

Effective Separation of Pt(IV), Pd(II), and Rh(III) in Acidic Solution by Using Phosphonium-based Ionic Liquid

Mochamad L FIRMANSYAH¹, Fukiko KUBOTA¹, Masahiro GOTO^{1,2,*}

¹Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motoooka, Fukuoka, 819-0395, Japan; ²Center for Future Chemistry, Kyushu University, 744 Motoooka, Fukuoka, 819-0395, Japan

An interest in utilizing ionic liquids for solvent extraction has been increasing over these recent years. A novel phosphonium-based ionic liquid, trioctyl(dodecyl)phosphonium chloride ($P_{88812}Cl$) has developed and used for the extraction of platinum group metals (PGMs) (i.e Pt(IV), Pd(II), and Rh(III)) from HCl media, and then compared to that of commercial trihexyl(tetradecyl)phosphonium chloride ($P_{66614}Cl$). The extraction performance with $P_{88812}Cl$ was comparable to that of $P_{66614}Cl$. However, the extraction with $P_{88812}Cl$ was comparably faster than that of $P_{66614}Cl$, due to its lower viscosity than the latter. The stripping of metal-loaded ionic liquid could be achieved with HNO_3 , $CS(NH_2)_2$, and HCl for Pt(IV), Pd(II) and Rh(III), respectively.

1. Introduction

Precious metals located in the columns V-VIII and period 5 and 6 are classified into platinum group metals (PGMs). Due to their unique physicochemical properties, various high-end technology industry requires PGMs¹. Nowadays, primary production of PGMs is through mining. However, in few decades, PGMs would face a supply shortage due to the difficulty in substituting PGMs with other elements².

In recent years, researches in sustainable and environmentally friendly secondary production of PGMs has gained more interest. Solvent extraction has emerged as a suitable process for the recovery of PGMs. Various reagents have been studied and proposed, including quaternary ammonium salts, organophosphorus, and sulphides extractants^{3,4}. Recently, many publications have appeared on the synthesis and applications of ionic liquids (ILs), which classified as green organic solvents due to their negligible vapor pressure. In a ILs extraction system, ILs were able to act not only as the solvent but also as the extracting agent. This was found to be appealing to replace the conventional extraction system, which uses massive amount of organic solvent. Various type of ILs has been explored, including ammonium, imidazolium, pyridinium, and phosphonium-based ILs. Not only possessed negligible vapor pressure, ILs are also non-flammable under normal storage conditions. ILs are therefore not expected to pollute the environment, safe to breathe and are neither flammable or explosives⁵. The most interesting feature of ILs is the tunability of their physicochemical properties by designing the structure of the cation and anion constituents. Various combination of cation and anion constituents was also one of the way to tune ILs properties.

ILs have also been used in PGMs extraction. Previously, imidazolium and phosphonium-based ILs have been able to quantitatively extract Au(III), Pt(IV), Pd(II), and Ir(IV)⁶⁻⁸. However, based on the previous results, Rh(III) was difficult to extract in a conventional extraction system with an organic solvent as a diluting agent. Different behavior of Rh(III) extraction was observed when using an undiluted ionic liquid. A phosphonium-based IL, namely trihexyl(tetradecyl)phosphonium chloride (P₆₆₆₁₄Cl) was able to extract Rh(III) quantitatively in a single metal model solution.

It is required for ILs to use as extraction solvents that the ILs are hydrophobic and show low viscosity. The work presented here deals with the investigation of extraction and separation of Pt(IV), Pd(II), and Rh(III) based on the newly designed and synthesized phosphonium-based IL, trioctyl(dodecyl)phosphonium chloride (P₈₈₈₁₂Cl). The physicochemical properties including the extraction performance was compared to that of commercially available P₆₆₆₁₄Cl. The extraction behavior was investigated under the undiluted IL conditions.

2. Experimental

2.1 Reagents

Newly designed and synthesized ionic liquid, trioctyl(dodecyl)phosphonium chloride (P₈₈₈₁₂Cl), obtained from Nippon Chemical Industrial Co. Ltd, (Tokyo, Japan) and commercial trihexyl(tetradecyl)phosphonium chloride (P₆₆₆₁₄Cl) obtained from Ionic Liquids Technologies GmbH (Heibronn, Germany) were used as received. HCl, HNO₃, H₂SO₄, NH₄OH, CS(NH₂)₂, Pt(IV) and a Pd(II) standard solution were obtained from Wako Pure Chemical Ltd, (Osaka, Japan). A Rh(III) standard solution was purchased from Kanto Chemical Co. Inc (Tokyo, Japan).

