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Ionogels as modular platform for metal extraction

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Abstract

In this study, we have explored a strategy to develop new ionogels as materials for metal extraction. The methodology applied here consists first in confining a commercial salt tetrahexylammonium bromide [THN][Br] in silica-based ionogels in order to determine their extracting properties. Anionic metathesis was then carried out *in-situ* on the [THN][Br] ionogels with sodium dicyanamide (NaDca) or lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to enhance their extracting efficiency or to bring selectivity to the extraction process. Treatment of [THN][Br] ionogels with those salts ensures a quasi-quantitative replacement of bromide ions by Dca⁻ and TFSI⁻. The replacement of bromide anions was confirmed by thermogravimetric analyses (TGA) and Infra-Red spectroscopy. Nitrogen adsorption-desorption isotherms measured before and after metathesis allow us to confirm that no major structural modification has been induced by the anionic exchange.

[THN][Br] ionogels were used for the extraction of Au(III), Pt(IV), Co(II) and Cr(VI). Au(III), Pt(IV) and Cr(VI) were fully extracted while the extraction of Co(II) did not exceed a few percent. Treatment of [THN][Br] ionogels with NaDca improved the extraction capabilities of the material with respect to Co(II) while treatment with LiTFSI allowed the separation of Au(III) from Pt(IV), with separation factors higher than 500. It also increased the separation of Au(III) from Cu(II) compared to the brominated ionogel. The extraction performances of each ionogel were compared to those of the pure similar ionic liquid. This work shows that, starting from the same ionogel, the extracting properties can be modulated as desired by simple anion exchange.

Keywords: ionic liquid, liquid-liquid extraction, ionogel, gold, platinum, cobalt

Introduction

The removal and recovery of 3d and noble metal ions from industrial wastewater is a major concern in most industries due to economic and environmental factors. Many treatment processes, such as chemical precipitation, electrodialysis, adsorption and liquid-liquid extraction are currently used. Among these methods, liquid-liquid extraction is one of the most efficient and economical methods and is widely applied in most hydrometallurgical processes [1-4]. The main disadvantage of liquid-liquid extraction is the extensive use of extractants and organic solvents (paraffin, toluene, etc.) as diluent. The loss of organic diluent through volatilization during the extraction process has a negative impact on the environment and can cause serious damage to human health. Therefore, greener extraction methods are being sought.

In recent years, ionic liquids (ILs) have attracted great interest in the field of metal extraction as alternative medium to molecular solvent in liquid-liquid extraction processes or as new extractants.[5,6] ILs are salts composed of asymmetric organic cations, liquid at room temperature.[5,6] Hydrophobic ILs form biphasic systems with aqueous effluents and constitute an extraction phase for metals. In the last decades, important works have highlighted the potential of room temperature hydrophobic ionic liquids (RTILs) for the separation of divalent metal ions [7-12] and the recovery of precious metals such as Pt(II), Pd(II) and Au(III) in liquid-liquid extraction processes . [4, 13-18] The modularity of ILs allows their design to be adapted to meet the needs of specific applications. Thus, several extraction strategies can be implemented, depending on the nature and coordinating properties of the metals to be extracted. For example, the extraction of 3d metals (Cu(II), Ni(II), Co(II)) requires the use of extractants dissolved in the IL phase or involves the use of coordinating ILs, also called task-specific ionic liquids (TSILs).[19] The extraction of noble metals (Au(III), Pt(IV), Pt(II)) is based on the ion-pairs formation between the noble metal halocomplexes (AuCl_4^- , PtCl_6^{2-} , PtCl_4^{2-}) and the IL's cation *via* an anion exchange mechanism.[15,17]

On the other hand, inorganic-organic hybrids offer very interesting potential applications in the field of metal extraction.[20-26] Due to their excellent thermal and mechanical stability, high specific surface area and the possibility of surface functionalization, silica gels have been widely used as inorganic solid matrices in inorganic-organic composite materials. The modification of the physical and chemical properties of the silica gel's surface by covalent grafting of various molecules functionalized with carboxylic, amine or amide groups has attracted much attention in the field of catalysis, separation and adsorption. The immobilization of active chemical groups leads to a substantial increase in the binding capacity of silica gels for a large panel of metal ions.[20-22,27] However, the development of

these materials requires post-synthesis grafting and the use of silylating agent such as (3-aminopropyl)triethoxysilane (APTES) or (3-iodopropyl)trimethoxysilane) which limits, to date, their large-scale applicability. In a previous work, we explored a new strategy to develop an adsorbent material consisting of confining a TSIL in a silica gel matrix.[28] These matrices allow ILs to retain their chemical activity. We have demonstrated that the confinement of the tetrahexylammonium dicyanamide [THN][Dca] in a silica-based ionogel is an interesting solution to improve the handling of IL. Indeed, the extraction properties and recyclability of the [THN][Dca] ionogel were found to be very close to those obtained with the neat IL, with an effective separation factor of Co(II) from Ni(II) in 4 mol.L⁻¹ NaCl. The recyclability and reusability of the material was also high, the material can be regenerated by simple metathesis with sodium dicyanamide and still functions as the original material (Boudesocque et al., 2020). The effectiveness of metathesis in recovering the extracting properties of the ionogel has led us to explore another strategy for the development of extractant materials. This strategy consists first in confining the low-cost commercial salt: tetrahexylammonium bromide [THN][Br] in a silica-based ionogel and then, in performing anionic metathesis directly on the ionogel, to exchange the bromide ions of the IL with other anions. Treatment with sodium dicyanamide (NaDca) is used to improve the extraction of 3d and noble metals compared to untreated [THN][Br] ionogel, while treatment with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) can improve the separation of Au(III) from Pt(IV) or Cu(II) (Boudesocque et al., 2019). This elegant strategy is also a way to avoid problems that may occurred during ionogels synthesis. Indeed, not all ILs can be confined in a silica matrix. For instance, ILs composed of carboxylate anions are known to be protonated during non-hydrolytic sol-gel synthesis while BF₄⁻ anions and, to a lesser extent, PF₆⁻ ones are known to hydrolyze in the presence of water leading to the release of some.[29]

In this study, the ionogels are characterized before and after bromide exchange by thermogravimetric analyses (TGA), Infra-Red (IR) spectroscopy and nitrogen adsorption-desorption isotherms after extraction of the IL. The comparison of their physical properties before and after the metathesis allow us to identify if any structural modifications have occurred during anionic exchanges. The extraction properties of [THN][Br] ionogels and of ionogels after anion exchange with NaDca and LiTFSI towards Co(II), Pt(IV), Au(III) and Cr(VI) are evaluated. The performance of the ionogels in terms of extraction capacity and selectivity are also compared to those of functionalized silica gels described in the literature and to those of neat ILs.

2. Experimental Section

2.1 Chemicals and reagents

All chemical and reagents used in this study were used as received without further purification. Sodium dicyanamide (99%) and bis(trifluoromethane)sulfonylimide lithium salts were obtained from Sigma-Aldrich (Diegem, Belgium). Tetrahexylammonium bromide [THN][Br] (98%), tetramethylorthosilicate (TMOS) and methyltrimethoxysilane (MTMS), were purchased from Acros Organics (Geel, Belgium). Copper and Cobalt nitrate metal salts have a purity of 99% or better and were purchased from Acros Organics (Geel, Belgium) or Sigma-Aldrich (Diegem, Belgium). $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.9%), K_2PtCl_6 (99.9%) Na_2PtCl_6 (98%) and $\text{K}_2\text{Cr}_2\text{O}_7$ (99%) were purchased from Aldrich. All chemicals and reagents used in this study were used as received, without further purification.

