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ARTICLE TYPE

Possibilities and limitations in separating Pt(IV) from Pd(II) combining imidazolium and phosphonium ionic liquids.

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The investigation on a process for separating Pt(IV) and Pd(II) dissolved in acidic aqueous solution containing HCl using two ionic liquids 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([OMIM][NTf₂]) and trihexyltetradecylphosphonium bromide (Cyphos 102) is presented. To that end, the
 10 single extraction of platinum in [OMIM][NTf₂] has been investigated as a function of the initial concentration of Pt(IV) ion dissolved in 1 M HCl. The distribution coefficient for Pt(IV), present in water as PtCl₆²⁻ anion, decreases with the concentration of Pt(IV). The extraction of Pd(II) towards [OMIM][NTf₂] or Cyphos 102 as a function of the concentration of HCl in the aqueous phase is also reported. Pd(II), present as PdCl₄²⁻ in water is not extracted using [OMIM][NTf₂]. On the other hand, the
 15 distribution coefficients of Pd(II) using Cyphos 102 are above 2000. In this ionic liquid, Pd(II) is extracted as a PdBr₄²⁻ anion. Separation of Pt(IV) from Pd(II) was then carried out starting from aqueous phases containing 1 M HCl and various initial concentrations of Pt(IV). The influence of the numbers of extraction steps using [OMIM][NTf₂] on the extraction of Pt(IV) was also studied. Unlike results obtained from the single extraction experiments of Pt(IV), consecutive extraction of Pt(IV) in water using
 20 [OMIM][NTf₂] does not improve significantly the extraction of this metal ion. The second step of the extraction process carried out using Cyphos 102 leads to the quantitative extraction of Pd(II) and Pt(IV) remaining in the aqueous phase.

Introduction

25 Platinum group metals (PGM) are precious metals that are located in columns V to VIII and period 5 and 6 of the periodic table. Their concentration in the earth crust is very low, typically in a few ppm in the most concentrated ores.¹⁻⁴ In such ores, PGM are present together, and due to similarities in hydrometallurgical
 30 properties, purification of these metals is tedious. Due to their unique physical chemical properties, they are used in very specific high technology applications ranging from aerospace to automotive catalytic converters.¹ Because the primary production of PGMs is located in very few mining spots on earth, because it
 35 will face shortage in a few decades and because these metals cannot be substituted by other more common metals, PGM are now listed as critical raw materials that present a high supply risk.⁵ With the development of a sustainable and environment-friendly chemistry and because the secondary production
 40 (recycling from wastes) is becoming a sustainable source of such metals, alternative processes for recovering and separating PGM from used devices, such as automotive catalysts, has nowadays become a relevant topic of research in chemistry.

In the production of PGM from ore or the recycling thereof from
 45 used devices, metals are first leached using acidic solutions. Pt and Pd are leached into water Pt(IV), Pd(II) ions. Since the leaching solution contains HCl, the metals are present in water as various anionic polychlorometallate complexes such as PtCl₆²⁻, PdCl₄²⁻.⁶ PGM in general are difficult to separate because they
 50 exhibit similar extracting properties. Besides, the processes used for separating and purifying the various PGM complexes raise several environmental concerns because hydrometallurgical processes require hazardous chemicals such as cyanide or volatile organic compounds and because the pyrometallurgical processes
 55 are very expensive in terms of energy consumption. Ionic liquids are now a well-known class of alternative solvents composed only with ions exhibiting melting points typically below 373 K.^{7,8} Most ionic liquids studied and reported so far are based on linear or cyclic quaternary ammonium cations, such as
 60 tetralkylammonium, 1-alkyl-3-alkylimidazolium, 1-alkylpyridinium, 1-methyl-1-alkylpyrrolidinium or 1-ethyl-1-alkylpiperidinium, and more rarely on quaternary phosphonium cations.⁹ Ionic liquids hardly exhibit any vapour pressure and are non flammable under normal storage conditions. They are
 65 therefore not expected to pollute the atmosphere, be breathed by

workers and are neither flammable nor explosive. For these reasons, ionic liquids have been used in all types of chemical and industrial applications in the last decade.¹⁰

