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# Liquid-liquid extraction of rare earths elements by use of ionic liquids.

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## ABSTRACT

Rare earth elements (REE) have a wide range of applications due to their unique chemical, electrical, magnetic, optical and catalytic properties. The continuous growing of technological applications of these elements has increased the interest for the development of an efficient technology for their recovery by extraction from wastes and aqueous effluents. Ionic Liquids (ILs) are considered as good alternative for organic solvents in extraction processes. However, the higher or lower extraction efficiency in ILs remains difficult to predict because of a lack of understanding of the extraction mechanisms in this class of diluents, which render their application difficult to generalize. We have studied and compared the extraction behavior of *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (DMDOHEMA) diluted in *n*-dodecane and ionic liquids (ILs), 1-ethyl-1-butylpiperidinium bis (trifluoromethylsulfonyl)imide [EBPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] and 1-ethyl-1-octylpiperidinium bis (trifluoromethylsulfonyl)imide [EOPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>], toward La(III) and Eu(III) dissolved in aqueous solution, at room temperature. Fe(III) was introduced to the aqueous phase in order to study the selectivity with regard to La(III) and Eu(III) and the effect of pH on extraction was investigated by using of several HNO<sub>3</sub> concentrations. We found that the ionic liquid with shorter alkyl chain [EBPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] shows a higher extraction ability than [EOPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] and that the use of ILs as organic solvent instead of *n*-dodecane, greatly enhances the extraction efficiency in all cases. Cation ([EBPip<sup>+</sup>] or [EOPip<sup>+</sup>]) and anion ([NTf<sub>2</sub><sup>-</sup>]) concentration in the aqueous phase, has been determined in order to elucidate the extraction mechanisms.

## INTRODUCTION

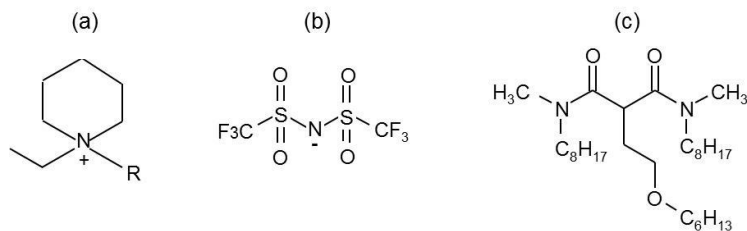
Rare earth elements (REE) are widely used nowadays in a large number of technological applications as hard disc drives, LCD panels, hybrid vehicles, wind turbines, surgical robots, etc (Zepf, 2016). They are rarely concentrated in mineral ores and only three minerals, monazite, bastnasite, and xenotime are sufficiently enriched with REEs for an economic viability in their refining (Hidayah & Abidin, 2018). China is the world most important supplier of REE with a market share that can reach 95%. Uncertain supply caused by this market monopolization together with their high economic importance, have led to considered REE as critical metals, generating great interest in the development of an efficient technology for their recycling from electrical and electronic wastes on an industrial scale.

Ionic liquids (ILs) are defined as organic salts with melting points below 100°C. Thanks to their ionic nature, they present unique properties as negligible vapor pressure, non-flammability, high degree of solubility for organic and inorganic substances, high thermal and chemical stability. Whatever the source, the extraction of rare earth elements involves dissolution and solvent extraction process that implies the use of acids and organic solvents, generating a large amount of chemical waste, VOC release in the atmosphere, water pollution and heat discharge (Omorodion & Baker, 2018). For this reason, ionic liquids arise as a promising alternative to common organic solvents because they possess favorable properties which are tunable with the adjustment of the cation/anion pair or by incorporation of functional groups into the cationic and/or anionic components of ILs.

ILs were used initially for the extraction of substituted-benzene derivatives thirty years ago (Huddleston et al., 1998). Dai and co-workers studied the strontium extraction into ionic liquids using crown ethers as extractant. They found that a higher extraction efficiency can be achieved using ionic liquids instead classical solvents (Dai, Ju & Barnes, 1999). Mechanistic studies showed that metal extraction in ILs can be carried out by several mechanisms such as anion (Ansari et al., 2015) or cation (Dietz & Dzielawa, 2001) exchange and a similar mechanism to that in classical systems (Cocalia et al., 2005).

