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ARTICLE TYPE

Extraction of iridium(IV) from aqueous solutions using hydrophilic/hydrophobic ionic liquids

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Anionic complexes of iridium(IV) were extracted from acidic solutions of HCl using ionic liquids (IL). Influence of the cation structure of IL and of the aqueous phase pH on the distribution coefficients of $IrCl_6^{2-}$ was investigated. Liquid-liquid extraction and precipitation of iridium(IV) were studied. Iridium(IV) was precipitated out from aqueous solutions using water-soluble ionic liquids by forming a water-insoluble salt composed of two cations from the ionic liquid. Pyridinium cations appear to be the most efficient at precipitating out iridium(IV). Iridium(IV) was found to be efficiently extracted using simple hydrophobic ionic liquids, exhibiting *D* values ranging up to 71. Investigations on the extraction mechanism tend to show that iridium(IV) is exchanged with two $[NTf_2]^-$ anions from the IL phase. Finally, elution of iridium(IV) from ionic liquid towards aqueous solutions was carried out from $[BMIM][NTf_2]$, $[OMIM][NTf_2]$ or $[OdMIM][NTf_2]$ into solutions containing high amounts of hydrochloric acid or nitric acid.

Introduction

Iridium is a rare and precious metal found in the earth crust in extremely low concentration, typically 2 ppb. It is found in primary ores of platinum, such as those found in South Africa. In such ores, iridium can be found in various proportions, ranging from above 25 % down to less than 1 %. It is however generally low, typically below 1 % in weight of the overall precious metals content, an amount similar to that of gold.[1-3]
Iridium, platinum and other platinum group metals, so-called PGMs, are generally present together in ores and are difficult to separate because they are very similar elements. Ir and Pt are neighbours in the periodic table and exhibit oxidation states of II and IV. Both Pt(IV) and Ir(IV) are able to form octahedral complexes such as $PtCl_6^{2-}$ or $IrCl_6^{2-}$. For the latter anions, typical extraction process involve ternary amines such as trioctylamine or phosphate compounds as extracting agents and kerosene as the extracting phase.[4-7]
Ionic liquids are now well-known organic salts melting at or near room temperature. The diversity of available cations and anions confers them very specific physicochemical properties. Used as extracting phases, and with or without extracting agents, ionic liquids have proven to be promising phases for the selective extraction of numerous metallic ions.[8] Even though the extraction mechanism are still the subject to discussions, the extraction of negatively charged metal complexes appears to be mainly due to some anion exchange between the anion from the ionic liquid (such as bis(trifluoromethanesulfonyl)imide) and the metal complex.[9-14] Removal of metal from water is also possible by forming a water-insoluble ion pair formed with one or more cations of the IL and a negatively charged metal complex.[11,14]

After having recently reported results on the extraction of gold(III) and platinum(IV) and their subsequent separation,[11,12,14] we focus here on the extraction of iridium(IV) from acidified aqueous solutions using ionic liquids.
Such a study is justified for several reasons. First, iridium is a precious metal with a high price (approximately 10^3 €/kg), which confers a significant added-value to any alternative extraction and purification process of the metal. Second, iridium is used in several industrial and high technology applications such as electronics and telecommunications. It is also used in several other applications including alloys with platinum to yield highly resistant anodes,[15] high temperature crucibles,[16] specific catalysts in organic chemistry[17] and even more recently catalysts for the electrocatalytic reduction of carbon dioxide.[18] It is also used as electrodes together with platinum in spark plugs in internal combustion engines. Such spark plugs electrodes usually range between 5 to 15 % in mass of iridium, the rest being composed of platinum.[19] Third, efficient and selective extraction of iridium from ores or wastes such as spark-plug electrodes is difficult using current processes. Fourth, on a more fundamental level, studying the extraction of iridium and its separation from gold or platinum, its immediate neighbour in the periodic table, is useful for gaining better insight into the extraction abilities of ionic liquids towards negatively charged metallic complexes. Our previous works dealing with Au(III) and Pt(IV) reported extraction of chloro-, bromo-, or thiocyanocomplexes of these metals.[11,14] However, the formation of $IrBr_6^{2-}$ starting from $IrCl_6^{2-}$

salt is the subject of contradictory reports in the literature. We were not able to obtain such hexabromoiridate(IV) complexes in water, even after heating a solution containing K_2IrCl_6 and an excess of KBr for a week at 60 °C. On the other hand, iridum(IV) was reported to oxidize thiocyanate anion in water leading to the formation of cyanide anion.[20] Therefore, the study reported in this article focussed on the extraction of $IrCl_6^{2-}$ in aqueous solutions containing 10^{-2} to 12 M HCl, using two ways of removing $IrCl_6^{2-}$, namely liquid-liquid extraction or precipitation.