In the specific case of liquid-liquid extraction, ionic liquids based on perfluorinated anions (PF_6^- , BF_4^- or bis(trifluoromethanesulfonyl)imide) and ammonium cations are considered to be promising alternative extracting phases because in addition to the above mentioned physical chemical properties, they exhibit low solubility in water and low viscosity. Numerous studies have thus reported the application of hydrophobic ionic liquids based on quaternary ammonium cations to extraction of metal ions or organic compounds.^{11–13} Recently, our team has reported successful extraction of precious metals such as Au(III), Pt(IV) or Ir(IV) using hydrophobic ionic liquids based on $[\text{NTf}_2]^-$ anions and without requiring any additional extracting agent.^{14–17} The family of ionic liquids based on large phosphonium cations, such as trihexyltetradecylphosphonium produced by Cytec, are another family of promising extracting phases. Such a large cation has the advantage of yielding water-immiscible ionic liquids even when the counter-anion, such as chloride or bromide for instance, is small in size and hydrophilic. Recent works have reported successful extraction of a range of metallic ions from water using ionic liquids based on cation $[\text{P}_{6614}]^+$ and various anions such as chloride, nitrate or dialkylphosphonate, accordingly and without adding any organic extracting agent in the process.^{18–23} Such ionic liquids have nevertheless the inconvenient of exhibiting a relatively high solubility in water, and an increased viscosity (typically above 500 cP at 298 K). Other works have therefore reported the use of Cyphos ionic liquids diluted in organic solvents such as toluene.^{24–26} Even if this latter approach solves the problem related to the viscosity of the extracting phase, important environmental concerns arise from the use of classical organic solvents. To the best of our knowledge, despite the fact that both families of ionic liquids present complementary properties in the field of metallic ion extraction, only one article reports extraction of metals using a combination of a hydrophobic ammonium- and a phosphonium-based ionic liquids.²⁷

The work presented here deals with the investigation of a simple separation process for Pt(IV) and Pd(II) based on 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[\text{OMIM}][\text{NTf}_2]$) and trihexyltetradecylphosphonium bromide (Cyphos 102). Structures and abbreviations are detailed in Fig. 1. No organic phase or additional extractant was used in this study. Because Pt(IV) and Pd(II) are difficult to separate from each other in classical hydrometallurgical processes, we chose to investigate first on the extraction of these two metallic ions using ionic liquids.

In this article, the single extraction of Pt(IV) and Pd(II) from aqueous solution using $[\text{OMIM}][\text{NTf}_2]$ or Cyphos 102, accordingly will be presented in a first section. Then, a two-step process for the separation of Pt(IV) from Pd(II) using $[\text{OMIM}][\text{NTf}_2]$ and Cyphos 102 will be presented. Discussion on the optimization of the process by modifying the volume ratio of aqueous and ionic liquid phases, or the initial concentration of metals will also be presented, followed by a short conclusion.

Experimental

Chemicals

All aqueous solutions were prepared using Millipore water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$). Na_2PdCl_4 , H_2PtCl_6 , LiBr and concentrated hydrochloric acid solutions were received from Sigma Aldrich or Alfa Aesar and used as received. Cyphos 102 was gratefully provided by Cytec. $[\text{OMIM}][\text{NTf}_2]$ was received from Solvionic. Both ionic liquids were used without further purification.

Instrumentation

Extraction experiments were carried out using an orbital shaker with a rotation speed of 260 rpm. Centrifugation was carried out on a Universal 320R centrifuge from Hettich. UV-Vis spectra were recorded on a Cary 50 from Varian using a 1 cm length quartz cell. ICP-OES analysis was performed using a ICP-OES 720ES apparatus from Varian.

Speciation of Pd(II)

A first aqueous solution of Pd(II) in water was prepared adding typically 25 mg of Na_2PdCl_4 into 10 mL of a solution of 1 M HCl. A second solution was prepared adding a large excess of LiBr to a sample of the first solution. A third solution of Pd(II) in Cyphos 102 was prepared by mixing 10 mg of Na_2PdCl_4 in 2 g Cyphos 102. For all three solutions mentioned above, UV-Vis spectra were recorded.

Extraction procedure

Single extraction of Pd(II)

Initial solutions containing 1 mM Na_2PdCl_4 and 1, 2, 4 and 8 M HCl were first prepared. Extraction was then carried out mixing in a tube 3 g of an aqueous solution with 1 g of Cyphos 102 or 1.3 g of $[\text{OMIM}][\text{NTf}_2]$, accordingly. The tube was left on a shaker for 12 h and then centrifuged at 3000 g for 20 minutes. After 2 h settling time, the aqueous phases obtained after extraction using $[\text{OMIM}][\text{NTf}_2]$ or Cyphos 102 were analysed by UV-Vis spectroscopy or ICP-OES respectively.

