Hydrometallurgical Process with Phosphonium-based Ionic Liquid for Selective Recovery of Platinum Group Metals from Automotive Catalyst

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Hydrometallurgical Process with Phosphonium-based Ionic Liquid for Selective Recovery of Platinum Group Metals from Automotive Catalyst

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CHAPTER 1 GENERAL INTRODUCTION

1.1 Platinum group metals (PGMs)

Platinum group metals (PGMs) consist of six elements: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt) [1]. They are extremely scarce and highly valuable metals due to their physical and chemical properties, offering considerable catalytic activity alongside high wear and high temperature resistances. Currently supplies of PGMs regularly fall below that of the demand and with newly emerging technologies such as hydrogen fuel cells demand for PGMs, in particular platinum, is likely to increase. As shown in Fig. 1.1, more than half of PGMs were used for automobile catalysts in this year, which were mainly used in automobile exhaust gas catalysts (Platinum, Palladium and Rhodium) followed by jewelry, industrial, and investment [2].

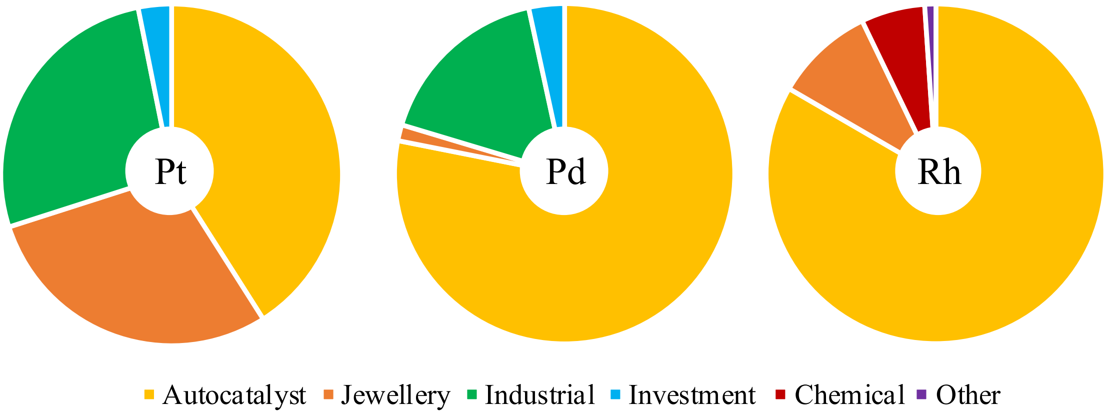

Figure 1.1. Platinum group metals market demand by application in 2019 [2].

Moreover, growing demand of PGMs is caused by the manadatory intallation of catalytic converter to suppress harmful vehicle emission since stricter regulation is being implement in various countries [3]. Moreover, even hydrogen fuel cell requires Pt to carry out the reactions needed to convert the hydrogen into electricity [4]. As PGMs deposits are highly uneven with nearly 90% of PGMs being supplied by South Africa and Russia and no reserves in Europe, as shown in Fig. 1.2 [5]. In the last decades, the value of Pd has increased over 9 times and Pt increased nearly 5 times [2]. In 2018 the gross demand for Pt due to rising demand from the automotive industry led to a deficit of 160 tones. Over the same period Pd experienced a deficit of 195 tones with slight increase of demand of 2% annually while the supply stays the same level since 2015 [6].

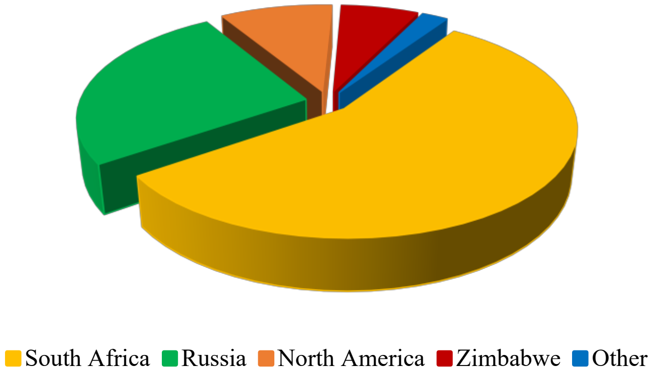

Figure 1.2. World PGMs Production in 2019 [2].

Due to the PGMs scarcity and soaring price, finding suitable inexpensive material with similar properties with PGM attracts researcheres from various fields. However, the effort was still in vain. In order to solve the PGMs demand-supply gap and reducing environmental impact, recycling and the recovery of PGMs from secondary sources seems indispensable. Apart from the economic aspect, producing PGMs from secondary sources, such as catalytic converter has distinct ecological benefits. Producing 1 kg of platinum from a crude ore requires high energy consumption and also produces 400 tons of waste that requires another process before it can be disposed [7]. On the contrary, processing spent catalytic converter requires less resource and generate less additional waste. Thus, recycling PGMs from secondary resources is greatly beneficial since it requires less energy expenditure and a lighter adverse effect on the environment compared to primary production [3,8].

1.1.1 Automotive Catalytic Converter

Cars are human most popular mode of transportation, which also bring many problems, especially air pollution. Ideally, modern cars produce harmless gas, such as carbon dioxide and vapor. However, incomplete combustion and over temperature are inevitable and produce harmful exhaust gas, such as carbon monoxide, nitrogen oxides, and unburned hydrocarbon [9]. Catalytic converters are fitted to the exhaust systems in order to reduce the toxicity of exhaust gasses. Catalytic converters consist of a ceramic honeycomb coated in reactive metals such as, Pt, Pd or Rh in which exhaust gasses were passed through. Due to the three reactions taking place within the converter they are often referred to as TWC's (three-way catalysts) [10]. Initially, reduction of nitrous oxide is occured by rhodium and platinum, then oxidation of unburnt hydrocarbons and carbon monoxide is proceeded by platinum and palladium.

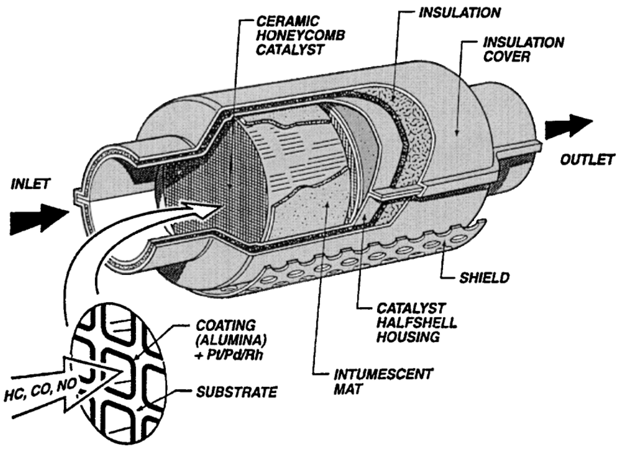

Figure 1.3. Automotive catalyst structural design including honeycomb support and mounting can. Reprints from ref. 8 with permission.

A typical honeycomb monolith of the catalytic converter is constructed within 400 cell in^{-2} and 0.004 in. wall thickness and 600 cell in^{-2} and 0.004 in. [9]. Improvements in the ceramic extrusion technology leading to thinner wall thicknesses of materials are now leading to cell densities around 900 cell in^{-2}. Figure 1.3 shows a typical automotive catalyst design. The honeycomb-shaped cordierite is coated with washcoat layers of the mixture of γ-alumina and PGMs [11]. Depending on the production method, this is achieved by either one layer of washcoat comprising all materials including alumina and catalytic metals, or two layers one comprising alumina (to increase the surface area of the catalytic converter) and one containing the catalytic metals. Washcoat layers are applied in various ways including dip coating or insipient wetness techniques [12].

1.2 Recovery of precious metals from secondary resources

Combination of metals in the secondary resource creates a new technological challenge for their recovery because it is often much different from the original deposits. Secondary resources, such as electronic wasted and spent catalytic converter are the great source of PGMs since they consist of PGMs in much larger quantity than natural resources. Mass produced consumer components such as computer motherboards contains around 200–250 grams per ton (g t^{-1}) of gold and around 80 g t^{-1} palladium; mobile phones contain up to 350 g t^{-1} gold and 130 g t^{-1} palladium; and automotive catalytic converters may contain up to 2000 g t^{-1} PGM in the ceramic catalyst brick, the active part of the converter [13]. This is significantly higher than the PGMs content in primary ores (on average < 10 g t^{-1}). The high intrinsic value of these secondary resources makes an attractive point for recycling. Moreover, recycling is not only beneficial in terms of economic aspect but also beneficial from environment point of view since it helps to reduce the environmental burden from mining and other metallurgical process. Even more valuable for recycling is PGMs used in jewelry, as these are typically concentrated at an even higher level.

1.3 Hydrometallurgical separation of precious metals

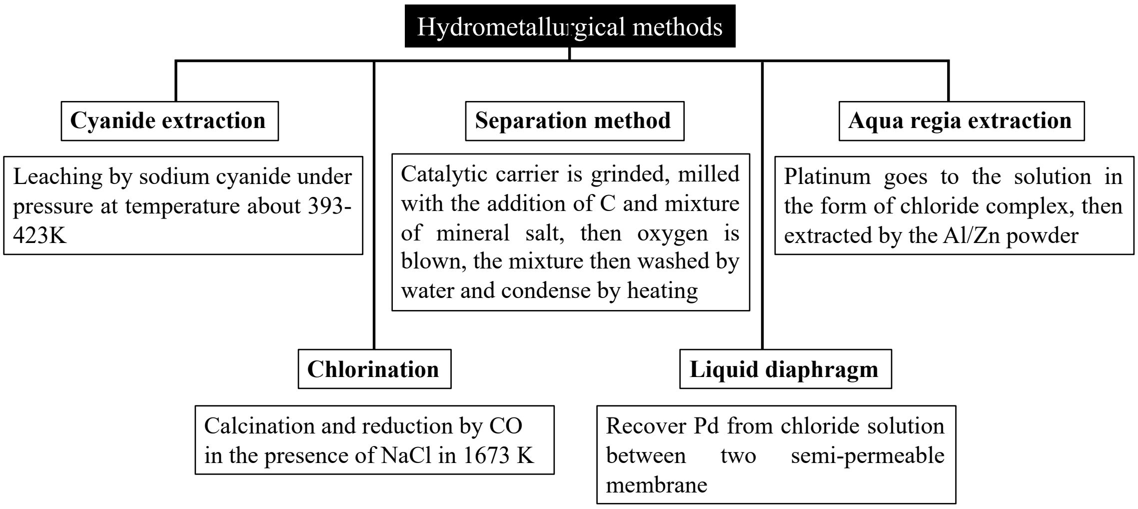

Figure 1.4. Short characteristic of available hydrometallurgical methods applied in recycling PGM from waste automotive catalyst. Reprints from ref. 14 with permission.

Hydrometallurgical treatment of spent catalyst wastes might be an alternative way to the currently applied - mechanical pretreatment and pyrometallurgical processes. Hydrometallurgical methods use various suitable acidic and alkaline solutions in the presence of oxygen, iodine, bromine, chlorine, hydrogen peroxide to dissolve a specific element from catalyst [15]. However, it is rarely applied in the PGMs recovery industry despite much effort being made, it is rarely applied in the PGMs recovery industry. Figure 1.4 presents available hydrometallurgical methods and their short characteristic.

The hydrometallurgical process is often worked as a crude extraction process, which is the most important step for the recovery of PGMs from the support of catalysts. It mainly divided into support dissolution and noble metal dissolution. In the first process; the support is dissolved with a non-oxidizing acid or base where the noble metals are not dissolved and remained as a sludge [16]. Then, the sludge is dissolved with a strong acid to extract the PGMs. This could achieve a high purity product and a high recovery rate. The carrier dissolution method is inexpensive and has a high metal recovery rate. Moreover, the byproduct of the process can be used in a paper industry and a wastewater treatment. However, this process requires a large number of reagents and only suitable to treat the alumina carrier, which has low dissolution ratio. In addition, the operation of solid-liquid separation is generally difficult, so it is rarely applied in practice [17].

In the second process, the noble metals are extracted from the support by using an acidic solution of an oxidant, leaving the bulk of the support. However, in most cases, due to heat, alumina support change its phase to γ-alumina which could be dissolved partially and interfere with the recovery process of the PGMs. However, the pre-treatment of the spent catalyst to promote the transformation of the acid soluble γ-alumina to the acid insoluble α-alumina usually suffers from low recovery of the precious metals [18]. Initially, soluble metals in the wastes were leached. Among different leaching agents, acidic chloride medium is an inexpensive medium in which most of platinum group metals can form soluble anionic chloro-complexes and has been extensively studied as model species. The most stable anionic chloro-complexes for Pt(IV), Pd(II) and Rh(III) are $PtCl_6^{2-}$ $PdCl_4^{2-}$ and $RhCl_6^{3-}$, respectively. As these chloro-complexes are negatively charged, most of the separation methods for the precious metals are involved in an anion exchange between anionic chloro-complexes and anion exchangers [19]. The tendency for metal-chlorocomplexes to form ion pairs with anion-exchangers is $[MCl_6]^{2-} > [MCl_4]^{2-} > [MCl_6]^{3-}$, which is determined by its charge density of the species. Densely charged species tend to have a larger hydration shell, which resulting in lower coulombic interaction with their counter anions (Figure 1.5). Thus, low charged density species are more easily paired than that with a higher charge density [20,21].

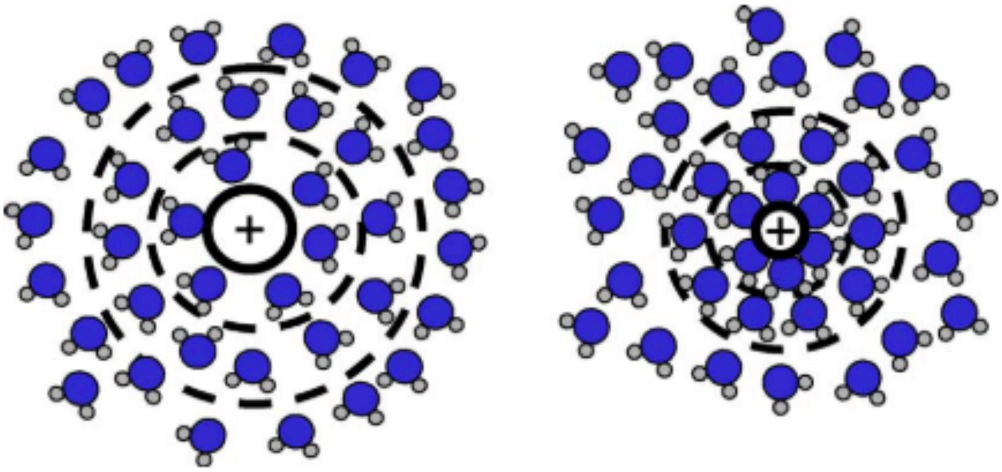

Figure 1.5 Schematic representation of hydration shells around a large and a small ion. Inner and outer circles represent the primary and secondary hydration shells, respectively. Reprints from ref. 21 with permission.

1.3.1 Solvent extraction

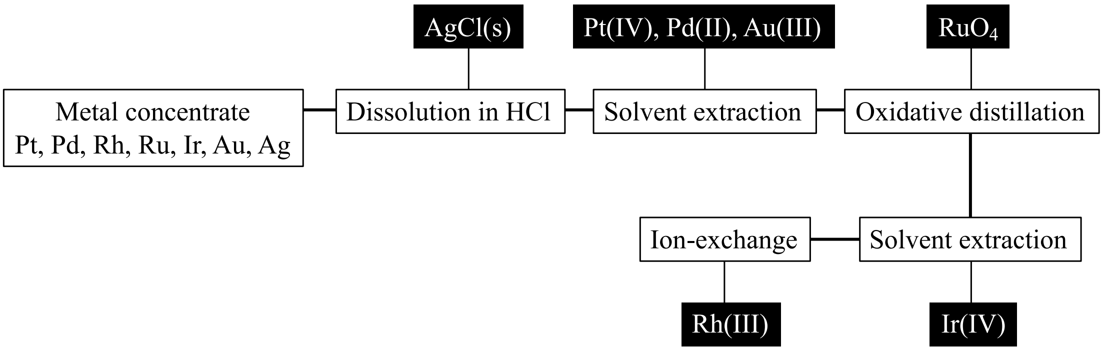

Figure 1.6 Modern refining method using solvent extraction. Reprints from ref. 14 with permission

Initial implementation of solvent extraction was in the petroleum industry in the beginning of 1930. Then, it was spreading to other industries such as pharmaceutical, petroleum, metallurgical and nuclear industries. Solvent extraction is partitioning of compounds in two different immiscible liquids. These immiscible liquids most often consist of an organic solvent that contains diluent and/or extractant, and an aqueous phase (feed) that contains the solute. The extractant is the active component in transferring the solute from one phase to another. Extraction of a solute is a reversible process by contacting the extractant with another immiscible solution that has higher affinity for the solute than the extractant (back extraction/stripping). The phase containing the extracted solute after extraction is called the extract while the depleted aqueous phase is called the raffinate. In comparison to the classical precipitation methods, solvent extraction offers advantages such as fast kinetics, continuous operation and high selectivity [22].

The main shortcoming of solvent extraction is that large amounts of organic solvents are used to dilute the extractants, from which secondary pollution might be caused by the evaporation and a leakage of organic solvents [23]. The solution to this problem, to put it simply, is to avoid the use of volatile organic compounds. Diethyl ether, benzene, and other hydrocarbons are common solvents that are usually used in solvent extraction and less dense than water and form a phase that sits on top of the aqueous phase. In a two phases mixture, some of each solvent are found in both phases, but one phase is predominantly water and another phase is predominantly organic. The volumes of each phase after mixing are not exactly equal to the volumes that were mixed.

1.4 Ionic liquids

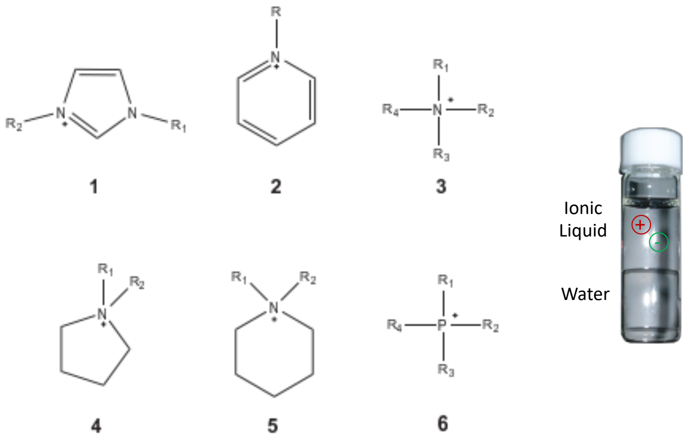

Figure 1.7. Most commonly used ionic liquid cations: 1,3-dialkylimidazolium (1), N-alkylpyridinium (2), tetraalkylammonium (3), N,N-dialkylpyrrolidinium (4), N,N-dialkylpiperidinium (5), tetraalkylphosphonium (6).

Ionic liquids (ILs) are a specific class of compounds that are defined as liquids that consist exclusively of ions[24,25]. In principle, this definition could be applied to any salts, organic or inorganic compounds, that have a melting temperature lower than 373 K. However, the term ionic liquid is usually used primarily to address organic salts with a low melting temperature. On the first glance, this group of compounds seems haphazardly defined. However, their remarkable properties and possible applications have made ionic liquids a booming business the past two decades, both in research and industry [7].

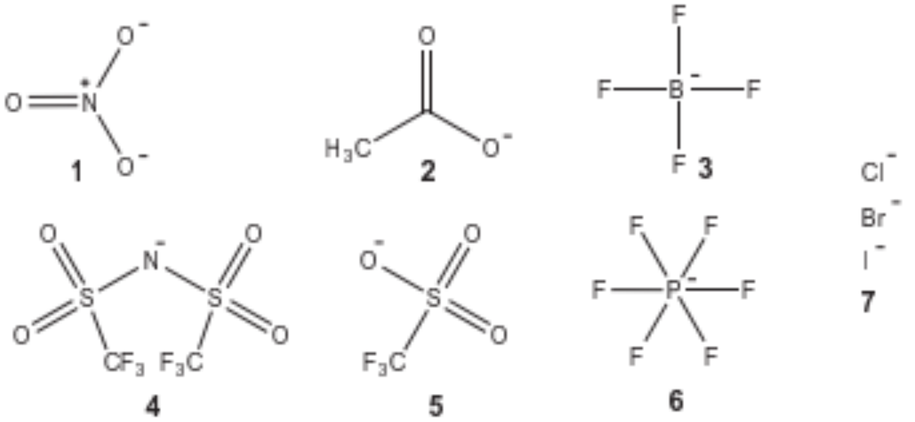

Figure 1.8. Most commonly used ionic liquid anion: nitrate ($[NO_3]^-$, 1), acetate (2), tetrafluoroborate ($[BF_4]^-$, 3), bis(trifluoromethylsulfonyl)imide (bistriflimide, $[Tf_2N]^-$, 4), trifluoromethanesulfonate ($[TfO]^-$, 5), hexafluorophosphate ($[PF_6]^-$, 6) and the halogenides chloride Cl^-, bromide Br^- and iodide I^- (7)

Ionic liquid properties can be tune by designing its structure or different combination of cations and anions. Thus, many researchers therefore also refer to ionic liquids as designer solvents. The low melting point is achieved by the right choice of cations and anions. A high degree of asymmetry or mismatch between the ion sizes, combined with a large charge distribution over the ions and the absence of physical interactions such as hydrogen bonds, inhibit crystallization [26]. Depending on the application, specific functional groups can be incorporated into the structure of the cation or anion. Figure 1.7 and 1.8 show cations and anions that are usually used in the component ionic liquids. The most interesting or important properties of ionic liquids include their negligible vapor pressure, low flammability, good electrochemical stability and conductivity [27]. Minimal coulombic interaction between ions, and innate ionic character of ionic liquids restricts ion pair formation required for volatilization resulting in low volatility character in ionic liquid. In addition, due to its low volatility, ionic liquid often deemed as green replacement for volatile organic compound. However, some ionic liquids are still harmful and toxic to the environment [28]. Furthermore, ionic liquids have low flammability which could prevent fire related problem due to the build-up of static electricity in the organic solvents, which makes them inherently safer than traditional organic solvents [29]. Their intrinsic electrical conductivity prevents the accumulation of static electricity.