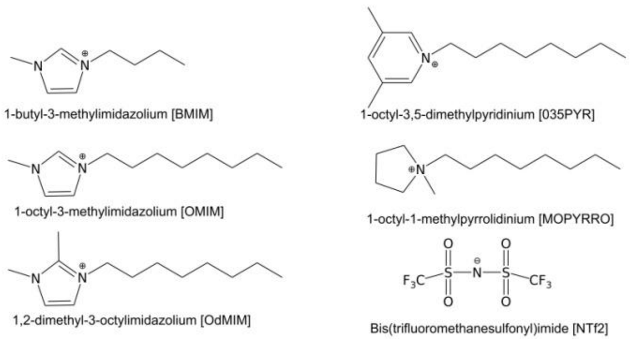

Fig 1 - Structures and abbreviations of ions used in this study.

Liquid-liquid extraction experiments were carried out using hydrophobic ionic liquids 1-butyl-3-methylimidazolium bis(trifluromethanesulfonyl)imide [BMIM][NTf_2], 1-octyl-3-methylimidazolium bis(trifluromethanesulfonyl)imide [OMIM][NTf_2], 1-octyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [OdMIM][NTf_2], 1-octyl-1-methylpyrrolidinium bis(trifluromethanesulfonyl)imide [MOPYRRO][NTf_2] or 1-octyl-3,5-dimethylpyridinium bis(trifluromethanesulfonyl)imide [O35PYR][NTf_2] as extracting phases. Structures and abbreviations of the ions used in this study are presented in Fig. 1. $[BMIM]^+$ and $[OMIM]^+$ cations are based on the same unsaturated heterocycle containing a delocalised positive charge, and two different alkyl chain lengths. $[OdMIM]^+$ cation includes a methyl group on the carbon bound to the two nitrogens, which replaces the labile hydrogen present on the $[BMIM]^+$ and $[OMIM]^+$ cations. These three cations were chosen because they belong to the family of ionic liquids studied the most in the literature. $[O35PYR]^+$ is a six-membred unsaturated heterocycle containing a delocalised positive charge. On the other hand, $[MOPYRRO]^+$ cation is a saturated five-membred heterocycle embedding a localized positive charge, as opposed to the unsaturated imidazolium cation.

Precipitation experiments were carried out using hydrophilic ionic liquids [OMIM][Br], [OdMIM][Br] or [O35PYR][Br], accordingly. Since no reaction of $IrCl_6^{2-}$ and bromide anions were observed in our studies, the presence of bromide anions did not modify the nature of the iridium(IV) complex during the time of the investigation.

The extraction mechanism for the liquid-liquid extraction of iridium(IV) using [OMIM][NTf_2] was studied experimentally adding Li[NTf_2] to aqueous phases containing K_2IrCl_6 prior to the extraction experiments.

Back extraction studies were carried out starting from several ionic liquid phases containing $IrCl_6^{2-}$ and several leaching phases containing either HCl or HNO_3.

Experimental

Materials

K_2IrCl_6 was provided by Johnson Matthey 39,37 % Ir titration), and used as is. 37 % HCl solution was purchased by Sigma Aldrich and used as is. Ionic liquids were sysnthesized using bromooctane (purity 99 %), 1-methylimidazole (purity 99 %) and 1,2-dimethylimdazole (purity 99%) provided by Alfa Aesar and used without further purification. Lithium bis(trifluoromothanesulfonyl)imide was provided by Solvionic and used as is. Ionic liquids were synthesized using reported procedure REF. Purity was checked using silver nitrate tests and NMR.

Instrumentation

Experiments were carried out using an orbital shaker with a rotation speed of 260 rpm.

Centrifugation was carried out on 3-10 centrifuge from Sigma.

UV-Vis spectra were recorded on a Cary 50 from Varian using a 1 -cm quartz cell.

^{1}H NMR spectra were recorded on a 400 MHz spectrometer from Brucker. Deuterated DMSO was used as solvent.

The pH of the aqueous solutions prior and after the extraction experiments carried out at 0.01 and 0.1 M HCl were measured using a HI221 pH meter from Hanna Instruments and a HI1131 pH electrode.

Extraction protocols

Precipitation of Ir(IV)

Precipitation of iridium(IV) complexes was carried out using aqueous solutions containing various concentrations of water-soluble ionic liquids. To that end, a stock solution containing 1 M HCl and 1.1 mM K_2IrCl_6 was first prepared. Precipitation experiments were then carried out typically mixing 2 cm^3 of the above mentioned aqueous solution with 2 cm^3 of a solution containing 1 M HCl and concentrations of [OMIM][Br], [OdMIM][Br] or [MOPYRRO][Br] accordingly, ranging from 10^{-3} to 2 10^{-2} M. The mixture was left on a shaker for one hour. When a precipitate of a red-brownish colour was observed, the tube was centrifuged for 15 min. The aqueous phase was then analysed by UV-Vis spectroscopy as detailed further.

