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Extraction of Lanthanides from Aqueous Solution by Using Room-Temperature Ionic Liquid and Supercritical Carbon Dioxide in Conjunction

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Abstract: For the first time, the study of a three-step extraction system of water/ionic liquid/supercritical CO_2 has been performed. Extraction of trivalent lanthanum and europium from an aqueous nitric acid solution to a supercritical CO_2 phase via an imidazolium-based ionic liquid phase is demonstrated, and extraction efficiencies higher than 87 % were achieved. The quantitative extraction is obtained by using different fluorinated β-diketones with and without the addition of tri(*n*-butyl)phosphate. The complexation phenomenon occurring in the room-temperature ionic-liquid (RTIL) phase was evidenced by using luminescence spectroscopy.

Keywords: carbon dioxide · ionic liquids · lanthanides · metal extraction · supercritical fluids

Introduction

Supercritical fluids and room-temperature ionic liquids (RTILs) are increasingly used in numerous fields of chemistry owing to their "green" characteristics.[1–7] Carbon dioxide is the most widely used gas for supercritical fluid extraction due to the fact that it has moderate critical constants and is commercially available with high purity at a low cost. The main "green" advantages of using this fluid are the inertness of carbon dioxide and the absence of waste-solvent generation. In the specific field of metal extraction, as the usual organic phases (mostly volatile organic compounds) can be replaced by supercritical carbon dioxide (Sc-CO_2), procedures using Sc-CO_2 can be regarded as "green processes". The potential of Sc-CO_2 for metal extraction has been extensively studied during the last decade. Numerous reports in the literature have demonstrated that (quantitative) extraction of metal species, from solid or liquid samples, can be accomplished by using proper chelating agents as extractants.[2,8] For example, actinides, lanthanides, and transition metals are easily extracted by using highly soluble fluorinated β-diketones in Sc-CO_2.[9,10] Adding an organophosphorus reagent such as tri(*n*-butyl)phosphate (TBP) to the β-diketone/Sc-CO_2 system could create a positive synergistic effect, further enhancing the metal-extraction efficiencies for both solid and liquid samples.[11,12]

RTILs also show unique "green" properties such as near-zero vapor pressure and nonflammability, in addition to their interesting physicochemical properties[4] (in particular, polarity, polarizability, and molar volume) including wide liquidus and high solubilities for a variety of compounds (both neutral and charged). These properties make RTILs good candidates to replace traditional volatile organic solvents in current extraction processes.[13–18] In the case of their potential nuclear fuel reprocessing applications, RTILs display the additional advantage of good radiation stability.[19] However, few studies have focused on the extraction abilities of water/RTIL systems for lanthanides and acti-

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nides[15,17,20] and very few back-extraction studies have been performed so far, which limits, at the moment, the potential interest of water/RTIL systems in this respect. From the studies that have been reported, the mechanism of the extraction process appears to strongly depend on the nature of the RTIL and on the extracting ligand used. The extraction occurs either through a cation exchange, by the loss of RTIL cations in the water phase,[21] or through an anion exchange and subsequent loss of RTIL anions in the water phase,[20] so that part of the RTIL is lost in water and cannot be recycled. The influence of the RTIL structure on the extraction mechanism has been highlighted in the case of Sr^{II}[18] and, in other cases, the extraction mechanism and extracted complex have been found to be identical in RTILs and classical solvents.[22]

Supercritical carbon dioxide is highly soluble in RTILs. Since Blanchard et al. carried out the first experiment involving both phases,[23] numerous investigations have been carried out on the thermodynamics and physicochemical properties (solubilization, polarity, solvent strength, nature of interactions) of biphasic systems composed of ionic liquids and supercritical carbon dioxide.[7,23–29] It has been shown that the RTIL anion dominates the interactions with CO_2 molecules and then influences the Sc-CO_2 solubility. By contrast to what is observed in water/Sc-CO_2 systems, due to the RTILs very low volume expansion and undetectable vapor pressure, a biphasic Sc-CO_2/RTIL system is observed up to 3100 bar of pressurized carbon dioxide.[30] The RTIL phase can be described as a strongly organized liquid, with CO_2 molecules circulating and penetrating into free interstices (also called free volume) formed by the cation–anion spatial arrangement.

