ionic liquids media is not consistent with the enhanced extraction properties obtained in our system. Indeed, we observed that a more hydrophobic cation [EOPip] is as efficient as a less one [EBPip], whereas the [EOPip] cation has never been observed in aqueous phase even at low nitric acid concentration.

Moreover, clear differences have been identified in the number of ligands per metallic cations obtained in Bn_2O and ILs. Only 3 ligands are necessary to extract quantitatively Ln in ionic liquids, whereas more than 9 are required in Bn_2O. These ratios have been corroborated by slope method and ^{31}P NMR analysis.

Solvation of the ligands and/or the complexes is thus very different in these two systems and could be the reason why ligands are more efficient in ionic liquids. Furthermore solvation has been found to be a dominant mechanism in the IL-based extraction system for REEs. Indeed, the efficiency is not dependent on the hydrophobicity of IL cations, which excludes the involvement of the classical ion-exchange mechanism associated with traditional IL-based extraction systems. To go further in the understanding of the mechanisms, supramolecular studies (SAXS, SANS, experiments…) would be necessary to evaluate the different organization behaviour of the ligands in Bn_2O and ILs.

It was also shown that reasonable stripping of Ln from IL diluent is possible using an aqueous solution of ammonium DTPA at 60°C.

Finally, we have demonstrated that such systems are able to selectively extract REEs from nitric acid media, as simulant leaching solutions of permanent sintered Nd/Fe/B/Dy permanent magnets. High selectivities are obtained in regards to other competitive ions such as boron and iron species.

Acknowledgements

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References

1 Report on critical raw materials for the EU, Critical raw materials profils, http://ec.europa.eu/enterprise/policies/rawmaterials/files/doc/crm-critical-material-profiles_en.pdf.
2 S. Dai, Y. H. Ju and C. E. Barnes, Journal of the Chemical Society, *Dalton Transactions*, 1999, 1201.
3 Y. Baba, F. Kubota, N. Kamiya and M. Goto, *Journal of Chemical Engineering of Japan*, 2011, 44, 679.
4 F. Kubota, Y. Baba and M. Goto, *Solvent Extraction Research and Development, Japan*, 2012, **19**, 17.
5 K. Nakashima, F. Kubota, T. Maruyama and M. Goto, *Industrial & Engineering Chemistry Research*, 2005, **44**, 4368.

