Extraction and Separation of Pt and Pd by an Imidazolium-Based Ionic Liquid Combined with Phosphonium Chloride

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Extraction and separation of Pt(IV) and Pd(II) from a hydrochloric acid solution was examined with a mixture of undiluted ionic liquids, 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ([C8mim][Tf2N]) and trihexyltetradecylphosphonium chloride ([P6,6,6,14][Cl]). Imidazolium-based [C8mim][Tf2N] shows a high selectivity for Pt(VI), whereas [P6,6,6,14][Cl] has a high extraction ability for both Pt(IV) and Pd(II). The addition of [P6,6,6,14][Cl] to [C8mim][Tf2N] improved the extraction efficiency for Pt and the separation factor between Pt and Pd also increased. This improvement was attributed to the presence of Cl− being more hydrophilic than Tf2N− in the [C8mim][Tf2N] extraction phase. Stripping of the metals was possible with HNO3 solution without any degradation of the ionic liquid extraction phase. The ionic liquid mixture was shown to be reusable for at least five extraction cycles.

1. Introduction

Platinum group metals (PGMs) play an important role in the development of high-tech industries, such as electronics, chemicals, and automobiles because of their unique physical and chemical properties. The production of PGMs is limited to a few countries [1] and recycling PGMs from secondary resources such as electronic waste (e-waste) and automotive catalysts has attracted much attention for ensuring a stable supply of PGMs [2,3]. However, the separation and purification of PGMs is difficult both from natural sources and when recycling, owing to the similarity of their chemical and physical properties.

Solvent extraction has been widely used for the separation and purification of a variety of metals including PGMs. The key to effective extraction and recovery of a target metal is the selection of an appropriate extraction media for the metal ions. Various processes have been developed for separation of PGMs, using commercial extractants; however, these processes still have problems that need to be solved [4-6]. Separation of Pt and Pd remains a challenging issue and more effective separation methods are needed.

Over the past few decades, ionic liquids (ILs), which are salts in a liquid state at room temperature, have been highlighted as “green” alternatives to conventional organic solvents owing to their unique properties such as high thermal stability, negligible vapor pressure, and flame resistance [7-10]. ILs are generally composed of organic cations and a variety of different anions. The physicochemical properties of ILs are highly tunable by varying the combination of the cationic and anionic partners. Typical organic cations are 1-alkyl-3-methylimidazolium (abbreviated as Cn mim, where n is the carbon number),
tetraalkylphosphonium (P_{n1,n2,n3,n4}), N-alkylpyridinium, and tetraalkylammonium ions. Chloride, bromide, hexafluorophosphate (PF_6^-), and bis(trifluoromethylsulfonyl)imide [(CF_3SO_2)_2N] are often used as IL anions. Since a marked improvement in the extraction ability of metal ions using ILs as a diluent in liquid-liquid extraction was reported in 1999, researchers have focused on the application of ILs to improve solvent extraction methods [11]. Commercial extractants such as crown ethers and octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and newly synthesized extractants have been used to extract cationic metal ions [10,12]. Furthermore, ILs have been used for extraction both dissolved in organic solvents [13-15] and as an undiluted extraction phase [16-22]. Phosphonium based ILs such as trihexyltetradecylphosphonium chloride, bromide and phosphinate have been applied to the separation of PGMs [21,22]. Recently, undiluted imidazolium based ILs have been reported to have a high extraction ability for Au(III) and Pt(IV), as well as the ability to separate these metals from Pd(II) [16,19,20]. Two different ILs [C_mim][Tf_2N] and a phosphonium-based IL, [P_{6,6,6,14}][Br], have been applied to a two-step extraction and separation of Pt(IV) and Pd(II) [21]. In this case, however, a multistep extraction operation was required for the separation of Pt and Pd. In the present study, we attempted to use a mixture of two different ILs to improve the separation efficiency between Pt and Pd. In cases using [C_mim][Tf_2N], the extraction has been shown to proceed via anion exchange of the IL anions with a metal chloro-complex anion in the chloride feed solution. Imidazolium-based ILs containing the PF_6^- anion have shown better Pt(IV) extraction performance than those containing Tf_2N^- because PF_6^- is more hydrophilic and is more readily released into the aqueous phase than Tf_2N^-.

If a more hydrophilic anion, such as Cl^-, existed in the extraction IL phase, the metal extraction may be promoted further. Imidazolium-based ILs containing Cl^- are solid at room temperature and have an affinity for water. In this work, a phosphonium-based IL [P_{6,6,6,14}][Cl], which is hydrophobic and contains Cl^-, was added to [C_mim][Tf_2N] to improve the extraction efficiency of Pt, and the extraction and separation of Pt and Pd was examined with the IL mixture. In the studies on the extraction using undiluted ILs, reports on stripping are very few [18]. In the present work, the stripping and reusability of the IL phase were also examined, and the potential uses of this mixed IL system are discussed.

2. Experimental

2.1 Reagents

The imidazolium-based ionic liquid, 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ([C_mim][Tf_2N], Lot No. 001641-IL-0099, L00219.1.1-IL-0099) was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). The phosphonium type ionic liquid, trihexyltetradecylphosphonium chloride

![Molecular structures of the ionic liquids used.](image-url)
([P₆,₆,₆,₁₄][Cl], Lot No. M00250.4.1-IN-0006) and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P₆,₆,₆,₁₄][Tf₂N]) were obtained from Ionic Liquids Technologies, GmbH Inc. The molecular structures of the ionic liquids are shown in Figure 1. Hydrogen hexachloroplatinate(IV) 6-hydrate and palladium(II) chloride, as the sources of Pt(VI) and Pd(II) ions, were purchased from Kishida Chemical Co., Ltd (Osaka, Japan). All other reagents were of analytical grade and were used as received.