Single extraction of Pt(IV)

Initial solutions containing 1 M HCl and concentrations of H_2PtCl_6 ranging from 1 to 8 mM were first prepared. Extraction was then carried out in a tube mixing 3 g of initial solution with 1 g of Cyphos 102 or 1.3 g of $[\text{OMIM}][\text{NTf}_2]$, accordingly. The tube was left on a shaker for 12 h and then centrifuged at 3000 g for 20 minutes. After 2 h settling time, the aqueous phases obtained after extraction using $[\text{OMIM}][\text{NTf}_2]$ or Cyphos 102 was analysed by UV-Vis spectroscopy or ICP-OES respectively.

Competitive extraction of Pd(II) and Pt(IV)

Four extraction experiments were carried out starting from aqueous solutions containing 1 M HCl, concentrations of H_2PtCl_6 ranging from 1 mM to 7.5 mM and concentrations of Na_2PdCl_4 ranging from 2.4 to 4.6 mM. 4 mL of each aqueous solution was contacted with $[\text{OMIM}][\text{NTf}_2]$. In experiments 1 and 4, the volumes of water (V_w) and of ionic liquid (V_{IL}) were adjusted so

that the volume ratio $V_w/V_{IL} = 1$. In experiments 2 and 3, $V_w/V_{IL} = 2$. In all experiments, the density of aqueous solutions was assumed to be equal to that of a 1 M HCl solution, namely 1.02 g.cm⁻³. For [OMIM][NTf₂], density was set to 1.30 g.cm⁻³.^{14,16}

The tubes were then left on a shaker for 12 h and centrifuged at 3000 g for 20 minutes.

In experiments 2 to 4, additional extraction cycles were carried out. To that end, after extraction of metals was carried out by contacting [OMIM][NTf₂] with an aqueous solution, the latter is removed and contacted again with a fresh volume of [OMIM][NTf₂]. Two extraction cycles were carried out in experiments 2 and 3 and three cycles in experiment 4.

Finally, 4 g of each remaining aqueous solution obtained after the extraction towards [OMIM][NTf₂] was contacted with 2.5 g of Cyphos 102 in a centrifuging tube. The tube was left on a shaker and centrifuged as detailed above.

The aqueous phases obtained after each extraction step was analysed using and ICP optical emission spectroscopy, as detailed in the following section.

Measurement

In the case of the single extraction of Pt(IV), the initial and final concentrations of PtCl₆²⁻ in the aqueous phases were determined by UV-Vis spectrophotometry. The Beer-Lambert's law was applied at the maximum absorption wavelength of each metal complex ($\lambda_{max} = 262$ nm for PtCl₆²⁻, $\lambda_{max} = 280$ nm for PdCl₄²⁻) using calibration solutions ranging from 10 to 100 μ M. In all cases, a correlation factor of 0.999 and above for the Beer-Lambert's law was obtained. For all other extraction experiments, initial and final concentrations for PtCl₆²⁻ and PdCl₄²⁻ were determined by ICP-OES. To that end, the Beer-Lambert's law was applied at selected emission wavelengths ($\lambda^{em} = 177.6$ nm for PtCl₆²⁻, $\lambda^{em} = 229.6$ nm for PdCl₄²⁻) using calibration solutions ranging from 1 to 100 μ M. In all cases, a correlation factor of 0.999 and above for the Beer-Lambert's law was obtained.

Percentage of extraction ($M_{extr}\%$) and distribution coefficients (D_M) of metals (platinum or palladium) were calculated using the following relations

$$M_{extr}\% = 100 \frac{[MCl_x^{2-}]^{Init} - [MCl_x^{2-}]^{Final}}{[MCl_x^{2-}]^{Init}} \quad (1)$$

where M stands for metal Pt or Pd accordingly, $[MCl_x^{2-}]$ refers to the concentration of PtCl₆²⁻ or PdCl₄²⁻ in water accordingly and the superscripts *Init* and *Final* refer to the values measured prior or after the extraction experiment, respectively. The value of $M_{extr}\%$ is calculated within $\pm 0.2\%$.

$$D_M = \frac{[MCl_x^{2-}]^{Init} - [MCl_x^{2-}]^{Final}}{[MCl_x^{2-}]^{Final}} \frac{V_w}{V_{IL}} \quad (2)$$

with V_w and V_{IL} the volumes of water and ionic liquid, respectively. The volume ratio V_w/V_{IL} used in the extraction experiments is 1 or 2, as specified above. The maximum D value measurable in this study by UV-Vis spectroscopy or ICP-OES was assumed to be 2.10² or 5.10³ respectively. The relative uncertainty on D_M is $\pm 5\%$.

