

Functionalized Ionic Liquids: New Agents for the Extraction of Actinides/Lanthanides

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Abstract – The potentialities of hydrophobic ionic liquids BumimPF₆ and BumimTf₂N for their use in the nuclear fuel cycle were investigated, in particular for the liquid liquid extraction. We demonstrate that the use of RTILs in replacement of the organic diluents for actinides partitioning is promising. In our contribution, we present the synthesis of several task-specific ionic liquids. Our results show that grafting metal complexing groups increases the affinity of metals to the IL phase and gives rise to suitable media for the liquid-liquid extraction of actinides.

INTRODUCTION

Room-temperature Ionic liquids (RTILs, Fig. 1.) are promising solvent alternatives in organic synthesis, catalysis, electrochemistry and separation processes [1]. The introduction of RTILs in the nuclear fuel cycle can be envisioned through different approaches. In this respect, the RTILs' stability under alpha and gamma irradiation and the enhanced safety they provide towards criticality are additional interesting "green" properties of this new class of solvents. In a rather classical way, RTILs can just be considered as alternative solvents [2], in replacement of the highly toxic and flammable kerosene mixtures that are in use nowadays [3]. In such a perspective, not all the potentials of RTILs are considered. The usefulness of RTILs for the extraction of simple organic compounds such as naphthalene has already been reported. However, the partitioning of metallic species is largely limited by the low complexation properties of the hydrophobic ionic liquids: in general, hydrophobic RTILs are non-coordinating, and the highly hydrated metal ions remain in the aqueous phase. Several attempts have been made to enhance the affinity of metal ions towards the IL phase. For example, the addition of organic coordinating compounds increases significantly the distribution ratios of metal ions between the ionic liquid and the aqueous phase [4].

Another very promising objective is the use of functionalized RTILs, which would behave both as the organic phase and as the extracting agent, simply suppressing the problems encountered with extractant/solvent miscibility and the recovery of both the extracting species and the solvent. This last concept has already been the subject of some studies [5].

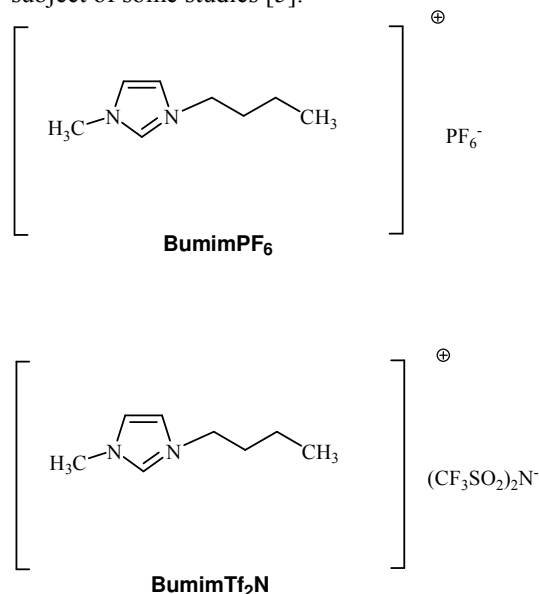


Fig. 1. Examples of Room Temperature Ionic Liquids (RTIL)

PARTITIONING OF ACTINIDES

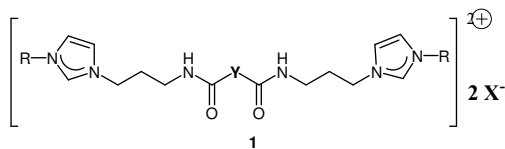
Actinides exhibit significant partitioning towards IL phases from aqueous solutions with the addition of an extractant. Partitioning of metal ions can also be achieved by grafting complexing moieties on the organic cation of the IL. ILs bearing urea, thiourea and thioether or ethyleneglycol groups enhance the partitioning of various metal ions to the IL phase from water. Various functions can be grafted on the RTIL giving rise to task-specific ionic liquids (TSILs) which allow a selective separation of targeted metal ions.

Functional RTILs can therefore be considered as new media for *f*-element chemistry. We focused on the synthesis of functionalized ionic liquids for the partitioning of actinides and lanthanides but we studied first the feasibility of the extraction of an actinide by a TSIL.

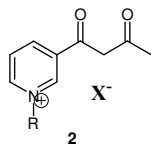
Functionalized Ionic Liquids

We synthesized three ionic compounds bearing different types of metal complexing groups, in particular malonamides, β -diketones and 2-hydroxy-benzylamine entities (Fig. 2.).

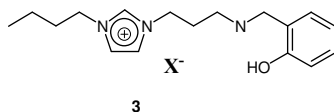
Malonamides



β -diketone



2-hydroxybenzylamine



$X^- = PF_6^-$ or NTf_2^-

Fig. 2. Examples of functionalized Ionic Liquids (TSIL).

These coordinating groups have widely been investigated for the complexation of various metallic species. They should increase the affinity of metals to the IL phase and give rise to suitable media for the liquid-liquid extraction of metals. These compounds, though too much viscous to be used only for liquid/liquid extraction, are easily soluble in Bumim whose anion is identical to that of TSILs synthesized (in our case, PF_6^-). By changing the nature of the counter anion of TSIL (Tf_2N^- instead of PF_6^-), it was possible to obtain a TSIL sufficiently fluid at ambient temperature to be employed in an experiment of liquid/liquid extraction.

Metal Ion Distribution Ratios

Metal ion distribution ratios were determined by mixing 1 mL of TSIL (or TSIL solubilized in the corresponding RTIL if too viscous) and 1 mL of an aqueous phase followed by vortexing (2 min) and centrifuging (2000 g, 2 min) to equilibrate the phases. Addition of the metal ion tracer (ca. 0.005 μCi , 5 μL) was followed by two intervals of vortexing (2 min) and centrifuging (2000 g, 2 min) to ensure that the phases were fully mixed and separated. The phases were separated and dispensed into shell vials from which 100 μL were removed for radiometric analysis. Because equal volumes of both phases were chosen for analysis, the distribution ratio for the metal was determined as the activity ratio:

$$D = \frac{\text{activity in the RTIL phase}}{\text{activity in the aqueous phase}}$$

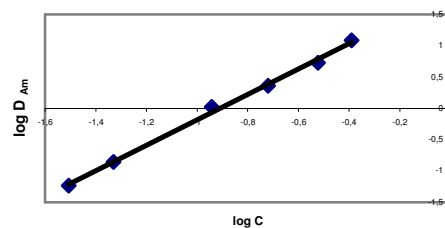


Fig. 3. Distribution ratios for Am^{3+} with increasing concentration of compound 3 in Bumim PF_6 at a fixed pH.

RESULTS

Our results show that grafting metal complexing groups increases the affinity of metals to the IL phase and gives rise to suitable media for the liquid-liquid extraction of actinides.

The preliminary results, which will be thorough in the near future, confirm that the extraction of Am (III) is possible (fig. 3.). This time, the extractant system presents a resolutely innovative character: the organic phase used is at the same time phase of reception of actinide and extracting agent.

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