The stock aqueous solutions of metals were prepared by dissolving the corresponding salt of the respective metals in double distilled and deionized water.

2.2 Elaboration of organo-silica ionogel

In a Teflon vial, the IL [THN][Br] (362 mg, 0.83 mmol) was dissolved under stirring in 1 mL formic acid for 5 min before adding 0.5 mL of a TMOS/MTMS mixture (50/50 v/v). The synthesis was performed by using 3.44 mmol of silica precursor and using the following molar ratio: 0.5 TMOS/0.5 MTMS/0.25 IL/7.8 HCOOH. The resulting solution was stirred at room temperature for 5 min. Gelation occurred within 24 hours. The Teflon vial was kept closed for 48 h and then opened. The aging process was followed by the weight loss over time and complete aging was reached when no more weight variation was noticed (around 15 days were found to be necessary).

2.3. Ionogel modifications by anionic metathesis

The treatment of the ionogel with sodium dicyanamide is modelled on that developed for the synthesis of the ionic liquid [THN][Dca] *i.e.* by anionic metathesis of [THN][Br]. 626 mg of the ionogel [THN][Br] were added to 100 mL of aqueous solution containing 2 eq of NaDca (150 mg). The mixture was gently stirred for 72 hours. Every 24 hours, the supernatant was removed from the reaction medium and replaced by 100 mL of an aqueous solution containing 0.5 eq NaDca (37 mg). This protocol ensures a rate of anionic exchange between the bromide ion and the dicyanamide ion greater than 98%. Metathesis of the tetrahexylbromide ionogel with the lithium salt of bis(trifluoromethane)sulfonylimide was carried out using a similar protocol using 1.2 eq of LiTFSI for the first exchange followed by 0.2 eq LiTFSI. The efficiency of the anion exchange was evaluated by determining the concentration of bromide ions released in the aqueous phase after metathesis and by determining the concentration of THN⁺ cations released into aqueous solutions before and after metathesis. [THN][Dca] and [THN][TFSI] have a lower solubility than [THN][Br] and the anionic exchange of the bromide ion by TFSI⁻ or Dca⁻ should induce a decrease in the release of the organic cation into aqueous solution after metathesis. The concentration of the

organic cation after anionic exchange of bromide can easily be related to the content of bromide anion in the ionogel after metathesis.

IL Extraction (Washed Gels). The removal of IL was performed by means of a Soxhlet extractor with refluxing acetonitrile. The efficiency of the extraction was checked by IR spectroscopy. A 48-h extraction was shown to be generally needed.

2.4 Physical measurements

The metal analyses were performed by UV-Vis spectroscopy using a Carry-5000 Varian spectrophotometer and by ICP-OES, Thermo Fisher ICAP Series. The bromide analyses were performed by ion chromatography (Metrohm 883 basic IC plus).

Thermogravimetric analyses (TGA) were carried out on a TA Instrument SDT Q600 by using platinum crucibles under an air flow, with a heating rate of 5 °C/min up to 850°C.

The nitrogen adsorption-desorption isotherms at -196°C were measured using a Micromeritics ASAP2420 surface and porosity analyser on monolith pieces degassed under vacuum at 120°C for 12h. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method and total pore volumes measured at the relative pressure $p/p^0 = 0.98$. Firstly, microporous volumes were estimated using the t-plot method. However, according to Galarneau's work [30] this method seems unsuitable (underestimation) for the determination of the microporous volume of these type of micro/mesoporous materials. Therefore, the microporous volume was determined from the N₂ adsorbed volume (in cm³/g STP) at $p/p^0 = 0.001$ using the Gurvich rule.[31]

$$V_{\text{pore}} = n_{\text{N}_2} / \rho^{\text{liq}}_{\text{N}_2} \quad (1)$$

where V_{pore} is the pore volume in cm³.g⁻¹, n_{N_2} is the specific amount of nitrogen adsorbed (g of N₂ / g of material) that is equal to $[(\text{N}_2 \text{ adsorbed volume in cm}^3/\text{g STP}) / (\text{molar volume in cm}^3.\text{mol}^{-1})] * \text{molar weight of N}_2 \text{ in g.mol}^{-1}$,

and $\rho^{\text{liq}}_{\text{N}_2}$ is the density of the liquid nitrogen (0.808 g/ cm³ liq).

The mesopore size distribution was evaluated with the Barrett-Joyner-Halenda (BJH) method applied to the adsorption and desorption branches of the N₂ adsorption-desorption isotherm.

Infrared spectra were recorded with a 2 cm⁻¹ resolution on a Bruker Vertex70 FTIR spectrometer with the use of a Platinum ATR accessory equipped with a diamond crystal. The ¹H NMR spectra were obtained on a Bruker AVANCE 400 HD instrument. The concentrations of ionic liquid cations in the aqueous phase were determined using quantitative ¹H NMR spectroscopy following this method: 100 μL of an aqueous solution of DMSO previously prepared at 100 mM were introduced into a conical tube. Then, 200 μL of the sample to analyze which is obtained after saturation of the aqueous phase with the ionic liquid or the ionogel were added. The mixture is dissolved in 700 μL of deuterated water (D₂O). The ¹H NMR spectrum of the DMSO solution shows a single peak at $\delta = 2.68$ ppm that corresponds to six protons. The DMSO is an internal reference so, its signals resonate in an area which is not overlapping the different studied ionic liquids signals. From the concentration of DMSO, the concentration of the sample can be deduced after integration of the different signals. The uncertainty range for this method is 1%. [32]

2.5 Extraction experiments

The extraction experiments were determined by mixing 0.3 g of ionogel and 2 mL of aqueous phase containing a metal salt. The mixture was stirred for 12 h to reach equilibrium. The ionogel was separated from the aqueous phase by decantation for analysis. The composition of the aqueous phase was analyzed by ICP-OES or UV-vis spectrophotometry. The metal ion concentration in the ionogel was deduced from the difference between the metal ion concentration in the aqueous phase before and after extraction. The efficiency of the

extraction process was evaluated by calculating the percentage extraction (%E) using the following equation (2):

$$E = 100 * \frac{(C_{in} - C_{fin})}{C_{in}} \quad (2)$$

C_{in} and C_{fin} (mol.L⁻¹) are the concentration of the aqueous metal solution before and after metal extraction, respectively. The percentages of metal extraction (%E) were determined at 25°C. The initial concentration of the Co(II) solutions was set to 1.5×10⁻² mol.L⁻¹ while the concentration of Au(III) and Pt(IV) solutions are 2×10⁻³ mol.L⁻¹. This ensures to be under the same conditions as those used with pure IL phases in order to facilitate the comparison of the performances between the confined and neat ILs. The experiments were performed in duplicate to ensure reproducibility of the assay, and the mean values of the extraction yields were considered for each system studied. The duplicate experimental results agree to within 5%. All experiments were performed with ground ionogels. The ionogel was ground in a ceramic mortar for a few minutes until a homogeneous powder was obtained. Extraction experiments using pure IL phases are performed under the same conditions as those described in our previous articles.[28]

