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# Quantitative extraction of Rh(III) using ionic liquids and its simple separation from Pd(II)

Lenka Svecova, Nicolas Papaiconomou and Isabelle Billard

The extraction of Pd(II) and Rh(III) from acidic solutions containing between 1 and 8 M HCl towards three ionic liquids, namely [P66614][Cl], [P66614][Br] and [P66614][DCA], based on the trihexyltetradecylphosphonium cation ([P66614]) and chloride, bromide or dicyanamide (DCA) anions, respectively, is reported. Extraction of Pd(II) is quantitative up to 6 M HCl ( $D > 3000$ ). A value of 258 for the distribution coefficient of Rh(III) extracted from 1 M HCl towards [P66614][Br] is also reported. [P66614][Cl] and [P66614][Br] were found to be very efficient at separating these two metals from aqueous solutions containing at least 6 mol L<sup>-1</sup> HCl.

## Introduction

Platinum group metals (PGM) include all elements from the 4th and 5th period and columns VIII to X. These metals exhibit very specific properties such as high conductivity, very high melting temperatures, high redox potentials and prominent catalytic properties. They are therefore used in a large range of applications including jewelry, electronics, hard-disks, chemical or fiber glass manufacturing and the automotive industry.<sup>1</sup>

Pt, Pd and Rh are currently used in automotive catalytic converters as catalysts in order to oxidize pollutants such as CO alkanes and NO<sub>x</sub> compounds present in exhaust gases. The amount of these metals in the present catalytic converters is far from negligible. Up to 10 g of PGM can be found in a diesel truck catalytic converter.<sup>2</sup>

Rhodium is amongst the rarest and most expensive metals on earth. Rhodium and other PGM are usually leached from ores using acidic solutions.<sup>3</sup> After the leaching steps, because of its size and speciation in water, Rh(III) is generally not quantitatively extracted (that is, extraction percentage below 98%, i.e.  $D < 49$ ) using classical extraction systems based on organic solvents and extracting agents. For instance, extraction of Rh(III) using toluene containing extracting agents such as TBP, CMPO, etc. yielded distribution coefficients ranging from 1 to 15 only.<sup>4–9</sup> Only a few studies reporting a quantitative Rh extraction were identified in the literature. In these studies, 99% of Rh(III) was extracted from aqueous solutions containing 1 and 2 M HCl using tin chloride and either Cyanex 923 in toluene,<sup>10</sup> a malonamide compound in 1,2 dichloroethane<sup>11</sup> or N,N-dioctylhexanamide in 1-octanol.<sup>12</sup> Therefore, new and simpler extracting systems for Rh(III) are still to be found.

Ionic liquids have become the subject of intense research over a decade now due to their unexpected physical and chemical properties such as hardly measurable vapor pressure, low melting point, high thermal stability, moderate viscosity, tunable solubility in solvents, relatively large conductivity and high electrochemical stability. ILs have therefore been used in all fields of chemistry including catalysis, electrochemistry or liquid–liquid extraction. In the latter case, extraction of metal ions has been studied by many groups either as a simple replacement to volatile organic solvents (VOC) in conjunction with an extracting agent,<sup>13–15</sup> or as a replacement to both extracting solvent and extracting agent.<sup>16–20</sup> Other studies have dealt with task-specific ionic liquids, ionic liquids that embed a functional group specifically designed to interact with a targeted metal ion.<sup>21–25</sup> In all these studies, ionic liquids based on imidazolium, pyrrolidinium, pyridinium or phosphonium cations were mostly investigated.

Regarding PGM, the extraction of Pt(IV) and Pd(II) using several neat ionic liquids, such as those based on trioctylammonium or alkyltrioctylammonium cations have been studied recently.<sup>26</sup> Neat hydrophobic ionic liquids based on imidazolium, pyridinium or pyrrolidinium cations were also found to be efficient at extracting Au(III)<sup>27</sup> or Ir(IV).<sup>28</sup> We also reported extraction of Pd(II) using neat phosphonium-based ionic liquids and showed that separation of Pt(IV) from Au(III)<sup>18</sup> or Pd(II)<sup>20</sup> was possible. Extraction of Pd(II) was also studied using ILs based on phosphonium or pyridinium cations diluted in kerosene or chloroform accordingly.<sup>29,30</sup>