A combination of RTILs and Sc-CO_2 extraction techniques could lead to new green processes in nuclear waste management. One can envision a “three-step” system (water/RTIL/Sc-CO_2) as a potential extraction medium for metals chelated with CO_2-philic extracting agents. We have thus undertaken a study of RTILs and Sc-CO_2 in view of their utilization in conjunction with the field of nuclear fuel reprocessing and this paper reports our first experiments in this area. By contrast to the work of Scurto et al.,[31] in which CO_2 is used to separate RTILs from water, in the present work, supercritical CO_2 is used to strip metal ions, the extraction from the water phase being performed through the water/RTIL system.

The ability of a water/RTIL/Sc-CO_2 system to significantly extract lanthanides is demonstrated in this paper. To this end, we first investigated some RTIL/Sc-CO_2 systems, evidencing the lanthanide complexes formed in RTILs and, secondly, we tested one water/RTIL/Sc-CO_2 three-step system. We have demonstrated that quantitative extraction of metals from ionic liquids (90–99 %) can be achieved by Sc-CO_2. Similar efficiencies were obtained for the water/RTIL/Sc-CO_2 systems investigated.

In our opinion, it is not the aim of this paper to present a three-step system already optimized in terms of extraction efficiencies and mechanism. We intend to demonstrate that such three-step systems do work and are a viable way to extract metallic species. Further work is needed to improve the characteristics of the system and to understand, on fundamental grounds, the mechanisms at work. To best demonstrate the potential of such systems, we limited ourselves to a series of very specific compounds, as explained below, and to classical-operation characteristics for the Sc-CO_2 part.

One imidazolium-based (1-butyl-3-methylimidazolium (BMIM)) ionic liquid, with bis(trifluoromethylsulfonyl)imide ($Tf_2N^- = (CF_3SO_2)_2N^-$) counteranions (Figure 1a), was chosen for this study because it is among the most commonly examined so far and because, owing to its counteranion, its complexing abilities are very weak.[32,33] The Tf_2N^- anion has characteristics that favor the solubilization of CO_2 molecules.[34]

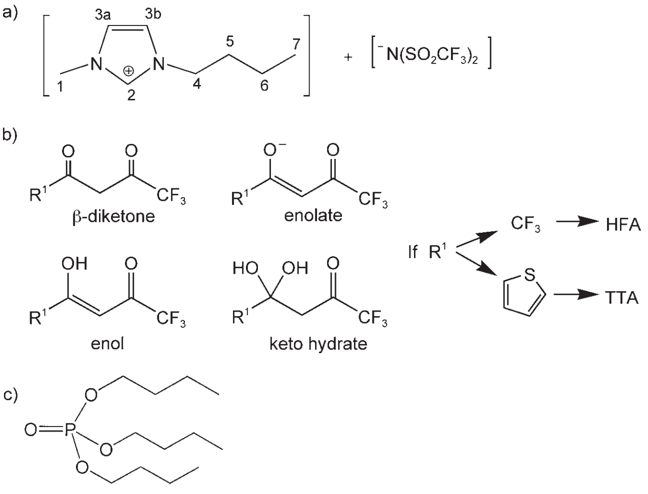

Figure 1. a) Chemical structure of the RTIL used in this study. b) Chemical forms of HFA and TTA in solution. c) Molecular structure of TBP.

In order to insure high extraction efficiencies, the extracting moieties and the synergist compound to be used should be very soluble in both Sc-CO_2 and in the chosen RTIL. The large amount of work on Sc-CO_2 that has already been performed by Wai and collaborators has guided us towards fluorinated β-diketones.[3,9,10] In this class of compounds, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) is also known to be soluble in $BMIMTf_2N$, in which it displays extracting properties towards Eu^{III}.[20] Hexafluoroacetylacetone (HFA) was also examined, because its solubility in Sc-CO_2 compares favourably with that of TTA (for molecular structures, see Figure 1b).