Due to the high degree of intermolecular interaction, the viscosity of ionic liquids is generally higher than that of common organic solvents. An ionic liquid with long alkyl chains will have a high viscosity due to increase in their Van der Waals interaction. Thus, ionic liquids can exhibit a wide range of viscosities depending on its cation and anion. Viscosity is an important parameter to consider when scaling-up the process, since highly viscous ionic liquid can exhibit the slow mass transfer and mess up the pumping system. Density is another important property to consider in the context of solvent extraction. Similar with viscosity, the structure of the cation and anion greatly influence this parameter. The presence of long alkyl chains decreases the density, while fluorinated anions increase the density. In the bulk of the ionic liquid, the anions and cations form clusters resulting in polar and apolar nanodomains. However, in contact with water or moisture from the air, ionic liquids take up water quite easily [30]. Due to this inhomogeneous structure, the presence of water does not interfere with the interactions between the ionic liquid and a solute [31].

1.4.1 Application of ionic liquid in metal extraction

The initial work on extraction using ionic liquids was the extraction of Sr(II) by crown ether dicyclohexyl-18-crown-6 (DCH18C6), a neutral extractant, dissolved in 1,3-dialkylimidazolium ionic liquids with $[Tf_2N]^-$ and $[PF_6]^-$ anions in 1999 [32]. Subsequently, it was found that the extraction mechanism involving ionic liquids was differed completely from that of extraction into molecular solvents [33]. These first observations showed that ionic liquids provide a large potential to broaden the possibilities for metal ion extraction.

The mechanism behind extraction of metal ions with ionic liquids may differ substantially from traditional solvent extraction systems. In contrast to traditional diluents, charged metal complexes also can be extracted to ionic liquids. Therefore, the extraction mechanism can be categorized according to the charge of the transferred metal complexes, either positive in the cation-exchange mechanism or negative in the anion-exchange mechanism. In the context of the extraction mechanism in ionic liquids, the term cation exchange is used when one or more positively charged ions from the ionic liquid phase are transferred (exchanged) to the aqueous phase upon extraction of a positively charged metal complex. Hence, the total charge of the complex is equal to the charge of the metal ion. Similarly, anion exchange refers to the exchange of a negatively charged metal complex with an anion of the ionic liquid phase. The extraction mechanism of metal extractions with basic extractants can all be categorized as the anion exchange of ionic liquids.

1.5 Research aim and thesis organization

The main research aim in this thesis is to develop an effective hydrometallurgical separation system for the separation and recovery of precious metals, by employing ionic liquid in liquid-liquid extraction

The present graduation thesis is composed of 5 chapters, which are the general introduction (Chapter 1), the research achievements (Chapter 2, Chapter 3 and Chapter 4) and the general conclusion (Chapter 5), together with references.

In Chapter 1, a general introduction was made on the recovery of precious metals from secondary resources. A brief review on the hydrometallurgical separation methods for precious metals was included as well. The application of ionic liquids in the recovery of PGMs was also discussed here.

Chapter 2 discusses the feasibility of using undiluted ionic liquids as an alternative of organic phases for the extractive separation of precious metals Pt(IV), Pd(II), and Rh(III). By varying the extraction conditions, the extraction mechanism and ionic liquid reusability were studied.

In Chapter 3, the performance of ionic liquids in the selective recovery of Pd(II) and Rh(III) was studied from the leachate of unused automotive catalyst. By changing the acid concentration and various combination of stripping solutions, selective recovery and removal of impurities were investigated.

In Chapter 4, the leaching process of spent automotive catalyst and the viability of using ionic liquids were studied for the selective recovery of Pt, Pd and Rh from the leachate.

In Chapter 5, summary was made based on the research achievements discussed in Chapter 2 ~ Chapter 4.

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CHAPTER 2. SOLVENT EXTRACTION OF PT(IV), PD(II), AND RH(III) WITH THE IONIC LIQUID TRIOCTYL(DODECYL) PHOSPHONIUM CHLORIDE.

2.1 Introduction

In recent years, there has been a notable increase in the consumption of noble metals, especially platinum group metals (PGMs), such as platinum (Pt), palladium (Pd), and rhodium (Rh) owing to rapid expansion of their industrial applications [1,2]. However, the limited nature of PGM resources has created a large gap between their supply and demand, which has increased over the years [3]. This value of PGMs has raised interest in their secondary resources [3,4]. Electronic and automobile waste, such as spent printed circuit boards and automotive catalysts, are potential secondary resources for PGMs. The recovery of PGMs from such waste is an important ecological and economical issue. For this reason, it is crucial to find efficient and effective separation methods for the recovery of Pt(IV), Pd(II), and Rh(III), because separation of PGMs from the waste is considered to be difficult owing to their similarities in terms of hydrometallurgical properties.

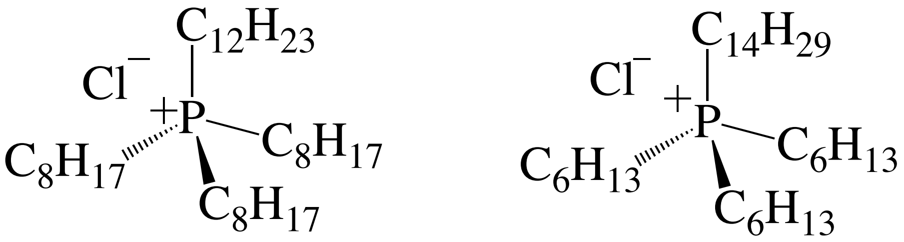
Recently, solvent extraction has become a viable technique for PGM separation owing to advantages such as high selectivity and ease of operation [5]. Various extractants have been used to extract PGMs, such organophosphorus compounds [6], ammonium salts and amine derivatives [7,8]. Ionic liquids (ILs) have also become widely used as an extractant or an extraction solvent. Several previous studies have reported on the extraction of Pt(IV) and Pd(II) by using ionic liquids such as imidazolium, pyridinium, or pyrrolidinium cation as the extractant [9-11]. In recent years, phosphonium-based ionic liquids have gained interest for their applications in PGM extraction. Commercially available trihexyl(tetradecyl)phosphonium chloride, bromide and bis(2,4,4-trimethylpenthyl)phosphinate dissolved in an organic solvent have been shown to have good extraction capabilities towards Pt(IV) and Pd(II) in hydrochloric acid media [12-15]. In conventional extraction, the extraction of Rh(III) is known to be difficult compared to Pt(IV) and Pd(II). However, a recent report from Svecova *et al.* detailed the use of undiluted trihexyl(tetradecyl)phosphonium chloride, bromide, and dicyanamide, which resulted in a high Rh(III) extraction efficiency [16], although the stripping was not described.

The aim of this chapter was to explore the potential of phosphonium-based ionic liquids as extraction solvents for PGMs. In the present chapter, a novel phosphonium based ionic liquid, trioctyl(dodecyl)phosphonium chloride ($P_{8,8,8,12}Cl$) was developed and its behavior in the extraction of Pt(IV), Pd(II), and Rh(III) from hydrochloric media was examined. The importance of hydrophobicity of ionic liquids based on the industrial application of solvent extraction by changing the molecular structure was also discussed.

2.2 Experimental

2.2.1 Reagents

The ionic liquid, trioctyl(dodecyl)phophonium chloride ($P_{8,8,8,12}Cl$)(Assay 98.0%), which was newly designed, was synthesized by Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan). A commercial analogue trihexyl(tetradecyl)phosphonium chloride ($P_{6,6,6,14}Cl$)(Assay >95%) was obtained from Ionic Liquids Technologies GmbH (Heilbronn, Germany). The molecular structures of these ionic liquids are shown in Figure 2.1, and both were used as received. Solutions of HCl, HNO_3, and H_2SO_4, NH_4OH, $CS(NH_2)_2$, and 1000 mg L^{-1} Pt(IV) and Pd(II) standard solutions in 1 mol L^{-1} HCl were purchased from Wako Pure Chemical Ltd (Osaka, Japan). A Rh(III) standard solution in 1 mol L^{-1} HCl was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan).



Trioctyl(dodecyl)phosphonium chloride

Trihexyl(tetradecyl)phosphonium chloride

Figure 2.1. Molecular structures of ionic liquids used in this study

2.2.2 Measurements

The density of the ionic liquids was analyzed by a density meter (DMA 35N, Anton Paar GmbH, Graz Austria). The viscosity of the ionic liquids was measured by a viscometer (Lovis M/ME 2000, Anton Paar GmbH, Graz, Austria). The water content in the ionic liquids was analyzed by a Karl–Fischer moisture meter (CA-200, Mitsubishi Chemical Analytech Co., Ltd., Tokyo, Japan). Ultraviolet-visible (UV-vis) spectroscopy was measured with a UV-Vis-NIR spectrophotometer (V-670, JASCO Co., Tokyo, Japan) in the range of 300–700 nm at room temperature. The concentration of precious metals and phosphorus (P) in the aqueous solution was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8300, Perkin Elmer Co., MA USA).

2.2.3 Extraction Procedure

Aqueous phases containing 100 mg L^{-1} of Pt(IV), Pd(II), and Rh(III) in 0.1–5 mol L^{-1} HCl were prepared by diluting their 1000 ppm standard solutions. Ionic liquids were used as received as the extraction phases. The volume ratio of the aqueous to the ionic liquid phases (V_{aq}/V_{IL}) was kept constant at 2, unless stated otherwise. Extractions were performed by mixing 2 mL of a metal solution (aqueous phase) with 1 mL of the ionic liquid solution (organic phases) in a propylene tube. The tube was mechanically shaken (160 rpm) for 3 h at 298 K before being centrifuged for 1 min at 5800 G to separate the both phases. All experiments went through a similar procedure unless mentioned otherwise. The metal concentrations in the aqueous phase were measured with ICP-OES. Extraction efficiency (E%) and distribution coefficient, D (-), were calculated as follows:

$$E\% = \frac{[M]_{IL}V_{IL}}{[M]_{IL}V_{IL}+[M]_{aq}V_{aq}} \text{ x } 100 \tag{1}$$

$$D = \frac{([M]_{0.aq}-[M]_{aq})}{[M]_{aq}}\frac{V_{aq}}{V_{IL}} \tag{2}$$

where V (L) and [M] (mg L^{-1}) were the volume and the metal concentration, respectively, and subscripts IL and aq denote the ionic liquid and aqueous phases, respectively. Ionic liquid was used as the organic phase in this study.

A loaded organic phase containing Pt(IV), Pd(II), and Rh(III) was prepared by extraction with 0.5 mol L^{-1} HCl solution mixed individually with various aqueous stripping solutions [HCl, HNO_3, H_2SO_4, NH_4OH, or $CS(NH_2)_2$] at a unit phase volume ratio, unless otherwise stated. The stripping experiments were performed in the same manner as the forward extraction. The stripping percentage (S%) was calculated as follows:

$$S\% = \frac{[M]_{st}V_{st}}{[M]_{st}V_{St}+[M]_{IL}V_{IL}} \text{ x } 100 \tag{3}$$

where subscript st denotes the stripping phase. The stripped organic phases were reused in further cycles of the extraction-stripping process.

2.3 Results and Discussion

2.3.1 Measurement of the Fundamental Properties of the Ionic Liquids

The physicochemical properties of the novel $P_{8,8,8,12}Cl$ as an extraction solvent were assessed along with the commercial analogue $P_{6,6,6,14}Cl$. As shown in Table 2.1, it was found that $P_{8,8,8,12}Cl$ had lower viscosity than that of $P_{6,6,6,14}Cl$, and the measurements of the viscosity and density of $P_{6,6,6,14}Cl$ agreed with results from several previous studies [17-19]. The viscosity of ionic liquids can affect the diffusion rate of metal ions into the organic phase. Thus, the low viscosity of $P_{8,8,8,12}Cl$ might be beneficial for metal ion transport [20]. The hydrophobicity of ionic liquids is another critical factor to gain the high extraction efficiency. To evaluate it, the water content in the ionic liquids and the phosphorus (P) release into the aqueous feed solution after contact with water were measured and the results are listed in Table 2.1. The new ionic liquid $P_{8,8,8,12}Cl$ featured lower water content than that of $P_{6,6,6,14}Cl$. Water molecules in ionic liquids can interact with the ionic liquid cations leading to their aggregation [21,22]. Thus, the low water content of $P_{8,8,8,12}Cl$ might prevent any decrease in extraction performance. $P_{8,8,8,12}Cl$ also showed a lower degree of P release into the aqueous phase than that of $P_{6,6,6,14}Cl$, which indicates the higher hydrophobicity of $P_{8,8,8,12}Cl$ compared with that of $P_{6,6,6,14}Cl$. The amount of P in aqueous media, such as waste water, is strictly regulated. Thus, the low release of P into the aqueous feed solution is a notable advantage of the new ionic liquid $P_{8,8,8,12}Cl$.

Table 2.1. Physicochemical properties of the ionic liquids

Sample	Density [g ml^{-1}]^a	Viscosity [mPa.s]	Water Content [wt%]	P Release [mg L^{-1}]^a
$P_{8,8,8,12}Cl$	0.8767	800.8	4.30	0.301
$P_{6,6,6,14}Cl$	0.8799	1930.5	6.26	6.887

measured at 298K
^{a} V_{IL}/V_{aq} = 2, time = 3 hours

2.3.2 Extraction rate (Effect of contact time)

Extraction kinetics of the metal ions with the ionic liquids was examined at 298 K. The extraction was performed with a metal concentration of 200 mg L^{-1} at 0.5 mol L^{-1} HCl, V_{aq}/V_{IL} ratio of 2, and all other parameters were unchanged. Figure 2.2 shows the time course of the extraction of metal ions. As shown in Figure 2.2 a and b, $P_{8,8,8,12}Cl$ achieved equilibrium within 30 min, while $P_{6,6,6,14}Cl$ required 60 min for Pt(IV) and Pd(II) extraction. In the Rh(III) extraction, the equilibrium was attained more slowly than that for Pt(IV) or Pd(II) extraction. However, $P_{8,8,8,12}Cl$ achieved equilibrium considerably faster than $P_{6,6,6,14}Cl$. Specifically, extraction equilibria were achieved within 80 min for the former ionic liquid, whereas more than 150 min was required for equilibria in the latter case (Figure 2.2c). Henceforth, extraction experiments were conducted after shaking mixtures of both phases for 3 h.

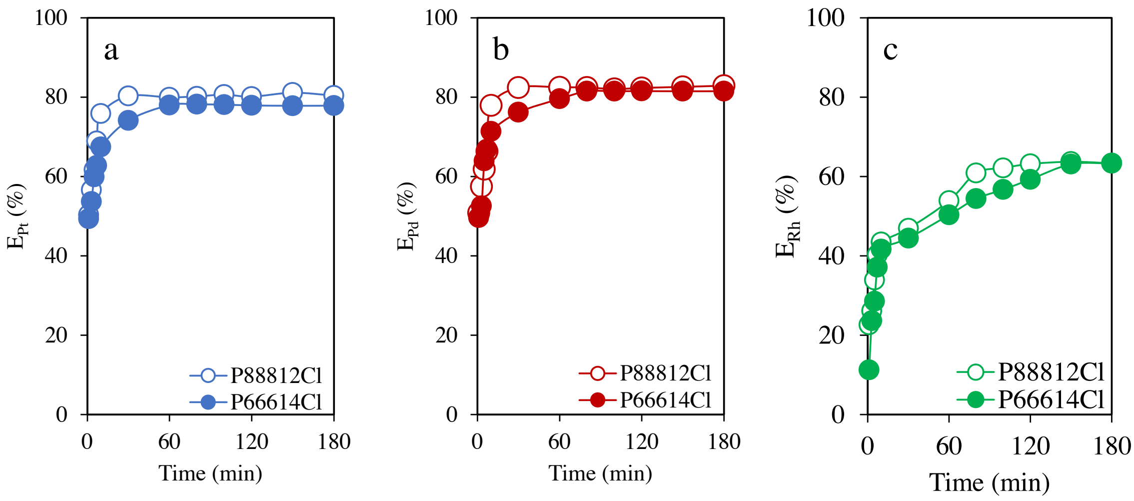


Figure 2.2. Effects of contact time on the Pt(IV), Pd(II), and Rh(III) extraction; $[M]_{aq}$ = 200 mg L^{-1}, V_{aq}/V_{IL} = 2, $[HCl]_{aq}$ = 0.5 mol L^{-1}

The kinetic parameters listed in Table 2.2 were determined through linear fitting in the initial stage of extraction according to Eq. (4):

$$\ln {}^{[M]_f}\!/_{[M]_i} = -kt, \tag{4}$$

where $[M]_i$ and $[M]_f$ are the metal concentrations (mg L^{-1}) in the aqueous phase initially and after reaching equilibrium, respectively, k (s^{-1}) is the rate constant, and t (s) is the extraction time.

Table 2.2. Reaction rate constants of metal extraction

Ionic Liquid	Reaction Rate Constant k (s^{-1}) ($\times10^{-4}$)		
	Pt	Pd	Rh
$P_{8,8,8,12}Cl$	6.73	7.55	1.23
$P_{6,6,6,14}Cl$	4.82	4.98	0.93

As expected from its low viscosity, listed in Table 2.1, $P_{8,8,8,12}Cl$ showed a considerably higher extraction rate than that of $P_{6,6,6,14}Cl$ for all metal species; however, the Rh(III) reaction rate constant was smaller than those of the other metals. Hence, the difference in the viscosity between the two ionic liquids, which can affect the diffusion rate of solute, is reflected by the extraction rate.

2.3.3 Extraction Behavior of Pt, Pd, and Rh

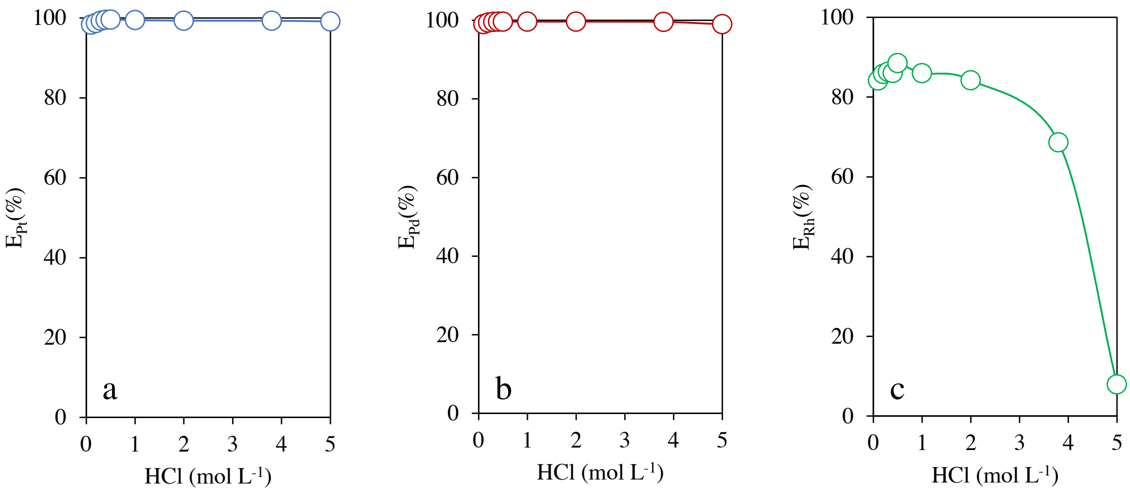


Figure 2.3. Effects of HCl concentration on the (a) Pt(IV), (b) Pd(II), and (c) Rh(III) extraction by $P_{8,8,8,12}Cl$; $[M]_{aq}$ = 100 mg L^{-1}, V_{aq}/V_{IL} = 2, time = 3 hours.

Figure 2.3 illustrates the extraction behavior of $P_{8,8,8,12}Cl$ for Pt(IV), Pd(II), and Rh(III) in the metal mixture system as a function of the HCl concentration. Quantitative extraction of Pt(IV) and Pd(II) was achieved over the whole pH range, although a slight decrease was observed at HCl concentrations greater than 1 mol L^{-1} (Figure 2.3 a and b). Notably, the extraction of Rh(III) showed a different trend from those of the other metal ions. As shown in Figure 2.3c, the extraction efficiency of Rh(III) by the ionic liquid increased as the HCl concentration was increased from 0.1 to 0.5 mol L^{-1} HCl. Further increases in the HCl concentration markedly decreases the extraction efficiency. At 5 mol L^{-1} HCl, the extraction efficiency of Rh(III) decreased to less than 10%. A similar trend was found for the extraction with $P_{6,6,6,14}Cl$. The extraction behavior of metal ions could be visually confirmed from the color change of the solution before and after extraction. The mixed metal solution of Pt(IV), Pd(II), and Rh(III) exhibited a yellow-brownish color, which became darker as the HCl concentration was increased from 0.1 to 5 mol L^{-1}, as seen in Figure 2.4.