Malonamides have been used in the DIAMEX solvent extraction process for the recovery of lanthanides and actinides from nuclear aqueous wastes with a high efficiency and stability in nitric acid media (Poirot, Bourgeois & Meyer 2015). Among the malonamides studied for the DIAMEX process, DMDOHEMA (see Figure 1 for the chemical structure) has shown a high extraction ability for REE in organic solvents as benzene (Mowafy & Aly, 2002), n-heptane (Ellis et al., 2014) and n-dodecane (Gannaz et al., 2007) . Several studies have been carried out for the extraction of REE in ILs using extractant molecules as TPO (Turgis et al., 2016), D2EHPA and HDEHDGA (Rout et al., 2011), CMPO (Nakashima et al., 2005) and DEHPA (Yoon et al., 2010). To our knowledge, no investigations for has been reported for REE extraction with DMDOHEMA in IL.

In this paper, we report the results for the extraction of two REE, La and Eu, from nitric acid media with DMDOHEMA dissolved in ionic liquid and compare it with the extraction in dodecane. Additionally, an investigation of the extraction mechanism in these ILs is presented.



**Figure 1** Chemical structures of the ILs and the extractant used in this work. (a) 1-ethyl-1-alkyl piperidinium cation, (b) NTf<sub>2</sub><sup>-</sup> anion, (c) DMDOHEMA

## METHODOLOGY

Four sets of samples were prepared for each organic solvent, having each of them the same initial nitric acid concentration in the aqueous phase (0, 0.01, 1 or 3M), and variable extractant content in the organic phase, between 0 to 0.4 M.

### Chemicals

High purity grade ILs ( $\geq 99.5\%$ ), 1-ethyl-1-butylpiperidinium bis (trifluoromethylsulfonyl)imide [EBPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] and 1-ethyl-1-octylpiperidinium bis (trifluoromethylsulfonyl)imide [EOPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] (see Figure 1 for the chemical structure), was obtained from Solvionic. N,N'- dimethyl- N,N'-dioctylhexylethoxymalonamide (DMDOHEMA) was provided by Pharmasynthèse. Dodecane and iron(III) nitrate nonahydrate (99%) were purchased from Acros Organics, lanthanum(III) nitrate hexahydrate (99.99%) and Europium(III) nitrate pentahydrate (99.99%) from Sigma Aldrich, and Nitric acid from Carlo Erba. All chemicals were used without further purification. Deionized water (Milli-Q) was employed for the aqueous phase preparation.

### Solvent extraction procedure

Aqueous stock solutions were prepared by dissolving weighted amount of the corresponding metal nitrate, La(NO<sub>3</sub>)<sub>3</sub>, Eu(NO<sub>3</sub>)<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>, in a nitric acid solutions at a desired concentration. A volume of 3 mL of the aqueous phase, was introduced in a plastic tube with the same volume of the organic phase in which a given concentration of extractant, DMDOHEMA, have been dissolved previously. The biphasic system was shaken mechanically in a tube rotator for 1.5 hours at 20 rpm and then separated by centrifuging at 4500 rpm for 30 minutes. All extraction experiments have been carried out at room temperature.

## Equipment

Metal and sulfur concentrations in the aqueous phase were determined before and after extraction, by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES). The percentage of metal extracted from the aqueous phase (E%) and the selectivity (S) were calculated as follows:

$$E\% = \frac{[M]_{initial} - [M]_{final}}{[M]_{initial}} \times 100 \quad (1)$$

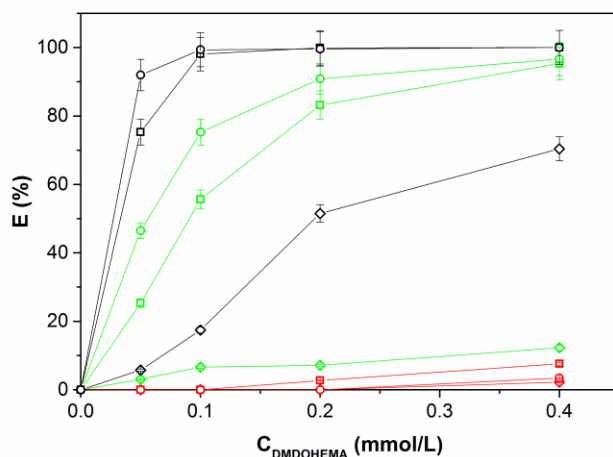
$$S_{M/Fe} = \frac{(E\%)_M \times [M]_{initial} \times [Fe]_{final}}{(E\%)_{Fe} \times [Fe]_{initial} \times [M]_{final}} \quad (2)$$

Where  $[M]_{initial}$  and  $[M]_{final}$  are the metal concentration in the aqueous phase before and after extraction, respectively.

The total carbon concentration in the aqueous phase was determined using a Shimadzu TOC-V CSH. For the carbon content determination, a known volume of sample was diluted with Milli-Q water into a glass vessel, and introduced in the sample holder of the instrument for the measure.