Among the stabilizing organophosphorus Lewis bases used to enhance the extraction process in water/Sc-CO_2 systems, tri(*n*-butyl)phosphate (TBP, see Figure 1c) has the strongest synergistic effect and CO_2-philic behavior for metal chelates.[35]

Interestingly, it is known that TBP dissolves well in RTILs and allows for UO_2^{2+} extraction.[36] TBP was thus chosen in our study. Finally, in view of demonstrating interest in the nuclear fuel cycle, we focused on Eu^{III} and La^{III}, as these lanthanides are known for their analogy with the actinides Am^{III} and Cm^{III} that are major long-lived, highly radioactive elements of high-level wastes.

Experimental Section

Elemental analysis: In order to accurately determine the elemental concentration of metals or chloride in our samples we used a nondestructive neutron activation analysis (NAA) method. To our knowledge, our group is the first to report the use of NAA for RTIL studies.[37] All samples were irradiated at the Nuclear Radiation Center at Washington State University (Pullman, WA) in a 1 MW General Atomics TRIGA nuclear reactor at a steady flux of 6×10^{12} neutrons$\,cm^{-2}s^{-1}$. After irradiation, the samples were cooled before being counted, until the total activity of the irradiated sample met security levels. Each sample was counted for a fixed time by using a large-volume Ortec Ge(Li) detector with a resolution of about 2.3 keV at the 1332.5 keV ^{60}Co peak. The following radioisotopes and their specific γ energies were used for the identification and quantification of metals: ^{152m}Eu ($t_{1/2}=9.3$ h; 121.8 keV), ^{140}La ($t_{1/2}=40.2$ h; 487 keV). For Ln and Eu, calibration of the signal was obtained by measuring reference RTIL solutions of known concentrations (107 and 98 ppm for Eu and La, respectively), which were irradiated and counted with the samples under identical conditions. For quantitative chlorine determination, a standard solution (ultra pure water, SRM 1549, NIST) containing 22 ppm of Cl was used. The amount of chlorine was calculated from the counted activity of the radioisotope ^{38}Cl ($t_{1/2}=37.2$ min; 1642 keV).

Spectroscopic analysis: Absorption spectra in the range 190–800 nm were recorded with a PSI spectrophotometer with 1 cm quartz cuvettes allowing 95% transmittance. Emission and excitation spectra were recorded with a standard spectrofluorimeter (Photon Technology International). In Table 3 (see below), emission data for europium are also presented as $R=I_{613}/I_{591}$, the ratio of the intensity of the $^5D_0$–$^7F_2$ transition (around 613 nm) with that of the $^5D_0$–$^7F_1$ transition (around 591 nm) for an excitation at $\lambda_{exc}=394$ nm. Background subtraction was performed prior to the calculation of R.

$BMIMTf_2N$: $BMIMTf_2N$ synthesis was based on a method by Moutiers and Billard,[38] however, an optimization of the washing step was performed. Before the anion-exchange step, the ionic liquid BMIMCl is usually washed with ethyl acetate. By adding dichloromethane to ethyl acetate (30% vol), the halide content was significantly decreased. Our homemade batch was almost colorless before starting the purification procedure.

Purification and characterization: The synthesized RTIL was purified according to published procedures.[39] The NAA analysis only showed chloride impurities (see Table 1) and FTIR spectra did not show organic impurities. Even after purification, our homemade ionic liquid still contained halides. After synthesis and purification, the RTIL was stored in a screw-capped flask on the bench at room temperature.

Table 1. Chloride and water contents as determined by NAA and Karl-Fischer titration, respectively.

$BMIMTf_2N$ ionic liquid	Chloride content	Water content	
basic synthesis	12 ppm	8 100 ppm	0.65 M
water-saturated	12 ppm	11 600 ppm	0.91 M

A structural characterization of $BMIMTf_2N$ was performed by using ^{1}H and ^{19}F NMR spectroscopy. The major findings are given in Table 2 and are in agreement with the expected structure. A singlet located at 2.47 ppm (not displayed in Table 2) is due to water molecules incorporated in the structure of the liquid by hydrogen bonds to the anion.[40,41]

Water titration: The water content of the samples was determined by Karl Fischer titration, using standard procedures (Mettler DL32 titrator, hydranal composite 5, Fluka, and analytical grade methanol) and is displayed in Table 1. For the three-step extraction system, the ionic liquid is equilibrated with an aqueous phase (see below). Therefore, we did not dry the ionic liquid batches before carrying out the experiments. The water saturation value obtained for our batch compares reasonably well with other values published in the literature.[42,43]

Table 2. ^{1}H and ^{19}F NMR chemical shifts using D_2O as solvent. The numbered protons refer to the chemical scheme of $BMIMTf_2N$.