Liquid-liquid extraction of $IrCl_6^{2-}$

Stock solutions of K_2IrCl_6 containing concentrations of HCl ranging from 10^{-2} to 12 M HCl accordingly, were prepared dissolving K_2IrCl_6 in aqueous solutions of HCl.

Liquid-liquid extraction experiments were then carried out contacting in a centrifuge tube, 3 g of each stock solution mentioned above with a volume of ionic liquid yielding a volume ratio V_w/V_{IL} of 5. Densities of HCl solutions are available in the literature.[21] Densities of ionic liquids were assumed to be 1.3 ± 0.02 $g.cm^{-3}$ for all octyl-based ionic liquids. The density of [BMIM][NTf_2] was taken as 1.40 ± 0.02 $g.cm^{-3}$.

The tube was then left on a shaker for 12 hours and then centrifuged for 15 min. An aliquot of the aqueous phase was then taken from the tube and the concentration of $IrCl_6^{2-}$ was measured with the help of UV-Vis spectroscopy as detailed below.

In addition, six aqueous solutions containing 0.01, 0.017, 0.024, 0.051, 0.074 and 0.1 M Li[NTf$_2$] were prepared by adding the desired mass of Li[NTf$_2$] into a solution at pH 1 and 10^{-3} M K_2IrCl_6. Then, 3 cm^3 of each solution was mixed with 0.6 cm^3 of [OMIM][NTf$_2$]. After mixing and centrifuging as detailed above, the aqueous phase was analysed using UV-Vis spectroscopy.

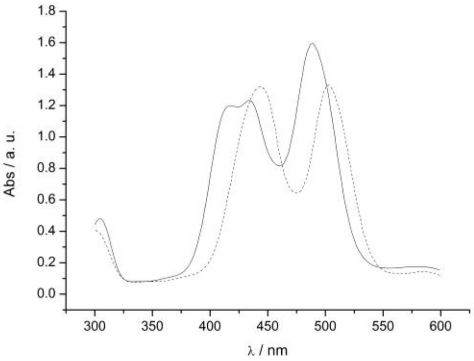

Fig. 2 – UV-Vis absorption spectrum for $IrCl_6^{2-}$ dissolved in a 1 M HCl solution (−) or in DMSO (---).

Back-extraction of Ir(IV) ions

Elution experiments were carried out starting from several ionic liquid phases obtained after liquid-liquid extraction, thus containing $IrCl_6^{2-}$. Typically, 0.5 cm^3 of the ionic liquid was mixed with 4 mL of an aqueous phase containing either 5 M HCl, 12 M of HCl or 5 M HNO_3. After mixing and centrifuging as detailed above, the aqueous phase was analysed using UV-Vis spectroscopy.

Measurements

The final concentration of $IrCl_6^{2-}$ was determined by UV-Vis spectrophotometry, applying the Beer-Lambert's law at the maximum absorption wavelength (λ_{max} = 489 nm) of iridium and using calibration solutions ranging from 10 to 100 µM. In all cases, a correlation factor of 0.999 and above for the Beer-Lambert's law was obtained. Values for the molecular extinction coefficients of 3400, 3900, 6380 and 1900 mol.L^{-1}.cm^{-1} were calculated for iridium (IV) dissolved in aqueous solutions containing 0.1, 1, 4 and 7.8 M HCl, respectively. Fig. 2 presents a typical UV-Vis spectra of iridium(IV) dissolved in an acidic phase.

For the precipitation experiments, the extraction efficiency of iridium from water ($Ir_{extr}\%$) is calculated as following:

$$Ir_{extr}\% = 100\frac{[IrCl_6^{2-}]^{Init} - [IrCl_6^{2-}]^{Final}}{[IrCl_6^{2-}]^{Init}} \qquad (1)$$

where $[IrCl_6^{2-}]$ refers to the concentration of $Ir_2Cl_6^{2-}$ in water, and the superscripts *Init* and *Final* refer to the values measured prior or after the extraction experiment, respectively. The value of $Ir_{extr}\%$ is calculated within ± 0.2 %.