## RESULTS AND DISCUSSION

### Rare earths element extraction in ionic liquid and dodecane



**Figure 2** Percentage of extraction as function of DMDOHEMA concentration, for  $[HNO_3]=1M$ , in:  $[EBPip^+][NTf_2^-]$  (black),  $[EOPip^+][NTf_2^-]$  (green) and dodecane (red). Metal: lanthanum ( $\square$ ), europium ( $\circ$ ) and iron ( $\diamond$ )

Figure 2 shows the percentage of metal extracted from the aqueous phase into the ionic liquids and dodecane. Lanthanum and europium are completely extracted in the  $[EBPip^+][NTf_2^-]$  when the DMDOHEMA concentration is 0.1 M, whilst for  $[EOPip^+][NTf_2^-]$  a concentration of extractant of 0.4

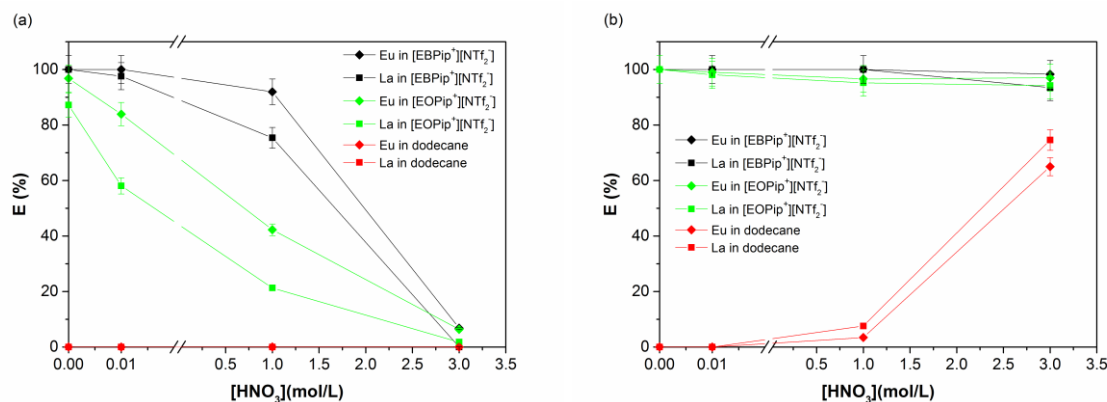
M is necessary for a complete extraction. In the case of dodecane, extraction of metals is negligible and do not reach 10% for the higher extractant concentration. A higher extraction efficiency for REE in ionic liquids with a shorter alkyl chain have been already reported by Kubota and co-workers (Kubota et al., 2008).

DMDOHEMA has higher affinity for europium than lanthanum in ILs, whereas in dodecane it shows an opposite behaviour. For both ionic liquids, a good selectivity toward REE is observed, with a negligible extraction of iron. However, for [EBPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>], when there are not remaining REE in the aqueous phase ([DMDOHEMA] = 0.1 M), iron extraction increases noticeably and attains values up to 70% (see Table 1).

**Table 1** Metal extraction percentage and selectivity values for [HNO<sub>3</sub>]=1M

Ionic liquid	[DMDOHEMA] (mol/L)	Extraction percentage (E%)			Selectivity (S)	
		La <sup>3+</sup>	Eu <sup>3+</sup>	Fe <sup>3+</sup>	S La/Fe	S Eu/Fe
[EOPip <sup>+</sup> ] [NTf <sub>2</sub> <sup>-</sup> ]	0	0	0	0	-	-
	0.05	25	46	3	9.2	23.8
	0.1	55	75	6	16.5	40.2
	0.2	83	91	7	60.5	121.4
	0.4	95	97	12	139.0	197.4
[EBPip <sup>+</sup> ] [NTf <sub>2</sub> <sup>-</sup> ]	0	0	0	0	-	-
	0.05	75	92	5	46.2	173.2
	0.1	98	99	17	233.5	696.0
	0.2	100	100	51	-	-
	0.4	100	100	70	-	-
Dodecane	0	0	0	0	-	-
	0.05	0	0	0	-	-
	0.1	0	0	0	-	-
	0.2	3	0	0	-	-
	0.4	8	3	2	2.9	1.3

Figure 3 display the effect of the nitric acid concentration over the extraction performance of La and Eu for two DMDOHEMA concentrations. In all cases, ILs present a higher extraction efficiency than dodecane. In the same way that the results reported by Shimojo and co-workers (Shimojo, Kurashi, & Naganawa), we observed a decrease of extraction with HNO<sub>3</sub> concentration for the ionic liquids whereas for the organic solvent, extraction of metals increases at high HNO<sub>3</sub> concentration (when [DMDOHEMA] = 0.4 M). For ionic liquids [EBPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>] and [EBPip<sup>+</sup>] [NTf<sub>2</sub><sup>-</sup>], a complete metal extraction can be already be achieved at low extractant concentration for low HNO<sub>3</sub> concentration, and on the whole range of HNO<sub>3</sub> concentration for higher extractant concentration. In comparison, for dodecane, a significant extraction can only be reached for high extractant concentration and high HNO<sub>3</sub> concentration. Therefore, use of these ILs as solvents for REE extraction with DMDOHEMA is very promising as it allows performing the extraction in a wider range of pH and extractant concentration, than dodecane (Tian & Huges, 1994).