3. Results and discussion

3.1 Synthesis and characterization of ionogels

In our previous work [28], we have shown that after metal extraction, [THN][Dca] ionogels can be easily regenerated by simply contacting them with a NaDca solution for a few hours. This operation restores the extracting properties of the ionogel even after several extraction-stripping cycles. The principle is based on the reversible anionic exchange between the dicyanamide anion and the anions (Cl⁻, NO₃⁻) coextracted with the metal cations during the

different extraction cycles and which progressively decreases the coordinating anion content of the material affecting its extraction properties. This is the reason why, in this work, we have developed ionogels starting from the commercial salt, tetrahexylammonium bromide [THN][Br] to avoid anionic metathesis. Moreover, the confinement, associated with the very low solubility of the organic cation salt, limits the loss of the IL from the ionogel. These ionogels were obtained by sol-gel reaction in the presence of [THN][Br] using a mixture of TMOS/MTMS as silica precursor to render the silica surface hydrophobic and to prevent IL leaching into the aqueous phase.[33] Different sol-gel methods have been used to prepare silica-based ionogels *i.e* the formic acid solvolysis and the hydrolytic method. [29]. It has been evidenced that, for IL with the short alkyl chain 1-butyl-3-methylimidazolium (BMIM^+) component, both methods can be used to prepare ionogels when the anions are halogenated ones. Our attempts to use the hydrolytic method to prepare ionogels with [THN][Br] failed. This result shows that, not only the nature of the counter-anion matters, but also, the bulkiness of the cation. Using the formic acid solvolysis methods, crack-free monolithic ionogels were obtained within 1 day. In this method, formic acid acts both as reactant and solvent. The molar ratio IL/Si was set at 0.25 for the whole study. To enhance the extracting properties of the ionogel we then performed anionic exchange on the [THN][Br] ionogel with (i) NaDca in order to introduce a coordinating Dca^- anion which has a higher affinity for 3d metals than the bromide anion and (ii) with LiTFSI to bring more selectivity thanks to the TFSI $^-$ anion.

Anionic metathesis was carried out on the [THN][Br] ionogel following the protocol described in the experimental section. The efficiency of anionic metathesis was evaluated by several methods. First, we determined the total concentration of bromide ions in aqueous solutions in contact with the ionogel and found that, in all cases, the exchange rates were higher than 90%. However, the handling conditions (loss of solutions caused by the different

manipulations) do not allow us to have a more precise estimation of the exchange rate and the proportion of residual [THN][Br].

We therefore determined the concentration of organic cations released into the aqueous solution after the anion exchange with TFSI (or Dca). Assuming that the aqueous solution is electrically neutral, the concentration of bromide anions should be, at most, equal to the concentration of organic cations. The concentration of TFSI(Dca) in the solution can be neglected because of the lower solubility of the two ILs [THN][TFSI(Dca)] compared to [THN][Br]. Since the concentration of the organic cation is lower than the solubility of [THN][Br] (Table 1), this means that the concentration of bromide ions in aqueous solution is due to the dissociation of [THN][Br] remaining in the ionogel after anionic metathesis. Considering the equality between the concentration of organic cations and bromide ions, the content of [THN][Br] remaining in the ionogel after metathesis can be determined by the following equation:

$$\% \text{Br (in ionogel)} = [\text{Br}^-] * V_{\text{aq}} * 100 * 434 / m_{\text{LI(ionogel)}} \quad (3)$$

N.B.: 434 is the molar mas of [THN][Br] (g.mol⁻¹)

Table 1: Concentration of the organic cation in the aqueous phase determined by quantitative ¹H NMR and estimation of the residual Br⁻ content after anionic metathesis V_{aq} = 2 mL; m_{IL}= 0.150 g (m_{ionogel} = 0.3 g).

Neat ionic liquid	S (mol.L ⁻¹)	Ionogel	[THN ⁺]aq mol.L ⁻¹	% Br ⁻ in ionogel
[THN][Br]	1.94×10 ⁻²	-	-	-
[THN][Dca]	9.16×10 ⁻⁴	[THN][Dca] in confined phase	1.54× ⁻³	0.9
[THN][TFSI]	8.75×10 ⁻⁴	[THN][TFSI] in confined phase	1.85× ⁻³	1.1

The concentration of the organic cation remains higher than the solubility of the pure ionic liquid, which means that the Dca (TFSI) exchange is not complete. The residual Br⁻ content is estimated (Table 1) to be less than 1%, indicating that anionic metathesis is efficient. Moreover, anionic metathesis strongly reduces the release of the organic cation in aqueous solution, at least by a factor of 8 (the solubility of [THN][Br] is 1.94×10⁻² mol.L⁻¹). By this way, it also improves the recyclability of the ionogel by decreasing the loss of IL during the extraction experiments. To our knowledge, this is the first time that anionic exchange is performed *in-situ* in silica-based ionogels.

The thermal properties of the confined ILs were determined by TGA (Figure 1). The three ionogels present different thermal behavior with the less thermally stable being the [THN][Br] one with a thermal decomposition starting at 160°C. After extraction, no step loss could be observed at this temperature for the [THN][Dca] and [THN][TFSI] ionogels confirming the efficiency of the anion exchange. The ILs contents, determined by TGA, are also different. This difference is explained by the different molecular weights of the anions. Based on this, we calculated the theoretical ILs contents after anion exchange according to equation 4:

$$\text{Theoretical ILs content} = \frac{100}{1 + \frac{m_{SiO_2} * M(THNBr)}{m_{THNBr} * M(THNX)}} \quad (4)$$

with m_{SiO_2} and m_{THNBr} are the mass of silica and [THN][Br] measured on the TGA of [THN][Br] ionogel (here $m_{\text{SiO}_2} = 37.41\text{g}$; $m_{\text{THNBr}} = 62.59\text{ g}$), $M(\text{THNBr}) = 434.58\text{ g mol}^{-1}$; $M(\text{THNX}) = 420.72\text{ g.mol}^{-1}$ (X = Dca) 634.82 g.mol^{-1} (X= TFSI)

The theoretical values of the IL contents are 61.8 and 70.9% for [THN][Dca] ionogel and [THN][TFSI] ionogel respectively. These values match very well with the experimental values of 60.2 and 69%.