For the liquid-liquid extraction experiments, the distribution coefficient (D) was calculated using the following formula.

$$D = \frac{[IrCl_6^{2-}]^{Init} - [IrCl_6^{2-}]^{Final}}{[IrCl_6^{2-}]^{Final}}\frac{V_w}{V_{IL}} \qquad (2)$$

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 5. The detection limit of our analytical method was set to 5 10^{-6} M. The maximum D value measurable in this study was assumed to be 10^3. The relative uncertainty on D is ± 5 %. All experiments are performed in duplicates

Results and discussions

Precipitation of Ir(IV)

Results show that no precipitation occurs when 1.1 mM $IrCl_6^{2-}$ and 2.2 mM of [OMIM][Br] or [OdMIM][Br] are mixed accordingly. Precipitation was observed using higher concentrations of ionic liquid of 0.01 M and above.

[O35PYR][Br] is the most efficient ionic liquid for precipitating $IrCl_6^{2-}$ out from a 1 M HCl solution. With this cation, iridium was removed so efficiently from the aqueous phase that the remaining concentration was below the detection limit of our analytical method. Such results are in agreement with those reported for Au(III) precipitation, which had shown that 1-octylpyridinium bromide was more efficient at removing $AuBr_4^-$ complexes from water than [OMIM][Br].

Replacing the labile hydrogen of the imidazolium cation by a methyl group yielded lower extraction percentages of $IrCl_6^{2-}$. For instance, using 0.01 M of [OMIM][Br] or [OdMIM][Br], extraction percentages of 81 or 23 % for $IrCl_6^{2-}$ were obtained accordingly. Increasing the concentration of ionic liquid in the solution leaded to a higher extraction efficiency. Values of 98 and 71 % were obtained using 0.02 M of [OMIM][Br] or [OdMIM][Br].

As reported previously for Au(III) or Pt(IV) in HCl media, these results fully support the assumption that precipitation of $IrCl_6^{2-}$ in presence of cations of ionic liquids yields the formation of an insoluble ionic liquid containing $IrCl_6^{2-}$ anion. The reaction of precipitation can then be written as following

$$2[OMIM]^+ + IrCl_6{}^{2-} \rightarrow [OMIM]_2[IrCl_6]_{solid} \qquad (3)$$

and the solubility product is then calculated as

$$K_s = [OMIM]^2[IrCl_6] \qquad (4)$$

A sample of the powder obtained mixing [OMIM][Br] or [OdMIM][Br] with K_2IrCl_6 in 1 M HCl solution was collected and ^{1}H NMR spectrum was recorded. As expected, the spectrum obtained was similar to that of [OMIM][Br] cation, confirming the presence of [OMIM]$^+$ cation in the precipitate and the formation of [OMIM]$_2$[IrCl$_6$] as shown in eqn (4).The UV-Visible spectrum of a sample of the precipitated salt dissolved in DMSO showed absorption bands similar to those recorded for K_2IrCl_6 in water. Since the cations of the ionic liquids do not exhibit any absorption band in the visible region, the absorption bands shown in Fig. 2 are due to the $IrCl_6^{2-}$ anion. Due to the DMSO, a small bathochromic shift was observed.

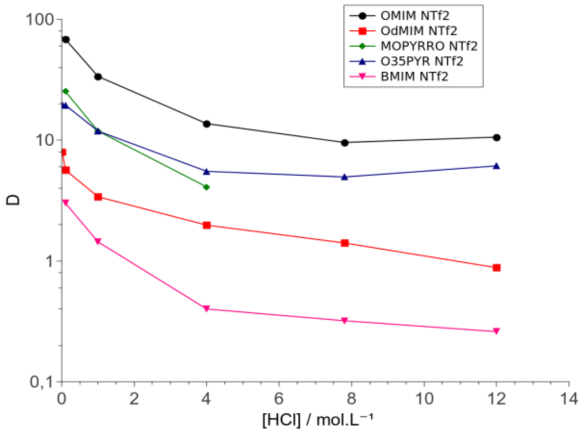

Fig. 3 - Distribution coefficients for $IrCl_6^{2-}$ as a function of HCl concentration in water. (●): [OMIM][NTf_2]. (♦): [MOPYRRO][NTf_2]. (▲): [O35PYR][NTf_2]. (■): [OdMIM][NTf_2]. (▼): [BMIM][NTf_2].

Solubility products calculated according to eqn (4) are reported in Table 2. The values are found to be below 10^{-8}, and are in the range of the K_s values reported previously for platinum(IV) at 1 M HCl. According to eqn (4), values of 1.35 10^{-8}, 0.62 10^{-8} and 1.16 10^{-8} for K_s were calculated from the results obtained using 0.01, 0.02 or 0.04 M [OMIM][Br], respectively. These values are close from one another and are within the experimental error of our analysis method. Therefore, an average value of 1.04 10^{-8} was assigned to the K_s (see Table 1). Similarly, an average value of 8.40 10^{-8} was calculated for $[OdMIM]_2[IrCl_6]$.