2.2 Measurements

The fundamental properties of the ionic liquids, which were density, viscosity, and water content, were analyzed by using the density meter (DMA 35N, Anton Paar GmbH, Graz Austria), the viscometer (Lovis M/ME 200, Anton Paar GmbH, Graz Austria), the Karl-Fischer moisture meter (CA-200, Mitsubishi Chemical Analytec, Co. Ltd, Tokyo Japan), respectively. The concentration of each element in an aqueous phase was measured by the inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8300, Perkin-Elmer Co., MA, USA).

2.3 Extraction procedure

A set of aqueous phases in 0.1-5 mol L⁻¹ HCl with 100 mg L⁻¹ of each Pt(IV), Pd(II), and Rh(III) was prepared. An aqueous phase and an undiluted IL phase were mixed at volume ratio 2 in a PP tube, and then shaken mechanically at 160 rpm for 3 hours. All parameters were kept constant, unless mention otherwise. the stripping was conducted with various stripping solution (HCl, HNO₃, H₂SO₄, NH₄OH, and CS(NH₂)₂) at a similar manner. The distribution ratio of the metal in both phases, D (-), and the stripping percentage, S (%), were calculated as follows:

$$D = \frac{C_{org}}{C_{aq}} \quad (1)$$

$$S\% = \frac{C_{st}V_{st}}{C_{st}V_{st} + C_{org}V_{org}} \times 100 \quad (2)$$

Where V and C were the volume and the metal concentration, respectively, and subscript aq , org ,

and *st* denote the aqueous, the organic, and the stripping phase, respectively.

3. Results and Discussion

3.1 Extraction behavior of Pt(IV), Pd(II), and Rh(III) with a phosphonium IL.

Figure 1 shows the distribution ratio of Pt(IV), Pd(II), and Rh(III) with P₈₈₈₁₂Cl as a function of the HCl concentration. As observed, Pt(IV) and Pd(II) were quantitatively extracted, whereas the extraction performance of Rh(III) seemed to be very low. The *D* values were increasing along with the increase in the HCl concentration until it reaches the highest point at 0.5 mol L⁻¹ HCl. Further increase in the HCl concentration caused a decrease in the *D* values of all the metal species. Rh(III) extraction seems to suffer the most upon the increase of the HCl concentration. The decrease in the high HCl concentration was probably due to the presence of massive amount of Cl ions. The high amount of Cl ions could also create extraction competition between metal and Cl ions¹³, leading to the decrease in the extraction performance of the ionic liquids in a high HCl concentration.

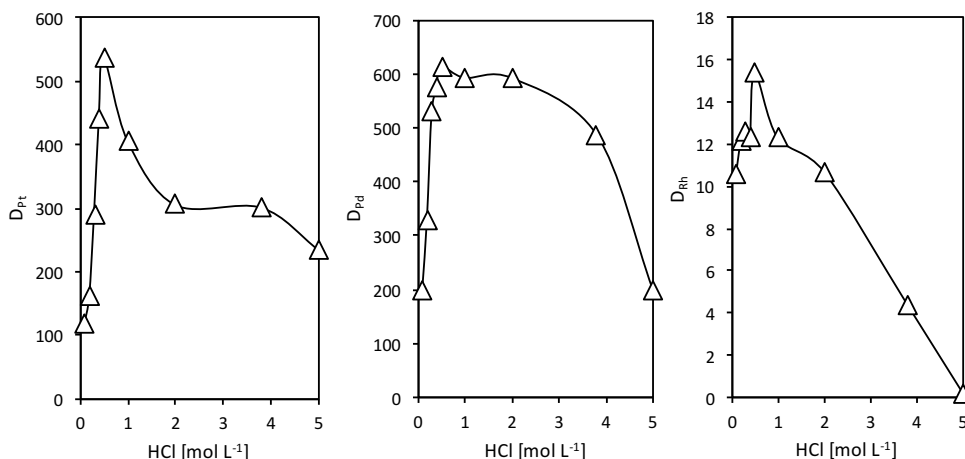


Figure 1. Effect of HCl concentration on the distribution ratio of the metals with P₈₈₈₁₂Cl