^{1}H NMR chemical shift [ppm]			
H1: 3.75 (s)	H3a: 7.30 (s)	H4: 4.02 (t)	H6: 1.19 (m)
H2: 8.43 (s)	H3b: 7.25 (s)	H5: 1.70 (m)	H7: 0.75 (t)
^{19}F NMR chemical shift [ppm]			
F: −80.3 (s)			

Other chemicals: Europium(III) trifluoromethanesulfonate (98%, Aldrich, $Eu(Tf)_3$) and lanthanum(III) trifluoromethanesulfonate (≥97%, Aldrich, $Ln(Tf)_3$) were used without further purification and were directly dissolved in $BMIMTf_2N$ by using an ultrasonic bath to accelerate the salt's solubilization. 2-Thenoyltrifluoroacetone (99%, Aldrich, TTA), hexafluoroacetylacetone (98%, Aldrich, HFA) and tri(*n*-butyl)phosphate (≥97%, Merck, TBP) were used as received. Ln concentrations were equal to 10^{-3} M (NAA) or 5×10^{-3} M (emission and excitation spectra). The ratio of metal/complexing moieties/TBP stoichiometries was 1:3:3.

All the solutions were stored under an air atmosphere in screwed glass vials on the bench at room temperature (25°C), but the samples containing TTA were stored in the dark to avoid photodecomposition.

Supercritical CO_2 extraction protocol

RTIL/Sc-CO_2 (two-step system): All experiments were performed with a lab-built supercritical-fluid extraction apparatus. The apparatus includes the following devices: a liquid-CO_2 tank, a high-pressure syringe pump, an extraction cell, and a collection vial. SFC-grade CO_2 was supplied with a syringe pump (ISCO, model 260 D, Lincoln, NB). A schematic diagram of the overall experimental apparatus is shown in Figure 2a. All the extraction experiments were performed with a stainless-steel high-pressure extraction vessel (13 mL) maintained at 50°C by placing it on a heater plate. The temperature inside the high-pressure cell is controlled by adjusting a thermocouple. The stainless-steel thermocouple probe (K type) penetrates into the cell wall. All extractions were performed on 1.5 mL aliquot solutions in a 3 mL beaker placed in the high-pressure vessel under stirring (see Figure 2b). When the extraction cell was set to 50°C, CO_2 was pressurized to 150 atm. The extraction process was allowed to occur under static supercritical fluid extraction for 10 min. After that time, the exit valve was opened and the CO_2 was flushed under dynamic conditions (flow rate equal to 0.5 mL$\,min^{-1}$ controlled at the Isco pump) for 50 min. When the extraction was complete, the system was allowed to slowly depressurize for about 2 h. The RTIL sample was then removed from the cell and analyzed by using NAA. The extraction efficiencies were calculated on the basis of the amount of the lanthanide measured in the solution samples before and after the extraction.

Water/RTIL/Sc-CO_2 (three-step system): HFA and TBP were dissolved in $BMIMTf_2N$ ($c=3\times10^{-3}$ M for both moieties). This RTIL solution (6 mL) was equilibrated with a HNO_3 aqueous phase (HNO_3: Aldrich, 0.1 M, 6 mL; ultra-pure water, pH 1) by vigorous stirring for 30 min. Then, an aliquot of this RTIL phase (3 mL) was put in contact with a fresh Eu^{III}/HNO_3/water phase ($c_{Eu}=10^{-3}$ M, $HNO_3=0.1$ M, 3 mL) under vigorous mechanical shaking for 5 min. The sample was decanted for 20 min and then centrifuged for 20 min (2500 rpm). This sequence (shaking, decantation, and centrifugation) was repeated once prior to phase separation. The aqueous phase was then measured by using NAA for residual Eu determination, while the RTIL phase was divided in two: one aliquot (0.5 mL) for NAA measurement, one (1.5 mL) for Sc-CO_2 extraction. The Sc-CO_2 extraction procedure was identical to that described above.