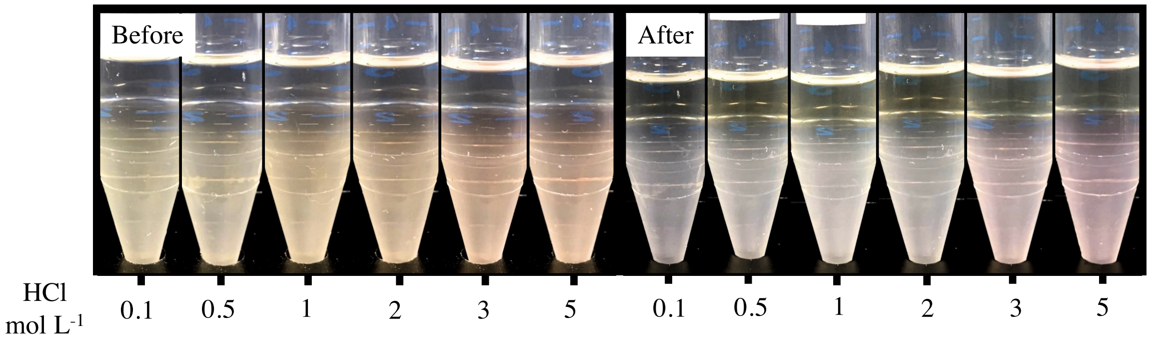


Figure 2.4. Color changes of phases of the metal mixture system before and after extraction with $P_{8,8,8,12}Cl$ in; $[M_i]_{aq} = 100$ mg L^{-1}, $V_{aq}/V_{IL} = 2$, time = 3 hours.

The color changes could be attributed to the presence of different Rh(III) species at high HCl concentrations [20]. After the extraction operation, the ionic liquid phase turned yellow. The aqueous phase became colorless at an HCl concentration of 0.1–2 mol L^{-1}. However, the aqueous phase of 3–5 mol L^{-1} HCl exhibited a light purplish color, which could be attributed to a large amount of unextracted Rh(III) in the aqueous phase. A considerable decrease in Rh(III) extraction might be caused by a change of the Rh(III) species in the aqueous phase. At high HCl concentrations (>3 mol L^{-1}), the main Rh(III) species shifted from $RhCl_5^{2-}$ to $RhCl_6^{3-}$. This transformation markedly affects the extraction efficiency of Rh(III), which is influenced by the anion charge density [23]. The molecular size of $RhCl_5^{2-}$ is much smaller than that of $RhCl_6^{3-}$, hence, the charge density of $RhCl_5^{2-}$ is higher than that of $RhCl_6^{3-}$. The difficulty of metal ion extraction is inversely proportional to the metal ion charge density. Thus, $RhCl_6^{3-}$ can be expected to be more difficult to extract than $RhCl_5^{2-}$ species.

Previously, several researchers have reported on the low extractability of Rh(III) by ionic liquids diluted with kerosene or toluene, and the extraction efficiency of Pt(IV) and Pd(II) was also shown to decrease at high HCl [13,14]. The decrease in the extraction efficiency at high HCl could be attributed to competition in the formation of metal-ligand complexes between the ionic liquid molecules with Pt(IV), Pd(II), or Rh(III). In an undiluted ionic liquid, the abundance of ionic liquid molecules should minimize this competition. The extraction percentage of Rh(III) was considerably increased with the use of the undiluted ionic liquid, however Rh(III) extraction was still lower than that of Pt(IV) and Pd(II).

2.3.4 Extraction Mechanism

The extraction mechanism for the metal ions with the novel ionic liquid, $P_{8,8,8,12}Cl$, was studied in toluene. The extraction mechanism in pure IL and diluted in toluene might not be identical. However, since it is difficult to discuss the extraction mechanism qualitatively in pure ILs, the extraction reaction was investigated in toluene to get a basic knowledge of complex formation with the ionic liquid. Figure 2.5 shows the effect of the $P_{8,8,8,12}Cl$ concentration on the distribution coefficients of Pt(IV), Pd(II), and Rh(III) at different HCl concentrations, 0.5 and 4 mol L^{-1} HCl, and a V_{aq}/V_{IL} ratio of 4. From the plots of log D versus log[$P_{8,8,8,12}Cl$] in Figure 2.5, linear relationships with gradients of 2 were obtained for Pt(IV) at both HCl concentrations. The gradient was found to change at low and high HCl for Pd(II) from nearly 1 to 2, respectively. That for Rh(III) was 2 at

0.5 M HCl, however, the extraction efficiency was too low to obtain the correlation at high HCl. These results indicate the number of ionic liquids bound with each metal ion.

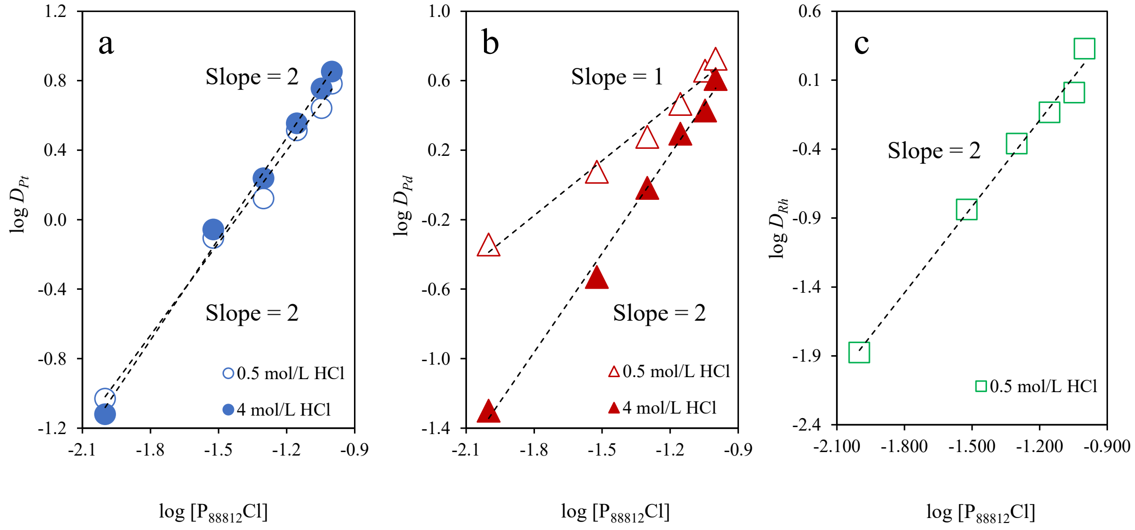


Figure 2.5. Effects of $P_{8,8,8,12}$Cl concentration on the (a) Pt(IV), (b) Pd(II), and (c) Rh(III) extraction; $[M]_{aq}$ = 100 mg L^{-1}, , V_{aq}/V_{IL} = 4, [$P_{8,8,8,12}$Cl] = 0.01– 0.1 mol L^{-1}, solvent = toluene, time = 3 hours

According to the stability constants, various chlorocomplexes form from Pt(IV), Pd(II) or Rh(III). However, in HCl media, the chlorocomplexes, i.e., $PtCl_6^{2-}$, $PdCl_4^{2-}$, and $RhCl_5^{2-}$ are the dominant species, according to their stability constant data and previous studies [12-14]. The extraction of each metal proceeds through an anion exchange mechanism as follows:

$$PtCl_6^{2-}+2\overline{(R_3R'P^+Cl^-)} \rightleftharpoons \overline{(R_3R'P)_2(PtCl_6)}+ 2Cl^-_{aq}, \quad (5)$$

$$PdCl_4^{2-}+2\overline{(R_3R'P^+Cl^-)} \rightleftharpoons \overline{(R_3R'P)_2(PdCl_4)}+ 2Cl^-_{aq}, \quad (6)$$

$$RhCl_5^{2-}+2\overline{(R_3R'P^+Cl^-)} \rightleftharpoons \overline{(R_3R'P)_2(RhCl_5)}+2Cl^-_{aq}, \quad (7)$$

where R and R' are alkyl groups, and horizontal bars indicate a species in the organic phase.

The formation of $(R_3R'P)_2(PtCl_6)$ expressed by Eq. (5) agrees with the obtained values from the slopes in Figure 2.5a. In the Pd(II) extraction, $PdCl_4^{2-}$ reaches a rapid equilibrium with $PdCl_3^-$ at low HCl concentrations (<2 mol L^{-1}) [13]. Thus, formation of $(R_3R'P)(PdCl_3)$ is formed according to Eq. (8) at low HCl range.

$$PdCl_4^{2-} + \overline{(R_3R'P^+Cl^-)} \rightleftharpoons \overline{(R_3R'P^+)(PdCl_3)} + 2Cl^-_{aq} \tag{8}$$

The formation of two different species corresponds with the gradient of two straight lines in Figure 5b. To confirm the extraction mechanism, the effect of Cl ion concentration on the distribution ratio D of the metal ions was examined. The log D shows a slope of -2 on the dependency of logarithmic Cl ion concentration for Pt(IV) and Pd(II), which is in agreement with the number of Cl ions involved in the extraction reaction as seen in Figure 6. As for Rh(III), the extraction mechanism expressed by Eq.(7) also agreed with the gradient obtained in Figure 2.5c and Figure 2.6.

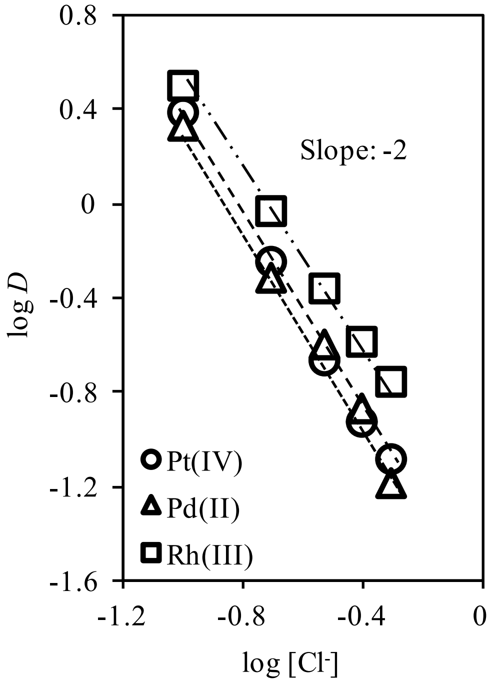


Figure 2.6. Effect of chloride ion concentration on the distribution ratio of Pt(IV), Pd(II), and Rh(III); Aqueous phase: $[M_i]_{aq}$ = 100 mg L^{-1}, $[H^+]_{aq}$ = 0.5 mol L^{-1}, $[Cl^-]$ = 0.1-0.5 mol L_{-1} (adjusted with 0.5 mol L^{-1} HCl and $HClO_4$): Organic phase; $[P_{8,8,8,12}Cl]$ = 0.07 mol L^{-1} (Pt(IV) and Pd(II)) and 0.12 mol L^{-1} (Rh(III)), toluene, V_{aq}/V_{IL} = 2, time = 3 hours.

According to UV-vis spectroscopy, $RhCl_5^{2-}$ was found to be the main species in the aqueous phase at low HCl concentrations (<3 mol L^{-1}), while, $RhCl_6^{3-}$ was the main species at high HCl concentrations (>3 mol L^{-1}) [24] (Figure 2.7). No changes were observed after contact with undiluted $P_{8,8,8,12}Cl$. This result, together with the gradient determined above, corroborated the Rh(III) extraction mechanism as presented in Eq (7). The reaction of $RhCl_6^{3-}$ with $P_{8,8,8,12}^+$, requires the formation of a complex with three $P_{8,8,8,12}^+$ units; the reactivity of this process is low compared with that for $RhCl_5^{2-}$ and the extraction efficiency declined at high HCl concentrations due to steric hindrance between 3 IL molecules and a metal ion [7]. A large amount of Cl ions in the aqueous phase could compete with extraction of the metal through the formation of chlorocomplex anions and Cl ions, according to the Eq (7).

Similar results were obtained for $P_{6,6,6,14}Cl$ (data not shown). These results in conjunction with previous reports and confirmed that the extraction mechanism of $P_{8,8,8,12}Cl$ for Pt(IV) Pd(II), and Rh(III) was similar to that of $P_{6,6,6,14}Cl$.

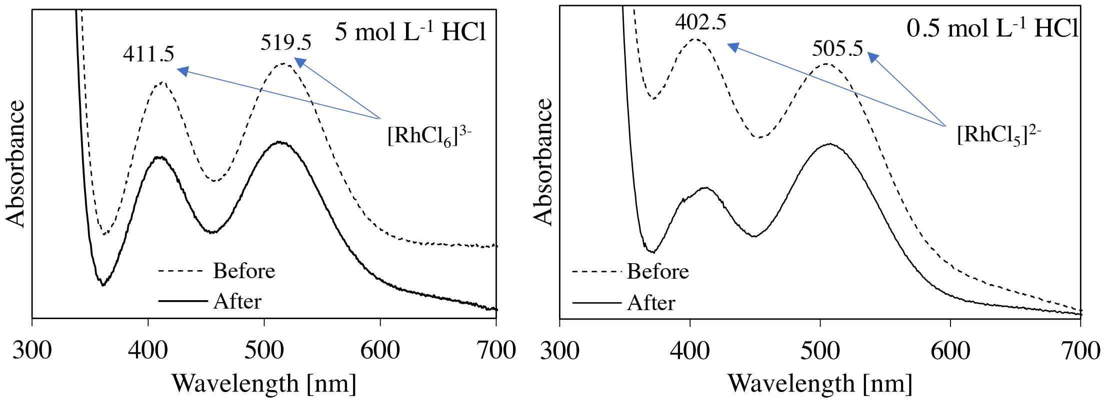


Figure 2.7. UV-vis spectral changes of the chlorocomplexes of Rh(III) in the aqueous phase before and after extraction with $P_{8,8,8,12}Cl$; $[Rh]_{aq}$ = 100 mg L^{-1}, V_{aq}/V_{IL} = 2, time = 3 hours.

2.3.5 Effects of Temperature on Metal Extraction

Many researchers have reported that temperature affects the extraction behavior of metal ions by ionic liquids [25,26]. The effects of temperature on the extraction behavior of Pt(IV), Pd(II), and Rh(III) with $P_{8,8,8,12}Cl$ and $P_{6,6,6,14}Cl$ were investigated. The effect of extraction temperature was also analyzed, and the results were shown in Figure 2.8. The temperature was varied over the range of 298–333 K, while other parameters were kept constant. The extraction efficiency for all metals decreased as the temperature was increased.

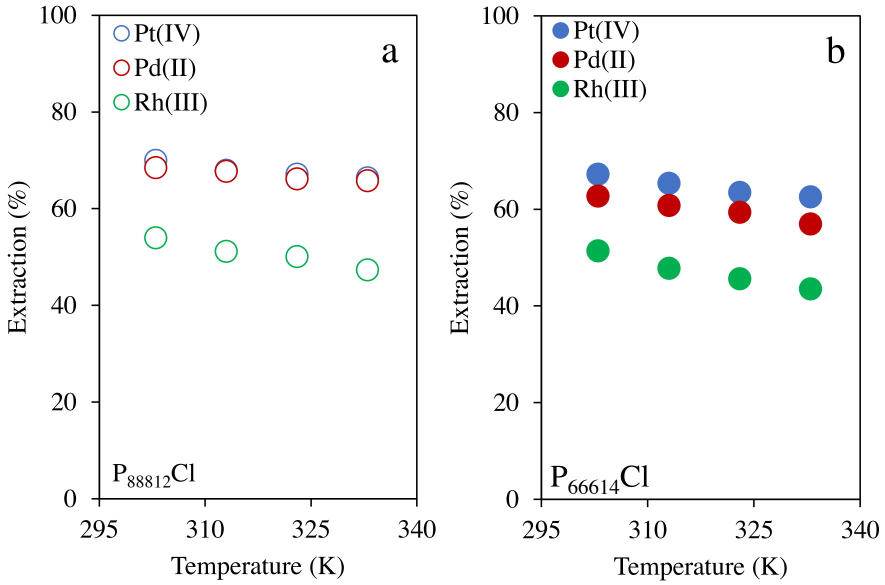


Figure 2.8. Effects of temperature on Pt(IV), Pd(II), and Rh(III) extraction with (a) $P_{8,8,8,12}Cl$ and (b) $P_{6,6,6,14}Cl$; $[M]_{aq} = 200$ mg L^{-1}, $[HCl]_{aq} = 0.5$ mol L^{-1}, $V_{aq}/V_{IL} = 2$, time = 3 hours.

Extraction equilibrium constants for the metal complexes, $K_{ex\text{-}MCl}$ are given by Eq (9) as:

$$K_{ex\text{-}MCl} = \frac{\overline{[(R_3R'P^+)_m(MCl^{m-})]} \cdot [Cl^-]^n_{aq}}{[MCl^{n-}_{aq}] \cdot \overline{[R_3R'P^+Cl^-]}^m} = \frac{D_{MCl^{n-}} \cdot [Cl^-]^n_{aq}}{\overline{[R_3R'P^+Cl^-]}^m} \qquad \begin{matrix}(Pt, Rh{:}m=n)\\(Pd\ {:}m=n-1)\end{matrix} \qquad (9)$$

where MCl is the metal chlorocomplex. Taking the logarithm and rearranging Eq (9), log K_{ex} is given as follows:

$$\log D_{MCl^{n-}} = \log K_{ex\text{-}MCl} + m\log\overline{[R_3R'P^+Cl^-]} - n\log[Cl^-]_{aq} \qquad (10)$$

In the aqueous phase, Cl ions exist in great excess of the metal ions, therefore the total Cl ion concentration can be considered to be constant. Thus, at a given temperature, the Gibbs free energy change of extraction (ΔG_{ex}) can be determined through the following equation:

$$\Delta G_{ex} = -2.303RT\log K_{ex} \tag{11}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the extraction temperature. The free energy change is related to the enthalpy and entropy changes, (ΔH^o) and (ΔS^o), by the following Gibbs–Helmholtz equation;

$$\Delta G_{ex} = \Delta H^o - T\Delta S^o \tag{12}$$

From Equations (11) and (12), the following equation is derived.

$$\log K_{ex} = \left(\frac{-\Delta H^o}{2.303R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Delta S^o}{2.303R}\right) \tag{13}$$

Figure 2.9 shows the effect of temperature on the distribution coefficient of Pt(IV), Pd(II), and Rh(III). The values of ΔH^o and ΔS^o can be obtained from the gradients and intercepts in Figure 2.9.

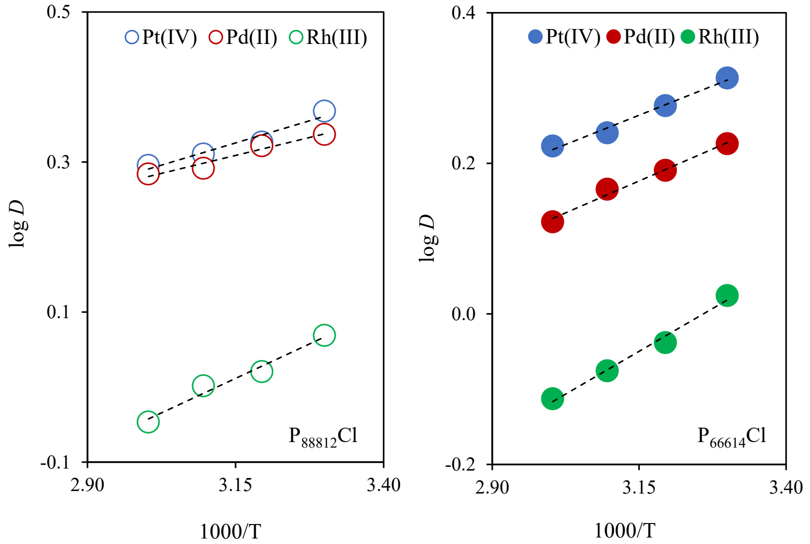


Figure 2.9. Log D vs 1000/T of Pt(IV), Pd(II), and Rh(III) extraction; $[M]_{aq}$ = 200 mg L^{-1}, $[HCl]_{aq}$ = 0.5 mol L^{-1}, V_{aq}/V_{IL} = 2, time = 3 hours.

The values of ΔH^o, ΔS^o, and ΔG_{ex} are listed in Table 2.3. A negative value of enthalpy, which indicates an exothermic extraction process, implies favorable formation of a metal-ligand complex. The change of entropy also derives from an association between the ligand and metal ions, and from the solvation of water molecules, where a negative value is unfavorable for the extraction process. According to the entropy values, $P_{6,6,6,14}$Cl is more ordered than $P_{8,8,8,1,2}$Cl. This result is in agreement with the water content of both ionic liquids, which was found to be highest in $P_{6,6,6,14}$Cl. The extractability depends on the overall enthalpy and entropy contribution to ΔG_{ex}, and a negative value indicates that the extraction process is spontaneous at a given temperature [13]. The novel $P_{8,8,8,12}$Cl ionic liquid was confirmed to be a favorable extractant for Pt(IV), Pd(II), and Rh(III).

Table 2.3. Thermodynamic parameters for metal extraction

Metal	ΔH° [kJ mol^{-1}K^{-1}]		ΔS [J mol^{-1} K^{-1}]		ΔG [kJ mol^{-1} K^{-1}]	
	$P_{8,8,8,12}$Cl	$P_{6,6,6,14}$Cl	$P_{8,8,8,12}$Cl	$P_{6,6,6,14}$Cl	$P_{8,8,8,12}$Cl	$P_{6,6,6,14}$Cl
Pt	-4.52	-5.96	-8.06	-13.70	-2.12	-1.87
Pd	-3.66	-6.49	-5.61	-17.06	-1.99	-1.41
Rh	-7.07	-8.69	-22.0	-28.37	-0.51	-0.24

2.3.6 Stripping Behavior

Metal stripping from the loaded ionic liquid phase is critical for recovery of the metals, and recycling of the extractant phase. In this chapter, 5 mol L^{-1} HCl, H_2SO_4, and HNO_3, 0.5 mol L^{-1} HN_4OH, and 1 mol L^{-1} $CS(NH_2)_2$ in 1 mol L^{-1} HCl were chosen as stripping reagents, and individually applied. Table 2.4 shows the percentage of PGMs stripped from the loaded $P_{8,8,8,12}$Cl and prepared by extraction with 0.5 mol L^{-1} HCl. As shown in Table 2.4, 5 mol L^{-1} HNO_3 was found to be efficient for stripping Pt(IV), and 90% stripping of Pd(II) was achieved with the use of 1 mol L^{-1} of $CS(NH_2)_2$. Significant decrease in the E(%) of Rh(III) in high HCl condition provides a good selectivity during the stripping. As for Rh(III), 70% of Rh(III) was recovered with 5 mol L^{-1} HCl under the present experimental conditions. Thus, HNO_3, $CS(NH_2)_2$, and HCl were effective stripping solutions for Pt(IV), Pd(II), and Rh(III), respectively. These results are similar to those for the $P_{6,6,6,14}Cl$ system as shown in Table 2.4. No emulsion formation or precipitation was observed for all stripping solutions and the aqueous and ionic phases remained transparent. Both phases rapidly separated.