The change in metal chlorocomplex species of Rh(III) was also one of the reason for the decrease in the extraction performance. According to the speciation diagram of several previous studies, in 5 mol L⁻¹ HCl, Rh(III) mainly exists in the form of RhCl₆³⁻ (70%) and RhCl₅²⁻ (30%). With the decrease of the HCl content, the species composition has been changed to RhCl₅²⁻ (80%) and RhCl₆³⁻ (20%). The significant difference in molecular sizes of RhCl₆³⁻ and RhCl₅²⁻ would affect their charge to the size ratio or the charge density¹⁴. The difficulty of the metal ion extraction was inversely proportional to their charge density. Thus, RhCl₅²⁻, which has higher charge density was ready to extract compared to that of RhCl₆³⁻. A similar extraction performance has been observed with commercial P₆₆₆₁₄Cl.

3.2 Properties of ionic liquids

The physicochemical properties of the ionic liquids are important to use as extraction solvents because they affect the extraction performance. As shown in Table 1, the density of the novel P₈₈₈₁₂Cl

was similar to that of P₆₆₆₁₄Cl. However, it was found that P₈₈₈₁₂Cl possesses a significantly lower viscosity compare to that of P₆₆₆₁₄Cl (Table 1), which would be effective for the extraction process of metal ions due to the increase in the diffusion rate⁹, as describe later.

Table 1. Physicochemical properties of the ILs

Ionic Liquid	Density [g mL ⁻¹]	Viscosity [mPa.s]	Water Content [wt%]	Cation Release [mg L ⁻¹]
P ₈₈₈₁₂ Cl	0.8799	800.8	7.72	0.301
P ₆₆₆₁₄ Cl	0.8767	1930.5	11.92	6.887

The water content of ionic liquids and the phosphorus (P) release into the aqueous phase after contacting ILs with water at the volume ratio of 2 (Water/IL) were analyzed and the results were listed in Table 1. The newly designed P₈₈₈₁₂Cl not only showed less P release, but also lower water content compared to those of P₆₆₆₁₄Cl. The lower release property could be associated with higher hydrophobicity and smaller loss of the ionic liquid constituent compare to P₆₆₆₁₄Cl¹⁰. Along with the low water content of P₈₈₈₁₂Cl, which would minimize the cation aggregation, these factor would minimize the decrease in their extraction performance of P₈₈₈₁₂Cl^{11,12}. In addition, P₈₈₈₁₂Cl appear to be environmentally friendlier compare to P₆₆₆₁₄Cl due to the lower release of phosphorus (P) to the aqueous phase. As for P element is heavily regulated in water environment, such as waste water.

3.3 Extraction rate

Time course of the extraction percentage was measured with 200 mg L⁻¹ metal concentration at 0.5 mol L⁻¹ HCl at V_{aq}/V_{IL} 4. Novel P₈₈₈₁₂Cl could achieve the extraction equilibrium of Pt(IV) and Pd(II) within 30 min, whereas the conventional P₆₆₆₁₄Cl took more than 60-80 min to achieve the equilibrium. Although the extraction rate of Rh(III) was slower compared to that of Pt(IV) or Pd(II), the extraction equilibrium with P₈₈₈₁₂Cl was attained at around 80 min, while more than 150 min was required to reach equilibrium with P₆₆₆₁₄Cl. As described earlier, the viscosity of the ILs also affected to the diffusion rate of the metal ions into the ILs phase. Three hours were deemed enough for the extraction process to reach equilibrium. The kinetic parameter of the extraction was determined through the linear fitting at the initial stage through equilibrium of extraction according to Eq. (3).

$$\ln \frac{C_f}{C_i} = -kt \quad (3)$$

Where C_i and C_f are the metal concentration in the aqueous phase at beginning and after reaching equilibrium, respectively.