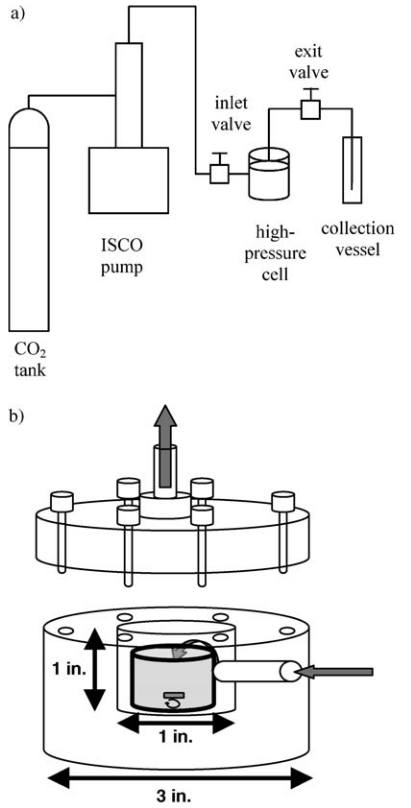

Figure 2. a) Schematic diagram of the experimental system used for the Sc-CO$_2$ extraction from BMIMTf$_2$N. b) Detailed diagram of the high-pressure cell.

Results

Two-step system—BMIMTf$_2$N/Sc-CO$_2$

Formation of Eu^{III} and La^{III} chelates in BMIMTf$_2$N: Figure 3 presents the emission spectra of Eu/TTA and Eu/TTA/TBP in BMIMTf$_2$N. Table 3 displays the position of the $^7F_2$ line and the value of the ratio of the $^5D_0 \rightarrow ^7F_2$ to the $^5D_0 \rightarrow ^7F_1$ line.

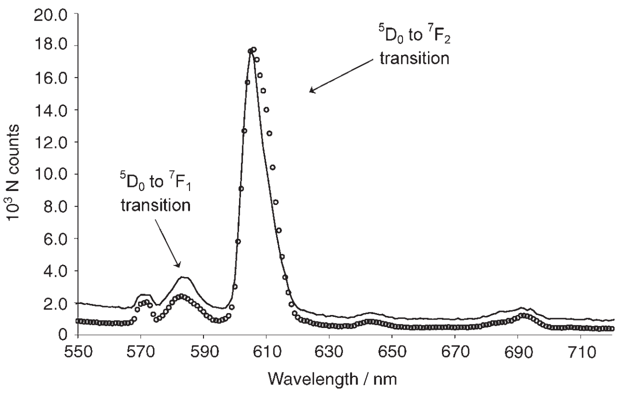

Figure 3. Emission spectra of Eu^{III}+TTA in BMIMTf$_2$N with (○) and without (——) TBP.

Table 3. Spectroscopic parameters of metallic solutions in BMIMTf$_2$N.

Chelating agent	Composition of the solutions in IL	Environment-sensitive transition wavelength ($^5D_0 \rightarrow ^7F_2$)	$\frac{I_{^5D_0 \rightarrow ^7F_2}}{I_{^5D_0 \rightarrow ^7F_1}}$[a]
none	Eu(Tf)$_3$	613 nm	0.5
HFA	Eu(Tf)$_3$+3 HFA, x H$_2$O[b]	612 nm	4.8
	Eu(Tf)$_3$+3 HFA+3 TBP	608 nm	8.2
TTA	Eu(Tf)$_3$+3 TTA, x H$_2$O[b]	605 nm	7.9
	Eu(Tf)$_3$+3 TTA+3 TBP	605 nm	9.7

[a] Ratio of absolute intensities. [b] $2 < x < 3$.

The emission spectrum of the Eu(Tf)$_3$ salt (not shown) reveals several peaks ascribable to 4f–4f transitions at $\lambda = 575$, 589, 613, and 700 nm and is in very good agreement with previously published data for the same system.[39] The small value (0.5) for the ratio R corresponds to hydrated europium dissolved in the IL, maybe in water clusters as emphasized in our previous work. Upon addition of three equivalents of HFA or TTA, the emission spectrum is strongly modified, providing evidence of a complexation process, which can also be followed through the changes in R (Table 3).