The case of Rh(III) is however specific among PGM. Until now, similarly to what was reported using classical extracting systems, extraction of Rh(III) towards ionic liquids remained low. Unlike Pd(II), Rh(III) is not extracted quantitatively towards hydrophobic ionic liquids based on ternary and quaternary linear ammonium cations.<sup>26</sup> The highest value for the distribution coefficient of Rh(III) was reported to be 16 only at 0.01 M HNO<sub>3</sub> using extracting agents such as TBP, CMPO and Aliquat 336 added to the ionic liquid.<sup>31</sup> Furthermore, such systems were found unable to extract Rh(III) at higher concentrations of nitric acid such as 6 M HNO<sub>3</sub>. More recently, thermomorphic ionic liquids were used as extracting phases for Rh(III).<sup>32</sup> Another approach investigated by Cieszyńska et al.,<sup>29</sup> consisting of diluting trihexyltetradecylphosphonium chloride in toluene, also appeared inefficient. Pd(II) was found to be extracted efficiently while Rh(III) remained again in the aqueous phase.<sup>33</sup>

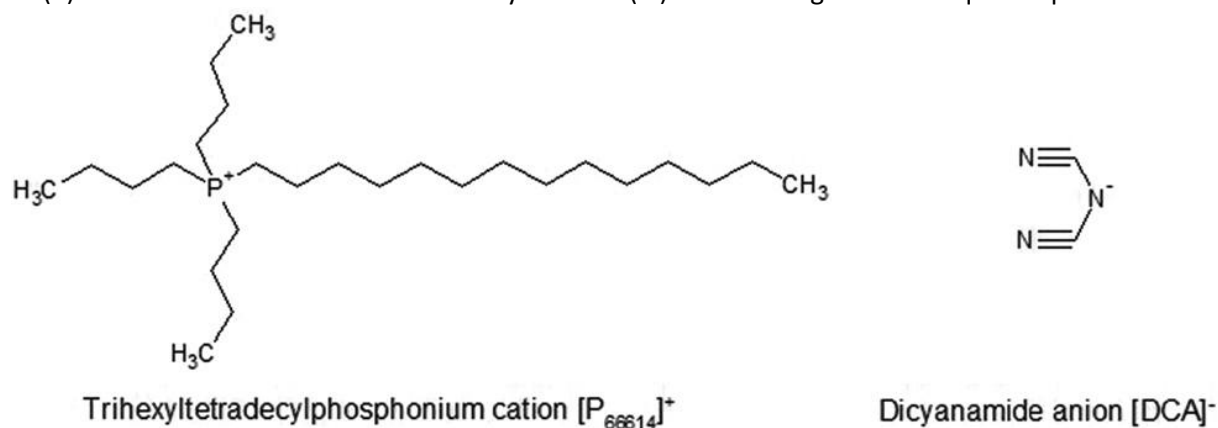


Fig. 1 Structure of ions used in this study.

Within our research group, new extracting systems based on ILs being capable of quantitatively separating PGM present in spent automotive catalytic converters are investigated. As no successful attempt at extracting rhodium quantitatively from acidic solutions using any type of extracting systems has been reported so far, we focused on the extraction of Rh(III) and its separation from Pd(II) using hydrometallurgical methods based on ionic liquids (IL) containing trihexyltetradecylphosphonium cations ([P66614]<sup>+</sup>). One advantage of such ionic liquids lies in the fact that because of the increased hydrophobicity of the cation, no hydrophobic and perfluorinated anion is required to yield water-immiscible ionic liquids. Small and environmentally benign anions<sup>34</sup> such as halide or dicyanamide are enough to obtain a hydrophobic ionic liquid.<sup>35–38</sup> Moreover, as these anions are good complexing agents of PGM ions, efficient extraction can be expected. New results dealing with the efficient extraction of Rh(III) and Pd(II) and their separation from aqueous phases containing between 1 and 8 M HCl towards three different hydrophobic ionic liquids based on the trihexyltetradecylphosphonium cation and chloride ([P66614][Cl]), bromide ([P66614][Br]) and dicyanamide ([P66614][DCA]) anions as extracting phases (structures and abbreviations for the ionic liquids are shown in Fig. 1) will thus be presented here.

## Experimental

### Chemicals

Potassium hexachlororhodate(III) (K<sub>3</sub>RhCl<sub>6</sub>) and sodium tetrachloropalladate( II) (Na<sub>2</sub>PdCl<sub>4</sub>·3H<sub>2</sub>O) were purchased from Alfa Aesar and used as received. Concentrated hydrochloric acid (37% solution) was purchased from Sigma Aldrich and used as received. Cyphos 101 ([P66614][Cl]), 102 ([P66614][Br]), and 105 ([P66614][DCA]) were gratefully provided by Cytec and were used without any further purification.

### Single metal extraction

Two sets of stock solutions containing 250 mg L<sup>-1</sup> of Rh(III) or Pd(II) accordingly, and 1, 2, 4, 6 and 8 M HCl were first prepared.