Interestingly, $[O35MPYR]_2[IrCl_6]$ exhibits a K_s value below 4 10^{-10}, which is two orders of magnitude lower than that obtained with [OMIM][Br]. Because similar observations had been reported with $AuCl_4^-$, our results confirm that the pyridinium cation generally interacts in a stronger way with polyhalogenometallate anions than imidazolium. Such a result might be explained by the important electron delocalisation on the pyridinium ring, which yields interactions between the π electrons and the electron pairs of the chloride anions from the anionic metal complex.

Industrial extraction processes regularly use selective precipitation procedures using ammonium chloride in order to precipitate iridium(IV) or platinum(IV) out from water under the form of $(NH_4)_2IrCl_6$ or $(NH_4)_2PtCl_6$, accordingly. The solubility of ammonium hexachloroiridate(IV), reported to be 7.7 or 12.1 g.kg^{-1} water at 20 and 30 °C respectively,[22] corresponds to K_s values of 9.10^{-6} and 3.5 10^{-5} respectively. In order to extract iridium(IV), typical concentrations of 0.5 M or 1 M NH_4Cl are therefore used in the process. The K_s values of $(NH_4)_2IrCl_6$ are therefore up to five orders of magnitude higher than those reported in this study. This implies that iridium(IV) could be precipitated out from water using a concentration of water-soluble ionic liquid one or two orders of magnitude lower than that of ammonium chloride classically used.

Overall, these results tend to confirm that water-soluble ionic liquids are promising alternative salts for the precipitation of iridium(IV) dissolved in an aqueous solution containing HCl.

Liquid-liquid extraction of $IrCl_6^{2-}$

All results are reported in Table 2. For comparison reasons, distribution coefficients have been plotted as a function of HCl concentration in Fig. 3.

Because [BMIM][NTf_2] has been used in several articles dealing with the extraction of metallic ions with ionic liquids, this IL was used for the extraction of $IrCl_6^{2-}$ in water. Results show that [BMIM][NTf_2] is a poor extracting phase for iridium(IV), yielding *D* values below 3 whatever the pH of the aqueous phase.

Replacing butyl with octyl yields higher distribution coefficients. At the same pH, the *D* values obtained with [OMIM][NTf_2] are systematically 20 to 30 times higher than those obtained with [BMIM][NTf_2]. Compared to other ionic liquids based on pyridinium, pyrrolidinium or dimethylimidazolium cations, [OMIM][NTf_2] yields highest D values reported in this study.

[OdMIM][NTf_2] corresponds to [OMIM][NTf_2] with an additional methyl group replacing the labile hydrogen on the imidazolium ring. Using this IL, distribution coefficients towards iridum(IV) appear to be one order of magnitude lower than those obtained using [OMIM][NTf_2], whatever the pH of the aqueous phase.

Obviously, the absence of a labile hydrogen reduces the interaction between $IrCl_6^{2-}$ and the imidazolium ring. This is most probably due to the fact that the labile hydrogen binds somehow with the iridium(IV) complex such as Im....H^+....$IrCl_6^{2-}$, either weakly or strongly, the hydrogen moving thus towards the $IrCl_6^{2-}$ anion. Because in the case of [OdMIM][NTf_2] such an interaction does not occur, $IrCl_6^{2-}$ is less attracted towards the imidazolium ring.

Using a different cation such as $[O35PYR]^+$ or $[MOPYRRO]^+$ yields extraction efficiencies that are lower than that obtained with [OMIM][NTf_2], but higher than that for [OdMIM][NTf_2]. Surprisingly, even though the *D* values measured here using [O35PYR][NTf_2] and [MOPYRRO][NTf_2] are of similar values. Even though this proves the influence of the structure of the cation ring (imdazolium vs. other cation ring) on the extraction efficiency of iridium(IV), there appears to be no significant difference between a pyridinium or a pyrrolidinium with regards to their extraction efficiency towards iridium(IV). The relatively low *D* values obtained with [O35PYR][NTf_2] are surprising because, as seen in the preceding section dealing with the precipitation of Ir(IV), $[O35PYR]^+$ cation appears to associate in a stronger way to $IrCl_6^{2-}$ anion than $[OMIM]^+$ cation does in order to form a neutral pair insoluble in water. The interactions involved in the liquid-liquid extraction of $IrCl_6^{2-}$ using ionic liquids are not necessarily the same as those involved in the precipitation of $IrCl_6^{2-}$.