The ratio reaches a value between four and ten depending on the nature of the β-diketone. The consecutive addition of TBP further modifies the emission spectra (see Figure 4; 4 nm shift for TBP+HFA relative to HFA alone, broadening of the 605 nm peak for TBP+TTA relative to TTA alone) and R ratio, from 7.9–4.8 to 9.7–8.2 for TTA and HFA, respectively.

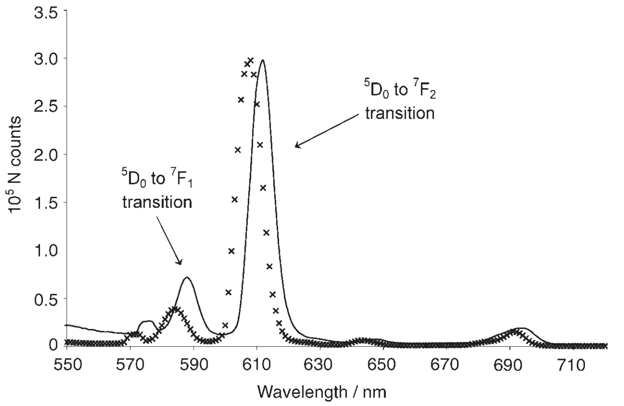

Figure 4. Emission spectra of Eu^{III}+HFA in BMIMTf$_2$N with (×) and without (——) TBP.

This is an indication of a second complexation process. Even if the metal ion/water molecule ratio is about 1:130, it is therefore reasonable to assume that TTA, HFA, and TBP are able to expel H$_2$O molecules from the lanthanide solvation sphere. The europium complexation with HFA or TTA, with or without TBP, is well known in Sc-CO$_2$ and RTILs.[3,9,20] Without a detailed study of the complex stoichiometry in BMIMTf$_2$N under our conditions and as RTILs have their own solvent properties (coordination, hydrophobicity, hygroscopy, viscosity), we cannot assume an exact stoichiometry for the complexes. Such a study is under progress and will be published separately. It can nevertheless be hypothesized that the CO_2-philic surface of the metal complex characterized by CF_3 groups and alkyl chains presents good properties to allow quantitative CO_2 extractions from the RTIL. For La, according to the well-known chemical similarities among the lanthanide series, we assume that complexation also takes place.

$BMIMTf_2N/Sc\text{-}CO_2$ extractions (two-step system): Eu^{III} and La^{III} extraction efficiencies with different β-diketones, with or without TBP, from $BMIMTf_2N$ by supercritical CO_2 are given in Table 4.

Table 4. Degree of extraction [%] of Eu^{III} and La^{III} from $BMIMTf_2N$ with different β-diketones (with or without TBP) by supercritical CO_2.

	Eu^{III}	La^{III}
HFA without TBP	90.5 ± 1	90.4 ± 1
HFA with TBP	99.9 ± 1	92.6 ± 1
TTA without TBP	–	87.1 ± 1
TTA with TBP	95.5 ± 1	90.5 ± 1

Quantitative extraction is achieved in all cases: La and Eu are extracted with at least 87 % efficiency. Even by considering the differences between the elements in the lanthanide group, whatever the system used, the selectivity of Eu versus La is not significant.

The extraction efficiencies of Eu and La are all in the range of 90.5–99.9 % when TBP is added. Overall, the most effective ligand appears to be HFA, which is capable of extracting more than 92 % of the two lanthanides, in conjunction with TBP. The mixed ligands show a preference for extracting the heavy lanthanide over the light one, but the difference is small compared with that observed for the individual fluorinated β-diketones. It is worth noting that the fluorine substitution in β-diketone plays a role in the synergistic extraction of lanthanides. For example, TTA with one CF_3 substitution shows a smaller synergistic effect with TBP for the lanthanides ($Eu^{III}/La^{III} = 95.5:90.5$) than HFA, which contains two CF_3 substitution groups ($Eu^{III}/La^{III} = 99.9:92.6$). Because of their electron-withdrawing fluorine substituents (CF_3), TTA and HFA show high miscibility with CO_2. As their extraction potential increases from TTA to HFA, it is confirmed that the more fluorinated groups the molecule has (one for TTA and two for HFA), the more acidic the molecule is, and then the solubility of the complex in CO_2 is enhanced. Moreover, HFA is only present as the enolate chemical form in Sc-CO_2, whereas TTA exists in two forms.