6 V. A. Cocalia, M. P. Jensen, J. D. Holbrey, S. K. Spear, D. C. Stepinski and R. D. Rogers, *Dalton Transactions*, 2005, 1966.
7 S. J. Yoon, J. G. Lee, H. Tajima, A. Yamasaki, F. Kiyono, T. Nakazato and H. Tao, *Journal of Industrial and Engineering Chemistry*, 2010, **16**, 350.
8 Y. Kikuchi, M. Matsumiya and S. Kawakami, *Solvent Extraction Research and Development, Japan*, 2014, **21**, 137.
9 Y. Zuo, Y. Liu, J. Chen and D.-Q. Li, *Journal of Chemical Technology & Biotechnology*, 2009, **84**, 949.
10 K. Shimojo, K. Kurahashi and H. Naganawa, *Dalton Transactions*, 2008, 5083.
11 M. P. Jensen, J. Neuefeind, J. V. Beitz, S. Skanthakumar and L. Soderholm, *Journal of the American Chemical Society*, 2003, **125**, 15466.
12 A. Rout and K. Binnemans, *Dalton Transactions*, 2015, **44**, 1379.
13 F. Yang, F. Kubota, N. Kamiya and M. Goto, *Solvent Extraction Research and Development, Japan*, 2013, **20**, 225.
14 M. L. Dietz and J. A. Dzielawa, *Chemical Communications*, 2001, 2124.
15 M. Bonnaffe-Moity, A. Ouadi, V. Mazan, S. Miroshnichenko, D. Ternova, S. Georg, M. Sypula, C. Gaillard and I. Billard, *Dalton Transactions*, 2012, **41**, 7526.
16 I. Billard, A. Ouadi and C. Gaillard, *Dalton Transactions*, 2013, **42**, 6203.
17 A. Rout, J. Kotlarska, W. Dehaen and K. Binnemans, *Physical Chemistry Chemical Physics*, 2013, **15**, 16533.
18 H. J. Cristau, D. Virieux, J. F. Dozol and H. Rouquette, *Journal of Radioanalytical and Nuclear Chemistry*, 1999, **241**, 543.
19 H.-J. Cristau, D. Virieux, P. Mouchet and A. Fruchier, *European Journal of Organic Chemistry*, 1999, 1561.
20 G. Chatel, C. Goux-Henry, A. Mirabaud, T. Rossi, N. Kardos, B. Andrioletti and M. Draye, *Journal of Catalysis*, 2012, **291**, 127.
21 Y. Marcus, and I. Abrahamer, *Journal of Inorganic and Nuclear Chemistry,* 1961, **22**, 141.
22 J. S. Preston and A. C. Du Preez, Solvent extraction processes for the separation of rare earths metals, in *Solvent Extraction 1990: proceedings of the International Solvent Extraction Conference* (ISEC '90), Kyoto, Japan, ed. T. Sekine, Part A, Elsevier, Amsterdam, 1990, pp. 883–894.
23 K.L. Nash, *Solvent Extraction and Ion Exchange,* 1993, **11**, 729.
24 A. N. Turanov, V. K. Karandashev and V. E. Baulin, *Radiochemistry*, 2001, **43**, 72.
25 I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard and S. Georg, *Solvent Extraction and Ion Exchange*, 2011, **29**, 577.
26 S. Dourdain, I. Hofmeister, O. Pecheur, J. F. Dufrêche, R. Turgis, A. Leydier, J. Jestin, F. Testard, S. Pellet-Rostaing and T. Zemb, *Langmuir*, 2012, **28**, 11319.
27 K. Nakashima, F. Kubota, T. Maruyama and M. Goto, *Analytical Sciences*, 2003, **19**, 1097.
28 K. Shimojo and M. Goto, *Analytical Chemistry*, 2004, **76**, 5039.
29 G.-T. Wei, J.-C. Chen and Z. Yang, *Journal of the Chinese Chemical Society*, 2003, **50**, 1123.
30 R. R. Chitnis, P. K. Wattal, A. Ramanujam, P. S. Dhami, V. Gopalakrishanan, A. K. Bauri and A. Banerji, *Journal of Radioanalytical and Nuclear Chemistry*, 1999, **240**, 721**.**
31 M. L. Dietz and D. C. Stepinski, *Green Chemistry*, 2005, **7**, 747.
32 M. L. Dietz and D. C. Stepinski, *Talanta*, 2008, **75**, 598.
33 A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin and R. D. Rogers, *Industrial & Engineering Chemistry Research*, 2000, **39**, 3596.
34 X. Sun, H. Luo and S. Dai, *Dalton Transactions*, 2013, **42**, 8270.
35 Y. Y. Yakubovich and V. G. Alekseev, *Russian Journal of Inorganic Chemistry* 2012, **57**, 911.
36 B. Moktli and C. Poitrenaud, Solvent Extraction and Ion Exchange, 1997, **15**, 455.

GRAPHICAL ABSTRACT

Performances and mechanistic investigations of triphosphine trioxide / ionic liquid system for rare earth extraction

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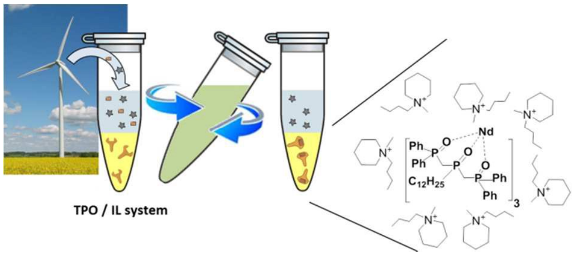
Triphosphine trioxide (TPO) / ionic liquid (IL) system for rare earth extraction: application for permanent magnet recycling.



Supplementary Information

Performances and mechanistic investigations of triphosphine trioxide / ionic liquid system for rare earth extraction

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Fig. SI-1 Extraction kinetic of Ln. $[HNO_3]$ = 6 M

Fig. SI-2 Effect of temperature on the extraction in [EBPip][NTf_2]. Initial aqueous phase: $[HNO_3]$ 6 M.
Ln D_{Ln} = f(1/RTx10^3) : Nd (y = 12.22x + 1.22); Eu (y = 11.67x + 0.73) ; La (12.65x + 1.04) ; Yb (y=-9.42x + 0.79)