Because the mutual solubilities of water and ionic liquids<sup>37,39</sup> are low and because in our study no variation in the volumes of aqueous and ionic liquid phases was observed upon mixing, no preliminary step consisting of saturating both phases with each other was carried out in this study. Extraction was then performed by mixing 4.1 grams of metal solution together with 1 g of [P66614]-based ILs in a PP tube. Taking into account the densities of the aqueous solution and the ionic liquid, the volume ratio of water and IL, so-called  $V_{aq}/V_{IL}$ , was thus equal to 3.4.

The tubes were then fixed on a horizontal shaker and left for 24 h at room temperature and 30 rpm before being centrifuged for 20 minutes at 3000 rpm in order to separate the two phases. The aqueous phases were then analysed using ICP-OES after appropriate dilution.

#### Separation of Rh(III) and Pd(II)

In order to study the separation of Rh(III) and Pd(II) under similar conditions, a first set of solutions using the same concentration for both metals (250 mg L<sup>-1</sup>) was prepared dissolving K<sub>3</sub>RhCl<sub>6</sub> and Na<sub>2</sub>PdCl<sub>4</sub> together in 1, 6 or 8 M HCl accordingly.

Taking into account that the mass of rhodium in a spent catalyst is generally 3 to 10 times smaller than that of palladium, a second set of solutions containing 50 mg L<sup>-1</sup> Rh(III) and 250 mg L<sup>-1</sup> Pd(II) was also prepared in 1, 6 or 8 M HCl. Extraction experiments starting from solutions containing 1 M HCl were carried out using [P66614][Cl], [P66614][Br] and [P66614][DCA]. At a higher HCl concentration, the extraction experiments were carried out using [P66614][Cl] and [P66614][Br].

Experiments were carried out in a way similar to that detailed in the preceding section (i.e. same contact time, same separation and analytical procedure).

#### Measurements

For all extraction experiments, initial and final aqueous concentrations for Pd(II) and Rh(III) were determined by ICP-OES. To that end, calibration solutions ranged from 0 to 50 and from 0 to 100 mg L<sup>-1</sup> for Rh(III) and Pd(II) ( $\lambda_{em} = 343.49$  nm for Rh(III),  $\lambda_{em} = 340.45$  nm for Pd(II)) respectively.

Distribution coefficients (D) and extraction efficiencies (E%) were calculated as follows:

$$D = \frac{(C_i - C_f) \times V_{aq}}{C_f \times V_{IL}} \quad (1)$$

$$E\% = \left(1 - \frac{C_f}{C_i}\right) \times 100 \quad (2)$$

where  $C_i$  and  $C_f$  are the initial and final metal concentrations respectively in the aqueous phase and  $V_{aq}$  and  $V_{IL}$  are the volumes of aqueous and ionic liquid phases, respectively. The extraction coefficients are given  $\pm 5\%$  and the maximum value for D that can be obtained following our analytical procedure is 3200.

For separation experiments, the separation factor  $\beta$  was also calculated:

$$\beta = \frac{D_{Pd}}{D_{Rh}}$$

## Results and discussion

### Single extraction of Rh(III)

As shown in Fig. 2, initial rhodium solutions exhibit colors changing gradually from brown pink at 1 M HCl to pink at 8 M HCl. This is in agreement with previous results dealing with the spectrophotometric study of Rh(III) solution in HCl and stating that  $[RhCl_5(H_2O)]^{2-}$  is predominant at concentrations of 1 to 4 M HCl whereas  $[RhCl_6]^{3-}$  is mostly formed above 3 M HCl.<sup>40–42</sup>

[P66614][Cl]. Snapshots of the extraction of Rh(III) towards [P66614][Cl] from acidic solution have been collected in Fig. 2. At 1 M HCl, the initially pink aqueous solution becomes colorless within few minutes. The ionic liquid then turns to an intense brown pink color. At 8 M HCl, the ionic liquid remains colorless while the aqueous phase remains unchanged.

Distribution coefficients and extraction efficiencies for Rh(III) using [P66614][Cl] are collected in Table 1 and Fig. 3. The rather high value of 73.9 (compared to the literature) for the distribution coefficient of Rh(III) obtained at 1 M HCl decreases sharply with the concentration of HCl and is mostly zero at 4 M HCl and above.

Previous articles dealing with the extraction of Rh(III) using extracting agents diluted in organic solvents such as kerosene also observed such a decrease at  $[HCl] > 4\text{ M}$ , however these articles have reported much lower  $D$  values compared to the studied system.<sup>4,10</sup> These observations were then related to the speciation of Rh(III) in HCl solutions. Because  $[RhCl_5(H_2O)]^{2-}$  is predominant below 4 M HCl and  $[RhCl_6]^{3-}$  is the major species above 4 M it is concluded that the higher the negative charge of the complex, the lower the distribution coefficient is.