For all ionic liquids studied here, *D* values decrease monotonously with the concentration of acid. This tends to show that the extraction mechanism is similar with all ionic liquids used here. As explained in the following sub-section, no straightforward explanation was found so far for the decreased in *D* with HCl concentration.

Because platinum and iridium are neighbour atoms in the periodic table, because they are always present together in ores and because they usually are extracted very similarly in classical solvent extraction process,[8] comparing the results reported here with those previously obtained for platinum(IV) is relevant. First, unlike previous reports dealing with the extraction of Ir(IV) and Pt(IV), ionic liquids provide extracting phases which are more efficient at extracting Ir(IV) than Pt(IV) at low concentration of [HCl]. For instance, at a pH of 0.1 and using [OMIM][NTf$_2$], *D* values of 68 and 5.5 have been obtained for Ir(IV) and Pt(IV) respectively. At higher pH, this trend changes with [OMIM][NTf$_2$].[14]

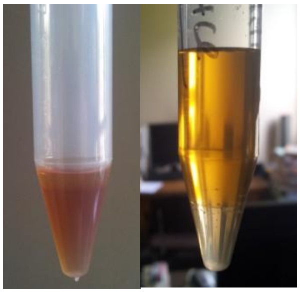

Fig. 4 - Snapshots of back extraction of iridium(IV). First snapshot: iridium(IV) extracted in 0.7 g [BMIM][NTf$_2$]. Second snapshot: back extraction of iridium(IV) after adding 4 mL of 37 % HCl solution to the ionic liquid phase from the first snapshot.

Second, the results obtained here are consistent with the assumption previously presented stating that the extraction of such anionic metal complexes can be qualitatively correlated with the solvation energy of the cation in water, hence with the charge density of metal complex. The distribution coefficients obtained with [OMIM][NTf$_2$] for $IrCl_6^{2-}$ is higher than those for $PtCl_6^{2-}$ but lower than those obtained for $PtBr_6^{2-}$. This trend is consistent with the thermochemical radius of $IrCl_6^{2-}$ (3.35 Å), compared to that of $PtCl_6^{2-}$(3.13 Å) and $PtBr_6^{2-}$ (3.42 Å).[23]

Mechanism of liquid-liquid extraction

Because the values for the molecular extinction coefficients at 489 nm calculated for iridium(IV) dissolved in water containing various concentrations of HCl vary significantly, the metallic ion is present under different forms in solution. In addition, since D decreases with the concentration of HCl in water, one can assume that the iridium(IV) complex is extracted under different protonated forms, namely $IrCl_6^{2-}$, $HIrCl_6^-$ or H_2IrCl_6. No significant variation of the UV-Vis spectrum has been found when increasing the concentration of HCl. In the UV region, however, a weak absorption band was found to slightly shift from 303 to 301 nm with [HCl] and the shape of the peak changed from a distinct peak to a shoulder. This might also be an insight into the formation of different protonated forms of the $IrCl_6^{2-}$ complex.

Plotting log(D) vs. Log([HCl]) yielded linear regressions with all ionic liquids studied here. Slopes ranged from -0.4 and -0.6. Such a behaviour has already been reported previously for metals in ILs or organic solvents.[7,12] This was generally attributed to the simultaneous and competitive extraction of Cl^- or HCl_2^- anions towards the organic phase. Nevertheless, in the absence of any pKa data for H_2IrCl_6, and without additional experiments, it is not possible at this point to elaborate further on the subject.

Extraction mechanism was thus further investigated by measuring the distribution coefficients for $IrCl_6^{2-}$ from an aqueous phase containing various amounts of Li[NTf$_2$] salt. Experiments were carried out using [OMIM][NTf$_2$] and aqueous solutions at pH 1, because a high value for *D* (68) was obtained under these conditions. Furthermore, the maximum concentration of Li[NTf$_2$] used in these experiments is 0.1 M, because above that concentration, no significant extraction of $IrCl_6^{2-}$ was observed and no reliable *D* values could be calculated. On the other hand, because the solubility product of [OMIM][NTf$_2$] in 0.1 M HCl was found to be 1.1 g.L^{-1} (corresponding to 2.3 10^{-3} mol.L^{-1} of [OMIM][NTf$_2$] in water, as reported very recently)[24] and because the concentration of [NTf$_2$]$^-$ anion originating from Li[NTf$_2$] added to the solution needs to be significantly higher than that initially present (2.3 mM), a minimum concentration of Li[NTf$_2$] 0.01 mol.L^{-1} was used.

Results are collected in Table 3 and show that extraction of iridium(IV) decreases with the concentration of salt added in water.