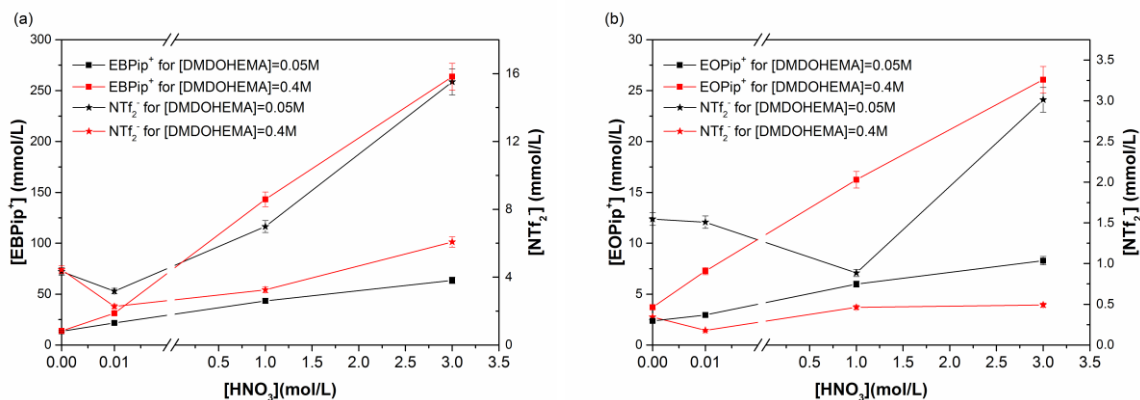


**Figure 3** Effect of pH on extraction of La and Eu for DMDOHEMA concentrations: (a) 0.05 M and (b) 0.4 M

### Extraction Mechanism

One of the possible extraction mechanisms of metals by ILs is due to an ion exchange. For this reason we determined the sulfur and total carbon concentration in the aqueous phase, to follow the cation (EBPip<sup>+</sup> or EOPip<sup>+</sup>) and the anion (NTf<sub>2</sub><sup>-</sup>) transferred to the aqueous phase by the extraction process. In figure 4 we show the concentration of ILs ions into the aqueous phase after extraction as function of HNO<sub>3</sub> concentration for two different extractant concentrations, 0.05 and 0.4 M. Increasing of the nitric acid concentration leads to an increase of ILs ions concentrations into the aqueous phase, likewise dissolution of DMDOHEMA in the ILs have the same effect on the cation concentration. This behaviour is caused for changes in the solubility of the ILs as has been suggested by several authors (Atanassova, Mazan & Billard, 2015), (Gaillard et al., 2016), (Ternova et al., 2016).

For both ILs, a decrease in the NTf<sub>2</sub><sup>-</sup> concentration with the [DMDOHEMA] is observed at each pH. This indicates that the quantity of anions in the aqueous phase is reduced with the extraction. The possibility of an anionic exchange can therefore be rejected in the extraction mechanism. Also, there is an increase of cation concentration, which could both be due to an increase of its solubility in the aqueous phase or to a cationic exchange between the complex extracted and the EBPip<sup>+</sup> or EOPip<sup>+</sup>. Therefore further investigations are required to clarify it.



**Figure 4** Cation and anion concentration in the aqueous phase after extraction as function of  $[\text{HNO}_3]$ , for extractant concentrations of 0.05 and 0.4 M: (a)  $[\text{EBPip}^+]$   $[\text{NTf}_2^-]$  and (b)  $[\text{EOPip}^+]$   $[\text{NTf}_2^-]$

## CONCLUSION

Our results show that the efficiency extraction of REE is enhanced by use of DMDOHEMA in ILs as organic solvent instead of an organic solvent as n-dodecane. The percentage of metal extracted is higher for the ILs at all pH and DMDOHEMA concentrations, which allows considering their use in a wide range of work conditions. The extraction of La and Eu is carried out with a high selectivity in regards to other competitive ion such as iron. Results obtained for the extraction mechanism studies, allows rejecting the idea of an anionic extraction mechanism but further investigations are necessary in order to clarify the possibility of a cationic exchange.

## ACKNOWLEDGEMENTS

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