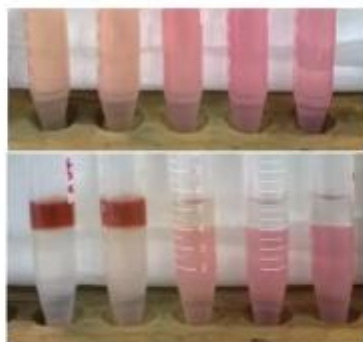


Fig. 2 Top: Snapshots of aqueous solutions containing rhodium(III). Bottom: Snapshots of the extraction of Rh(III) towards  $[P_{66614}][Cl]$  (IL in the top phase). From left to right for all snapshots: 1, 2, 4, 6 and 8 M HCl  $[Rh(III)] = 250\text{ mg L}^{-1}$ .

**Table 1** Influence of IL nature and of HCl concentration on extraction efficiency of Rh(III)

IL	$[HCl]\text{ mol L}^{-1}$	$D$	Efficiency (%)
$[P_{66614}][Cl]$	1	73.9	95.1
	2	11.9	76.5
	4	<0.05	0.6
	6	<0.05	0
	8	<0.05	0
$[P_{66614}][Br]$	1	258	98.7
	2	224	98.5
	4	66.7	95.3
	6	0.32	8.8
	8	<0.05	0
$[P_{66614}][DCA]$	1	12.9	81.3
	2	10.9	73.2
	4	2.5	43.4
	6	<0.05	0
	8	<0.05	0

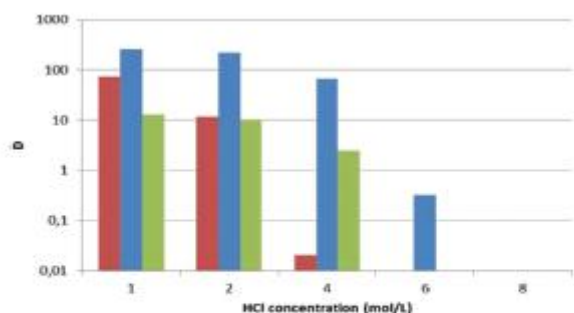
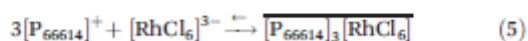
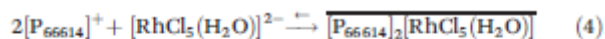


Fig. 3 Distribution coefficient for Rh(III) as a function of HCl concentration.  $[Rh(III)] = 250\text{ mg L}^{-1}$ . Red:  $[P_{66614}][Cl]$ . Blue:  $[P_{66614}][Br]$ . Green:  $[P_{66614}][DCA]$ .

As all hydrophobic ionic liquids,  $[P66614][Cl]$  exhibits a low but not negligible solubility in water.<sup>39</sup> The IL cations can therefore interact directly with the metal complex to be extracted in the aqueous phase. On this basis and similarly to what was previously presented for Pt(IV) or Pd(II) ions extracted

towards hydrophobic ionic liquids based on [NTf<sub>2</sub><sup>-</sup>] anions,<sup>17</sup> or phosphonium cations<sup>20</sup> and taking into account the change in Rh(III) speciation, the extraction can be explained using the following equations:



where the bar over the species indicates their presence in the organic phase. Eqn (4) is expected to occur mainly at  $[\text{HCl}] \leq 3 \text{ M}$ , while eqn (5) occurs at  $[\text{HCl}] \geq 6 \text{ M}$ . In addition, the reaction described in eqn (5) is expected to occur at a much lesser extent than that described in eqn (4). This is due to the fact that  $\text{RhCl}_6^{3-}$  is a trivalent anion and its solvation energy is expected to be higher in absolute value than that of  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ .  $\text{RhCl}_6^{3-}$  is thus less easily extracted out from an aqueous phase compared to  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ . Furthermore, the ionic liquid phase plays the role of a reservoir of ionic liquid cations. Therefore, any such cation extracted together with Rh(III) according to eqn (4) or (5) is expected to be replaced by another cation from the ionic liquid phase. A very recent article by our group has also shown that extraction of  $\text{PtCl}_6^{2-}$  occurred even when the concentration of this complex was above that of the ionic liquid cation and that the distribution coefficients were very well described using equations similar to eqn (4) or (5).<sup>43</sup>

Please note that the extraction mechanism for Rh(III) could also be discussed in terms of an ion exchange mechanism. However, according to the same paper mentioned above<sup>43</sup> and to that of another group dealing with the extraction of Au(III),<sup>44</sup> these two extraction mechanisms are indeed equivalent. We therefore decided to describe our results in terms of an ion pair formation mechanism.