Since Li[NTf$_2$] can be regarded as a hydrophilic salt, Li$^+$ and NTf$_2^-$ ions were assumed to remain in the aqueous phase during the extraction experiment. Even though we are aware this assumption is not completely true, it is valid as a first approximation.[25] The concentration of [NTf$_2$]$^-$ anion was then calculated taking into account the solubility in water of [OMIM][NTf$_2$]

$$K_s = x(x + [LiNTf_2]) \qquad (5)$$

with *x* the concentration of [OMIM]$^+$ cation, and [*LiNTf$_2$*] the concentration of Li[NTf$_2$] salt added to the solution. K_s is the solubility product of [OMIM][NTf$_2$]. The concentration of [NTf$_2$]$^-$ anion in the solution is here simply

$$[NTf_2^-]_{aq} = x + [LiNTf_2] \qquad (6)$$

Similarly to previous reports dealing with the extraction of gold(III) and platinum(IV),[11,14] such a behaviour is assumed to be related to an ion exchange between the iridium complex and [NTf$_2$]$^-$ anions. Due to electroneutrality during the extraction process, this exchange can be described as following

$$2\overline{NTf_2{}^-} + IrCl_6^{2-}{}_{aq} \rightarrow 2NTf_2{}^-{}_{aq} + \overline{IrCl_6^{2-}} \qquad (7)$$

where the subscript *aq* refers to the aqueous phase and the overline represents the ionic liquid phase. Following eqn (7), one writes

$$K_{ex} = \frac{[NTf_2^-]_{aq}^2\overline{[IrCl_6^{2-}]}}{[IrCl_6^{2-}]\overline{[NTf_2^-]}^2} \qquad (8)$$

where K_{ex} is the equilibrium constant of eqn (6). Taking into account eqn (2), one obtains

$$D = \frac{\overline{[NTf_2^-]}^2}{K_{ex}} \frac{1}{[NTf_2^-]_{aq}^2} \qquad (9)$$

D is therefore expected to vary linearly with 1/[NTf$_2^-$]^2. Plotting *D* as a function of [NTf$_2^-$]^2 as suggested in eqn (9) yields a linear regression with a good correlation factor (r^2=0.997). This confirms that the extraction of iridium follows an anion exchange with ILs based on [NTf$_2$] anions.

Back-extraction of Ir(IV) ions

Starting from the results provided in this study, simple back extraction procedures were carried out as presented in Table 4.

First, after extraction of iridium(IV) at 0.01 M HCl using [BMIM][NTf$_2$], the ionic liquid pregnant with iridium(IV) was contacted with a 12 M HCl aqueous phase. The volume of water was equal to five times that of the ionic liquid. The ionic liquid lost its brown colour upon contact, and after 2 minutes, most iridium was back extracted in the aqueous phase. Fig. 4 presents two snapshots, one from [BMIM][NTf$_2$] taken after iridium(IV) is extracted towards the ionic liquid phase, and one after [BMIM][NTf$_2$] was contacted with a concentrated HCl solution. Spectrophotometric analysis revealed that approximately 80 % of the iridium(IV) was recovered from [BMIM][NTf$_2$] by this method. Because the distribution coefficients at 8 M HCl are very close to those obtained at 12 M, similar results were obtained when contacting [BMIM][NTf$_2$] containing iridium(IV) with a solution of 12 M HCl.

Similar experiments were carried out with [OdMIM][NTf$_2$]. Results showed that at approximately 56 % of the iridium previously extracted in [OdMIM][NTf$_2$] could be back extracted in an 8 M HCl solution.

Considering the distribution coefficients reported here for iridium(IV) complexes with [OMIM][NTf$_2$] are always above 9 whatever the pH, back extraction of iridium(IV) from this ionic liquid using HCl solutions was not possible. Instead, aqueous solutions containing HNO_3 were used. In this case, 67 % of $IrCl_6^{2-}$ was back extracted in a 33 % HNO_3 solution. This is due to the fact that nitrate anions are extracted more significantly towards the ionic liquid phase than chloride ions do.

Conclusion

Five hydrophobic and three hydrophilic ionic liquids have been used for removing $IrCl_6^{2-}$ from water containing various concentrations of HCl. Ionic liquids based on the $[NTf_2]^-$ anion appear to be promising phases for the extraction of iridium from solution containing platinum(IV) and Au(III).