Results and discussions

Speciation of Pd(II)

Pd(II) can form several complexes in presence of HCl in water. However, at high concentrations of HCl, typically above 1 M HCl, Pd(II) is mainly under the form of PdCl₄²⁻.²⁸ The UV-Vis spectrum of Na₂PdCl₄ dissolved in an aqueous solutions of 1 M HCl is plotted in Fig. 2. A large absorption band centred on 280 nm is observed. Similar spectrum is obtained whatever the concentration of HCl used in this study. Previous reports have clearly assigned this absorption band to the presence of a PdCl₄²⁻ complex.²⁹

The UV-Vis spectrum recorded for a solution containing 10 mM Na₂PdCl₄, 1 M HCl and a large excess of LiBr is on the other hand different from that discussed above. In agreement with the change in colour observed for the solution which turns from orange to red upon addition of LiBr, a significant bathochromic shift is observed. The UV-Vis spectrum exhibits one absorption band centred around 331 nm. In agreement with previous reports, the bathochromic shift observed between the spectra obtained in absence and presence of LiBr is due to the formation of PdBr₄²⁻.²⁹ Such a bathochromic shift is also in agreement with previous results dealing with the formation of PtBr₆²⁻ or AuBr₄⁻ in water, starting from PtCl₆²⁻ or AuCl₄⁻ accordingly.^{14,15,30}

Similarly, when mixing Na₂PdCl₄ in Cyphos 102, the ionic liquid turns to a dark red colour upon mixing. The UV-Vis spectrum of the ionic liquid loaded with Na₂PdCl₄ exhibits an absorption band centred on 343 nm and appears to be similar to that observed for PdBr₄²⁻ in water. Such a result is in agreement with the fact that Cyphos 102 is based on bromide anion, which then interacts with the PdCl₄²⁻ complex in order to form PdBr₄²⁻, as it is observed in water. Therefore, it can be stated that Pd(II) in Cyphos 102 is under the form of a PbBr₄²⁻ anionic complex under our experimental conditions. The small bathochromic shift observed between the spectra obtained for PdBr₄²⁻ in water or in Cyphos 102 is due to the solvent. Similar bathochromic shift has been previously observed for PdBr₄²⁻ dissolved in 1-butyl-1-methylpyrrolidinium NTf₂ ionic liquid, exhibiting an absorption band centred on 350 nm.²⁹

Single extraction of Pt(IV) and Pd(II)

Extraction using [OMIM][NTf₂]

Previous results from our group have shown that extraction of 5 mM Pt(IV) in acidic aqueous solutions using [OMIM][NTf₂] yields a value of 5.5 for the distribution coefficient of PtCl₆²⁻ at 0.1 M HCl,¹⁵ but decreases with the concentration of HCl in the aqueous phase. Aiming at developing a process for the separation of Pt(IV) from Pd(II) because leachates from spent automotive catalysts are expected to contain various levels of Pt(IV), the influence of the initial concentration of PtCl₆²⁻ in an aqueous phase containing 1 M HCl on the distribution coefficient of Pt(IV) was first studied. Results, collected in Table 1, show that a value of 11.2 for the distribution coefficient of PtCl₆²⁻ using [OMIM][NTf₂] was obtained starting from an aqueous solution containing 1 M HCl and 1 mM PtCl₆²⁻. They also reveal that the initial concentration of PtCl₆²⁻ in the aqueous phase is indeed of significant importance, since D values decrease from 11.2 at 1 mM Pt(IV) down to 2.8 at 8 mM Pt(IV). Such a result has also

been observed previously. However, no specific value for the distribution coefficients were calculated.³¹

Even though the reason for the sharp decrease in D_{Pt} is not yet clearly understood, this result shows clearly that the design of a separation process using ionic liquids requires precise knowledge on the initial concentrations of metallic ions in the aqueous phase. In addition, because the distribution coefficients for Pt(IV) are not high, quantitative extraction of the latter is expected to require repeated extraction cycles using [OMIM][NTf₂]. Furthermore, one expects the higher the initial concentration of Pt(IV) in the leaching solution, the higher the numbers of extraction steps.