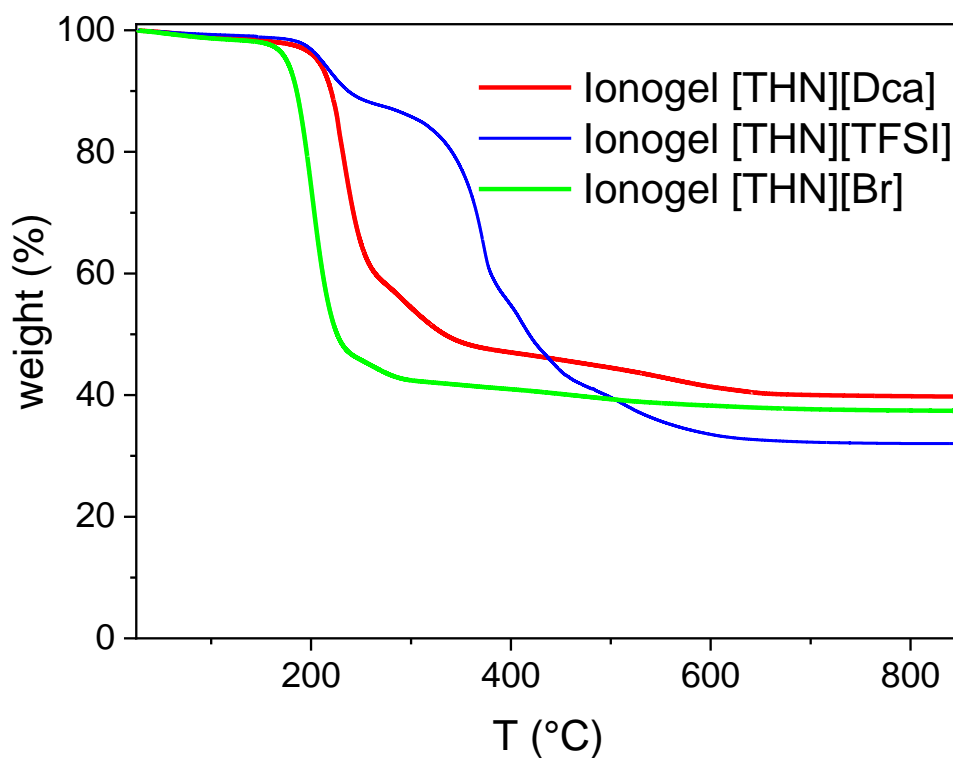


Figure 1. TGA curves of the ionogels [THN][Br], [THN][Br] treated NaDca, [THN][Br] treated LiTFSI

Infrared spectroscopy was also used to confirm the anionic exchange. Figure 2 compares the IR spectra of ionogel [THN][Br], ionogel [THN][Br] treated LiTFSI and ionogel [THN][Br] treated NaDca. The spectrum of the ionogel [THN][Br] treated LiTFSI presents new characteristic bands of TFSI at 1350 and 1132 cm^{-1} (ν_{as} and ν_{s} SO_2), 1180 cm^{-1} (ν_{as} CF_3), 615 cm^{-1} (δ_{a} SO_2) [34] while the spectrum of the ionogel [THN][Br] treated NaDca presents two peaks at 2128 and 2225 cm^{-1} that correspond to the antisymmetric and symmetric $\text{C}\equiv\text{N}$ stretch of the dicyanamide anion.[35]

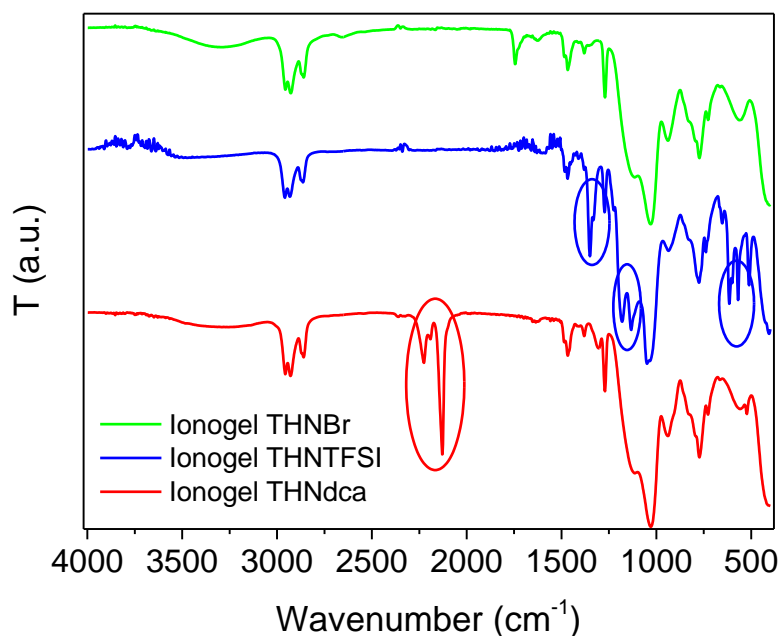


Figure 2. FT-IR spectra of ionogels [THN][Br], [THN][Br] treated NaDca, [THN][Br] treated LiTFSI

The ILs were then removed from the ionogels by means of Soxhlet extraction using acetonitrile for two days. The efficiency of the extraction was checked by IR spectroscopy (see Figures S1-S3 ESI). After extraction of these ILs, all washed gels presented a combination of types Ib, II and IVa isotherms characteristic of microporous and mesoporous materials as well as a type H2a hysteresis loop (Figure 3A), according to the IUPAC classification.[36] Textural properties such as total pore volume, specific surface area and

average mesopore diameter of the ionogels are summarized in Table 2. As seen in Figure 3B and Table 2 mesopore diameters determined by the BJH method on the desorption branches fall in the range 3.4-4.1 nm which correspond to relative pressure (P/P_0) values of 0.41-0.48. The sudden drop observed in the volume adsorbed along the desorption branch at these pressure range might be due to the Tensile Strength Effect (TSE) that often generates a tall and sharp peak in the pore size distribution (PSD) (Figure 3B).[37] This artefact may be misinterpreted as evidence to the presence of mesopores whose pore size is very narrow. In this case, the BJH method is not suitable when applied on the desorption branch. Therefore, the BJH model was applied on the adsorption branch of our isotherms where the TSE phenomenon is absent. In this case, the pore size distribution (Figure 3C) evidences a much broader peak with an increase of the mean pore size from 3.0 nm for the ionogel [THN][Br] to 4.2 nm for the ionogel [THN][Dca] and 4.7 nm for the ionogel [THN][TFSI]. An increase of pore size is thus observed with the increase of the anion's size. Differences are also noticed concerning the specific surface areas and total pore volumes. When the size of the anion increased ($\text{Br}^- < \text{dca}^- < \text{TFSI}^-$), the total pore volume and specific surface area increased from 0.90 to 1.15 $\text{cm}^3.\text{g}^{-1}$ and from 1126 to 1223 $\text{m}^2.\text{g}^{-1}$, respectively. The increase of total pore volume is also concomitant with an increase of the IL mass loading from 61.8% ([THN][Br]) to 70.9% ([THN][TFSI]). Moreover, the microporous volumes determined at $P/P_0 = 0.001$ are the same (0.13 $\text{cm}^3.\text{g}^{-1}$) whatever the ionogels.

Note also that the IR spectrum, TGA curve and N_2 -adsorption-desorption isotherms of the ionogel [THN][Dca] obtained after metathesis compared well with those obtained when [THN][dca] was directly confined in the silica matrix.[28]