Precipitation of iridium(IV) using water-soluble ionic liquids was carried out successfully starting from 1 mM $IrCl_6^{2-}$ and concentration of IL ranging from 2 to 40 mM. The precipitate was composed of two ionic liquid cations and one $IrCl_6^{2-}$ complex. K_s values obtained in this study were found to be up to five orders of magnitude lower than that obtained for $(NH_4)_2IrCl_6$. At low HCl concentration (pH 2), liquid-liquid extraction of iridium(IV) ranged between 7 and 70 using octyl-based ionic liquids. Distribution coefficient for $IrCl_6^{2-}$ was found to generally decrease with the HCl concentration. [BMIM][NTf$_2$] yielded low *D* values, because it embeds a short butyl chain, reducing the hydrophobicity of the ionic liquid, compared to its octyl homologues presented here. Except for [OMIM][NTf$_2$] at 12 M HCl, extraction of iridium(IV) was found to be more efficient than that of platinum(IV). Study of the extraction mechanism suggests that $IrCl_6^{2-}$ exchanges with two $[NTf_2]^-$ anions of the ionic liquid.

Back extraction of iridium(IV) from [BMIM][NTf$_2$] or [OdMIM][NTf$_2$] was also proven to be possible using 8 or 12 M HCl solutions. With [OMIM][NTf$_2$], back extraction was efficient using nitric acid.

Ionic liquids therefore have proven once again to be very versatile compounds for the extraction of a precious metal such as iridium(IV), yielding very different *D* values depending on their ion structure.

Further works, including separation of Ir(IV) from Au(III) or Pt(IV) using ionic liquids, the influence of interfering ions on the extraction of Ir(IV), as well as the selective electrochemical deposition of these metal complexes within an ionic liquid, and the influence of Au(III), Pt(IV) and Ir(IV) contaminants on the electrochemical deposition of each metal will shortly be carried out.

Notes and references

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Table 1 - Precipitation of $IrCl_6^{2-}$ in 1M HCl solutions using water-soluble ionic liquids.

Ionic liquid	[IL] / mol.L-1	$Ir_{extr}\%$	$10^8\ K_s$
[OMIM][Br]	0.0022	0	1.04 ±0.42
	0.0101	81.3	
	0.0194	98.6	
	0.0400	99.4	
[O35PYR][Br]	0.0100	>99.9	<0.04
	0.0200	> 99.9	
[OdMIM][Br]	0.0022	0	8.40 ±1.06
	0.0100	22.7	
	0.0195	71.5	

Table 2 - Extraction efficiency ($Ir_{extr}\%$) and distribution coefficients (*D*) for $IrCl_6^{2-}$ extracted from water using several ionic liquids.

Ionic Liquid	$[HCl]\ /\ mol.L^{-1}$	*D*
$[OMIM][NTf_2]$	0.01	71.4
	0.1	68.5
	1	33.7
	4	13.7
	7.8	9.57
	12	10.6
$[OdMIM][NTf_2]$	0.01	7.98
	0.1	5.67
	1	3.40
	4	1.98
	7.8	1.41
	12	0.88
$[MOPYRRO][NTf_2]$	0.1	25.3
	1	11.9
	4	4.10
$[O35PYR][NTf_2]$	0.01	19.6
	0.1	19.5
	1	11.9
	4	5.52
	7.8	4.96
	12	6.12
$[BMIM][NTf_2]$	0.01	3.25
	1	1.44
	4	0.42
	7.8	0.34
	12	0.28

Table 3 - Distribution coefficients for $IrCl_6^{2-}$ obtained using $[OMIM][NTf_2]$ and aqueous phase containing various concentrations of $LiNTf_2$. [HCl] = 0.1 $mol.L^{-1}$.

$LiNTf_2$ / 10^{-3} $mol.L^{-1}$	10^6 Ks	$[NTf_2^-]$ / $10^{-3} mol.L^{-1}$	*D*
10.02	5.36	10.53	3.354
16.94	5.36	17.25	1.610
24.32	5.36	24.54	0.865
50.73	5.36	50.83	0.415
74.44	5.36	74.51	0.337
101.4	5.36	101.5	0.250

Table 4 - Back-extraction of $IrCl_6^{2-}$ from $[BMIM][NTf_2]$, $[OdMIM][NTf_2]$ or $[OMIM][NTf_2]$ into acidic solutions

Ionic Liquid	Acid	$[H^+]\ /\ mol.L^{-1}$	% *E*
$[OMIM][NTf_2]$	HNO_3	5	67.3
$[OdMIM][NTf_2]$	HCl	7.8	56.4
$[BMIM][NTf_2]$	HCl	7.8	80.5

Removal of iridium(IV) using hydrophilic or hydrophobic ionic liquids was studied. $IrCl_6^{2-}$ anionic metal complexes were precipitated out from water using bromide-based ionic liquids, yielding water-insoluble salts with low K_s values. Liquid-liquid extraction of Ir(IV) using $[NTf_2]$-based ionic liquids yielded distribution coefficients up to 70 with $[OMIM][NTf_2]$ at pH 2.