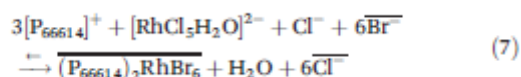
The decrease in D observed here can however also be interpreted by assuming a competitive extraction between  $\text{Cl}^-$  and the rhodium complex as proposed previously.<sup>20</sup> In this case, it is expected that the higher the concentration of  $\text{Cl}^-$ , the higher its extraction towards the ionic liquid, and the lower the extraction of the targeted Rh(III) complex. Such a competition between Rh(III) and  $\text{Cl}^-$  can be described by assuming extraction of  $\text{Cl}^-$  occurring simultaneously with that of the Rh(III) complexes and following the same extraction mechanism:



Such an equation was used previously to successfully describe the influence of the concentration of HCl on the extraction of  $\text{PtCl}_6^{2-}$ .<sup>43</sup> The competitive extraction of  $\text{Cl}^-$  has also been reported by several groups dealing with the extraction of such metal complexes towards classical organic solvents such as kerosene or chloroform containing an extracting agent (trioctylamine, tributylphosphate, etc.).<sup>33,45</sup> The two mechanisms described by eqn (4) to (6) are expected to occur simultaneously. At this point of discussion, it is however not possible to distinguish which mechanism is predominant and responsible for the decrease in extraction observed here.

[P66614][Br]. Distribution coefficients and extraction efficiencies are collected in Fig. 3 and Table 1. The distribution coefficient for Rh(III) at 1 M HCl is high (more than three times higher compared to [P66614][Cl] system), reaching a value of 258. Again, D decreases drastically when the concentration of HCl exceeds 4 M. No extraction is observed at 8 M HCl. As observed visually using [P66614][Cl], the aqueous phase becomes colorless within minutes upon coming into contact with the aqueous phases at 1 and 2 M HCl with [P66614][Br]. However the color of the Rh(III) loaded IL is different in this case as the IL turns into a dark green color. At 6 and 8 M HCl no significant extraction appears to occur as the aqueous solutions remain pink.

The dark green color observed in [P66614][Br] corresponds to the formation of a  $[\text{RhBr}_5(\text{H}_2\text{O})]^{2-}$  complex<sup>46</sup> formed consecutively to the extraction of a pentachloroaquorhodate(III) complex towards [P66614][Br] followed by its reaction with bromide ions from the ionic liquid, as depicted by the following equation:



This equation is proposed for two reasons. First, a UV-Vis spectrum of  $[\text{P}_{66614}][\text{Br}]$  recorded after extraction of Rh(III) in 4M HCl revealed an absorption band centered around 535 nm, as seen in Fig. 4. Such an absorption band is very similar to that reported previously for  $\text{RhBr}_6^{3-}$  in aqueous solutions.<sup>41</sup>

Therefore, the Rh(III) complex in the ionic liquid phase is most probably  $\text{RhBr}_6^{3-}$ . However, the exact metals' speciation in ILs is still very much unknown and should be studied more in detail soon. In addition, one  $\text{Cl}^-$  from the aqueous phases extracted together with the Rh(III) complex has been proposed in order to retain electroneutrality both in aqueous and ionic liquid phases. We are aware that the extraction mechanism is not explained in detail and gaining a clear and definite insight into the extraction mechanism, such as what specific polybromorhodate(III) complexes are extracted and what is the exact speciation of Rh(III) in the ionic liquid phase is of importance. This task is however very tedious, and far from the scope of this article.

This extraction mechanism is similar to that presented recently in our previous work dealing with the extraction of  $\text{PdCl}_4^{2-}$  by  $[\text{P}_{66614}][\text{Br}]$ , and involving the formation of a  $\text{PdBr}_4^{2-}$  complex in the ionic liquid.<sup>20</sup>

The presence of bromide anions in eqn (7) is due to the fact that above 6 M HCl, no extraction of Rh(III) occurs and no change in color of the aqueous solution is observed. This implies that Rh(III) does not bind with  $\text{Br}^-$  that are present in the aqueous phase due to the limited solubility in water of  $[\text{P}_{66614}][\text{Br}]$ . The change in the color of the ionic liquid phase along with the quantitative extraction of Rh(III) observed when it came into contact with an aqueous solution containing up to 4 M HCl is therefore necessarily related to the interaction between  $\text{Rh}^{3+}$  and the bromide anions from the ionic liquid.

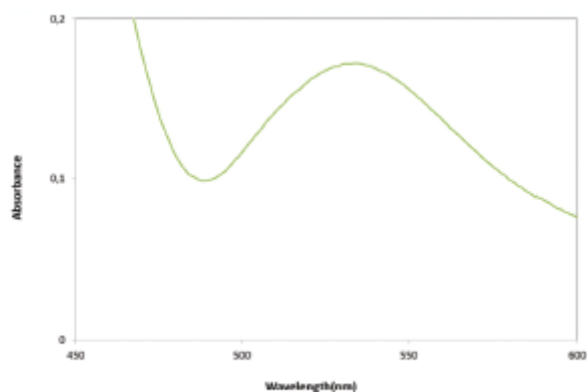


Fig. 4 UV-Vis spectrum of  $[\text{P}_{66614}][\text{Br}]$  after extraction of Rh(III) from an aqueous solution containing 4 M HCl. Blank is pure  $[\text{P}_{66614}][\text{Br}]$ .