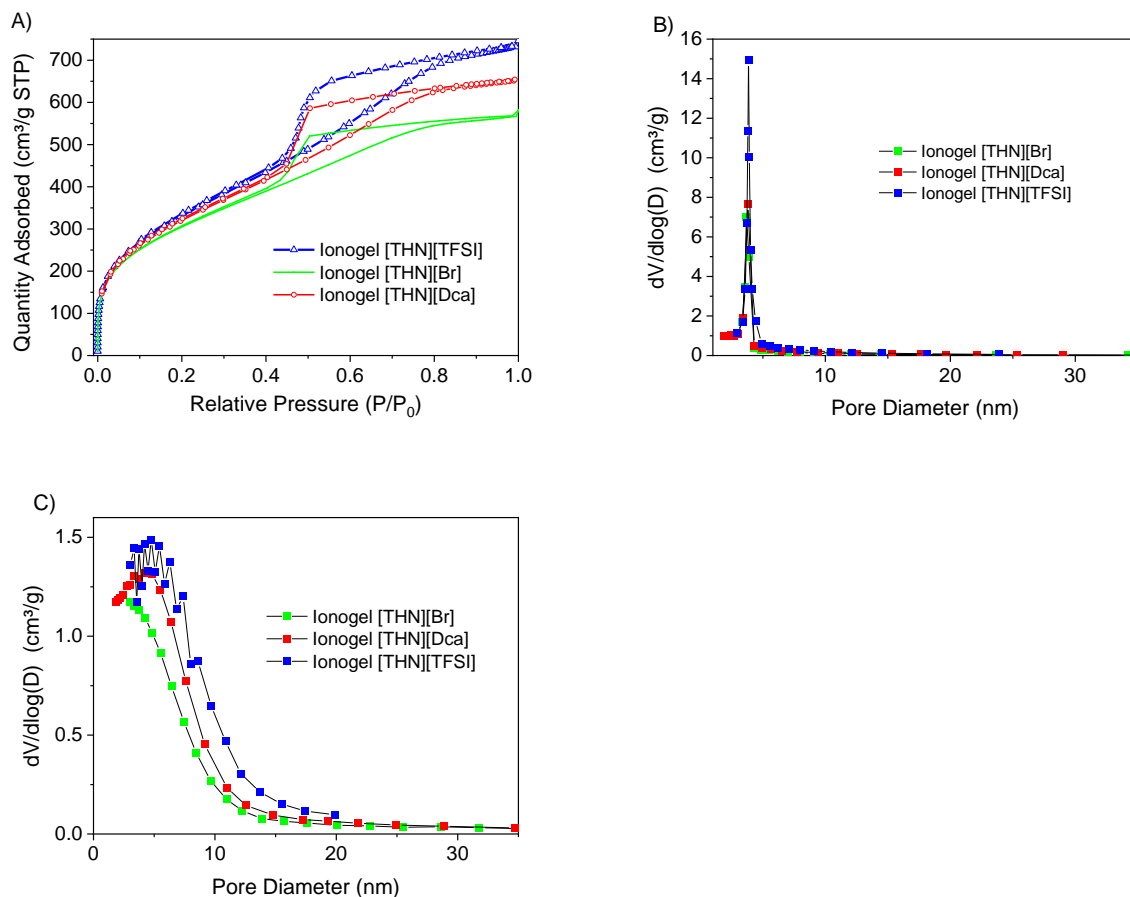


Figure 3. N₂ sorption isotherms at -196°C of washed gels (A) and pore size distribution determined from (B) the desorption branch and (C) from the adsorption branch.

Table 2: Textural characteristics of the ionogels before and after anion exchange determined from adsorption/desorption isotherm at -196°C and IL content determined from TGA

Ionogel	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$) ^b	V_p ($\text{cm}^3 \cdot \text{g}^{-1}$) ^c	D_{BJH} (nm) ^d	D_{BJH} (nm) ^e	IL content ^f (%)
[THN][Br]	1126	0.90	3.9	3.0	61.8
[THN][Dca]	1176	1.01	3.4	4.2	62.6
[THN][TFSI]	1223	1.15	4.1	4.7	70.9
[THN][Dca] ^a	1021	1.05	4.6		

^a values from [28], i.e. when the IL [THN][Dca] was used directly in the synthesis of the ionogel

^b determined using the BET method

^c determined at $p/p^0 = 0.98$

^d determined from the desorption branch of the isotherms

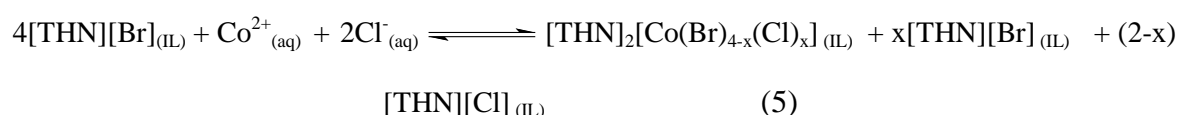
^e determined from the adsorption branch of the isotherms

^f determined by TGA

3.2 Extraction of Co(II), Au(III), Pt (IV) and Cr(VI) by [THN][Br] and treated ionogels

3.2.1 Co(II) extraction in 4 mol.L⁻¹ NaCl

The extraction properties of the ionogel containing [THN][Br] towards Co(II) in 4 mol.L⁻¹ NaCl were examined. As shown in our previous work,[19] the use of a background electrolyte such as NaCl improves the extraction yield and limits the loss of IL in the aqueous phase by favoring an ion pair extraction mechanism. The ionogel, after contact with a cobalt solution, turns sky blue (Figure 4), a characteristic shade of Co(II) in a tetrahedral environment (probably related to the formation of a $[\text{Co}(\text{Br})_{4-x}(\text{Cl})_x]^{2-}$) meaning a change in metal coordination sphere and geometry around the metal. The extraction process involves the formation of an anionic complex and an ion pair with the cation of the IL according to the following equilibrium 5:



The extraction yield of Co(II) obtained with the [THN][Br] ionogel is 47.8% whereas extraction efficiency obtained with pure [THN][Br] in the same medium is 64%, which means that the confinement of the IL in the ionogel decreases slightly its extraction efficiency .

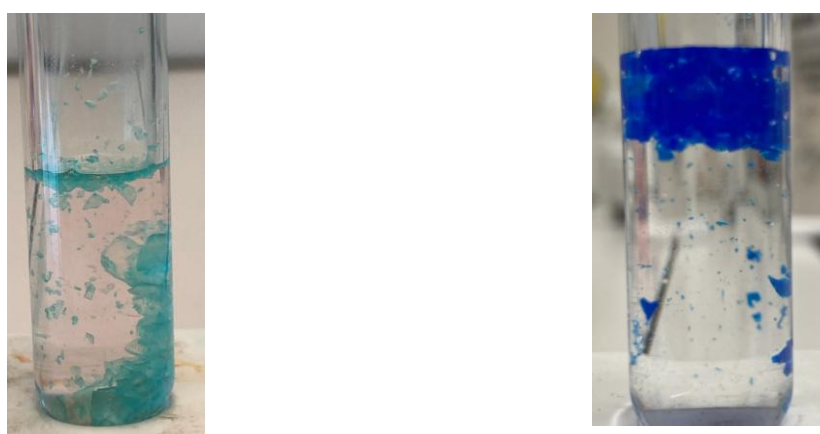


Figure 4: Snapshot after extraction of Co(II) of ionogel [THN][Br] (left) and of the ionogel [THN][Br] treated by NaDca (right). $[\text{Co}(\text{II})] = 1.5 \times 10^{-2} \text{ mol.L}^{-1}$; $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{ionogel}} = 0.300 \text{ g}$

In the presence of Co(II) the ionogel treated by NaDca is colored night blue (Figure 4) indicating the presence of dicyanamide ion in the coordination sphere of the metal with the formation of a $[\text{Co}(\text{Dca})_{4-x}(\text{Cl})_x]^{2-}$ complex species in the ionogel. The Co(II) extraction experiments performed with this ionogel under the same conditions ($\text{NaCl } 4 \text{ mol.L}^{-1}$) show an improvement in extraction efficiency with an extraction yield at 71%. Nevertheless, this value is lower than those found previously for the ionogel prepared by direct confinement of $[\text{THN}][\text{Dca}]$ (Figure 5) and pure $[\text{THN}][\text{Dca}]$ which show extraction yields of 89 and 98%, respectively. [28] In all experiments, the conditions were adjusted so that the ratio of moles of IL to moles of metal was equivalent for all three systems. Metathesis significantly improves the extraction properties of the ionogel and at the same time, induces a decrease in the IL loss due to the lower solubility of $[\text{THN}][\text{Dca}]$ compared to $[\text{THN}][\text{Br}]$. Despite this loss of efficiency due to the confinement of the ILs, the extraction rate of Co(II) ions by the treated ionogel corresponds to an extraction capacity of about $0.25 \text{ mmole.g}^{-1}$ of ionogel (15 mg.g^{-1}) which is comparable to extraction capacities of silica gel functionalized with chelating agents of the polyamine and polyaminocarboxylate type. [20-22,27]