Values for the distribution coefficients for PdCl₄²⁻ extracted towards [OMIM][NTf₂] are collected in Table 2. One can observe that whatever the concentration of HCl in the aqueous phase, PdCl₄²⁻ remains in water using [OMIM][NTf₂]. The distribution coefficients obtained here are in good agreement with a recent report dealing with the extraction of Pt(IV) and Pd(II) using [OMIM][NTf₂].³¹

The difference in extraction between Pt(IV) and Pd(II) observed here is related to the fact that the diameter of PtCl₆²⁻ is larger than that of PdCl₄²⁻.³² This results in a lower absolute value of the Gibbs energy of solvation for PtCl₆²⁻ compared to that for PdCl₄²⁻. Comparison with literature results shows that extraction of Pt(IV) or Pd(II) using classical liquid-liquid extraction systems, such as trioctylamine and kerosene follows the same trend as that reported there, namely that Pt(IV) is better extracted than Pd(II).^{6,26} On the other hand, these results are different from those obtained using trioctylammonium nitrate dissolved in ionic liquid trioctylammonium [NTf₂]. In this previous work, Pd(II) was found to be extracted more efficiently than Pt(IV) for concentrations of HCl ranging from 0.1 M HCl to 4 M. The influence of the HCl concentration on the distribution coefficient of Pd(II) was much more pronounced than on the distribution coefficient of Pt(IV).^{33,34} Even though no explanation was provided for these results, the difference with our data is most probably due to the formation of metal nitrate complexes due to the presence of trioctylammonium nitrate in the ionic liquid phase.

Because the hydrophobicity of a complex is related to its size, charge density and also its ability to form hydrogen bonds with water, metal complexes based on nitrate anions are expected to behave differently from those based on chloride or bromide anions. In addition, the stability of metal nitrate complexes as a function of HCl concentration is expected to differ from that of bromide homologues, hence modifying the influence of the concentration of acid on the distribution coefficient for Pt(IV) or Pd(II).

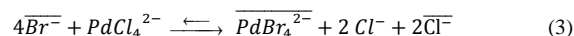
Overall, [OMIM][NTf₂] appears to be a promising extracting phase for separating Pt(IV) from Pd(II) dissolved in an acidic aqueous phase.

Extraction using Cyphos 102

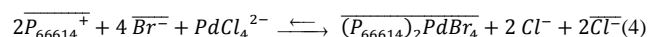
The extraction of PdCl₄²⁻ from aqueous HCl solutions was carried out using Cyphos 102 starting from aqueous solutions containing

various concentrations of HCl. Values for the distribution coefficients are collected in Table 2.

Results show that Pd(II) is quantitatively extracted using Cyphos 102. Values are very high, close to the experimental limits of our analysis method. As shown in Fig. 3, it is interesting to note that the colour of the aqueous phase prior to extraction differs from that of the ionic liquid phase after extraction. Prior to extraction, the colour of the aqueous phase is light orange. The UV-Vis spectrum presents an absorption band centred around 280 nm (see Fig. 2) which corresponds to the presence of a PdCl₄²⁻ complex. After extraction within Cyphos 102, the latter turns to a red colour. The UV-Vis spectrum exhibits an absorption band centred around 343 nm, revealing the presence of PdBr₄²⁻ complex within the ionic liquid phase. Pd(II) is therefore extracted towards Cyphos 102 as a PdBr₄²⁻ complex. The simplest mechanism in agreement with our results can be detailed as follows



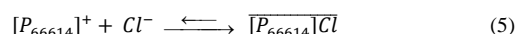
In this equation, the extraction mechanism involves two concomitant reactions. First, PdCl₄²⁻ reacts with Br⁻ from the ionic liquid to form PdBr₄²⁻. Second, PdBr₄²⁻ is extracted towards the ionic liquid phase at the expense of two chloride anions that are released in the aqueous phase. Please note that eqn (3) is fully compatible with the type of mechanism involving a phosphonium cation as proposed by other groups dealing with the extraction of various metals such as Co(II) or trivalent lanthanides towards phosphonium ionic liquids in presence of complexing ions Cl⁻ or NO₃⁻ ions.^{19,23}



This is linked to the question of the immediate surrounding of metallic ions in an ionic liquid, which has been discussed at length for actinides and lanthanides and can be applied too for PGM and other metallic ions.³⁵

It is not our intention in this article to confirm whether eqs. 3 or 4 describe most accurately the extraction mechanism for Pd(II). Noteworthy is that in any case, the process is environmentally favourable, since only two chloride anions are released in the aqueous phase.

When such an extraction mechanism occurs and when extraction is carried out in presence of such high concentrations of HCl, one must also consider the competitive extraction of Cl⁻ under the form of [P₆₆₆₁₄][Cl].