Table 2.4. Stripping behavior of metals from organic phases with various strip solution

		Stripping [%]				
	Metal	5 mol L^{-1} HCl	HNO_3	H_2SO_4	0.5 mol L^{-1} NH_4OH	1 mol L^{-1} $CS(NH_2)_2$
$P_{8,8,8,12}Cl$	Pt	0.30	**74.9**	35.8	0.15	21.2
	Pd	0.07	13.6	18.8	39.1	**91.2**
	Rh	**73.7**	31.8	45.2	19.4	3.71
$P_{6,6,6,14}Cl$	Pt	0.24	**71.3**	10.5	0.98	11.1
	Pd	0.29	0.81	0.12	31.8	**83.4**
	Rh	**72.3**	26.4	31.1	26.7	4.46

2.3.7 Regeneration of the Ionic Liquids

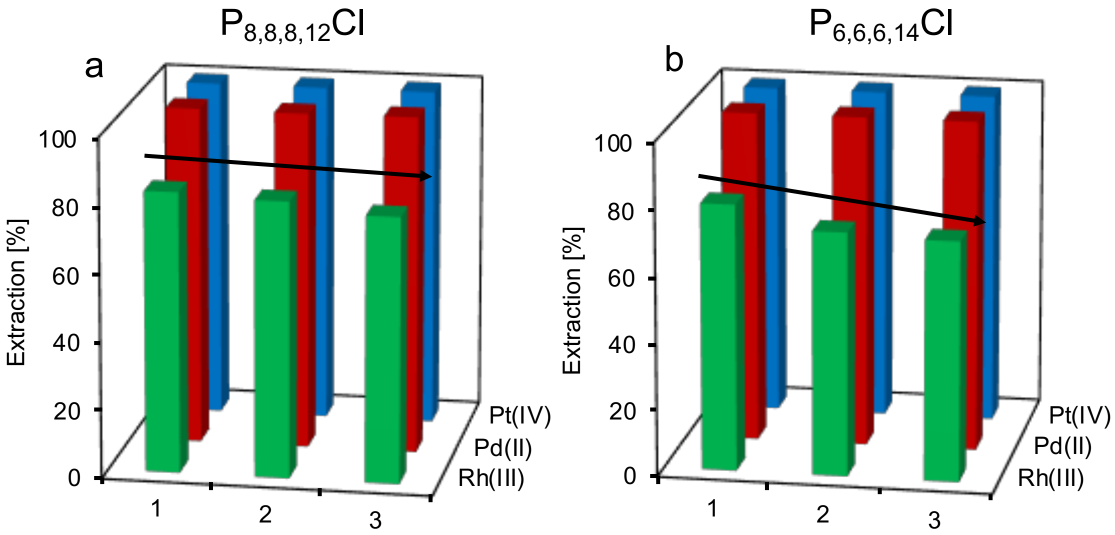


Figure 2.9. Extraction of Pt(IV), Pd(II), and Rh(III) with fresh and regenerated (a) $P_{8,8,8,12}Cl$ and (b) $P_{6,6,6,14}Cl$; IL= $P_{8,8,8,12}Cl$, $[M]_{0,aq}$= 100 mg L^{-1}, $[HCl]_{aq}$ = 0.5 mol L^{-1}, V_{aq}/V_{IL} = 2.

The ability to regenerate and reuse the ionic liquids for subsequent extraction steps is an important environmental and economical consideration. To assess the viability of regeneration, fresh and/or regenerated ionic liquid was equilibrated with a fresh aqueous solution at V_{aq}/V_{IL}= 2. Then, the loaded ionic liquids were stripped with HCl, HNO_3, and $CS(NH_2)_2$, successively. The stripped ionic liquid was then reused for an extraction cycle under similar experimental conditions. These cycles were performed three times. Figure 2.9 shows the extraction performance of the regenerated ionic liquid over three cycles for $P_{8,8,8,12}Cl$ along with the results for $P_{6,6,6,14}Cl$. As shown in Figure 2.9, $P_{8,8,8,12}Cl$ showed a slight decrease (~2%) in the extraction percentage compared with fresh solution over 3 cycles. Conversely, $P_{6,6,6,14}Cl$ which was subjected to a similar extraction-stripping cycles, showed a noticeable decrease (~8%) in the extraction percentage. The decrease in the

$P_{6,6,6,14}Cl$ extraction percentage could be attributed to greater leaching of the ionic liquid cations into the aqueous feed solution.

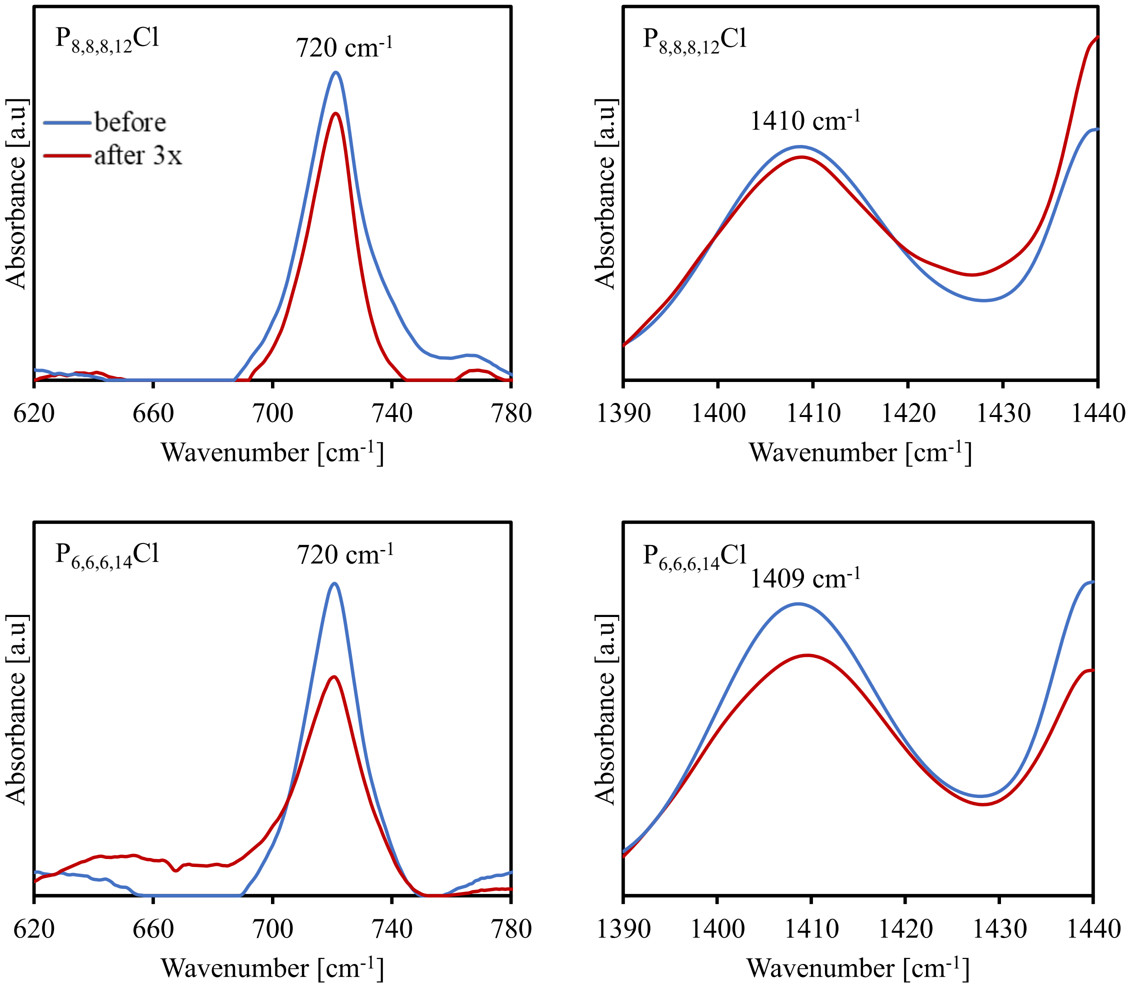


Figure 2.10. Infra-red spectroscopy of the ionic liquid before and after recycling three times.

The degree of cation leaching was assessed by IR spectroscopy through the change of P-C vibration band intensity between before and after three times recycling. P-C stretching vibration appear in the range of 754-634 cm^{-1} [27]. P-CH_2-CH_3 and P-CH_2-R deformation band appear in the range of 1440-1400 cm^{-1}[28]. As presented in Figure

2.10, both ionic liquids show a peak at 720 cm^{-1} which could be associated with P-C stretching band and peak at 1410 cm^{-1} that could be associated with P-CH_2-CH_3/P-CH_2-R deformation band. $P_{8,8,8,12}Cl$ shows no change in the peak intensity even after three times of recycling, while $P_{6,6,6,14}Cl$ shows significant decrease in the peak intensity. Similar trend could also observe for peak at 1410 cm^{-1} which could indicate the level of cation leaching in $P_{6,6,6,14}Cl$ and $P_{8,8,8,12}Cl$.

To validate the cation leaching evidence, both ionic liquids were contacted several times with a fresh aqueous phase (0.5 mol L^{-1} HCl) and then the phosphorous content in each aqueous phase was measured (Figure 2.11). $P_{8,8,8,12}Cl$ exhibited a considerably lower cation release compared with that of $P_{6,6,6,14}Cl$, which might explain the lower decrease of the extraction capability of $P_{8,8,8,12}Cl$ than that of $P_{6,6,6,14}Cl$. Thus, it was showed that $P_{8,8,8,12}Cl$ is highly stable as an extraction solvent and reusable with negligible or only a slight change to its extractive properties.

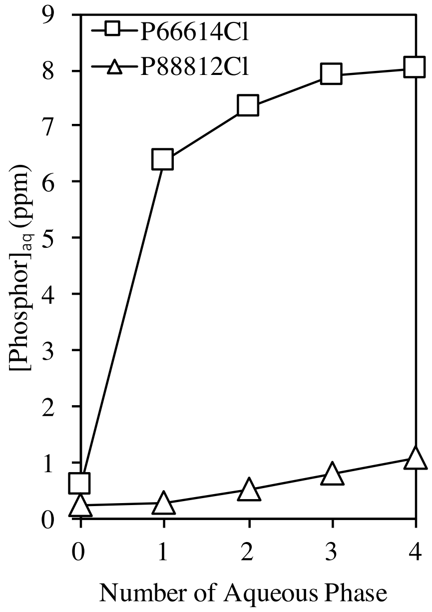


Figure 2.11. Ionic liquid cation release to the aqueous phase after repeated contact with an aqueous phase.; $[M]_{aq} = 0$ mg L^{-1}, $V_{aq}/V_{IL} = 2$, time = 3 hours, Aq phase= 0.5 mol L^{-1} HCl

2.4 Conclusion

The results obtained in this chapter highlight the ability to design ionic liquids with favorable properties for solvent extraction. Based on the hydrophobic design of the cationic moiety in ionic liquids, trioctyl(dodecyl)phosphonium chloride ($P_{8,8,8,12}Cl$) shows higher hydrophobicity and lower viscosity compare to that of its commercial analogue, trihexyl(tetradecyl)phosphonium chloride ($P_{6,6,6,14}Cl$). The novel ionic liquid, $P_{8,8,8,12}Cl$, developed in this chapter was applied to the extraction of Pt(IV), Pd(II), and Rh(III). Owing to its enhanced properties, $P_{8,8,8,12}Cl$ showed a better extraction performance than that of $P_{6,6,6,14}Cl$. Extraction with $P_{8,8,8,12}Cl$ is fast, effective and influenced by hydrochloric acid and chloride ion concentration, which also proceeds according to the anion exchange mechanism. $P_{8,8,8,12}Cl$ could also be effectively regenerated and reused without degradation of the extraction performance, and release of the phosphonium cation was not observed in recycling tests, contrary to results for the conventional ionic liquid $P_{6,6,6,14}Cl$. Hence, the novel ionic liquid is more environmentally friendly because of the low amount of P released. The advantages of $P_{8,8,8,12}Cl$ as an extraction solvent were also confirmed by thermodynamic studies. $P_{8,8,8,12}Cl$ shows potential for use as an extraction solvent for PGMs, and present results demonstrate advantages related to properties that can be readily tuned by changing the molecular structure of the ionic liquid.

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CHAPTER 3. APPLICATION OF A NOVEL PHOSPHONIUM-BASED IONIC LIQUID TO THE SEPARATION OF PLATINUM GROUP METALS FROM AUTOMOTIVE CATALYST LEACHATE

3.1 Introduction

Platinum group metals (PGMs), which occur naturally along with nickel and copper in minerals such as sperrylite or copperite [1], are of significant technological importance. The worldwide demand for PGMs is also steadily increasing owing to the widespread use of these materials in various applications. Presently, 70% of PGMs are consumed by the automobile industry, primarily as components of autocatalytic converters intended to reduce exhaust pollution [2]. However, such catalysts are eventually deactivated, either because of surface coke formation or the loss of active components, and simply become waste materials [3]. Spent catalysts are potentially harmful to the environment because of the presence of soluble/leachable organic and inorganic compounds, and so their disposal in landfills is restricted [3-5]. In addition, as a result of the scarcity and high value of PGMs, there is an increasing interest in recycling spent catalysts.

The recycling and recovery of spent automotive catalysts has become a growing secondary source of PGMs, and various methods have been developed for this purpose, such as hydrometallurgical or pyrometallurgical processes [4]. However, the physical and chemical properties of these metals are very similar and thus they are difficult to separate. Traditional PGM recovery methods involve physical treatments, including acid dissolution, chemical separation and refining [6,7], but have several disadvantages, such as poor selectivity, a high degree of complexity, and numerous recycling streams and refining steps. In contrast, hydrometallurgical leaching followed by solvent extraction offers greater selectivity, a scrubbing step that increases the product purity, and complete removal of metals via multi-stage extraction steps [8,9].

Ionic liquids (ILs) are salts composed of organic cations and inorganic anions that are liquid at room temperature, and these substances have potential applications to metal extraction due to their unique properties. ILs also tend to have negligible vapor pressure relative to more common organic solvents and their properties can be tuned by varying the cation and anion [10]. Hydrophobic ILs are also able to solvate species with a net charge, such as metal complexes [11], and thus can be suitable alternatives to organic solvents in extractions.

The high production cost of ILs often create a large controversy regarding its practical application on industrial scale. However, the use of ILs could lower operating cost (e.g reduce material consumption) and disposal cost (e.g recycling and reuse) than conventional method [12]. Strict regulation over volatile organic compound in various countries bring another advantage to ILs. Therefore, the high investment cost for ILs could be compensated through the additional value of ILs for the process.

Various ILs, such as those based on imidazolium, ammonium, pyridinium and phosphonium cations, have been applied to the extraction of metal ions [13]. Although these ILs have been employed successfully as catalysts and extractants, there are certain limitations associated with their use, such as their high viscosities and the use of organic solvents to decrease its viscosities. Svecova *et al.* reported the extraction of Pd(II) and Rh(III) with an undiluted trihexyl(tetradecyl)phosphonium IL, although the subsequent recovery of these metals from the IL has not yet been demonstrated [14]. Previously, a new phosphonium-based IL demonstrated excellent performance during the extraction of Pt(IV), Pd(II) and Rh(III) [15]. This trioctyl(dodecyl)phosphonium chloride ($P_{8,8,8,12}Cl$)

possesses low viscosity and high hydrophobicity, which allows for rapid transfer between aqueous and organic phases. $P_{8,8,8,12}Cl$ can also be effectively regenerated and reused with only a slight performance degradation and is more environmentally friendly than some other ILs owing to the minimal number of cations released to the environment.

The present chapter assessed the extraction, separation and recovery of PGMs from an automotive catalyst leachate containing a variety of other metals in addition to Pd(II) and Rh(III), some at high concentrations. These extractions were carried out using undiluted $P_{8,8,8,12}Cl$ as the solvent and the conditions were optimized for each extraction step. On the basis of the results, an optimum process for the recovery of Pd(II) and Rh(III) from automotive catalyst leachate is proposed.

3.2 Experimental

3.2.1 Reagents

$P_{8,8,8,12}Cl$ was supplied by Nippon Chemical Ind. Co., Ltd., Tokyo, Japan. Physicochemical properties of $P_{8,8,8,12}Cl$ was shown in Table 3.1.

A model leachate was prepared using a Pd standard solution, $FeCl_3.6H_2O$, $AlCl_3.6H_2O$, $ZrCl_4$ and $MgCl_2.6H_2O$ (all from Wako Pure Chemical Industries, Ltd., Osaka, Japan), $LaCl_3.7H_2O$, $CeCl_3.7H_2O$ and $BaCl_2.2H_2O$ (Kishida Chemical Co., Ltd., Osaka, Japan), a Rh standard solution, and $PrCl_3.7H_2O$ (Kanto Chemical Co., Inc., Tokyo, Japan). All other chemicals used were reagent grade, obtained from commercial sources and used without further purification.

Table 3.1. Physicochemical properties of $P_{8,8,8,12}Cl$[15]

Sample	Viscosity [mPa.s]	Density [g ml^{-1}]	Water content in wet IL [wt%]	Solubility in water [mg L^{-1}]^a
$P_{8,8,8,12}Cl$	800.8	0.8767	4.30	0.218

[a] IL solubility in water was determined by measuring the P concentration.

3.2.2 Automotive catalyst leachate

An automotive catalyst leachate was prepared by crushing an automotive catalyst into a coarse powder. This material was subsequently milled with 20 mm alumina balls at 90 rpm for 30 min until a fine powder (d_{90} = 75 μm) was achieved. A specific mass of the catalyst powder was added to a quantity of 5 mol L^{-1} HCl and refluxed at 343 K for 24 h with constant stirring [16]. After filtration of the mixture, the concentrations of metal ions in the filtrate (the leachate) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 8300, Massachussets, USA), and the resulting values are provided in Table 3.2. A model leachate was subsequently prepared by dissolving these same metal salts at the same concentrations in 5 mol L^{-1} HCl.

Table 3.2. Composition of automotive catalyst leachate

Metal	Pd	Rh	Ce	La	Pr	Ba	Al	Zr	Mg	Fe
Conc. [mg L^{-1}]	367.6	32.5	107.9	39.3	77.7	379.2	3898	52.9	555.4	32.2

3.2.3 Solvent extraction procedure

All extraction experiments were performed by mixing the aqueous phase (model or actual leachate) and the IL at a 2:1 volume ratio unless otherwise noted. Each mixture was vigorously agitated using a vortex mixer (Vortex Genie 2, Scientific Industries, New York, USA) for 1 min and then placed in a 298 K water bath shaker (NTS-4000, Eyela, Tokyo, Japan) for a defined period of time at 160 rpm, where the time when both phases were mixed was defined as time 0. In order to attain equilibrium for all metals, the mixture was shaken more than 12 h. The mixture was centrifuged at 5800 G for 5 min at 298 K for phase separation. The metal ion concentrations in the aqueous phase before and after extraction were determined by ICP-OES. The forms of iron species present in the ionic liquid phase were measured qualitatively using an Ultraviolet-visible (UV-vis) spectrometer (V-670 JASCO Co., Tokyo, Japan) with 1 nm resolution. The Fe(III) concentration in each sample solution was kept around 0.4 mmol L^{-1}. Impurities from the extraction process was removed from the IL phase through scrubbing process. The scrubbing process was performed in similar manner with extraction. Stripping of the Pd(II) and Rh(III) from the IL was performed in a similar manner but using $CS(NH_2)_2$ or 5 mol L^{-1} HCl, respectively, at a defined volume ratio, unless stated otherwise. The extraction (E), stripping (S) and scrubbing (Scrub) efficiencies were calculated from the equations

$$E\% = \frac{[M]_{IL}V_{IL}}{[M]_{IL}V_{IL}+[M]_{aq}V_{aq}} \times 100 \tag{1}$$

$$S\% = \frac{[M]_{st}V_{st}}{[M]_{st}V_{St}+[M]_{IL}V_{IL}} \times 100 \tag{2}$$

$$Scrub\% = \frac{[M]_{sc}V_{sc}}{[M]_{sc}V_{sc}+[M]_{IL}V_{IL}} \times 100 \tag{3}$$

where V (L) and C (mg L^{-1}) are the volume and metal ion concentrations, respectively, and the subscripts aq, IL, st and sc denote aqueous, ionic liquid, stripping and scrubbing phases, respectively.

3.3 Results and Discussion

3.3.1 Extraction of metal ions

The extraction of metal ions from the leachate using this novel ionic liquid was assessed at various HCl concentrations. As noted, the metal concentrations in the model leachate were determined based on the analysis of leaching from an actual automotive catalyst. The results of the extraction trials are presented in Figure 3.1.