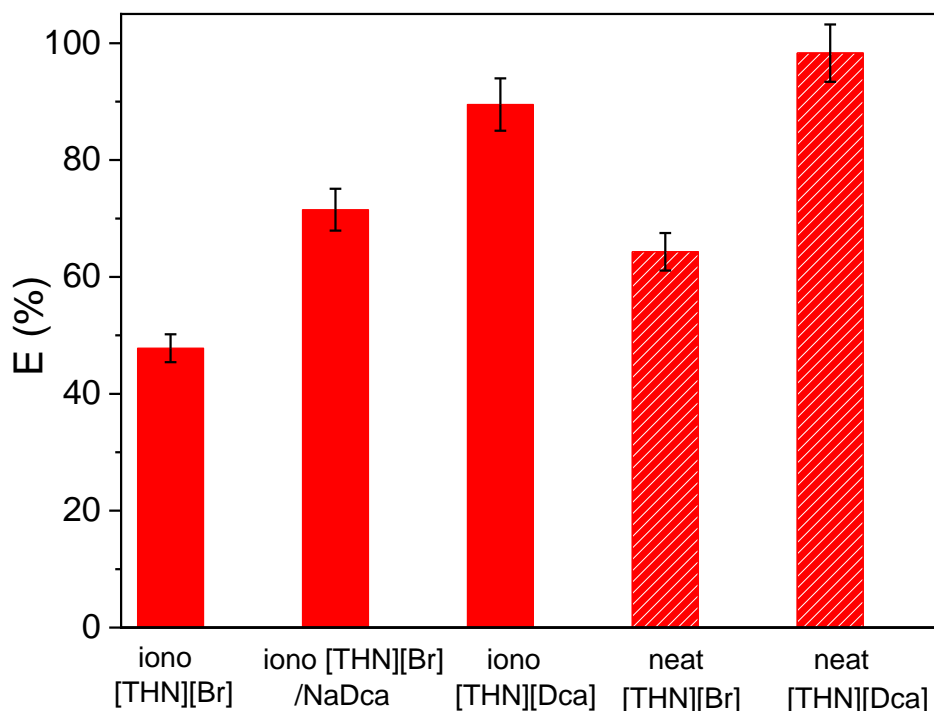


Figure 5. Extraction yields (%E) of Co(II) in NaCl 4 mol.L⁻¹ with ionogel [THN][Dca] and [THN][Br] treated with NaDca and with neat [THN][Dca]. $C_{\text{metal}} = 0.05 \text{ mol.L}^{-1}$; extraction with neat IL $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{IL}} = 0.5 \text{ g}$; extraction with ionogel $V_{\text{aq}} = 1.5 \text{ mL}$, $m_{\text{ionogel}} = 0.35 \text{ g}$ (0.15 g of IL in ionogel).

3.2.2 Recovery of Au(III), Pt(IV) by [THN][Br] and treated ionogels

3.2.2.1 Extraction of AuCl_4^- and PtCl_6^{2-} by [THN][Br] ionogels

Solutions of HAuCl_4 and K_2PtCl_6 were brought into contact with the [THN][Br] ionogels and gently stirred. A decolorization of the aqueous phase is observed within a few minutes. Snapshots of the extraction of AuCl_4^- and PtCl_6^{2-} are shown in Figure 6. After contacting the ionogels with HAuCl_4 and K_2PtCl_6 solutions, they turned orange in both cases, revealing that Au and Pt are efficiently extracted from the aqueous phases. The extraction percentages of AuCl_4^- and PtCl_6^{2-} are reported in Table 3. The values in the table indicate in both cases a

quantitative extraction of AuCl_4^- and PtCl_6^{2-} , close to those obtained with the pure IL, which means that the confinement of $[\text{THN}][\text{Br}]$ does not significantly alter its extraction properties.

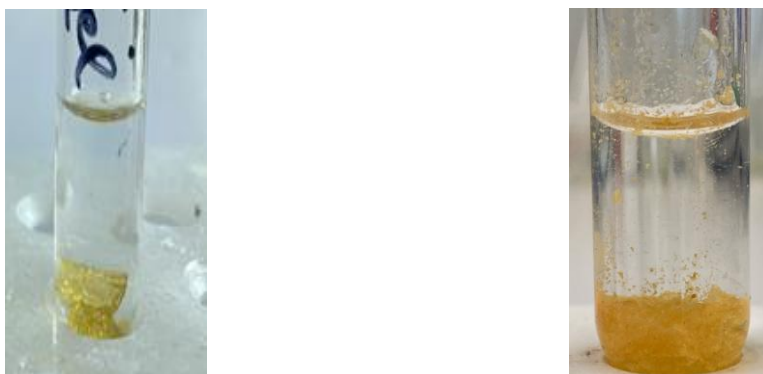


Figure 6. Snapshot of ionogel after extraction of AuCl_4^- (left) and PtCl_6^{2-} (right) from $[\text{THN}][\text{Br}]$ ionogel. $[\text{Au(III)} (\text{Pt(IV)})] = 1.5 \cdot 10^{-3} \text{ mol.L}^{-1}$; $V_{\text{aq}} = 2\text{mL}$, $m_{\text{ionogel}} = 0.300 \text{ g}$

Table 3: Extraction yields (%E) for Pt(IV), Au(III), and Cr(VI) for ionogel $[\text{THN}][\text{Br}]$ /water system . $V_{\text{aq}} = 2\text{mL}$ $[\text{Au(III)}, \text{Pt(IV)}, \text{Cr(VI)}] = 1.5 \cdot 10^{-3} \text{ mol L}^{-1}$, $m_{\text{IL}} = 0.3 \text{ g}$

	%E Au(III)	%E Pt(IV)	%E Cr(VI)
Ionogel $[\text{THN}][\text{Br}]$	99.7	98.0	98.6
Neat $[\text{THN}][\text{Br}]$	99.2	98.4	98.9

The extraction of halogenated noble metal complexes by IL has been extensively studied in the literature.[13, 15-18] It is now widely established that the driving force of the extraction process is governed by the formation of an ion-pair between the organic cation (THN^+) and the tetrahaloaurate anion and an anion exchange mechanism described by the equilibria (6):



The greater stability of the $[\text{THN}][\text{AuCl}_4]$ ion pair, compared to $[\text{THN}][\text{Br}]$, facilitates the extraction of halogenated complexes. In addition, the presence of bromide ions can lead to substitution of chloride with bromide ions to form AuBr_4^- within the ionogel due to the softer

character of bromide ion. A similar process and equilibria may be involved to explain the extraction efficiency obtained with PtCl_6^{2-} .

3.2.2.2 Extraction of AuCl_4^- and PtCl_6^{2-} by treated ionogels

Figure 7 shows the extraction efficiency of the ionogel $[\text{THN}][\text{Br}]$ treated with NaDca and LiTFSI towards Au(III) and Pt(IV). The extraction yields of Au(III) and Pt(IV) with neat $[\text{THN}][\text{Dca}]$ and $[\text{THN}][\text{TFSI}]$ are also reported.