Such a competition between Cl⁻ and anionic complexes has been discussed extensively for classical solvent extraction systems using trialkylamines in molecular solvents.⁶ In our case, a slight decrease in the distribution coefficients with the concentration of HCl is indeed observed, validating eqn (5). Not surprisingly, this influence is rather small because PdBr₄²⁻ is significantly more hydrophobic than chloride anion.

Extraction of PtCl₆²⁻ using Cyphos 102 was found to be quantitative. As presented in Table 1, no specific value was assigned to the distribution coefficients for PtCl₆²⁻ because the concentration of Pt(IV) in the aqueous phase after extraction was

found to be below the detection limit of our method of analysis. The initial colour of the aqueous phase was yellow, indicating the presence of a PtCl_6^{2-} complex. After extraction, the aqueous phase became transparent while the ionic liquid turned to an orange colour, indicating the presence of a PtBr_6^{2-} complex. The change in colour was similar to the colour observed for PtBr_6^{2-15} and is in agreement with the results discussed for Pd(II) discussed above. The extraction mechanism of Pt(IV) towards Cyphos 102 is thus similar to the one presented in eqn 3 for Pd(II).

Overall these results show that Pd(II) and Pt(IV) can be extracted quantitatively from water using Cyphos 102.

Separation of Pt(IV) from Pd(II)

According to the results obtained in the preceding sections, a simple extraction process for the separation of palladium and platinum is studied. The first step of the extraction process corresponds to separation of Pt(IV) from Pd(II) using [OMIM][NTf₂]. Removal of all remaining metal ions is then carried out in a second step towards Cyphos 102.

In order to study several extraction parameters such as the volume ratio of aqueous and ionic liquid phases, the initial concentration of Pt(IV) in water and the number of extraction cycles using [OMIM][NTf₂], four experiments (so-called experiments 1 to 4 in Table 3) were carried out starting from four aqueous solutions containing various concentrations of metals. The above mentioned parameters, the concentrations of each metal and the percentage of extraction for each metal have been collected in Table 3.

In all four experiments carried out here, Pd(II) was not significantly extracted during the first step of the separation process. A maximum value of 19 % for the percentage of extraction of Pd(II) was obtained in experiments 3 and 4, which is due to the fact that several extraction cycles with [OMIM][NTf₂] were carried out.

In the first step of the separation process carried out in experiment 1, only one extraction cycle towards [OMIM][NTf₂] was performed. Under our experimental conditions, 89 % of Pt(IV) was extracted.

This result was found to be in general agreement with the results reported in Table 1 dealing with the single extraction of Pt(IV).

Because extraction of platinum was not quantitative, repetitive extraction using the same ionic liquid, namely [OMIM][NTf₂] was envisaged. Nevertheless, keeping in mind that the extraction of platinum, and more generally of metal ions towards [OMIM][NTf₂] occurs via an ion exchange mechanism,^{14,36} the aqueous phase obtained after extraction is loaded with the ion of the ionic liquid, typically [NTf₂]⁻, exchanged with the PtCl_6^{2-} anion. After extraction, the aqueous phase containing [OMIM]⁺, [NTf₂]⁻, HCl and PtCl_6^{2-} is in equilibrium with the ionic liquid phase. Further extraction of metallic ions using a fresh sample of the same ionic liquid as that used in the first extraction step is not expected to be similar efficient because the aqueous phase is already equilibrated with the ionic liquid phase and "saturated" with the ions responsible for the ion exchange. Considering this fresh ionic liquid phase contains no platinum, further extraction of PtCl_6^{2-} towards the ionic liquid phase will only be due to the

presence of a chemical gradient between the two phases. To fulfil with the assumption of an ion exchange, PtCl_6^{2-} might then be extracted as a neutral species associated with a cation present in the aqueous phase.

Such an assumption is verified experimentally with experiments 2 to 4. In experiments 2 and 3, two extraction cycles with [OMIM][NTf₂] were carried out. According to the results obtained in Table 1, and taking into account a volume ratio (V_w/V_{IL}) of 2 and the initial concentrations of Pt(IV) in the aqueous phase, the values for the percentage of extraction of Pt(IV) in experiments 2 and 3 are expected to be 90 and 97 % respectively. Results show that only 72 and 82 % Pt(IV) were removed from the aqueous solutions from experiments 2 and 3, respectively.