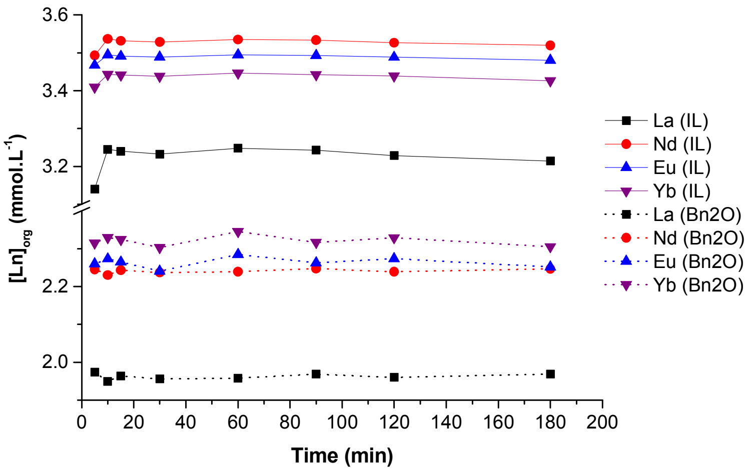
Fig. SI-3 Nitric acid extraction following the solvent used: a) after pre-equilibrium step and b) after metal extraction

Fig. SI-4 Theoretical (dot line) and experimental extraction in IL of La vs number of ligands

Fig. SI-5 a) variation of the ligand concentration vs Eu extracted in organic phase [TPO]-(IL) =f ([Eu]org): y = 2.94 + 0.3, R^2 = 0.998; [TPO]-(Bn_2O) =f ([Eu]org): y = 8.58x + 4.3, R^2 = 0.997; b) Theoretical (dot line) and experimental extraction in IL of Eu vs number of ligands

Fig. SI-6 variation of the ligand concentration vs Yb extracted in organic phase. [TPO]-(IL) =f ([Eu]org): y = 2.86 + 0.15, R^2 = 0.982; [TPO]-(Bn_2O) =f ([Eu]org): y = 8.8x + 0.38, R^2 = 0.996

Fig. SI-7 a) Comparison of water extraction with different ILs vs $[HNO_3]$; b) Extrapolation of the nitric acid extracted in organic phase vs $[HNO_3]$



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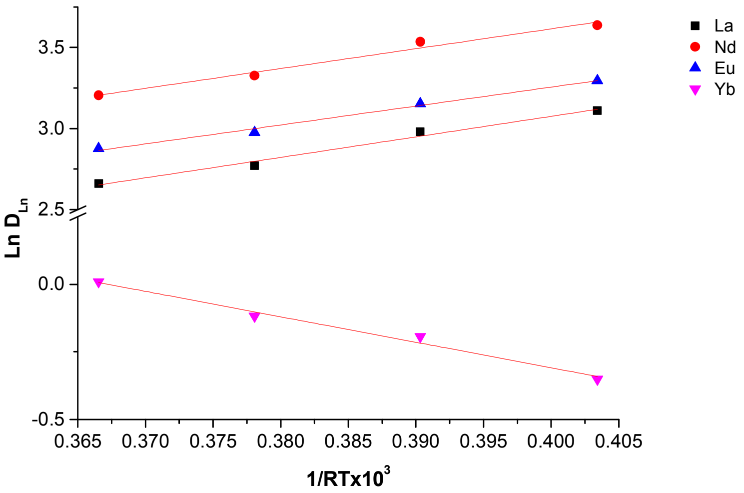