Below 4 M HCl, the distribution coefficients obtained using  $[\text{P}_{66614}][\text{Br}]$  are always higher than those obtained using  $[\text{P}_{66614}][\text{Cl}]$ . This is due to the larger size and lower solvation energy of the  $[\text{RhBr}_5(\text{H}_2\text{O})]^{2-}$  complex compared to  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ . The latter is thus less keen on being extracted towards the ionic liquid. Above 6 M HCl, Rh(III) forms mostly  $\text{RhCl}_6^{3-}$  species that is preferentially solvated by water and is thus not extracted towards  $[\text{P}_{66614}][\text{Br}]$ . The decrease in extraction of Rh(III) above 6 M HCl is also related to some competition of  $\text{Cl}^-$  as discussed in the preceding subsection and described in eqn (6).

$[\text{P}_{66614}][\text{DCA}]$ .

Results for the extraction of Rh(III) using  $[\text{P}_{66614}][\text{DCA}]$  are also collected in Table 1 and Fig. 3. This ionic liquid was selected because it exhibited a low viscosity compared to  $[\text{P}_{66614}][\text{Cl}]$  and because dicyanamide is known to be coordinated with metallic ions.<sup>47</sup>



Results show that this ionic liquid is generally less efficient at extracting Rh(III) than its bromide and chloride homologues. Similarly to the previous observations using [P66614][Cl] and [P66614][Br], a decrease in D with the increasing concentration of HCl was observed. In addition, the kinetics of extraction appeared to be slower than that observed using [P66614][Cl] and [P66614][Br]. Upon coming into contact with the aqueous and IL phases, nearly no transfer towards the IL phase was observed within the first 30 min.

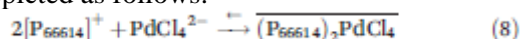
Moreover, during the extraction experiments, the IL first became turbid or gelatinous depending on the concentration of HCl. After a few days of ageing, a white precipitate was observed at the interface between the two phases. Similar observation was made after a sample of [P66614][DCA] came into contact with a 5 M aqueous HCl solution not containing any metal ion. This reveals that the white precipitate is not due to the presence of Rh(III). This phenomenon can be easily explained taking into account the fact that dicyanamide exhibits a pKa of approximately 5.48. The white precipitate is therefore expected to be dicyanoamine (HN(CN)<sub>2</sub>) which is not soluble in water. Moreover, in such a case, upon formation of dicyanoamine, the dicyanamide anion from the ionic liquid phase is necessarily replaced by another anion, namely chloride. Thus, [P66614][DCA] reacting with HCl will form [P66614][Cl] and dicyanoamine. A final confirmation of this assumption lies in the fact that an increase in viscosity is observed after coming into contact with the aqueous phase and [P66614][DCA]. Indeed, [P66614][Cl] is known to be significantly more viscous than its dicyanamide homologue.<sup>49</sup>

Obviously, because the distribution coefficients obtained with [P66614][DCA] differ from those obtained using [P66614][Cl], the dicyanamide anion is able to coordinate, at least partially, with Rh(III). Nevertheless, at this point of study, and because of the various phenomena described above, the reasons why the extraction of Rh(III) towards [P66614][DCA] is as reported are not clear.

#### Single extraction of Pd(II)

Extraction of Pd(II) using [P66614][Cl] starting from aqueous solutions containing between 1 and 8 M HCl has been carried out. Distribution coefficients and extraction yields are collected in Table 2 and in Fig. 5. Results show that extraction of palladium(II) is quantitative when the concentration of HCl is below or equal to 6 M, with D values ranging from 3200 to 363 at 1 and 6 M HCl, respectively. Please note that the maximum value is most probably above 3200, since the latter is the maximal value given according to our analysis protocol. At 8 M HCl, D reaches a value of 28.3, which is two orders of magnitude lower than that obtained below 4 M HCl.

As observed for Rh(III), extraction is high at low concentrations of HCl (up to 4 M) and decreases with the concentration of the acid. Following the results detailed above for Rh(III) and knowing that Pd(II) forms mostly a PdCl<sub>4</sub><sup>2-</sup> in aqueous HCl solutions,<sup>50</sup> the extraction of PdCl<sub>4</sub><sup>2-</sup> can be depicted as follows:



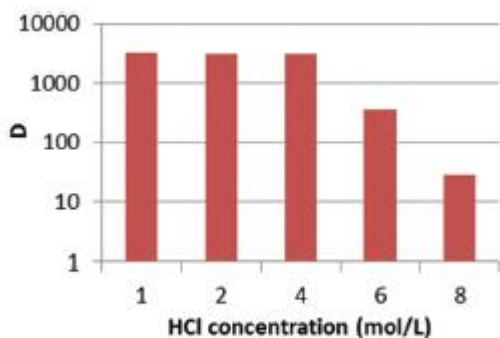
The occurrence of a competition between PdCl<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> according to eqn (6) accounts for the decrease in D reported here.