This small influence of the number of consecutive extraction cycles using [OMIM][NTf₂] on the extraction of Pt(IV) was further evidenced carrying out experiment 4, in which three consecutive extraction cycles with [OMIM][NTf₂] were carried out. According to Table 1, an extraction efficiency of 99 % is expected. Experimentally, despite an initial concentration of Pt(IV) of 5 mM and a volume ratio of 1, only 85 % of Pt(IV) was extracted.

The results shown here reveal that when distribution coefficients are not significantly high enough, the ion exchange mechanism occurring in the extraction of Pt(IV) using [OMIM][NTf₂] is a drawback to the elaboration of efficient separation processes. Consecutive extraction cycles, such as those classically used in hydrometallurgical processes involving an extracting agent and extracting phase, are not usable with ionic liquids.

In experiments 2 to 4, the second step of the process was carried out using Cyphos 102 and starting from the aqueous phases obtained after extraction towards [OMIM][NTf₂]. Over 99.9 % of Pd(II) and Pt(IV) remaining in water were extracted. Because the extraction of platinum is not quantitative using [OMIM][NTf₂] in the first step of the process proposed here, Cyphos 102 necessarily contains Pt(IV) and Pd(II). Pt(IV) is found to be extracted quantitatively.

This also represents a limitation to the development of industrially relevant separation processes based solely on [OMIM][NTf₂] and Cyphos 102. Nevertheless, because of the ionic nature of ionic liquids, electrodeposition of Pt(IV) and Pd(II) can be envisaged.^{29,37–39} This solution, if proved feasible would have the advantage of providing a straightforward separation of Pt(IV) from Pd(II) without requiring any additional hydrometallurgical or pyrometallurgical process.

Conclusion

The extraction of Pt(IV) from 1 M HCl aqueous solutions using [OMIM][NTf₂] was studied with respect to the initial concentration of Pt(IV). It appears that the distribution coefficient of Pt(IV) decreases with the initial concentration of PtCl_6^{2-} in water. Extraction of Pt(IV) using Cyphos 102 leads to distribution coefficients above 5000.

Pd(II) was not extracted towards [OMIM][NTf₂] whatever the concentration of HCl in the aqueous phase. On the other hand, extraction of Pd(II) was quantitative using Cyphos 102. The

extraction mechanism appears to involve a modification of the palladium complex changing from PdCl_4^{2-} to PdBr_4^{2-} and an ion exchange.

Starting from the above mentioned results, a process for the separation of Pt(IV) and Pd(II) from aqueous solutions containing 1 M HCl was proposed using [OMIM][NTf₂] and Cyphos 102 as selective extracting phases. In the first step of the process, Pt(IV) was extracted as PtCl_6^{2-} using [OMIM][NTf₂]. Because the distribution coefficient for Pt(IV) is relatively low under our experimental conditions and because an ion exchange mechanism is involved in the extraction of these anionic metal complexes, we observed that quantitative extraction of Pt(IV) could not be achieved, even carrying out repeated extraction cycles using [OMIM][NTf₂]. Palladium, on the other hand, was not significantly extracted towards [OMIM][NTf₂].

In a second step of the process, extraction of Pd(II) and of the remaining Pt(IV) ions was carried out contacting the aqueous phase using Cyphos 102. In this case, quantitative extraction of Pd(II) and Pt(IV) was achieved.

Investigation on the low distribution coefficients for Pt(IV) observed after carrying out a second and third extraction step will be carried out shortly. Electrochemical reduction of PtCl_4^{2-} within [OMIM][NTf₂] and PdBr_4^{2-} within Cyphos 102 will be the subject of a forthcoming article.

Finally, the separation of Rh(III) from Pt(IV) and Pd(II), and the application of ionic liquids to the recycling of PGM from spent automotive converters will be under investigation shortly.

Acknowledgements

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Notes and references

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Table 1 - Distribution coefficients for Pt(IV) from aqueous solutions containing 1 M HCl and different initial concentration of Pt(IV) using [OMIM][NTf₂] or Cyphos 102.

| | 1 mM Pt(IV) | 3 mM Pt(IV) | 4.5 mM Pt(IV) | 8 mM Pt(IV) |
|---------------------------|---------------------|---------------------|---------------|-------------|
| [OMIM][NTf ₂] | 11.2 | 6.4 | 4.5 | 2.8 |
| | 2.5 mM Pt(IV) | 6 mM Pt(IV) | | |
| Cyphos 102 | > 5 10 ³ | > 5 10 ³ | | |