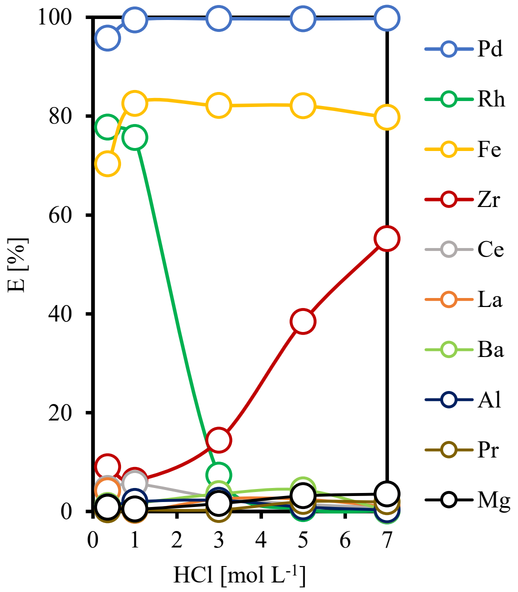

Figure 3.1. Data for the extraction of a model leachate with $P_{8,8,8,12}Cl$. Conditions: $V_{aq}/V_{IL} = 2$, time = 8 h, T= 298 K. Concentrations in the model leachate (mg L^{-1}) were: Pd 300, Rh 26.5, Ce 88, La 32.1, Pr 63.4, Ba 309.5, Al 3181, Zr 43.17, Mg 453.3 and Fe 26.3.

Presently, Pd(II) was quantitatively extracted over the entire pH range tested, and the presence of various other metal ions in the model leachate had no effect. In chapter 2, it was shown by slope analysis that two $P_{8,8,8,12}Cl$ molecules extract one Pd(II) by anion exchange with two Cl^- at high HCl concentration, where the primary Pd(II) species is $PdCl_4^{2-}$. Thus, under the present experimental conditions, the Pd(II) extraction mechanism is believed to be

$$[PdCl_4]^{2-}{}_{aq} + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2PdCl_4} + 2Cl^-{}_{(aq)} \tag{4}$$

where the horizontal bars denote the organic phases. In contrast, Rh(III) was readily extracted at HCl concentrations below 1 mol L^{-1}. The extraction efficiency was 80% at 1 mol L^{-1} HCl, but only several percent above 3 mol L^{-1}. This trend is attributed to the distribution of Rh(III) chlorocomplex species. According to the complex speciation diagram of Rh(III), at 5 mol L^{-1} HCl, about 70% of Rh(III) complex was present as $[RhCl_6]^3$. This species is particularly difficult to extract due to steric effects as well as its high charge density and significant energy of hydration [18]. At HCl concentrations less than 3 mol L^{-1}, $RhCl_5^{2-}$ is the dominant Rh(III) species under the present experimental conditions [19]. Thus, the Rh(III) extraction mechanism with $P_{8,8,8,12}Cl$ could be

$$[RhCl_5]^{2-}{}_{(aq)} + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2RhCl_5} + 2Cl^-{}_{(aq)} \tag{5}$$

the extraction mechanism is supported by slope analysis shown in chapter 2 [15]. The above results demonstrate that the Pd(II) and Rh(III) extraction processes are unchanged even in the presence of other metal ions.

Selective extraction of PGMs such as Pd(II) and Rh(III) from the leachate was found to be possible using $P_{8,8,8,12}Cl$. Two additional metals (Fe(III) and Zr(IV)) were also readily extracted under certain conditions, but could be completely separated from the Pd(II) and Rh(III) via a single extraction operation. Figure 2 demonstrates that Fe(III) was absorbed into the $P_{8,8,8,12}Cl$ at especially high concentrations, and that the extent of this extraction increased along with the HCl concentration to a constant value of 80% at 1 mol L^{-1} HCl.

The iron chloride species generated in HCl will vary with the chloride concentration, and it can be studied by using UV-vis spectrometry. The spectrum of the 5 mol L^{-1} HCl solution in Figure 3.2 showed a distinct peak at 360 nm and small shoulder peak at 316 nm, which can be attributed to the presence of $FeCl_3$ in the solution[20].

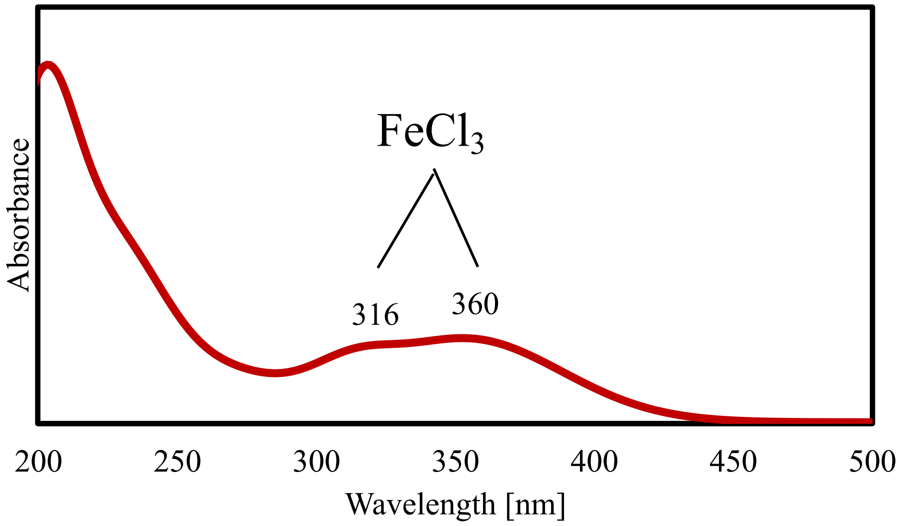

Figure 3.2. UV-vis spectra of Fe(III) in 5 mol L^{-1} HCl

This result was consistent with the speciation diagram of Fe(III) complex. Meanwhile, the typical peaks for $[FeCl_4]^-$ were observed in the spectrum of $P_{8,8,8,12}Cl$ after extraction, as described later. Thus, the extraction of Fe(III) could follow the process shown in Eq (6) [21].

$$FeCl_{3(aq)} + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2FeCl_4} \qquad (6)$$

The data in Figure 3.1 also show that the amount of Zr(IV) extracted into the IL steadily increased with increases in the HCl concentration. Solvation likely played an important role in the extraction of Zr(IV) at HCl concentrations above 0.1 mol L^{-1}, based on the process in Eq. (7) or (8) [22].

$$Zr(OH)_2{}^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} + 2\ \overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2Zr(OH)_2Cl_2} \tag{7}$$

$$Zr(OH)_2{}^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} + 2\ \overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2Zr(OH)_2Cl_4} \tag{8}$$

eq. (7) and (8) indicates that an increase in the chloride ion concentration would have a positive effect on the extraction of Zr(IV). The extraction pathway would likely depend on the amount of Cl- ion present. This occurs because Zr(IV) is a hard Lewis acid while the chloride ion is a hard Lewis base, and so the two have a strong tendency to form chlorocomplexes [23] that subsequently migrate to the IL phase [24]. None of the other metals were extracted regardless of the HCl concentration, but it was evident that the PGMs would have to be separated from the Fe(III) and Zr(IV) to permit the recycling of automotive catalysts by solvent extraction using $P_{8,8,8,12}Cl$.

3.3.2 Extraction kinetics

Figure 3.3 shows the time dependence of the degree of extraction of the metals from the model leachate (at 5 mol L^{-1} HCl), holding all other parameters constant. The extraction of Pd(II) with $P_{8,8,8,12}Cl$ was rapid, such that equilibrium was attained within 5 min. Funahashi shows that Pd(II) has significantly higher reaction rate compare to other metals [25]. Moreover, complex geometry of Pd(II) might also influence its extraction rate. Schumann and Elias shows that square planar has significantly higher reactivity even when compare to similar geometry with 4 coordination number, such as tetrahedral [26]. Thus, $[PdCl_4]^{2-}$ complex with square planar geometry has higher extraction rate compare to that of $[FeCl_4]^-$ with tetrahedral geometry. Although Fe(III) was also readily extracted, a longer time span was required to reach equilibrium. Zr(IV) also exhibited a similar trend to Fe(III), such that equilibration required extraction for 5 h or more, while very little Rh(III) was obtained from the liquor at this HCl concentration. These results suggest that an extraction of approximately 10 min allows the efficient separation of Pd(II) from Fe(III) and Zr(IV) under the present experimental conditions.

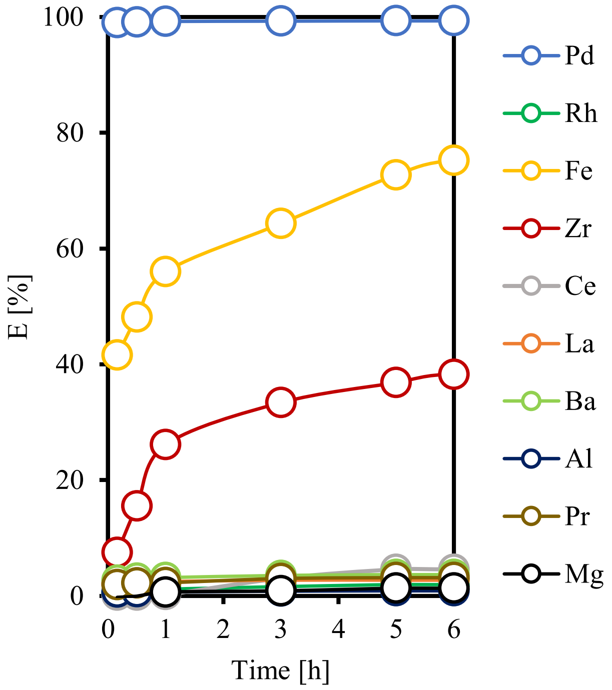

Figure 3.3. Effect of contact time on the extraction of metals from the model leachate. Conditions: $V_{aq}/V_{IL} = 2$, $[HCl]_{aq} = 5$ mol L^{-1}, T= 298 K. The metal concentrations in the aqueous phase were the same as those provided in the caption to Figure 2.

3.4.3 Scrubbing of Fe(III) from the loaded ionic liquid

The scrubbing of metallic impurities from the loaded phase is sometimes an effective means of enhancing the separation efficiency. As an example, Sun et al. reported the efficient scrubbing of Fe(III) from the solvent tri-n-octylamine using 5 mol L^{-1} H_2SO_4 [27]. In this case, tri-n-octylamine facilitates the transfer of H_2SO_4 in between the two interface of extractant and stripping phase. Mishra et al. determined that water is an effective scrubbing solvent for the removal of Fe(III) from Aliquot 336 [28]. Because the data show that the transfer of Fe(III) to the IL phase from the leachate is unavoidable, the selective removal of Fe(III) from the Pd(II)-loaded IL phase is required. Therefore, we examined the removal of Fe(III) using 0.1 mol L^{-1} HCl, 0.5 mol L^{-1} HNO_3, 0.5 mol L^{-1} H_2SO_4, 1 mol L^{-1} Na_2SO_3 and water. As shown in Figure 3.4A, 0.1 mol L^{-1} HCl, 0.5 mol L^{-1} H_2SO_4 and water all showed some capacity to remove Fe(III), although the scrubbing efficiencies with these solutions were lower than 40%.

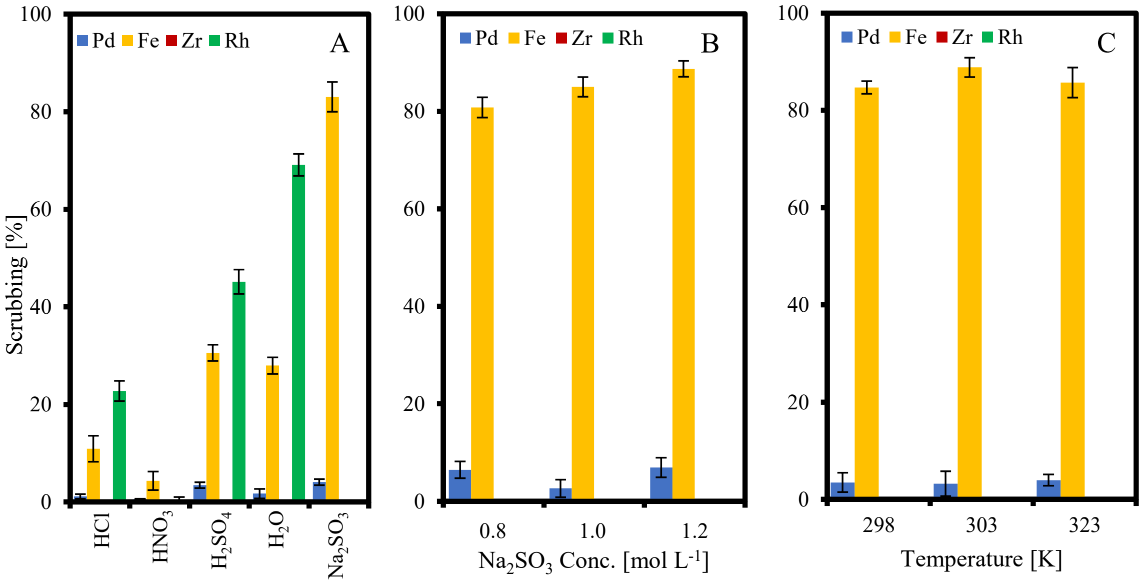

Figure 3.4. Fe scrubbing from loaded $P_{8,8,8,12}Cl$. (A) The results obtained using 0.1 mol L^{-1} HCl, 0.5 mol L^{-1} HNO_3 and H_2SO_4, water and 1.0 mol L^{-1} Na_2SO_3 at 323 K. (B) The effect of Na_2SO_3 concentration at 323 K and 30 min. (C) The effect of temperature using 1 mol L^{-1} Na_2SO_3 at 30 min and $V_{aq}/V_{IL} = 2$.

The effect of Na_2SO_3 concentration on the Fe(III) scrubbing efficiency was also investigated, and Figure 3.4B demonstrates that in the extent of Fe(III) removal was directly correlated with the concentration. As the Na_2SO_3 level was increased to 1.2 mol L^{-1} the efficiency gradually increased to 88%. As shown in Figure 3.4C, the scrubbing efficiency was not greatly altered by changing the solution temperature and Fe(III) was removed almost exclusively at all temperatures.

The highest Fe(III) scrubbing efficiency was achieved using Na_2SO_3, with approximately 85% removal of the impurity. This superior performance can be attributed to a combination of the hydrolysis of Na_2SO_3 and the reduction of Fe(III) to Fe(II) [20]. In addition to promoting the reduction of Fe(III), Na_2SO_3 could also prevent the precipitation of Fe(III) [29]. UV-visible spectra of the Fe(III)-loaded $P_{8,8,8,12}Cl$ were recorded before and after scrubbing (Figure 3.5A) to assess the removal of Fe(III) species. The primary peaks in these spectra at 242, 320 and 368 nm prior to scrubbing confirm the presence of $[FeCl_4]^-$ species in the IL phase [21], while the new absorption band at 280 nm after scrubbing can be assigned to SO_2 [20]. Based on these results, the scrubbing of Fe(III) is believed to proceed via the processes shown in Eqs. (9-12).

$$SO_3^{2-} + H_2O \rightarrow 2OH^- + SO_2 \tag{9}$$

$$\overline{[P_{88812}]FeCl_4} + 3OH^- \rightarrow Fe(OH)_3 + 3Cl^- + \overline{P_{88812}Cl} \tag{10}$$

$$2Fe(OH)_3 + SO_3^{2-} \rightarrow Fe(OH)_2 + SO_4^{2-} + H_2O \tag{11}$$

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + 4H^+ + SO_4^{2-} \tag{12}$$

Fe(III) stripping is therefore directly correlated with the extent of Fe(III) reduction, and the presence of SO_2 enhances the removal process [29]. Formation of Fe(II) was confirmed by using UV-vis spectra with 1,10-phenanthroline. The reagent of 0.01 mol L^{-1} was added to the scrubbing solution, showing a translucent reddish color. A distinct peak at 518 nm which is the signature peak for $(phen)_3Fe(II)$ complex, was observed, as shown in Figure 3.5B [30]. This further support the underlying mechanism of Fe(III) scrubbing with Na_2SO_3. Furthermore, Na_2SO_3 could be used to remove Fe(III) from the IL phase without reducing the Pd(II) concentration.

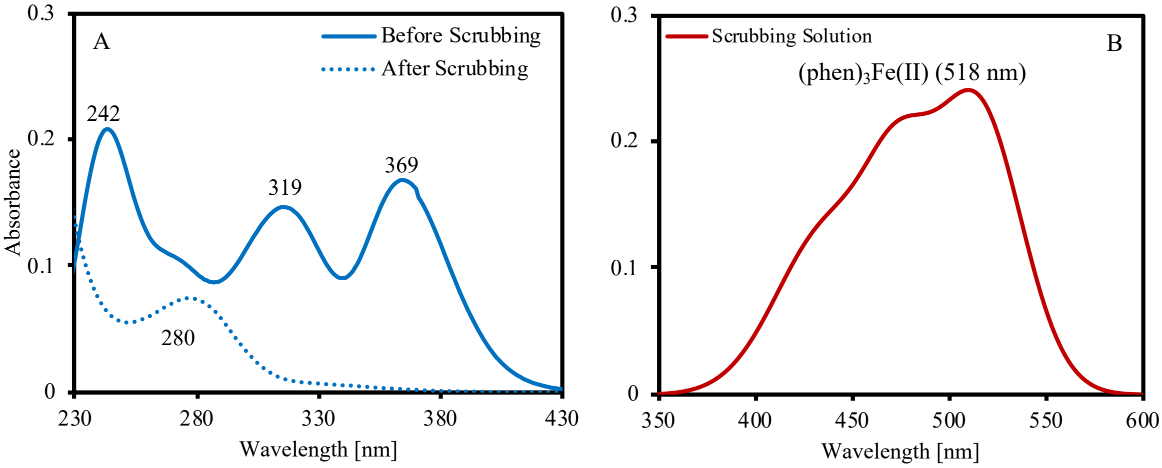

Figure 3.5. UV-visible spectra of (A) iron(III)-chlorocomplexes in $P_{8,8,8,12}Cl$ before and after scrubbing with Na_2SO_3. Conditions: $[HCl]_{aq} = 5$ mol L^{-1}, $V_{aq}/V_{IL} = 2$. Spectra were acquired in ethanol. (B) iron(II)-phenanthroline compelexes from scrubbing solution. Conditions: 1,10-phenanthroline = 0.01 mol L^{-1}

3.3.4 Pd(II) stripping

The recovery of Pd(II) from the loaded IL phase is an important aspect of the recycling process. In chapter 2, it was determined that Pd(II) could be selectively stripped from an IL phase loaded with several PGMs (Pd(II), Pt(IV) and Rh(III)) with an efficiency of greater than 90% using $CS(NH_2)_2$. This compound was therefore applied as a stripping reagent for Pd(II) in the present chapter, immediately after scrubbing Fe(III) from the IL phase.

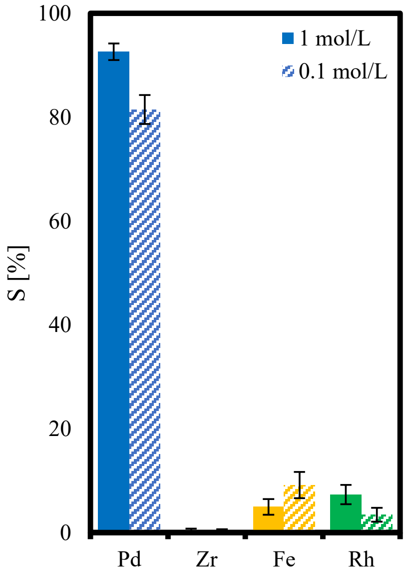

Figure 3.6. Stripping of Pd(II) from loaded $P_{8,8,8,12}Cl$ using $CS(NH_2)_2$. Conditions: $V_{aq}/V_{IL} = 2$ and T= 298 K.

As shown in Figure 3.6, the $CS(NH_2)_2$ concentration had a slight effect on the stripping efficiency, such that increasing the level from 0.1 to 1 mol L^{-1} enhanced the removal efficiency by 10%. However, both stripping solutions produced high purity Pd(II) (approximately 97%). In prior work, $CS(NH_2)_2$ has shown a similar capability to remove Pd(II) from several extractants, such as di-(2-ethylhexyl) thiophosphoric acid (DEHTPA), Alamine 336, trihexyl(tetradecyl)phosphonium chloride (Cyphos IL101) and N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl] glycine/phenylalanine (D2EHAG/F) [31-34]. Some of these studies also used HCl along with $CS(NH_2)_2$ to depress metal hydrolysis during the stripping operation. However, $CS(NH_2)_2$ shows a more pronounced effect than HCl for the recovery of Pd(II) [32]. The effectiveness of $CS(NH_2)_2$ as a Pd(II) removal agent is related to its soft ligand properties. According to the hard-soft acid base theory, Pd(II) is categorized as a soft metal and so forms a water-soluble complex with thiourea, $Pd(CS(NH_2)_2)_4^{2+}$ [31]. The dissociation of Pd from Pd-thiourea complex can be achieved through several steps. $[Pd(CS(NH_2)_2)_4]^{2+}$ is hydrolyzed under alkaline solution, to a metastable intermediate complex $[Pd(OH)_2(CS(NH_2)_2)]$ [35], which is decomposed rapidly and form PdS [36], followed by the reaction with HCl solution to from palladium chlorocomplex, $PdCl_2$ [37].

3.3.5 Rh extraction and stripping

The recovery of Rh(III) from the leachate is also desirable. After the first extraction operation at 5 mol L^{-1} HCl, the aqueous raffinate was mixed with a fresh portion of IL to allow Rh(III) extraction. Simultaneously, the HCl concentration of the aqueous phase was adjusted to 1 mol L^{-1} so as to increase the extraction efficiency, based on the results shown in Figure 2. The extraction was carried out at a V_{aq}/V_{IL} ratio of 2 for 5 h.

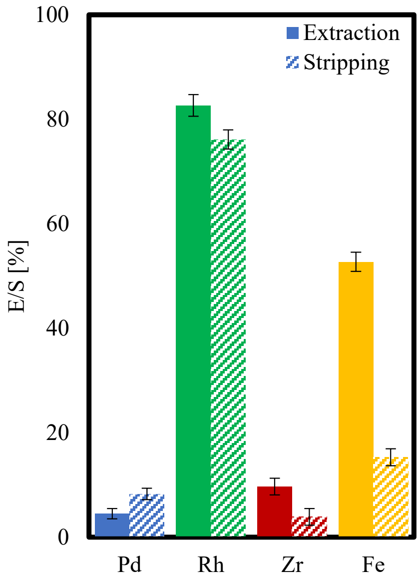

Figure 3.7. Extraction of Rh(III) from the raffinate (1 mol L^{-1} HCl) and stripping of Rh(III) using 5 mol L^{-1} HCl. Conditions: V_{aq}/V_{IL} = 2, T = 298 K, time = 5 h.