As listed in Table 2, P₈₈₈₁₂Cl exhibits a higher reaction rate constant compared to that of P₆₆₆₁₄Cl. This supported the fact that P₈₈₈₁₂Cl achieved equilibrium faster than P₆₆₆₁₄Cl. As expected, the Rh(III) rate constant was small compared to that of Pt(IV) and Pd(II). This result was in accordance with the degree of viscosity for each ionic liquid, which P₈₈₈₁₂Cl has a lower viscosity than that of P₆₆₆₁₄Cl. This could affect the diffusion rate of the solutes, hence affecting the extraction rate using the ionic liquid.

Table 2. Reaction rate constants for both ionic liquids

Ionic Liquids	Reaction Rate Constant k [s^{-1}] (10^{-4})		
	Pt	Pd	Rh
P ₈₈₈₁₂ Cl	6.73	7.55	1.23
P ₆₆₆₁₄ Cl	4.82	4.98	0.93

3.4 Stripping behavior

Stripping of the meta-loaded extractant phase is an essential step for the metal recovery and an ionic liquid recycling. In this study, the ionic liquid extracted from 0.5 mol HCl was used for evaluating the stripping behavior, where the initial concentration of Pt(IV), Pd(II), and Rh(III) were 157, 175, 189 mg L⁻¹, respectively. Various strip solutions, such as 5 mol L⁻¹ HCl, HNO₃, HCl, 0.5 mol L⁻¹ NH₄OH, and 1 mol L⁻¹ CS(NH₂)₂ in 1 mol L⁻¹ HCl, were used. Table 3 presents the stripping results of P₈₈₈₁₂Cl. Among them, 5 mol L⁻¹ HNO₃ showed the highest percentage of Pt(IV), with 78.5% stripping from P₈₈₈₁₂Cl. As for Pd(II), 1 mol L⁻¹ CS(NH₂)₂ in 1 mol L⁻¹ HCl was able to achieve the highest stripping percentage with 98.9%. In case of Rh(III), 5 mol L⁻¹ HCl was able to selectively strip Rh(III), and more than 70% of the metal was recovered. Thus, HNO₃, CS(NH₂)₂ and HCl were effective for stripping Pt(IV), Pd(II) and Rh(III) from the meta-loaded ionic liquid phase. The performance in the stripping test was equal or comparable to that for P₆₆₆₁₄Cl. After the stripping operation, neither emulsion nor precipitation were observed, and both phases were transparent and separated quickly.

Table. 3 Stripping from the ionic liquid with various strip solutions

Ionic Liquids	Metal	Stripping [%]				
		5 mol L ⁻¹		0.5 mol L ⁻¹		1 mol L ⁻¹
		HCl	HNO ₃	H ₂ SO ₄	NH ₄ OH	CS(NH ₂) ₂
P ₈₈₈₁₂ Cl	Pt	0.41	78.5	3.50	0.15	20.5
	Pd	0.06	0.28	2.09	39.1	98.9
	Rh	72.6	23.5	23.4	19.4	0.08
P ₆₆₆₁₄ Cl	Pt	0.39	64.5	0.11	0.98	22.7
	Pd	0.74	0.21	0.25	31.8	92.7
	Rh	76.6	20.6	39.2	26.7	0.84

4. Conclusion

An ionic liquid having favorable properties in the liquid-liquid operation with two immiscible solvents could be prepared by designing its alkylstructure. The extraction performance of newly designed trioctyl(dodecyl)phosphonium chloride (P₈₈₈₁₂Cl) was comparable in the extraction of Pt(IV), Pd(II), and Rh(III) compared to that of commercial trihexyl(tetradecyl)phosphonium chloride (P₆₆₆₁₄Cl). Both ionic liquids exhibit a significant decrease in Rh(III) extraction at a high HCl

concentration due to the extraction competition and the change of Rh(III) species with Cl⁻ in a high HCl concentration. P₈₈₈₁₂Cl was able to extract the metals faster than that of P₆₆₆₁₄Cl due to its low viscosity. It was also more hydrophobic and environmentally friendly due to the less release of phosphonium cation into the feed aqueous phase than P₆₆₆₁₄Cl. The stripping test of the metals was achieved with HNO₃, CS(NH₂)₂, and HCl for Pt(IV), Pd(II), and Rh(III), respectively. Thus the obtained results indicate that P₈₈₈₁₂Cl possesses several advantages compared to P₆₆₆₁₄Cl, as for a new task specific extractant.

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