The results obtained with [P66614][Cl] are in agreement with, though systematically lower than, those previously obtained by our group when using [P66614][Br].<sup>20</sup> The lower values for D obtained using [P66614][Cl] can be explained similarly as above: Pd(II) is extracted towards [P66614][Br] in the form of PdBr<sub>4</sub><sup>2-</sup>, whereas it remains as PdCl<sub>4</sub><sup>2-</sup> within [P66614][Cl] (see eqn (8)). Because PdCl<sub>4</sub><sup>2-</sup> is smaller, it is more solvated by water than PdBr<sub>4</sub><sup>2-</sup>, and less extracted towards [P66614][Cl] than towards [P66614][Br]. Moreover, because PdCl<sub>4</sub><sup>2-</sup> is smaller than PdBr<sub>4</sub><sup>2-</sup> (hence a higher solvation energy in absolute value), one can expect the competition between PdCl<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> to play a more prominent role than in the case of PdBr<sub>4</sub><sup>2-</sup> extracted towards [P66614][Br]. We believe thus that the extraction of PdCl<sub>4</sub><sup>2-</sup> is more affected by the competition with Cl<sup>-</sup> than its bromide homologue.



**Table 2** Influence of IL nature and of HCl concentration on extraction efficiency of Pd(II)

IL	[HCl] mol L <sup>-1</sup>	<i>D</i>	Efficiency (%)
[P <sub>66614</sub> ][Cl]	1	3200	99.9
	2	3100	99.9
	4	3100	99.9
	6	363	99.2
	8	28.3	89.7
[P <sub>66614</sub> ][DCA]	1	91.4	96.5



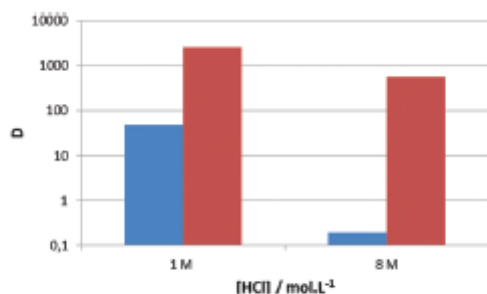
**Fig. 5** Influence of HCl concentration on Pd(II) extraction by [P<sub>66614</sub>][Cl]. [Pd] = 250 mg L<sup>-1</sup>,  $V_{aq}/V_{IL}$  = 3.4.

Extraction of Pd(II) towards [P<sub>66614</sub>][DCA] was also investigated. According to the stability issues observed using [P<sub>66614</sub>][DCA] at a high concentration of the acid, extraction was only carried out at 1 M HCl. Under these conditions, a value of 91.4 for *D* was obtained. This ionic liquid is therefore also a good extracting phase for Pd(II). Unlike what was observed with Rh(III), extraction of Pd(II) using this ionic liquid occurred within minutes, which might suggest a possible separation between Rh(III) and Pd(II) using [P<sub>66614</sub>][DCA] based on different extraction kinetics. Overall, these results show that ionic liquids based on trihexyltetradecylphosphonium cations are good extracting phases for palladium(II), whatever the acidity of the aqueous solution.

Separation of Rh(III) from Pd(II)

Taking into account the high values for the distribution coefficients of Pd(II) and the major influence of the concentration of HCl on the extraction of Rh(III) towards ionic liquids, separation of these two metals using ionic liquids was investigated. Values for the distribution coefficients and the separation factors are collected in Table 3. Plots of these data as a function of the concentration of HCl are also presented in Fig. 6 and 7.

As expected from the results gathered from single extraction studies, both metals are quantitatively extracted towards [P<sub>66614</sub>][Cl] and [P<sub>66614</sub>][Br] at 1 M HCl and the separation factor is low. The picture is very different at 6 or 8 M HCl. Here, [P<sub>66614</sub>][Cl] and [P<sub>66614</sub>][Br] quantitatively separate Pd(II) from Rh(III), the latter remaining in the aqueous phase. These results are in good agreement with the values for the distribution coefficients collected in the two preceding sections.



**Fig. 6** Distribution coefficients for the separation of 250 mg L<sup>-1</sup> Rh(III) from 250 mg L<sup>-1</sup> Pd(II) using [P<sub>66614</sub>][Br] and aqueous solutions containing 1 or 8 M HCl. Blue: Rh(III). Red: Pd(II).