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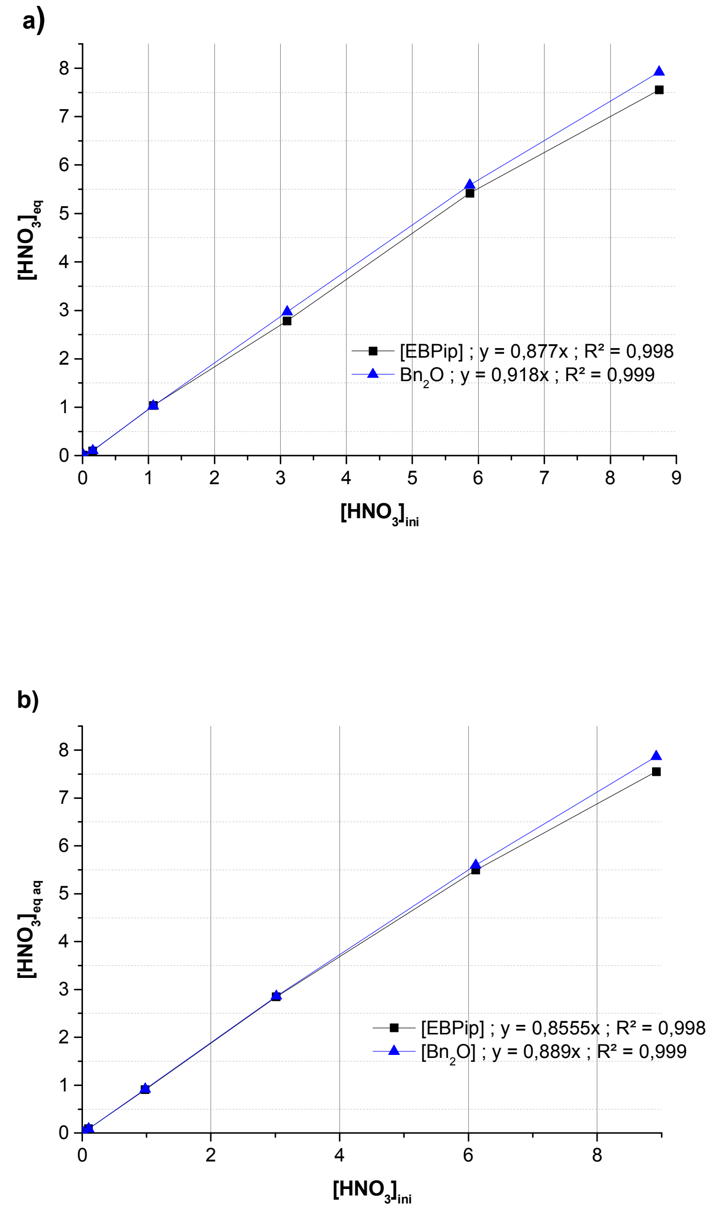

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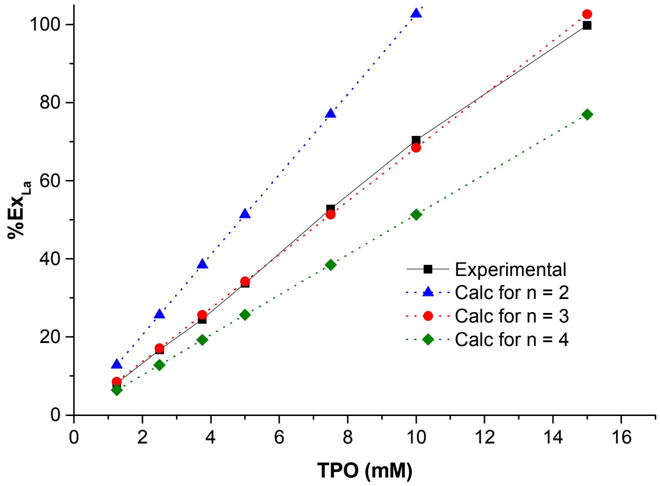

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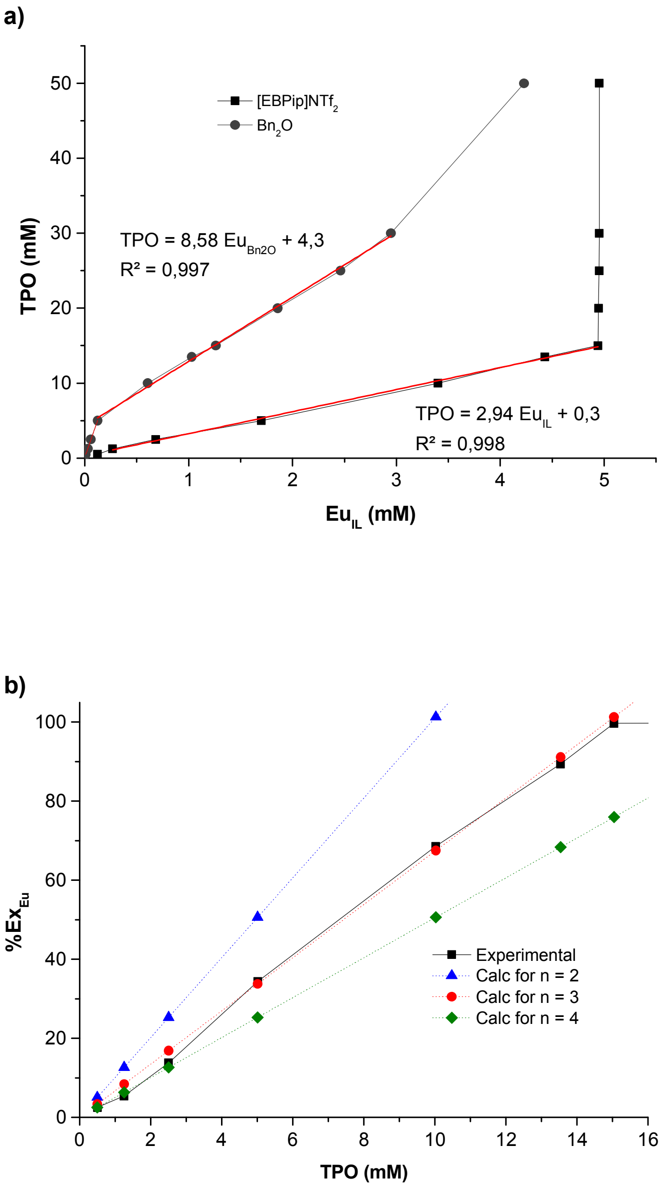