After contacting the NaDca-treated $[\text{THN}][\text{Br}]$ ionogel with solutions of HAuCl_4 and K_2PtCl_6 , the ionogels turn yellow and orange, respectively, revealing that gold and platinum are efficiently extracted from the aqueous phases. As shown in Figure 7, the treatment of the ionogel with NaDca does not affect the extraction properties of the ionogel, the extraction of Au(III) and Pt(IV) is almost quantitative with extraction yields of 99.9 and 98.4% similar to those found with the ionogel $[\text{THN}][\text{Br}]$ before treatment and those obtained with the neat IL $[\text{THN}][\text{Dca}]$.^[19] This result shows that the dicyanamide anions can be exchanged as readily as bromide ions by the halogenated Au(III) and Pt(IV) complexes to form an ion pair with the tetrahexylammonium cation. Although anionic metathesis with NaDca does not significantly improve the extraction properties of the ionogel towards Au(III) and Pt(IV) ions, the treatment of the ionogel with NaDca is relevant, as it decreases the aqueous solubility of the ionic liquid and limits the release of IL from the ionogel.

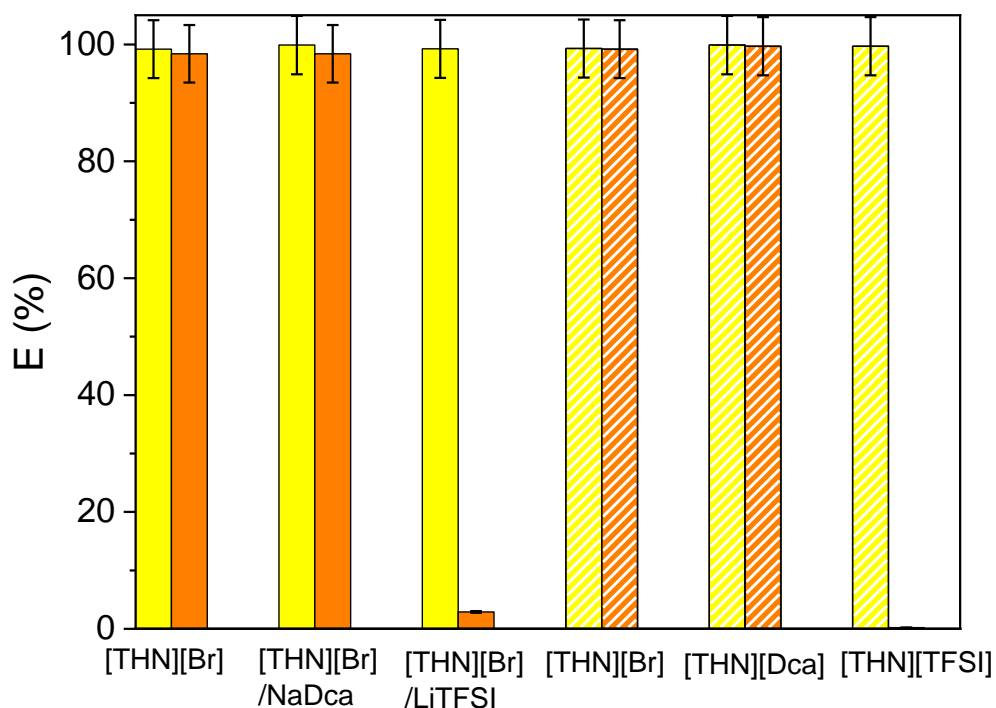


Figure 7. Extraction yields of AuCl_4^- and PtCl_6^{2-} in ionogels and neat ILs: $[\text{Au(III)}] = [\text{Pt(IV)}] = 1.5 \times 10^{-3} \text{ mol.L}^{-1}$; $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{ionogel}} = 0.3 \text{ g}$. The cross hatched curves represent the extraction yields with neat ionic liquids (Boudesocque et al, 2019).

After contacting the LiTFSI-treated [THN][Br] ionogel with HAuCl_4 solution, it turns yellow confirming a strong extraction of AuCl_4^- . However, the aqueous K_2PtCl_6 solution remains slightly orange meaning that the extraction of PtCl_6^{2-} is low. The extraction yield values of Au(III) and Pt(IV) depicted in Figure 7 confirm this observation. The extraction of Au(III) is quantitative with an extraction yield of 99.2% and Pt(IV) is extracted with a yield of 2.5%. These results show that anionic metathesis with LiTFSI is a useful tool to provide selectivity between Au(III) and Pt(IV). The selectivity of TFSI-based IL towards gold over platinum has already been observed with the neat [THN][TFSI] also by other authors.[16,17] This selectivity is due to the fact that Pt(IV) anions are divalent and have a higher charge density and a higher standard Gibbs energy ($-668.2 \text{ kJ.mol}^{-1}$ for PtCl_6^{2-}) than monovalent anions such

as TFSI⁻ and Au(III) anions ($-243.6 \text{ kJ.mol}^{-1}$ for AuCl_4^-). The Au/Pt separation factor calculated from the extraction rates is above 1000, comparable to that obtained with the neat IL indicating an efficient Au/Pt separation with this ionogel.

3.2.2.3 Back extraction of Au(III), Pt(IV)

Stripping experiments were performed by contacting the ionogel containing the extracted metal with 2 mL of aqueous thiourea solutions (0.2 mol.L^{-1} in 0.5 mol.L^{-1} HCl) for 4 hours and placed under gentle agitation. The percentage of stripped metal was determined from the analysis of the aqueous phases. The extraction of Au(III) from ionogel [THN][Br] treated with LiTFSI is almost quantitative with a percentage of 95%. Stripping is less efficient with ionogel [THN][Br] treated with NaDca with a percentage of metal recovered equal to 72.5% and 55.5% for Au(III) and Pt(IV). It is important to note that under the same conditions, thiourea stripping from pure ionic [THN][Dca] does not lead to complete metal recovery with percentages of back extraction equal to 76% for both Au(III) and Pt(IV).

3.2.3 Separation of Au(III) and Cu(II) by [THN][Br] and treated ionogels

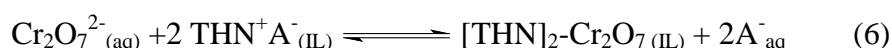
Copper is a metal often present in gold leachates, and as such, an efficient method of separating these two metals may be of industrial interest, particularly for the recovery of metals from Print Circuit Board (PCB) and Jewelry.[38,39] The ability of the ionogels to achieve Au/Cu separation was tested with the [THN][Br] ionogel before and after treatment with TFSI. The Au(III)/Cu(II) separation factors were determined from the extraction rates of the bimetallic solution at a concentration of $4 \times 10^{-3} \text{ mol.L}^{-1}$ for Au(III) and 0.05 mol.L^{-1} for Cu(II). The extraction yield of Cu(II) by the [THN][Br] ionogel is 8%, while, as seen previously, the extraction of Au(III) is quantitative ($E = 98\%$). The separation factor thus calculated with these data is higher than 500 indicating an efficient separation of Au(III) other Cu(II). The extraction rates of Au(III) and Cu(II) from the same solution by the LiTFSI-treated ionogel are respectively 99 and 1.2 % for Au(III) and Cu(II) leading to an increase in

the separation factor compared to that of the untreated ionogel. The separation factor found in this case is higher than 1000, meaning that the separation has been improved by the LiTFSI treatment.