Figure 3.7 shows the extraction of metals from the raffinate and results obtained from stripping the metal-loaded IL solution. The $P_{8,8,8,12}Cl$ was able to extract more than 80% of the Rh(III) from the aqueous phase, and the recovery of this Rh(III) from the loaded IL phase was investigated using 5 mol L^{-1} HCl for 24 h. The data in Figure 3.7 demonstrate that approximately 80% of the Rh(III) was recovered from the loaded IL solution. After the stripping operation was completed, neither an emulsion nor a precipitate was present, and both phases were observed to rapidly separate.

3.3.6 Recovery of Pd and Rh from actual automotive catalyst leachate

Because both Pd(II) and Rh(III) were successfully removed from the model solution, the novel IL was applied to a real-world automotive catalyst leach solution. Based on the results obtained using the model solution, a process for the recovery of Pd(II) and Rh(III) from the actual catalyst leachate (at 5 mol L^{-1} HCl) was developed, and is summarized in Figure 3.8.

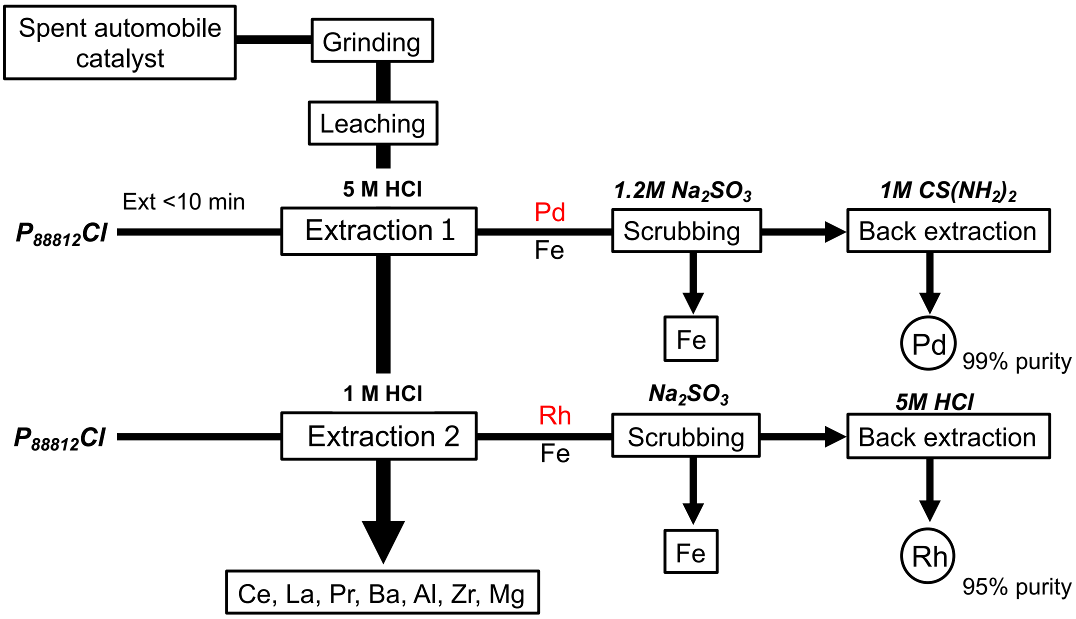

Figure 3.8. Flow chart summarizing the separation and recovery of Pd(II) and Rh(III) from an automotive catalyst leachate.

In the first extraction stage, the leachate (at 5 mol L^{-1} HCl) is mixed with $P_{8,8,8,12}Cl$ for less than 10 min, to allow for Pd(II) extraction. This short extraction time is intended to limit the extraction of Zr(IV), due to the slower extraction rate of this species. The metal-loaded $P_{8,8,8,12}Cl$ is then moved to the scrubbing stage, which uses 1.2 mol L^{-1} Na_2SO_3 at 303 K to remove Fe(III) from the IL. Subsequently, Pd(II) is selectively recovered from the IL using 1 mol L^{-1} $CS(NH_2)_2$. Rh(III) is extracted from the raffinate left over from the first extraction stage by adding a fresh quantity of $P_{8,8,8,12}Cl$ while also adjusting the HCl concentration to 1 mol L^{-1}. Finally, the Rh(III) is recovered by mixing the loaded $P_{8,8,8,12}Cl$ with 5 mol L^{-1} HCl.

In subsequent trials, Pd(II) and Rh(III) were recovered from an actual automotive catalyst leachate (as shown in Table 3.2) using the above process. During the first stage 10 min extraction, the $P_{8,8,8,12}Cl$ was able to extract Pd(II) almost quantitatively (approximately 99%), along with the removal of some Fe(III) (approximately 50%) and only a small amount of the other metals (Figure 3.9A). In the following scrubbing stage, about 90% of the Fe(III) was removed from the IL solution with Na_2SO_3 during a 30 min operation, as can be seen from Figure 3.9B. Following the scrubbing and the reduction of Fe(III) to Fe(II), a high recovery of Pd(II) (approximately 90%) was achieved using 1 mol L^{-1} $CS(NH_2)_2$, as shown in Figure 3.9C. In the second extraction stage, fresh $P_{8,8,8,12}Cl$ was able to extract 80% of the Rh(III) from the raffinate, as is evident from Figure 3.9D, along with the extraction of more than 50% of the Fe(III). Therefore, the metal-loaded $P_{8,8,8,12}Cl$ was also scrubbed to remove Fe(III) in a similar manner to the first scrubbing step. This process removed almost 90% of the Fe(III), as seen in Figure 3.9E. Subsequent to the Fe(III) scrubbing, 5 mol L^{-1} HCl was used to recover almost 80% of the Rh(III) from the IL solution (Figure 3.9F). Overall, the novel $P_{8,8,8,12}Cl$ was able to selectively recovered Pd(II) and Rh(III) from the automotive catalyst leachate in high purities (approximately 99% for Pd(II) and 95% for Rh(III)).

It has been confirmed that $P_{8,8,8,12}Cl$ after stripping is regenerated by contacting with a high concentration of HCl and is reusable with a small loss [15]. The facts that $P_{8,8,8,12}Cl$ is stable as an extraction solvent and is readily regenerated also suggest the potential use of ILs which have been known to be expensive.

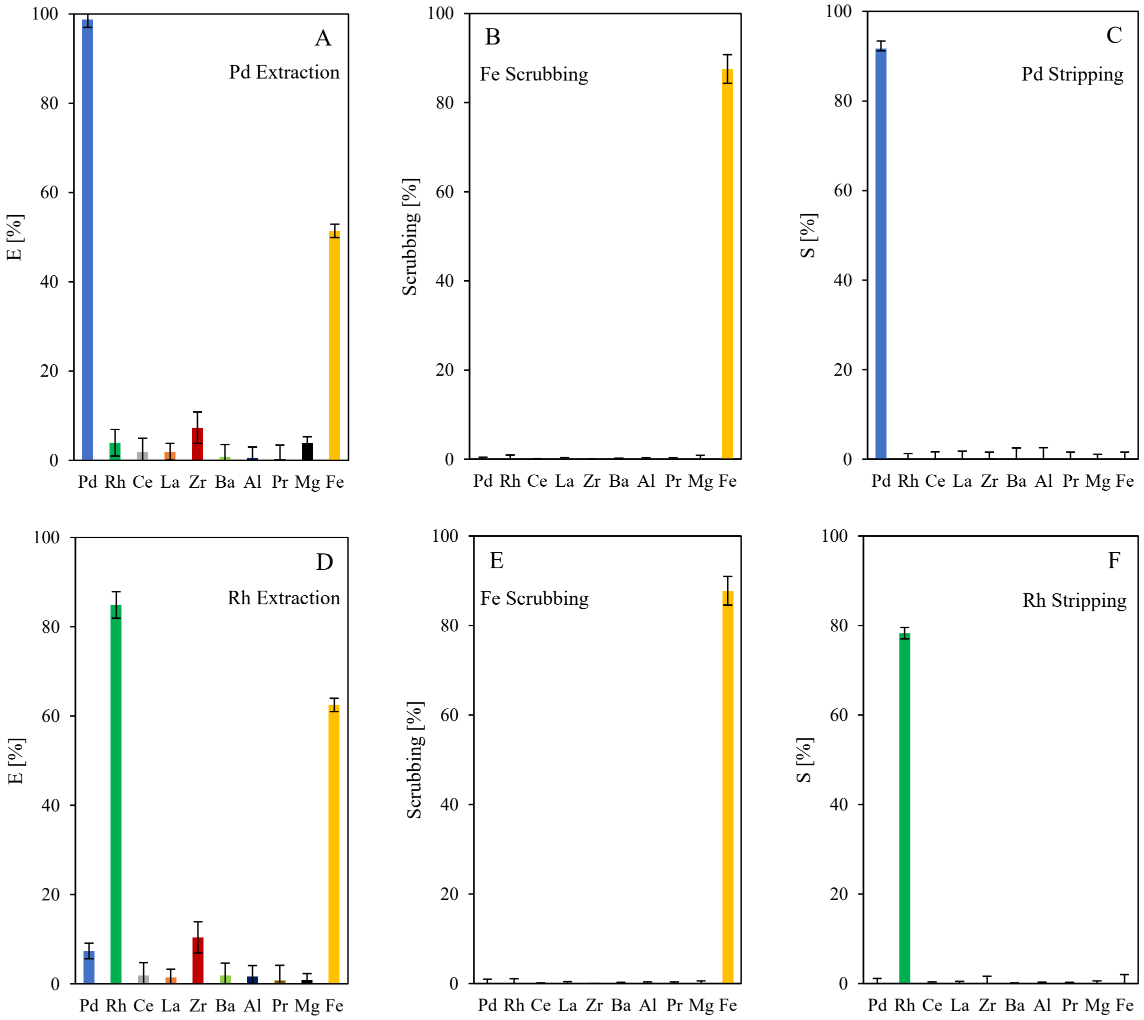

Figure 3.9. Data for the processing of an automotive catalyst leachate. (A) Pd extraction using $[HCl]_{aq}$: 5 mol L^{-1}, time: 10 min. (B) First Fe(III) scrubbing using Na_2SO_3: 1.2 mol L^{-1}, T: 323 K, time: 30 min. (C) Pd stripping using $CS(NH_2)_2$: 1 mol L^{-1}. (D) Rh extraction using $[HCl]_{aq}$: 1 mol L^{-1}, time: 5 h. (E) Second Fe(III) scrubbing using Na_2SO_3: 1.2 mol L^{-1}, T: 323 K, time: 30 min. (F) Rh(III) stripping using HCl: 5 mol L^{-1}. $V_{aq}/V_{IL} = 2$, T = 298 K.

3.4 Conclusion

A complete hydrometallurgical process for the separation and recovery of Pd(II) and Rh(III) from automotive catalyst leachate containing chloride was developed. This process was examined using laboratory-scale solvent extraction with the newly developed phosphonium-based ionic liquid trioctyl(dodecyl)phosphonium chloride ($P_{8,8,8,12}Cl$). Separation of both metals was achieved by adjusting the acid concentration of the solution. Pd(II) was recovered using a combination of thiourea and a low acid concentration, while Rh(III) was recovered using a high acid concentration. In both cases, Fe(III) scrubbing was required but this was readily achieved using Na_2SO_3. The recovered Pd(II) and Rh(III) were highly pure (99% and 95%, respectively). The present approach demonstrates the capability of the newly designed $P_{8,8,8,12}Cl$ to recover precious metals from automotive catalyst leachate, thus addressing an important environmental issue.

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CHAPTER 4. SELECTIVE RECOVERY OF PLATINUM GROUP METALS FROM SPENT AUTOMOTIVE CATALYST BY LEACHING AND SOLVENT EXTRACTION

4.1 Introduction

Platinum group metals (PGMs) are crucially important in various fields, especially in the automotive industry as the key components of exhaust catalysts. Development of exhaust catalysts has significantly increased in recent years because of environmental concern caused by air pollution. Exhaust catalysts mainly use platinum (Pt), palladium (Pd), and rhodium (Rh) as one of their main components. The catalytic activity decreases over time and the deactivated catalysts eventually become waste. Disposal of spent catalysts in landfill is restricted because of the presence of harmful leachable substances [1]. Accordingly, recycling of spent catalyst waste not only provides economic benefits, but it also contributes to material sustainability [2]. Efficient and cost-effective methods to recover PGMs from various spent materials are being pursued. The importance of recovery and recycling approaches for spent industrial and automotive catalysts is also increasing owing to their potential harmful effects.

The main process technologies for recovery of PGMs are categorized as pyrometallurgical methods, selective chlorination processes, and hydrometallurgical methods, such as solvent extraction. Recovery of PGMs by pyrometallurgy requires various processes, which take a long time and consume a large amount of energy. In pyrometallurgical methods, the ceramic carrier of the catalyst is ground and then melted with addition of other metals in the solid or vapor state to produce a PGM alloy and a ceramic waste slag. In recent years, hydrometallurgical methods have attracted attention for PGM recovery. This method has a number of advantages, such as high selectivity, high metal purity, and complete recovery of metals by multi-stage operation [3]. The solvent extraction process makes it possible to recover valuable metals, such as platinum and palladium, from secondary resources or spent materials, or remove environmentally harmful compounds [4]. When the technique is applied to PGM recycling, the metals contained in the scrap are dissolved in a mineral acid and the leachate is subjected to solvent extraction [5]. The leachate from such wastes contain a variety of metal ions along with PGMs. Thus, an efficient process for selective recovery of PGMs with low environmental impact is required.

In recent years, various studies have reported synthesis and application of ionic liquids (ILs). The growing interest in ILs is because of their unique properties, such as their low volatility, low flammability, and low melting point [6]. It has recently been found that ILs themselves possess high extraction ability and selectivity for some metal ions, and their application as an extraction solvent (extractant) without dilution has been intensively studied [7-9]. Undiluted phosphonium-based ILs have been applied to recovery of various metals, such as precious and transition metals [10-12]. In a previous chapter, the phosphonium-based IL trioctyl(dodecyl)phosphonium chloride ($P_{8,8,8,12}Cl$) was synthesized and applied it to metal extraction. This IL compound was first synthesized in 2011 for other purposes [13]. The phosphonium-based IL exhibits excellent performance for extraction and separation of Pt(IV), Pd(II), and Rh(III) in chloride solution. $P_{8,8,8,12}Cl$ possesses low viscosity and high hydrophobicity, which allows for rapid metal transfer between the aqueous and organic phases. Regeneration and reuse of $P_{8,8,8,12}Cl$ are also possible with a slight decrease in performance. $P_{8,8,8,12}Cl$ has also been applied to selective recovery of Pd(II) and Rh(II) from the leachate of a unused automotive catalyst containing Pd(II) and Rh(II) as PGMs and various other metals [14].

The aim of this chapter is to develop an efficient and eco-friendly process for recovering the PGMs from spent automotive catalysts using an IL extraction solvent. The metal components of the waste catalyst depend on the type, model, and year of the vehicle, and the working conditions. In the present chapter, leaching from a used catalyst was investigated and the metal components were analyzed. Extraction, separation, and recovery of Pt, Pd, and Rh from a real waste automotive catalyst leachate was investigated using undiluted $P_{8,8,8,12}Cl$ as the extraction solvent. The feasibility of using ILs to recycle valuable metals, such as PGMs, is also discussed.

4.2 Experimental

4.2.1 Reagents

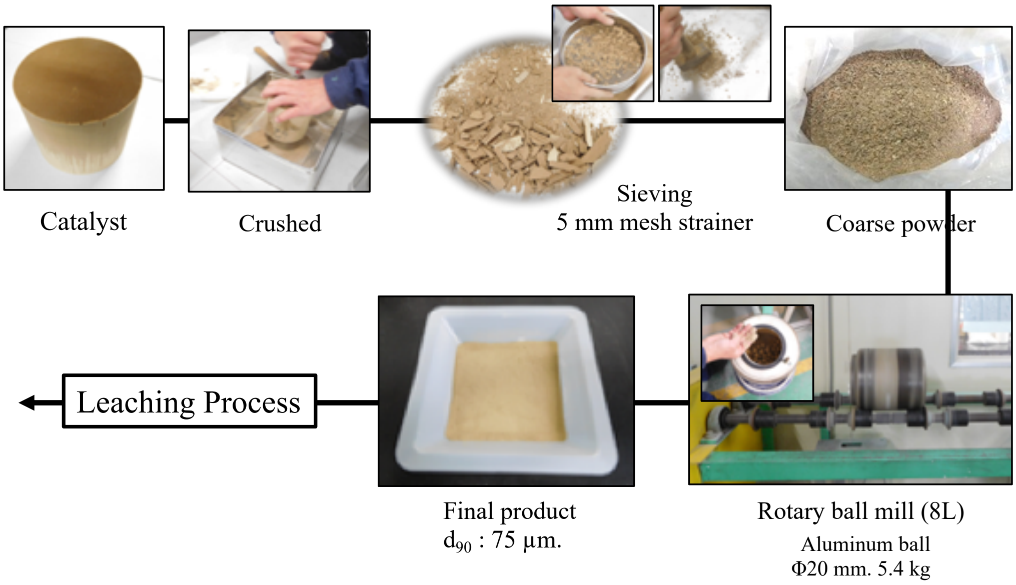
$P_{8,8,8,12}Cl$ was supplied by Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan). Pt and Pd standard solutions, $FeCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, $ZnCl_2$, $CuCl_2 \cdot 2H_2O$, and $MgCl_2 \cdot 6H_2O$ were supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan). $LaCl_3 \cdot 7H_2O$, $CeCl_3 \cdot 7H_2O$, and $BaCl_2 \cdot 2H_2O$ were supplied by Kishida Chemical Co., Ltd. (Osaka, Japan). Rh standard solution and $PrCl_3 \cdot 7H_2O$ were supplied by Kanto Chemical Co., Inc., (Tokyo, Japan). Na_2SO_3, H_2SO_4, HNO_3, HCl, NH_3, and $NaClO_4$ were supplied by Kishida Chemical Co., Ltd. All of the other chemicals were reagent grade, obtained from commercial sources, and used without further purification.

4.2.2 Spent automotive catalysts

A spent catalyst from a gasoline powered vehicle made in Japan was supplied by West-Japan Auto Recycle Co., Ltd. (Kitakyushu, Japan). The model year, run distance, and weight of the catalyst are 2000, 85,807 km, and 570 g, respectively. The catalyst carrier is ceramic with a honeycomb structure. The spent automotive catalyst block was cut in half lengthwise. The cut surface of the catalyst was analyzed by X-ray fluorescence spectrometry (µXRF, M4 TORANDO plus, Bruker, MA, USA).

4.2.3 Leaching metals from the spent automotive catalyst

Before the leaching process, so that the PGMs could be readily dissolved in acidic solution, the catalyst was mechanically crushed into a fine powder at Seishin Enterprise Co., Ltd., Hibiki Factory (Kitakyushu, Japan) as follows. After crushing the catalyst with a hammer, it was sieved with a 5 mm mesh strainer to produce a coarse powder. The powder was placed in a rotary ball mill with aluminum balls, which was operated for 0.5 to 5.5 h to obtain a fine powder with particle sizes below 75 µm (Scheme 1) [15,16].



Scheme 4.1. Spent automotive catalyst pre-leaching treatment.

The leaching test was performed by mixing a specific amount of the powder sample with 50 mL HCl solution in a round-bottom flask for a given time at a controlled temperature on a magnetic stirrer with a dry thermostatic bath (EYELA RCH-20L, Rikakikai Co, Ltd., Tokyo, Japan). The resultant mixture was filtrated and the concentrations of the metal ions in the clear filtrate (i.e., the leachate) were measured by inductively coupled plasma–atomic emission spectroscopy (ICP-OES, Optima 8300 Perkin Elmer Co., MA, USA).

4.2.4 Solvent extraction procedure

The extraction experiment was performed by mixing the aqueous feed solution (leachate) with undiluted $P_{8,8,8,12}Cl$. The mixture was agitated with a vortex mixer (Vortex Genie 2, Scientific Industries, NY, USA) for 1 min. It was then shaken in a water bath shaker (NTS-4000, Eyela, Tokyo, Japan) at 298 K for a period of time. The mixture was centrifuged at 5800 G for 5 min at 298 K. Metal removal from the loaded IL was performed in a similar manner with each stripping solution. All of the experiments were performed at a 2:1 aqueous phase to IL phase volume ratio, unless otherwise stated. The metal concentrations in the aqueous solution were measure by ICP-OES. The degrees of extraction E (%) and stripping S (%) were calculated with the following equations:

$$E\% = \frac{[M]_{IL}V_{IL}}{[M]_{IL}V_{IL}+[M]_{aq}V_{aq}} \times 100 \tag{1}$$

and

$$S\% = \frac{[M]_{st}V_{st}}{[M]_{st}V_{St}+[M]_{IL}V_{IL}} \times 100 \tag{2}$$

where V (L) and C (mg L^{-1}) are the volume and metal ion concentration, respectively, and the subscripts aq, IL, and st denote the aqueous, IL, and stripping phases, respectively.

4.3 Results and Discussion

4.3.1 Elemental analysis of the catalyst

The elemental distribution maps of the cross-section of the catalyst determined by µXRF analysis are shown in Figure 4.1.