Table 2 – Distribution coefficient for Pd(II) as a function of the acidity of the aqueous solution using Cyphos 102 or [OMIM][NTf₂]. Initial concentration of Pd(II) is 5 mM.

| | 1 M HCl | 2 M HCl | 4 M HCl | 8 M HCl |
|---------------------------|---------|---------|---------|---------|
| [OMIM][NTf ₂] | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| Cyphos 102 | 3400 | 2983 | 3020 | 2024 |

Table 3 - Separation of Pt(IV) and Pd(II) in a two step process using first [OMIM][NTf₂] and second Cyphos 102. Number of extraction cycles, volume ratio (V_w/V_{IL}), concentration of metals and percentage of extraction for each metal after extraction step.

| Exp. n° | Ionic liquid | Number of cycles | V_w/V_{IL} | Initial conc. mM | | % E | |
|---------|---------------------------|------------------|--------------|------------------|--------|--------|--------|
| | | | | Pt(IV) | Pd(II) | Pt(IV) | Pd(II) |
| 1 | [OMIM][NTf ₂] | 1 | 1 | 200 | 465 | 89 | 4 |
| | Cyphos 102 | 1 | | 24 | 450 | > 99.9 | > 99.9 |
| 2 | [OMIM][NTf ₂] | 2 | 1.9 | 1445 | 240 | 71 | < 5 |
| | Cyphos 102 | 1 | | 416 | 245 | > 99.9 | > 99.9 |
| 3 | [OMIM][NTf ₂] | 2 | 1.9 | 500 | 320 | 92 | 19 |
| | Cyphos 102 | 1 | | 44 | 256 | > 99.9 | > 99.9 |
| 4 | [OMIM][NTf ₂] | 3 | 1 | 1000 | 335 | 85 | 19 |
| | Cyphos 102 | 1 | | 150 | 300 | > 99.9 | > 99.9 |

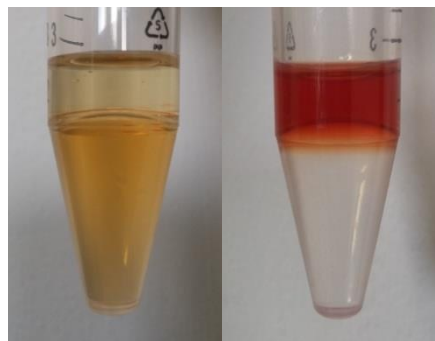
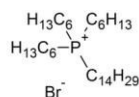
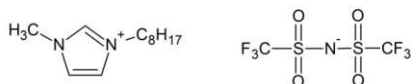


Fig. 3 – Snapshots prior and after extraction of Pd(II) from 1 M HCl towards Cyphos 102. Ionic liquids phase is on top.



Trihexyltetradecylphosphonium bromide [Cyphos 102]



1-octyl-3-imidazolium bis(trifluoromethanesulfonyl)imide [OMIM][NTf₂]

Fig. 1 – Structure of ionic liquids used in this study

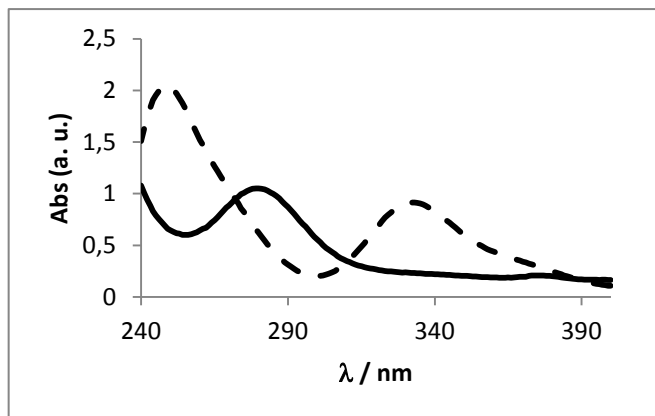


Fig. 2 – UV-Vis spectra of PdCl₄²⁻ (full line) and PdBr₄²⁻ (dashed line) in aqueous solutions containing 1 M HCl.

Graphical abstract

Extraction of Pt(IV) using 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and of Pd(II) using trihexyltetradecylphosphonium bromide (Cyphos 102) is reported. Extraction of Pd(II) using Cyphos 102 was found to be quantitative. Separation of Pt(IV) from Pd(II) was carried out in a simple two step process. Nevertheless, quantitative separation of both metals were not achieved due to limitations related to the extraction mechanism of metallic ions using ionic liquids.