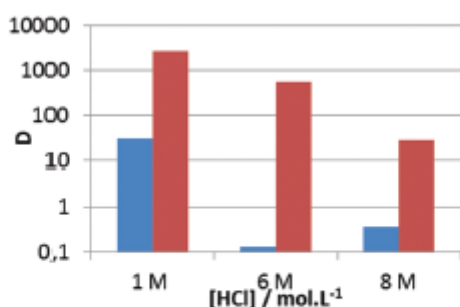


Fig. 7 Distribution coefficients for the separation of 50 mg L<sup>-1</sup> Rh(III) from 250 mg L<sup>-1</sup> Pd(II) using [P<sub>66614</sub>][Cl] and aqueous solutions containing 1, 6 or 8 M HCl. Blue: Rh(III). Red: Pd(II).

Only the D value for Pd(II) at 6 M HCl is slightly lower than that obtained from the single extraction experiments.

The separation factors ( $\beta$ ) range from ca. 30 to 13 300. Low separation factors, typically below 100, occurred starting from aqueous solutions containing 1 M HCl. In these cases, according to the results obtained from single extraction experiments, both Rh(III) and Pd(II) are extracted efficiently. High separation factors, typically above 3000 were obtained using 6 or 8 M HCl and yielded a quantitative extraction of Pd(II) towards [P<sub>66614</sub>][Cl] or [P<sub>66614</sub>][Br] while Rh(III) remained in the aqueous phase. Highest values for  $\beta$  are obtained using either [P<sub>66614</sub>][Br] at 8 M HCl or [P<sub>66614</sub>][Cl] at 6 M HCl.

Table 3 Influence of the nature of the ionic liquid and the HCl concentration on Pd/Rh competitive extraction at different Rh/Pd ratios

[Rh(III)] mg L <sup>-1</sup>	[Pd(II)] mg L <sup>-1</sup>	IL	[HCl] mol L <sup>-1</sup>	E% Rh	E% Pd	D <sub>Rh</sub>	D <sub>Pd</sub>	$\beta$
250	250	[P <sub>66614</sub> ][Cl]	1	93.7	99.87	47.7	2532	53.1
			6	5.34	99.41	0.19	570	3000
		[P <sub>66614</sub> ][Br]	1	96.5	99.9	95.5	>3000	>30
			6	31.5	99.6	1.38	740	536
		[P <sub>66614</sub> ][DCA]	8	5.07	99.9	0.2	2663	13 300
			1	40	99.9	2.30	>3000	>1300
		[P <sub>66614</sub> ][Cl]	1	91.7	99.9	31.3	2698	86.2
			6	5.68	99.6	0.13	552	4250
50	250	[P <sub>66614</sub> ][Br]	8	5.07	99.9	0.34	29.1	162
			1	96.7	99.9	103	>3000	>34
		[P <sub>66614</sub> ][Br]	6	11.5	99.6	0.39	825	2115
			8	5.26	99.8	0.2	2248	11 240

Usual leaching processes of PGM involve the use of concentrated acidic solutions such as aqua regia or HCl containing H<sub>2</sub>O<sub>2</sub>.<sup>51,52</sup> In these cases, [P<sub>66614</sub>][Cl] and [P<sub>66614</sub>][Br] are best suited to separate quantitatively Pd(II) from Rh(III). The extraction of Rh(III) is then achieved by simply diluting the aqueous phase in order to reach 4 M HCl for instance, allowing a quantitative extraction of Rh(III) towards [P<sub>66614</sub>][Cl] or [P<sub>66614</sub>][Br].

## Conclusion

The results presented here show that ionic liquids based on the trihexyltetradecylphosphonium cation are extremely good extracting phases for the extraction of Rh(III) and its separation from Pd(II).

To the best of our knowledge this is the first time that such high distribution coefficients for the extraction of Rh(III), reaching a value of 258 at 1 M HCl, are reported. A significant influence of the concentration of HCl on the distribution coefficient was observed. This seems to be directly linked to the change in speciation of Rh(III) from [RhCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> to RhCl<sub>6</sub><sup>3-</sup> when the concentration of HCl in water exceeds 4 M, and to the competitive extraction of Cl<sup>-</sup>. Moreover, the separation of Pd(II) from Rh(III) was obtained in one simple step using [P<sub>66614</sub>][Cl] or [P<sub>66614</sub>][Br] and starting from aqueous solutions containing 6 or 8 M HCl.

Stripping of these metal ions extracted towards [P<sub>66614</sub>][Cl] and [P<sub>66614</sub>][Br] as well as the electrodeposition of these PGM within these ionic liquids are currently under study. Application of such extracting systems to the recycling of PGM from end-of-life devices such as used catalytic converters will be carried out soon.

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