3.2.4 Extraction of Cr(VI) by [THN][Br] and treated ionogels

3.2.4.1 Extraction of Cr(VI) by neat [THN][Br] and [THN][Br] ionogels

The extraction yield was first determined with pure [THN][Br] under the conditions used for the extraction of AuCl_4^- or PtCl_6^{2-} . Under these conditions, the extraction is almost instantaneous, and the extraction yield was found to be 99.2%. Spectroscopic analysis of the [THN][Br] phase after extraction from $\text{K}_2\text{Cr}_2\text{O}_7$ allowed us to identify the extraction mechanism (Figure 8). For convenience, the IL extraction phase was first dissolved in ethyl acetate before spectroscopic analysis. Figure 8 shows that the [THN][Br] phase after extraction presents the specific transitions of $\text{Cr}_2\text{O}_7^{2-}$ meaning that this ion is directly transferred from the aqueous to the organic phase and that the anionic exchange between the bromide and the dichromate anion is the predominant process of the extraction mechanism. This mechanism follows the same scheme as those proposed for AuCl_4^- and PtCl_6^{2-} . Equilibrium (6) is related to the extraction mechanism of $\text{Cr}_2\text{O}_7^{2-}$.



The red shift of the transitions compared to those observed in aqueous media seems to indicate a strong interaction between the tetrahexylammonium cation and the dichromate anions.

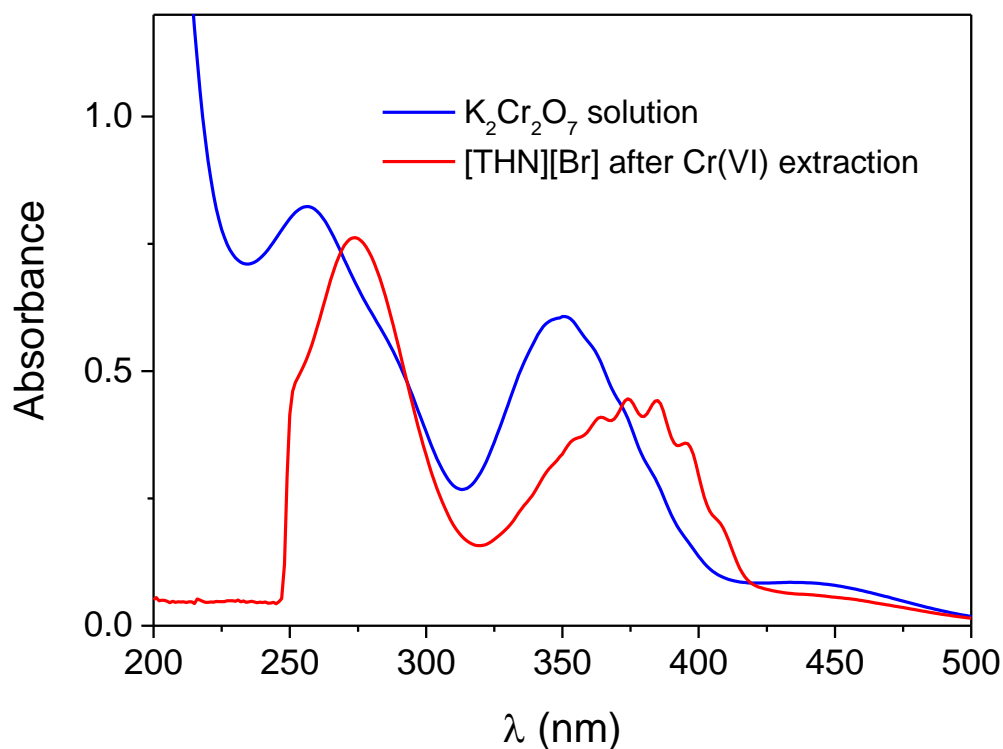


Figure 8: UV-vis spectra of dichromate anion of an aqueous solutions of $K_2Cr_2O_7$ and of the $[THN][Br]$ phase after extraction. ($[THN][Br]$ ionic liquid was dissolved in EtOAc)

With the $[THN][Br]$ ionogel, the transfer of $Cr_2O_7^{2-}$ from the aqueous phase to the organic phase is slower than with the pure ionic liquid, in accordance with the slower dynamic of IL confined in silica matrix .[40] After contact, the ionogel turns orange and the color of the potassium dichromate solution gradually fades within a few minutes. The extraction is quasi-quantitative after 4 hours with an extraction yield of 98.6% close to the one found with the neat molten salt (Table 3).

3.2.4.2 Removal of hexavalent chromium from treated ionogel

Table 4 gives the extraction yield of $Cr_2O_7^{2-}$ ions by $[THN][Br]$ ionogel before and after treatment with LiTFSI and NaDca.

Table 4: extraction yields for Cr(VI) by ionogels. $V_{\text{aq}} = 2 \text{ mL}$, $m_{\text{IL}} = 0.3 \text{ g}$, $[\text{Cr}_2\text{O}_7^{2-}] = 1.5 \times 10^{-3} \text{ mol.L}^{-1}$.

Ionogel	Treatment	%E (Cr(VI))
[THN][Br]	-	98.6
[THN][Br]	NaDca	97
[THN][Br]	LiTFSI	6.0

The ionogels treated with NaDca show the same extraction capacities as the untreated ionogel confirming the fact that the Dca^- anion has the same exchangeability capacities as the Br^- anion towards $\text{Cr}_2\text{O}_7^{2-}$. Treatment with LiTFSI strongly decreases the affinity of the ionogel for $\text{Cr}_2\text{O}_7^{2-}$ with an extraction yield of 6%. The TFSI⁻ anion is more hydrophobic than dicyanamide anion and leads to the formation of a stable ion pair with the tetrahexylammonium cation, which cannot be displaced by $\text{Cr}_2\text{O}_7^{2-}$.

Conclusion

In this work, we have developed an easy to implement strategy to modulate the extracting and separation properties of silica-based ionogels that do not require grafting functionality. This strategy is based on the synthesis of ionogels from a commercial salt [THN][Br] and their subsequent *in-situ* anions metathesis with LiTFSI or NaDca salts. We have confirmed the efficiency of anions exchange by different method and have also shown that the treatment of the ionogels does not affect their textural and their mechanical characteristics. This demonstrates that confined ILs have comparable flexibility properties to their unconfined analogues. To illustrate the interest of our methodology, we chose to perform

different metal extraction experiments. Ionogels containing [THN][Br] extract efficiently anionic complexes of Au(III), Pt(IV) and Cr(IV). However, the treatment by NaDca enhances the extraction efficiency of the ionogel towards 3d metals, giving extraction capabilities comparable to functionalized silica gel. At the same time, the treatment by TFSI, allows the separation of Au(III) and Pt(IV) and improves the separation Au(III)/Cu(II). The Au(III)/Cu(II) and Au(III)/Pt(IV) separation factors are similar to those obtained with neat ILs. Thus, we have demonstrated that before or after anions metathesis, ionogels have similar extraction properties to neat ionic liquids. All this work was carried out under conditions of equilibrium between the aqueous and extractant phases. One of the points that we will be developed in a later work is to use ionogels in processes working in continuous non-equilibrium mode. We believe this method can be used for other applications like catalysis and sensing for instance.

Acknowledgments

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Appendix A : supplementary data

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