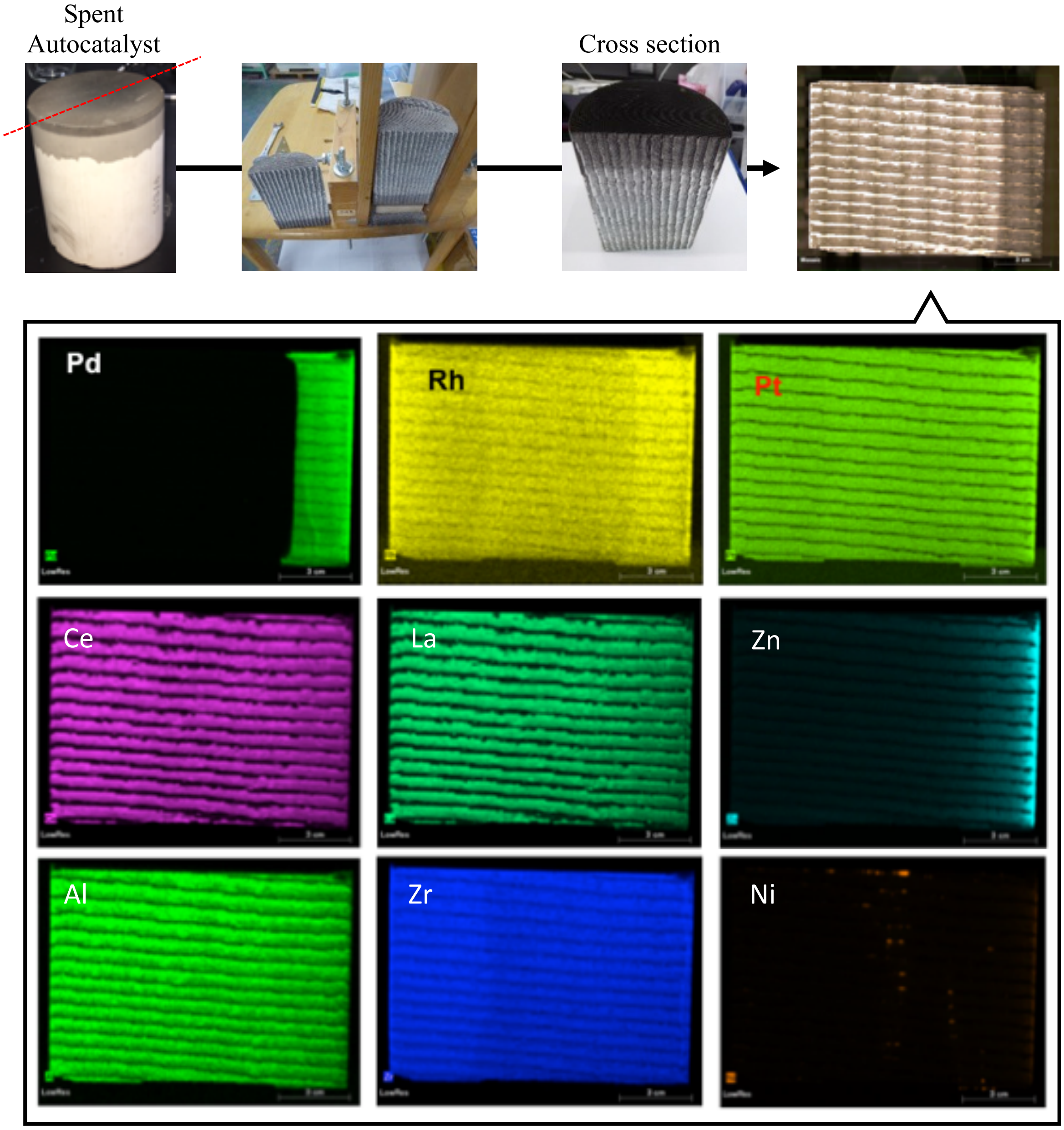


Figure 4.1. Elemental distribution maps of the cross-section of the catalyst.

The interior of the catalyst has a honeycomb shape divided into a number of elongated cylinders. The catalyst material is attached to the surface of the wall of the cylinder. Pd, Pt, and Rh are located on the surface, where Pd is only present up to a few centimeters from the end of the catalyst following the engine room. Rare earth metals, such as cerium (Ce) and lanthanum (La), added as a co-catalyst are also present on the entire surface. Zirconium (Zr) and aluminum (Al) are the main components of the catalyst support. The quantitative results are given in Table 4.1.

Table 4.1. Metal composition of the catalyst determined by µXRF analysis

Metal	Pt	Pd	Rh	Fe	Zn	Cu	Ce	La	Ni	Zr	Mg	Al
[wt%]	0.77	1.52	0.34	0.25	0.09	0.04	6.03	3.37	0.03	15.1	2.61	22.5

4.3.2 Preparation of the leachate from the spent automotive catalyst

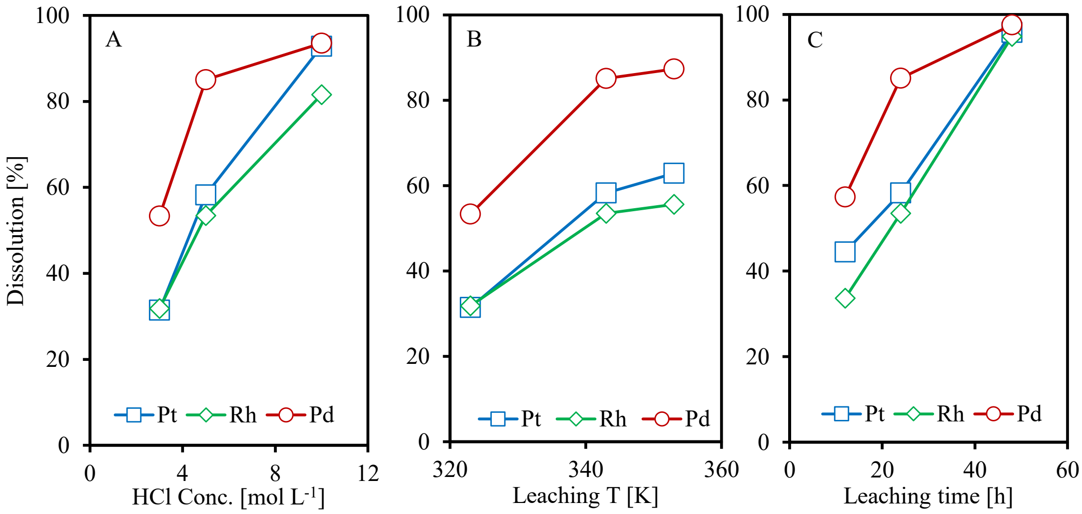


Figure 4.2. Effects of various parameters on the dissolution efficiency of PGMs (2.5 g catalyst powder in 50 mL HCl). (A) HCl concentration (time = 24 h, T = 343 K). (B) Leaching temperature (time = 24 h, $[\mathrm{HCl}]_{aq}$ = 5 mol L^{-1}). (C) Leaching time ($[\mathrm{HCl}]_{aq}$ = 5 mol L^{-1}, T = 343 K).

Leaching from the spent automotive catalyst was investigated using HCl solution. PGMs are difficult to directly dissolve in acids, but they can be dissolved as a ≤75 μm powder [16]. The effect of the HCl concentration on the dissolution efficiencies of the PGMs is shown in Figure 4.2A. PGM dissolution increases with increasing HCl concentration. However, taking into account that the leachate is subjected to an extraction procedure, a feed solution with too high HCl concentration is not favorable. Therefore, 5 mol L^{-1} HCl was chosen as the leaching solution. Pd readily dissolves in HCl, but the dissolution efficiencies of Pt and Rh are lower than that of Pd. Thus, the leaching conditions were further optimized by investigating the effects of the leaching temperature and time. Dissolution of the PGMs increases with increasing leaching temperature (Figure 4.2B). However, PGM dissolution does not significantly improve at temperature above 70 °C. Increasing the leaching time has a favorable effect on PGM dissolution. Increasing the leaching time from 12 to 48 h significantly improves the degree of PGM dissolution (Figure 4.2C). Quantitative PGM dissolution can be achieved using 5 mol L^{-1} HCl for 48 h operation at 343 K. The composition of the leachate is given in Table 4.2.

Table 4.2. Composition of the leachate from the spent automotive catalyst (50 g sample/L 5 mol L^{-1} HCl)

Metal	Pt	Pd	Rh	Fe	Zn	Cu	Ce	La	Ni	Zr	Mg	Al
[ppm]	78.7	156.2	26.8	50.2	21.6	8.2	399	523	0.03	0	1016	3792

The results show that the spent automotive catalyst contains 5.3 g PGMs/kg catalyst, demonstrating that the spent automotive catalyst is a high-grade ore compared with natural resources, such as pentlandite, pyrrhotite, and pyrite [17]. The leachate contains high concentrations of rare earth metals, such as Ce and La, and large amounts of common metals, such as Al and Mg, along with the PGMs.

4.3.3 Extraction of the metal ions contained in the leachate

Among the PGMs in the leachate, Pt and Pd are readily separated from Rh using $P_{8,8,8,12}Cl$ by changing the HCl concentration in the aqueous feed phase, as described in a previous paper [12]. It has also been reported that quantitative extraction of Pd is achieved in a short time [14]. Automotive waste catalysts contain a variety of metals depending on the type, model, and year of the car. Thus, the changes of the metal concentrations in the leachate (5 mol L^{-1} HCl) with extraction time were measured (Figure 4.3). The large amounts of Al and Mg in the leachate are not extracted at all. Rare earth metals are also not extracted. However, Fe, Cu, and Zn are extracted along with the PGMs.

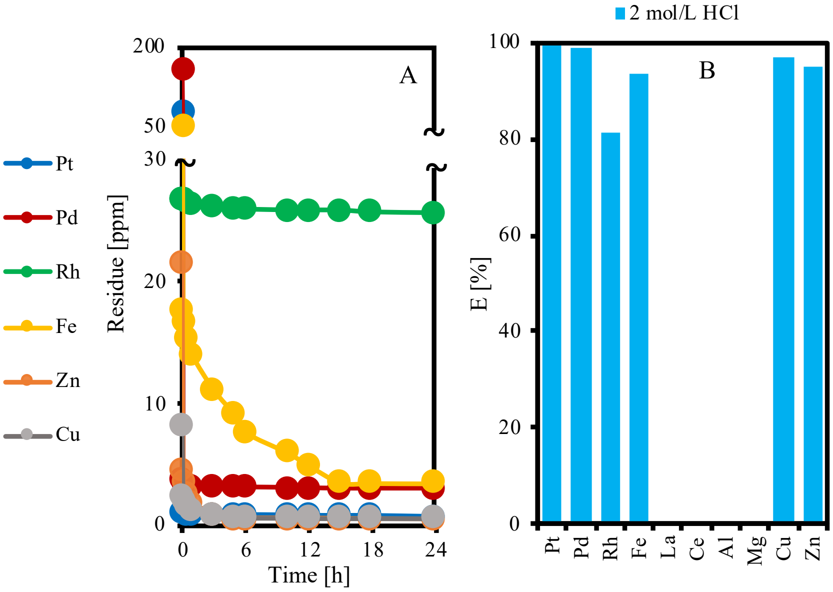


Figure 4.3. (A) Effect of contact time on model leachate extraction ($V_{aq}/V_{IL} = 2$, $[HCl]_{aq} = 5$ mol L^{-1}, T = 298 K). (B) Data for extraction from the spent catalyst leachate using $P_{8,8,8,12}Cl$ ($V_{aq}/V_{IL} = 2$, time = 8 h, T = 298 K).

The concentrations of Pt(IV) and Pd(II) rapidly decrease, and quantitative extraction is achieved within 10 min. $[PtCl_6]^{2-}$ is the dominant Pt species in a wide HCl concentration range [12], which is supported by the ultraviolet (UV) spectrum of the aqueous phase (Figure 4.4A). The extraction mechanism of Pt(IV) by $P_{8,8,8,12}Cl$ is considered to be

$$[PtCl_6]^{2-}{}_{(aq)} + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2PtCl_6} + 2Cl^{-}{}_{(aq)} \tag{3}$$

The extraction mechanism of Pd(II), whose dominant species under the present conditions is $[PdCl_4]^{2-}$ from the UV spectrum (Figure 4.4B), is likely to be anion exchange:

$$[PdCl_4]^{2-}{}_{(aq)} + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2PdCl_4} + 2Cl^{-}{}_{(aq)} \tag{4}$$

Pd(II) has a significantly higher reaction rate than other metals [18]. Deeth et al. reported that Pt(IV) also has a high reaction rate, although it has a slightly higher activation energy than Pd(II) [19]. The geometry of $[PdCl_4]^{2-}$ also enhances the reactivity of Pd compared with other metals [20]. Thus, rapid extraction of Pt is also achieved, with quantitative extraction within 10 min. Fe, Cu, and Zn are simultaneously extracted with high efficiency along with Pt and Pd, although the extraction rates are slightly lower than those of Pt and Pd.

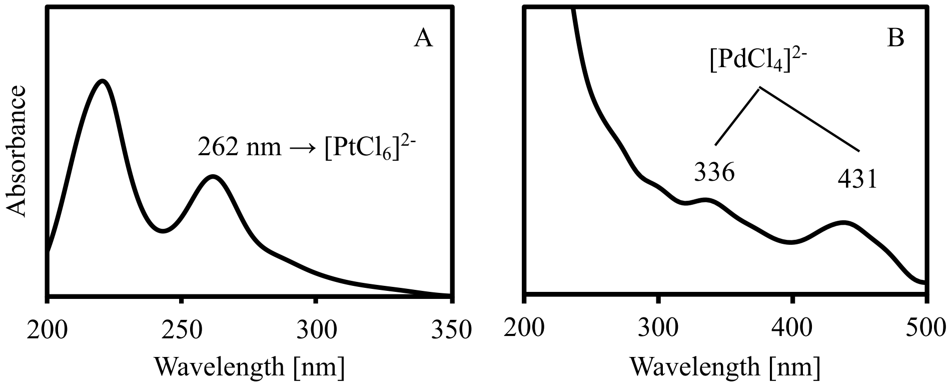


Figure 4.4. UV–vis spectrum of (A) Pt and (B) Pd in 5 mol L^{-1} HCl solution

The metal–chloro complex species, which depends on the HCl concentration, determines the extraction mechanism. As reported in chapter 3, extraction of $FeCl_3$, which is the dominant Fe species in the aqueous feed solution, occurs by ion association of the IL cation with $[FeCl_4]^-$:

$$FeCl_{3(aq)} + \overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2FeCl_4} \quad (5)$$

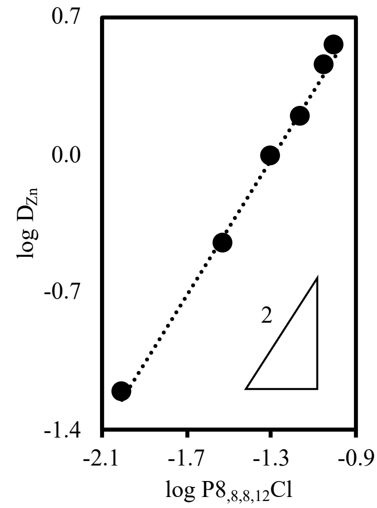


Figure 4.5. Effect of $P_{8,8,8,12}Cl$ concentration on (A) Zn(II) extraction ($[M]_{aq}$ = 50 mg L^{-1}, V_{aq}/V_{IL} = 2, $[P_{8,8,8,12}Cl]$ = 0.01–0.1 mol L^{-1}, solvent = toluene).

According to the literature [21], extraction of Zn(II) from chloride solution can proceed by two different mechanisms depending on the HCl concentration, which are the ion association mechanism and the anion exchange mechanism:

$$ZnCl_2 + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2ZnCl_4} \quad (6)$$

$$[ZnCl_4]^{2-} + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2ZnCl_4} + 2Cl^- \quad (7)$$

According to slope analysis, two molecules of $P_{8,8,8,12}Cl$ are required to extract one divalent Zn(II) ion (Figure 4.5). This is in agreement with the complex speciation diagram of Zn(II), which shows that $[ZnCl_4]^{2-}$ is the dominant species in 5 mol L^{-1} HCl solution. Thus, extraction of Zn(II) is by the anion exchange mechanism (Eq. (7)).

For Cu(II), $CuCl_2$ is dominant in a wide HCl concentration range based on the speciation diagram. In slope analysis of an organic solvent system in Figure 4.6A, two $P_{8,8,8,12}Cl$ molecules are required to extract one Cu(II) ion. The presence of $CuCl_2$ in the HCl solution was confirmed by UV–visible (vis) spectroscopy, where an absorption band at 265 nm attributed to $CuCl_2$ is present in the spectrum (Figure 4.6B) [22]. Extraction of Cu(II) might proceed by the ion association mechanism:

$$[CuCl_2] + 2\,\overline{P_{88812}Cl} \rightarrow \overline{[P_{88812}]_2CuCl_4} \qquad (8)$$

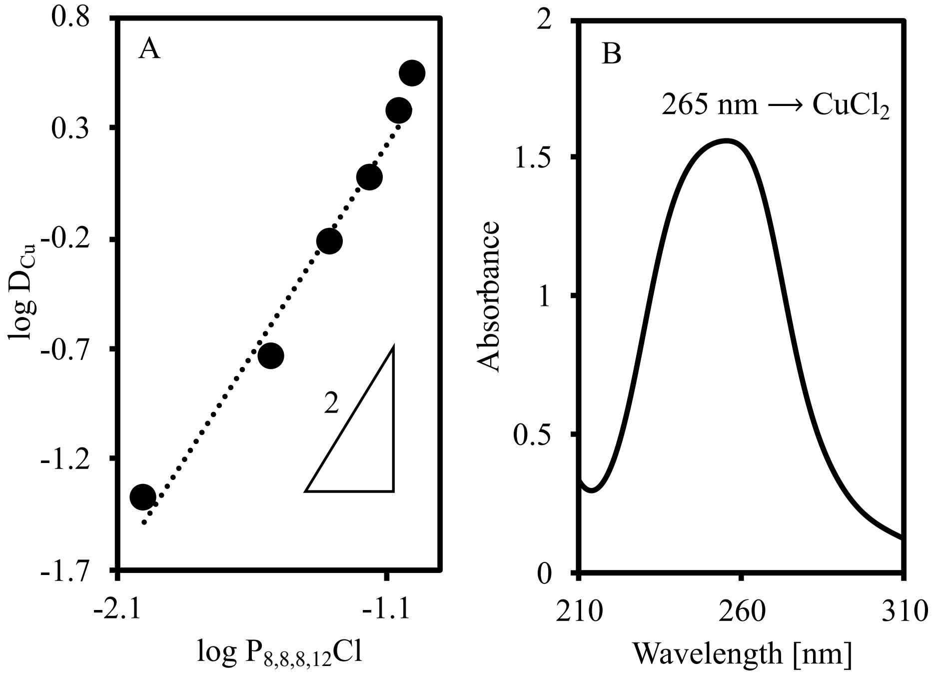


Figure 4.6. (A) Cu(II) extraction ($[M]_{aq}$ = 50 mg L^{-1}, V_{aq}/V_{IL} = 2, $[P_{8,8,8,12}Cl]$ = 0.01–0.1 mol L^{-1}, solvent = toluene). (B) UV–vis spectrum of Cu(II) in 5 mol L^{-1} HCl.

Rh extraction is significantly affected by the HCl concentration. The low extraction efficiency of Rh in Figure 4.3A can be attributed to formation of $[RhCl_6]^{3-}$ in the aqueous feed solution at high HCl concentration. Formation of the $[RhCl_5]^{3-}$ complex with three $P_{8,8,8,12}Cl$ molecules is difficult because the geometry has steric hindrance and high charge density [12]. In the previous chapter, extraction was achieved at below 3 mol L^{-1} HCl, where $[RhCl_5]^{2-}$ is the dominant Rh species in aqueous solution [14]. Formation of the 1:2 complex of $[RhCl_5]^{2-}$ with $P_{8,8,8,12}Cl$ is preferable under such conditions. The extraction rate of Rh with $P_{8,8,8,12}Cl$ is slower than those of Pt and Pd. Thus, the extraction behavior of the metal ions in the raffinate after extracting Pt and Pd was investigated after adjusting the HCl concentration to 2 mol L^{-1} (Figure 4.3B). 80% of Rh is extracted to the IL phase, but impurity metals, such as Fe, Zn, and Cu, also move to the IL if they are contained in the raffinate.

4.3.4 Stripping of the metals from the IL phase

As described above, the leachate from spent automotive catalysts contains a variety of metals other than PGMs. Efficient recovery of the PGMs from the IL and removal of the impurity metals co-extracted with the PGMs are crucially important for PGM recycling. Therefore, the stripping performance of the metals from metal-loaded $P_{8,8,8,12}Cl$ using different stripping reagents was investigated. The results are given in Table 4.3.

Table 4.3. Stripping of metals from loaded $P_{8,8,8,12}Cl$ with various stripping solutions

S [%]	**Pt(IV)**	**Pd(II)**	**Rh(III)**	**Fe(III)**	**Cu(II)**	**Zn(II)**
H_2O	0	0	0	0	0	0
3 mol L^{-1} HNO_3	**58.4**	11.4	0	0	0	0
5 mol L^{-1} HNO_3	**82.1**	14.1	0	1.2	0	0
0.5 mol L^{-1} $NaClO_4$	**15.4**	1.0	0	0	0	0
1 mol L^{-1} $CS(NH_2)_2$ in 1 mol L^{-1} HCl	18.8	**86.6**	0	0	0	0
0.1 mol L^{-1} $CS(NH_2)_2$ in 1 mol L^{-1} HCl	10.1	**90.9**	0	0	0	0
0.1 mol L^{-1} $CS(NH_2)_2$ in 0.5 mol L^{-1} HCl	2.7	**88.6**	0	0	0	0
1.2 mol L^{-1} Na_2SO_3	1.4	3.9	0	**90.2**	0	0
1 mol L^{-1} H_2SO_4	6.2	3.5	0	20.5	**66.4**	**73.9**
3 mol L^{-1} H2SO4	8.4	4.5	0	21.0	**83.5**	**82.7**
5 mol L^{-1} H_2SO_4	25.8	13.7	0	23.6	**88.4**	**83.3**
0.5 mol L^{-1} NH_4OH	0.2	15.7	0	0	**98.2**	**95.2**
5 mol L^{-1} HCl*	0.3	0.1	**81.7**	7.8	0.1	0

*Stripping after second extraction.