The impact of adding TBP has to be examined carefully. TBP is currently used as a synergist in liquid/liquid extraction processes involving an aqueous phase to enhance partitioning coefficients towards traditional nonpolar organic phases in the reprocessing nuclear field. TBP has an effect on the stability of the metal β-diketonate complex in Sc-CO_2[11] by modifying its polarity, therefore enhancing the extraction efficiencies. For example, it was reported that La^{3+} and Eu^{3+} (at 3×10^{-4} M) in 6 M HNO_3 could be extracted by TTA in TBP-modified Sc-CO_2. In 10 % TBP-modified Sc-CO_2 at 60 °C and 350 atm, La^{3+} and Eu^{3+} were extracted by 1 and 30 %, respectively, whereas in a 30 % TBP-modified system, the extraction efficiencies were increased to 61 and 92 %, respectively.[44] In our study, however, large extraction efficiencies are obtained already without TBP. Therefore, the relatively low impact of TBP on the extraction efficiencies cannot be ascribed to a poor synergetic effect of TBP but rather to an already well-functioning system. The effect of TBP is thus minimized in our case.

Extraction from the aqueous phase followed by supercritical extraction (three-step system): The NAA results show that for the water/RTIL step, (98 ± 1) % of the europium is extracted to the RTIL phase. The mechanism of such an extraction is not known at the moment and is outside the scope of this paper. Nevertheless, it can be hypothesized that an ionic exchange occurs between water and the RTIL as has been demonstrated in other water/RTIL systems.[18,20,45] We suggest that HFA is in an enol form in $BMIMTf_2N$. Upon addition of Eu^{III} in water, an ionic exchange–complexation process occurs at the interface so that the HFA proton is left in the water and the enolate-complexed europium is transferred to $BMIMTf_2N$. The exact charge balance cannot be inferred from this work.

An extraction efficiency of (100 ± 1) % for Eu from the RTIL to Sc-CO_2 was then obtained, so that the overall extraction efficiency from water to Sc-CO_2 reached 98 %. It is worth noting that the extraction efficiency is even larger when the RTIL phase is fully equilibrated with water (the RTIL is not water-saturated in the two-step system experiments). It implies that the complex is further expelled from the RTIL as the amount of water is increased, owing to its apolar properties.

Discussion

In this section, we compare the three-step system water/RTIL/Sc-CO_2 with the water/RTIL and water/Sc-CO_2 systems to emphasize the advantages and disadvantages of all procedures, so as to highlight trends for possible improvements.

First, it is important to note that in our experiments, the β-diketone ligands were dissolved in the RTIL, not in the water or Sc-CO_2 phases. As compared to usual water/Sc-CO_2 systems, our experiment demonstrates that TBP (as a synergist) is not needed to get high extraction efficiencies. At this stage of our work it can be expected that by varying the β-diketone, extraction as high as 99 % could be obtained, even though TBP is not used. Moreover, quantitative extraction is obtained in our case without modified Sc-CO_2, which is commonly used to enhance the extraction coefficient in Sc-CO_2 systems. TBP-modified Sc-CO_2 systems for extraction of trivalent lanthanides from nitric acid solutions and methanol-modified Sc-CO_2 for extraction of lanthanides from solid samples are known examples reported in the literature.[2] In our case, neat Sc-CO_2 is good enough and this has to be ascribed to the use of the intermediate phase, namely, $BMIMTf_2N$, in which HFA is dissolved. The solubility of Sc-CO_2 in $BMIMTf_2N$ under the temperature and pressure conditions of our work (50 °C, 150 atm) can be extrapolated from the data obtained by Aki et al.[29] and should be in the range of 0.74 (mole fraction). This value is roughly the maximum CO_2 solubility observed in dry $BMIMTf_2N$ and these authors have shown that water has very little influence on this parameter. It is thus possible that the high solubility of Sc-CO_2 in $BMIMTf_2N$ and the very low vapor pressure of the ionic liquid allows for large extraction efficiencies of the lanthanides with no use of modifiers.