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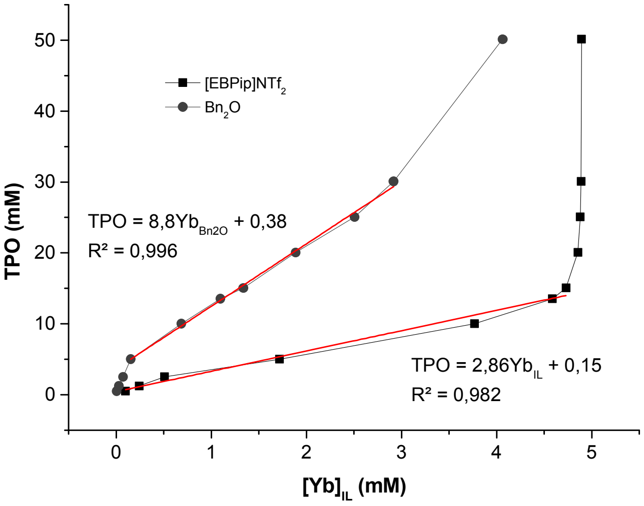

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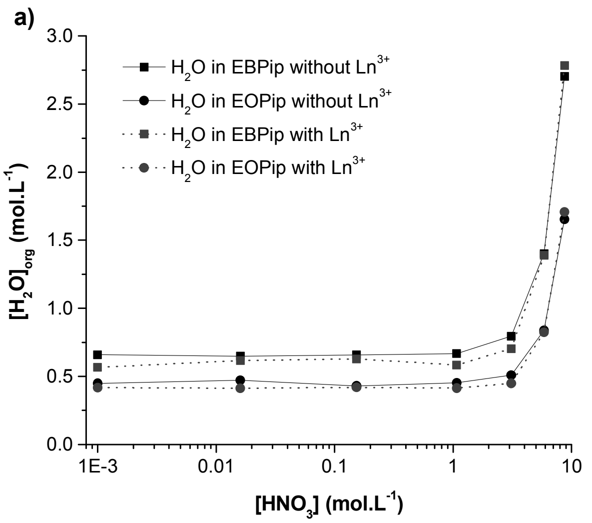

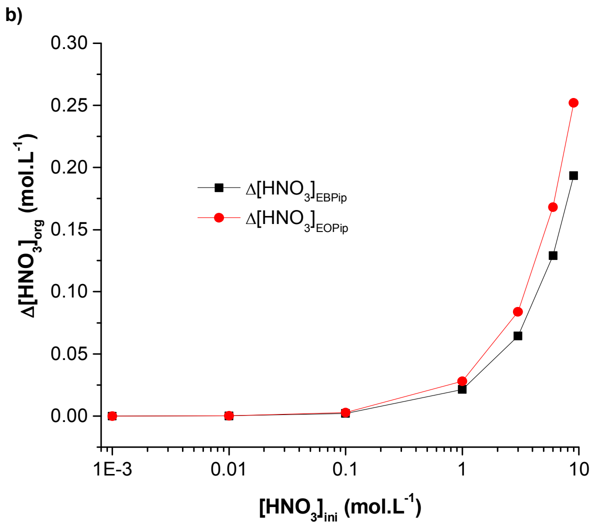

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