Water is ineffective in stripping any of the metals from the IL because of the strong bonds between the IL cations and metal–chloro complexes. The absence of exchangeable anion species in water and the interface barrier may prevent recovery of the metal–chloro complexes [23].

In chapter 3, it was found that Fe(III) can be stripped from the $P_{8,8,8,12}Cl$ phase by reducing Fe(III) to Fe(II) using Na_2SO_3 [14]. About 90% of Fe can be removed from the metal-loaded IL phase by contact with 1.2 mol L^{-1} Na_2SO_3 at 303 K, while Pt and Pd remain in the IL phase (Table 4.3). NH_4OH can quantitatively strip Zn and Cu, which have high affinity for $P_{8,8,8,12}Cl$. However, a white precipitate formed at the interface between the IL and the aqueous phase after the operation, which could limit the reusability of $P_{8,8,8,12}Cl$.

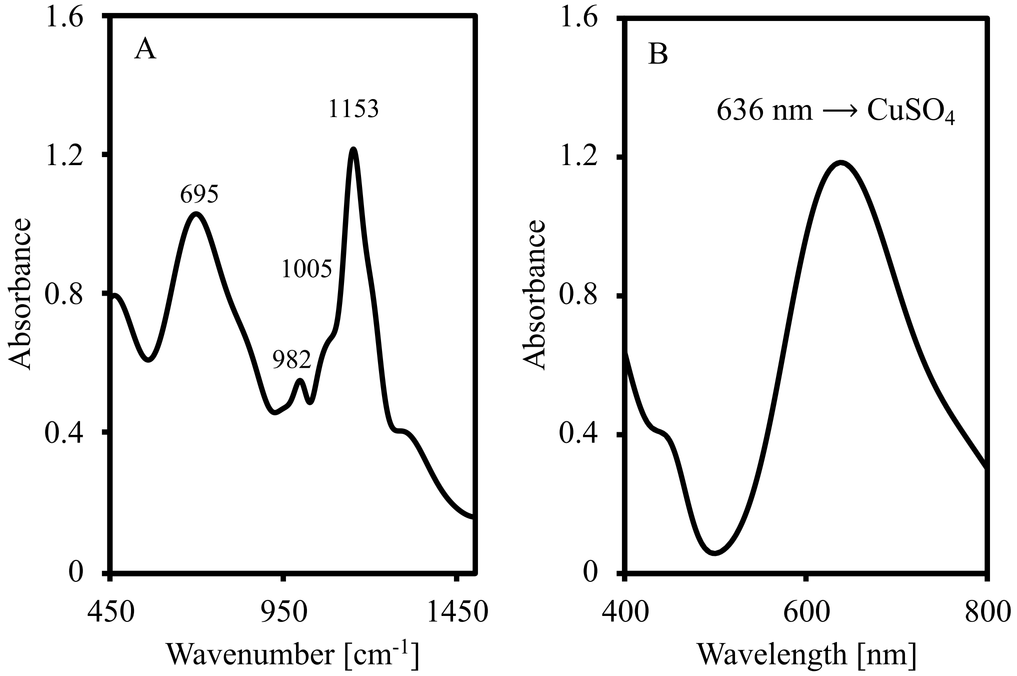


Figure 4.7. (A) FTIR spectrum of Zn(II) in 3 mol L^{-1} H_2SO_4. (B) UV–vis spectrum of Cu(II) in 3 mol L^{-1} H_2SO_4.

High stripping efficiencies of Zn and Cu are also achieved using 3 and 5 mol L^{-1} H_2SO_4, where the efficiency increases with increasing acid concentration. However, removal of such metals using 5 mol L^{-1} H_2SO_4 is accompanied by stripping of Pt and Pd. The stripping process is facilitated by formation of $ZnSO_4$ and $CuSO_4$. The presence of

$ZnSO_4$ in the stripping solution was confirmed by Fourier transform infrared (FTIR) spectroscopy as shown in Figure 4.7A, which shows $ZnSO_4$ signature peaks at 1194, 1150, and 1080 cm^{-1}. Thus, stripping of Zn from metal-loaded $P_{8,8,8,12}Cl$ most likely occurs by

$$\overline{[P_{88812}]_2ZnCl_4} + H_2SO_4 \rightarrow ZnSO_4 + 2\,\overline{P_{88812}Cl} + 2HCl \qquad (9)$$

The stripping solution was then subjected to UV spectroscopy. The UV spectrum shows a major absorption band at 638 nm, which can be ascribed to the presence of $CuSO_4$ (Figure 4.7B) [24]. Thus, stripping of Cu most probably occurs by

$$\overline{[P_{88812}]_2CuCl_4} + H_2SO_4 \rightarrow CuSO_4 + 2\,\overline{P_{88812}Cl} + 2HCl \qquad (10)$$

Selective stripping of PGMs is essential for efficient PGM recovery. HNO_3 can recover a significant amount of Pt. Because other common co-extracted metals are not recovered, HNO_3 is considered to be a suitable recovery agent for Pt. As previously reported, $CS(NH_2)_2$ shows good performance in quantitative stripping of Pd from metal-loaded $P_{8,8,8,12}Cl$.

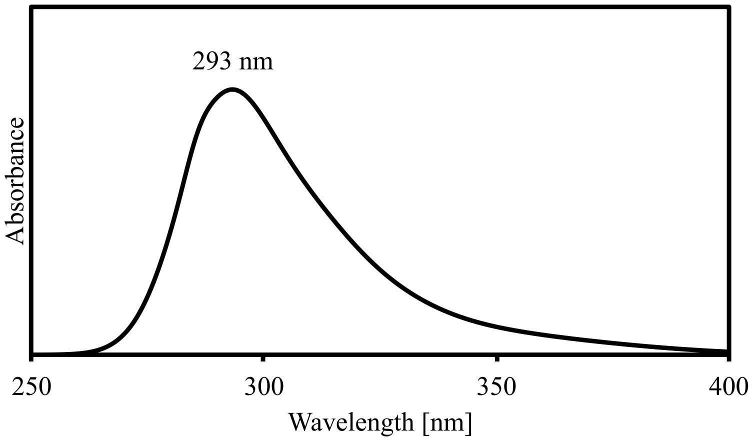


Figure 4.8. UV–vis spectrum of the Pd–thiourea complex in the stripping solution ($V_{aq}/V_{IL} = 2$, $[CS(NH_2)_2] = 0.1$ mol L^{-1} in 0.5 mol L^{-1} HCl).

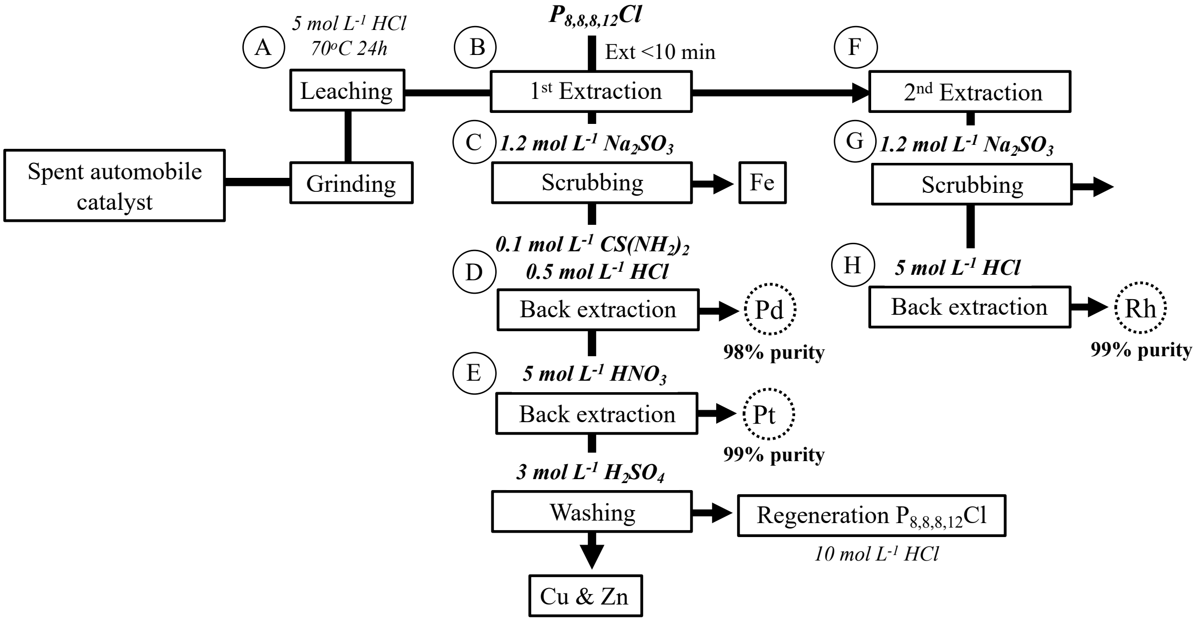
The nature of Pd as a soft acid and $CS(NH_2)_2$ as a soft base promotes formation of $[Pd(CS(NH_2)_2)_4]^{2+}$. UV spectrum of the stripping solution in Figure 4.8 shows the presence of Pd-thiourea complex at around 300 nm [25]. Thus, Pd is stripped by the coordination–substitution reaction between $CS(NH_2)_2$ and Cl^- [26]:

$$\overline{[P_{88812}]_2PdCl_4} + 4(NH_2)_2CS \rightarrow 2\,\overline{P_{88812}Cl} + [Pd((NH_2)_2CS)_4]^{2+} + 2Cl^- \tag{11}$$

A mixture of HCl and $CS(NH_2)_2$ has been used to strip Pt and Pd from different loaded organic phases [25,27]. When both Pt and Pd are present, substitution between $CS(NH_2)_2$ and Cl^- competitively occurs and depends on the concentration of the metal ion complexes [28]. Recovery of Pd with 1 mol L^{-1} $CS(NH_2)_2$ dissolved in 1 mol L^{-1} HCl occurs with recovery of a significant amount of Pt (Table 4.3). Thus, the composition of $CS(NH_2)_2$ and HCl was adjusted to minimize stripping of Pt. Decreasing the $CS(NH_2)_2$ concentration from 1 to 0.1 mol L^{-1} hardly affects Pd stripping but stripping of Pt is significantly reduced (Table 4.3). Stripping of Pt can be further suppressed by adjusting the HCl concentration [25,26]. Pt is rarely stripped by decreasing the HCl concentration from 1 to 0.5 mol L^{-1}, although the stripping efficiency of Pd slightly decreases.

In the competitive substitution reaction, Cl in the $\overline{[P_{88812}]_2PdCl_4}$ complex is substituted by $CS(NH_2)_2$ faster than the Pt–$CS(NH_2)_2$ complex [28]. Thus, Pd can be efficiently stripped at a low $CS(NH_2)_2$ concentration, while stripping of Pt gradually increases as the $CS(NH_2)_2$ concentration increases. Selective stripping of Rh from metal-loaded $P_{8,8,8,12}Cl$ can be achieved using 5 mol L^{-1} HCl.

4.3.5 Recovery of the PGMs from the leachate of the spent automotive catalyst



Scheme 4.2. Flow chart summarizing separation and recovery of PGMs from an automotive catalyst leachate.

Based on the extraction and stripping test results, the process for recovery of Pt, Pd, and Rh from the spent automotive catalyst leachate (5 mol L^{-1} HCl) is shown in Scheme 4.2. All of the extraction and stripping operations were performed at $V_{aq}/V_{IL} = 2$. The metal concentrations in the solution after each process are given in Table 4.4. The leachate (Table 4.4, A) was directly mixed with $P_{8,8,8,12}Cl$ to allow for Pt and Pd extraction. After the first extraction stage, Pt and Pd are almost quantitatively extracted in 10 min, followed by Cu, Zn (approximately 90%), and Fe (approximately 65%) (Table 4.4, B).

Table 4.4. Metal concentrations in the respective phase after certain processes (V_{aq}/V_{IL} = 2, T = 25 °C)

	Step	Pt (mg/L)	Pd (mg/L)	Rh (mg/L)	Fe (mg/L)	Zn (mg/L)	Cu (mg/L)	Ce (mg/L)	La (mg/L)	Mg (mg/L)	Al (mg/L
A	Initial conc.	78.7	156.2	26.8	50.2	21.6	8.2	399	523	1016	3792
B	1st extraction (in IL phase)	153.5	298.9	0	50.2	35.2	13.1	0.3	2.1	2	2.0
C	Scrubbing (IL phase)[a]	153.3	297.7	0	2.4	35.2	13.1	0.3	2.1	2	2.0
D	$CS(NH_2)_2$ (Pd stripping)[b]	2.1	139.9	0	0	0	0	0	0	0	0
E	HNO3 (Pt stripping)[c]	67.1	0.2	0	0	0	0	0	0	0	0
F	2nd extraction (IL phase)*	0	0.1	15.1	14.0	0	0	0.6	0.3	0.1	0.6
G	Scrubbing (IL phase)a	0	0	15.1	1.4	0	0	0	0	0	0
H	HCl (Rh stripping)	0	0	6.8	0	0	0	0	0	0	0

*Diluted from 5 to 2 mol L^{-1}.

[a] 1.2 mol L^{-1} Na_2SO_3, 303 K, 30 min.

[b] 0.1 mol L^{-1} $CS(NH_2)_2$ in 0.5 mol L^{-1} HCl.

[c] 5 mol L^{-1} HNO_3.

[d] 5 mol L^{-1} HCl.

The metal-loaded $P_{8,8,8,12}Cl$ was then moved to the scrubbing stage. Fe is almost completely removed from the IL phase by operation for 30 min at 303 K using 1.2 mol L^{-1} Na_2SO_3 while leaving Pt and Pd in the IL (Table 4.4, C). Pd and then Pt are recovered from the IL using 0.1 mol L^{-1} $CS(NH_2)_2$ in 0.5 mol L^{-1} HCl and 5 mol L^{-1} HNO_3, respectively. About 94% of Pd and 90% of Pt are selectively recovered from the IL phase, where the purities in the recovery solutions are >98% for both Pd and Pt (Table 4.4, D and E). After stripping Pd and Pt, the IL phase was washed with 3 mol L^{-1} H_2SO_4 to remove Cu and Zn. The raffinate of the first extraction stage with remaining Rh was subjected to a second extraction stage. The raffinate of 5 mol L^{-1} HCl was diluted to 2 mol L^{-1} HCl, followed by mixing with fresh $P_{8,8,8,12}Cl$, resulting in 80% extraction of Rh (Table 4.4, F). After scrubbing with Na_2SO_3, the extraction IL phase (Table 4.4, G) was placed in contacted with 5 mol L^{-1} HCl for 24 h. About 80% of Rh is selectively recovered from the IL at 99% purity (Table 4.4, H).

Regeneration of $P_{8,8,8,12}Cl$ is possible using high concentration HCl solution and the IL is reusable with minimal degradation in performance, as suggested by the previous chapter. Overall, $P_{8,8,8,12}Cl$ can selectively recover Pt, Pd, and Rh from the spent automotive catalyst leachate in high purities (approximately 99% for Pt and Pd).

4.4 Conclusion

A hydrometallurgical process for separation and recovery of PGMs from the leachate of spent automotive catalysts has been developed based on solvent extraction using the $P_{8,8,8,12}Cl$ IL, which was recently developed as an extraction solvent for PGMs. The phosphonium-based IL extracts both Pt and Pd in high efficiency. In addition, selective recovery of Pt and Pd, which are usually difficult to separate, is achieved by a stripping process. Pt is selectively recovered using high concentration nitric acid, while Pd is recovered with thiourea in low concentration hydrochloric acid. Rh is extracted from the raffinate to $P_{8,8,8,12}Cl$ after removing Pt and Pd in the first extraction stage and then recovered by high concentration hydrochloric acid solution. Some common metals co-extracted into $P_{8,8,8,12}Cl$ can be removed by using an effective stripping reagent for each metal. The results demonstrate the potential of well-designed ILs as extraction solvents for recycling valuable metals, such as PGMs, from waste products, which will contribute to solving environmental issues.

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Chapter 5. Conclusions

5.1 Summary

In the last several years, the demand-supply for PGMs is widening. Technical and operational cost makes mining PGMs much more difficult than before. In order to fulfill the supply, recovering PGMs from wastes is an attractive option. By doing this, the environmental burden due to mining could be lightened. Recovering PGMs from wastes also produces less byproduct that needs treatment prior to disposal. Not only beneficial in ecological aspect, recovering PGMs from wastes would also be beneficial in an economic aspect. PGMs content in waste is several times higher than that in their natural deposit. Solvent extraction is one of the good alternatives to the classical approach in metal processing. It consumes less energy, has better selectivity and lower environmental burden. The drawback of solvent extraction could be solved through the use of ionic liquids because it does not require additional solvent unlike conventional extractants. In the present thesis, based on the aim of developing effective hydrometallurgical separation systems for the separation and recovery of PGMs from a waste automotive catalytic converter, three subjects were investigated for their feasibility.

In chapter 2, the potential of undiluted phosphonium-based ionic liquid in the extraction of Pt(IV), Pd(II) and Rh(III) was explored. Trioctyl(dodecyl)phosphonium chloride ($P_{8,8,8,12}Cl$) was firstly reported as an extractant in this chapter and its performance was compared to that of its commercial counterpart, trihexyl(dodecyl) phosphonium chloride ($P_{6,6,6,14}Cl$). A slight modification in the structure of the cation moiety showed a notable difference in their physicochemical properties. A shorter asymmetrical alkyl chain and a longer symmetrical alkyl chain of $P_{8,8,8,12}Cl$ contribute to its low viscosity and their high hydrophobicity than that in $P_{6,6,6,14}Cl$, respectively. Lower mass transport barrier due to its low viscosity allows faster extraction on $P_{8,8,8,12}Cl$. Pt and Pd extraction was quick and followed by Rh extraction. Rh extractability was improved as the chloride concentration decreased due to the change in dominant chlorocomplex species as evidenced by the spectroscopic study. The extraction of the metals was proceeded according to the anion exchange mechanism and their extractability was strongly influenced by the chloride concentration. The extraction performance with $P_{8,8,8,12}Cl$ was also consistent after several cycles of regeneration unlike its counterpart which showed a significant decrease after the several cycles. This could be caused by the loss of the phosphonium cation, which was higher in $P_{6,6,6,14}Cl$ than in $P_{8,8,8,12}Cl$. Thus, $P_{8,8,8,12}Cl$ shows the potential for the use as an extraction solvent for PGMs, and the present results demonstrate advantages related to the properties that can be readily tuned by changing the molecular structure of the ionic liquid.

Chapter 3 focused on the recovery of Pd(II) and Rh(III) from the chloride leachate of an unused automotive catalytic converter. Separation of Pd(II) and Rh(III) was successfully achieved by adjusting the chloride concentration in the feed in order to change the dominant chlorocomplex species in the feed solution. The recovery of Pd(II) and Rh(III) was achieved by using $CS(NH_2)_2$ and HCl, after removing co-extracted Fe(III) with Na_2SO_3. A spectroscopic study shows that reduction of Fe(III) to Fe(II) plays an important role. The whole process resulted in a high purity PGMs product, which is 99 and 95% for Pd(II) and Rh(III), respectively. Simple treatment of contacting $P_{8,8,8,12}Cl$ with the high concentration of HCl was enough to regenerate the $P_{8,8,8,12}Cl$. $P_{8,8,8,12}Cl$ also shows remarkable stability after going through the whole process since there is almost no changes in the structure of the phosphonium part of $P_{8,8,8,12}Cl$.

The actual practicability of $P_{8,8,8,12}Cl$ in recovering PGMs from the actual waste automotive catalyst was investigated in Chapter 4. The spent automotive catalyst was leached under the acidic conditions and mild temperature of 343K. It was found that the acid concentration, temperature and leaching time significantly influenced the leaching efficiency, with the optimal conditions for leaching are 5 mol L^{-1} HCl at 343 K for 24 hours. Extraction of Pt and Pd was achieved efficiently and both metals were selectively recovered through the stripping process. The Pt recovery was done with nitric acid while selective Pd recovery was achieved with combination of thiourea and low acid concentration. However, it was also followed with extraction of Cu, Zn, and Fe. Removal of Cu and Zn was achieved through complexation with H_2SO_4 which has stronger affinity towards Cu and Zn. Extraction of Rh(III) was successfully done by dropping the chloride concentration and recovered by using a high concentration hydrochloric acid. Through the whole process, high purity of PGMs was obtained, which was 99, 99, and 98% for Pt, Pd, and Rh. The results demonstrate the potential of well-designed ILs as extraction solvents for recycling valuable metals, such as PGMs, from waste products, which will contribute to solving environmental issues.

5.2 Future work

Potential ideas that have not been carried out include variation of cation-anion combination and its effect on extraction of various metals. By using different anions, type of metals that can be extracted is greatly increased. Phosphonium-based ionic liquid with anion, such as malonamide, diethyl(hexyl)phosphate, and trimethypentyl phosphinate, was able to extract actinides and lanthanides. The effect of cation-anion combination on the physicochemical properties of the ionic liquid itself can be investigated. Incorporating

$P_{8,8,8,12}Cl$ into a polymeric membrane is also interesting topic. It would allow the 1-step recovery process of PGMs from various source solutions. It would decrease the operational cost and material loss during the solvent extraction process. Selectivity of the process can be adjusted by using various stripping solutions and a polymeric membrane technique such as polymer inclusion membrane (PIM), supported liquid membrane (SLM), or polymeric plasticized membrane (PPM), and by adjusting the operation conditions therein including the selection of stripping solution.

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APPENDIX A

Metal complex speciation in chloride solution