Furthermore, the total amount of Ln that is extracted in our case is in the order of 10^{-3} M compared with the usual 10^{-4} M range obtained in water/Sc-CO_2 experiments. Another important point is the pressure required for the extraction process. In our case, extraction is completed within 10 (static) + 50 (dynamic) minutes of Sc-CO_2 contact under 150 atm, while 350 atm of pressure are usually required for the best extraction efficiencies reported so far (350 atm and 60 °C, Eu from acidic solutions with TTA and 30 % TBP).[44] Thus, although our system may appear to be rather complex, because of the three-step procedure it seems to compete favourably with water/Sc-CO_2 systems already known, as far as pressure, extracted amount, and efficiencies are concerned.

The comparison with water/RTIL systems must also be conducted with caution. In the work carried out by Jensen et al.,[20] an anion-exchange mechanism is described in which a large excess of TTA relative to the Eu^{III} concentration is introduced in $BMIMTf_2N$. The high complexing ability of this fluorinated β-diketone has been highlighted by the formation of the $[Eu(TTA)_4]^-$ complex. In our case, however, such a complex may not form as the maximum ratio of Eu/TTA is 1:3, therefore we can reasonably assume that this limits the stoichiometry of the complex under our experimental conditions. Our experiments do not allow us to examine the possible Ln extraction mechanisms from water into the RTIL phase in detail. Therefore, the question of the possible loss of some of the ionic liquid components (either the cation or the anion) into the aqueous phase is still pending in our case. As already stressed in the introduction, the system presented here is not optimized and this would require an extension to this feasibility study.

From the above discussion, it cannot be concluded, however, that the Sc-CO_2 phase is not needed and does not bring any advantages. As a matter of fact, the problem of back-extraction is not solved in any of the three systems under comparison. In our opinion, this point needs to be documented more with regard to water/RTIL and water/Sc-CO_2 systems and was not examined in our work either. This difficult question has to be addressed in order to increase the interest in any of these systems. In our case, depressurization of the Sc-CO_2 phase will allow recovery of the lanthanide in a solid or liquid form but it is probable that the lanthanide will still be complexed to the ligand, which thus could not be recovered for another extraction cycle. One possible solution would be to attain the metallic form of the element. At present, promising experiments demonstrating the deposition of metallic species onto silicon wafers from a Sc-CO_2 phase in which the metal is complexed with β-diketone are under progress.[46] Such a procedure, if confirmed for lanthanides, would be a key point for the future industrial use of a water/RTIL/Sc-CO_2 system.

Conclusion

For the first time, the feasibility of an extraction process, in which trivalent lanthanum and europium are extracted quantitatively (more than 90 %) using fluorinated β-diketones in a three-step system water/$BMIMTf_2N$/Sc-CO_2 is established. The lanthanides are extracted from the water phase towards an intermediate phase with the help of the extractants directly dissolved in the RTIL. Although the stoichiometries are not determined, this work presents some insights into the structure of the complexes formed in the RTIL phase. The last extracting step corresponds to the transfer of the complex to the Sc-CO_2 phase following a classical procedure which has also been successful for copper.[37]

Despite the absence of selectivity for Eu versus La, thanks to the RTIL properties, there is no need to add a synergist moiety (TBP) or a modifier (MeOH) to the Sc-CO_2 to reach high extraction efficiencies. Nevertheless, in the Sc-CO_2 phase the extracted metals are still in chelated forms. Several methods can be foreseen to strip the metals from the supercritical phase. Among them, in order to finalize the process and complete an extraction cycle with no waste, the chelating agents should be freed and reused. This can be envisioned by reduction–deposition of the metal form of the lanthanides, while the extractants are still loaded in the supercritical phase. A depressurization of the Sc-CO_2 phase would allow the ligands to be recycled, to be dissolved again in a fresh ionic-liquid phase for further extraction processes. The last point counter balances the fact that the β-diketones cannot be considered as perfectly "green" due to their fluorine content.

For long-term development of such a method, an improvement would be to simplify the current three-step system into a two-step system, thus avoiding water. Sonochemical dissolution of the species to be extracted might be a potential way to this new route of reprocessing.[47,48] In order to optimize either the three-step system of this study or the proposed two-step systems suggested above, a fundamental understanding of the extraction mechanisms at work is of paramount importance. Work is under progress to answer these questions.

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