2.2 Extraction procedure

An aqueous feed solution containing metal ions was prepared by dissolving the metal salts in HCl or HNO₃ solution. For the ionic liquid extraction phase, weighted amounts of the two types of ionic liquid were mixed and used after washing with water or 0.1 M HCl to remove water soluble compounds. The extraction IL phase and the aqueous feed phase were mixed in a sealed tube at a volume ratio ($V_{aq}/V_{IL}$) of 2, unless otherwise stated. After mixing for 60 s in a vibrating mixer, the mixture was gently shaken at 298 K for more than 3 h in a temperature-controlled bath to attain equilibrium. After phase separation, the metal concentrations in the aqueous phases were determined with an inductively coupled plasma (ICP)-atomic emission spectrometer (Optima 8300; Perkin Elmer Inc., MA, USA). The stripping of metal ions from the extraction phase was also examined using HCl or HNO₃ solutions. The extraction efficiency and degree of stripping of the metal ions, $E$ (%) and $S$ (%), respectively, are defined as follows:

$$E = \frac{C_{MIL}}{C_{Maq,0}} \times 100 = \frac{C_{Maq,0} - C_{Maq}}{C_{Maq,0}} \times 100$$

(1)

$$S = \frac{V_{STR}C_{MSTR}}{V_{IL}C_{MIL,0}} \times 100$$

(2)

where $C_M$ is the metal concentration, $V$ is the phase volume, and the subscripts aq, str, and IL indicate the aqueous feed, stripping aqueous, and IL extraction phases, respectively. The subscript 0 denotes the initial state.

3. Results and Discussion

3.1 Extraction ability of Pt and Pd with a variety of ionic liquid systems

An imidazolium based ionic liquid, [C₈mim][Tf₂N] has been reported to have an extractive selectivity for Pt(IV) in a previous publication [19]. As shown in Figure 2, Pt was selectively extracted into the [C₈mim][Tf₂N] phase; however, the extraction performance of Pd was low. In a mixture of [C₈mim][Tf₂N] and [P₆,₆,₆,₁₄][Cl], the extraction efficiency of Pt was improved; however, the efficiency of the extraction of Pd also slightly increased. The extraction was considered to proceed via anion exchange of a Pt chloro-complex with the IL anion [16,19], therefore the existence of Cl⁻ in the extraction phase facilitated anion exchange by releasing Cl⁻ into the aqueous phase preferentially (Cl⁻ is more hydrophilic than Tf₂N⁻). When [C₈mim][Tf₂N] was combined with [P₆,₆,₆,₁₄][Tf₂N], instead of [P₆,₆,₆,₁₄][Cl], the extraction performance of Pt was not improved, therefore the increase in the extraction performance was attributed to the promotion of anion exchange by the release of Cl⁻. Although the selectivity for the two metal ions by [P₆,₆,₆,₁₄][Cl] was very low, the selectivity for Pt was maintained in the mixture of
Here, the distribution ratios of the metal ions $D_M(-)$, defined in Eq. (3), were obtained for the [C8mim][Tf2N] and the mixed [P6,6,6,14][Cl] systems.

$$D_M = \frac{V_{aq}(C_{Maq,0} - C_{Maq})}{V_{IL}C_{Maq}}$$  \hspace{1cm} (3)

Under the experimental conditions, described in Figure 2, the values for Pt and Pd were 4.07 and 0.10 in the single IL system, whereas the values were 37.2 and 0.27 in the mixed IL system, respectively. The separation factor of Pt and the separation factor between Pt and Pd were increased by adding [P6,6,6,14][Cl].

Figure 3 shows the effect of the [P6,6,6,14][Cl] concentration, initially added to the [C8mim][Tf2N], on the degree of metal ion extraction. The extraction percentage increased as the concentration of [P6,6,6,14][Cl] was increased, reaching a constant value at approximately 10 wt% [P6,6,6,14][Cl] addition. Under these experimental conditions Pd was only slightly extracted. Henceforth, the [C8mim][Tf2N], to which 10 wt% of [P6,6,6,14][Cl] was added, was used as the IL extraction phase. Figure 4(a) shows the extraction behavior of Pt and Pd in the mixed IL system compared with that of the [C8mim][Tf2N] single IL system, as a function of the HCl concentration in the aqueous feed phase. The extraction efficiency of Pt increased as the HCl concentration increased at lower HCl
concentrations; however, above 1 M HCl, the Pt extraction efficiency declined gradually. Among the Pt species in the chloride solution, PtCl$_6^{2-}$ was predominant and increased with increasing Cl$^-$ concentration [23,24]. At around 1 M chloride concentration, most species were PtCl$_6^{2-}$. The extraction profile was similar to the speciation profile of PtCl$_6^{2-}$ in aqueous solution as a function of Cl$^-$ concentration. At a higher acid concentration, competition between the extraction of the Pt chloro-anion and Cl$^-$ occurs. The degree of Pd extraction decreased with increasing HCl concentration. The Pd extraction curve was analogous to the speciation profile of PdCl$_3^-$, which was expected to form an active species with the imidazolium ILs. From the nitric acid feed solution, neither of the metal ions were extracted under acidic conditions under the present experimental conditions (Figure 4(b)).

### 3.2 Stripping of metal ions

Stripping tests for Pt in the mixed IL system were performed with stripping agents including HNO$_3$, HCl, NaCl, NH$_4$Cl, and ammonia. More effective stripping performance was obtained with acids such as HCl and HNO$_3$, and the stripping behavior of Pt with these two acids was examined in detail. Figure 5(a) shows the effect of each acid concentration on the stripping efficiency of metals from the IL phase at $V_{str}/V_{IL} = 4$, where the metal loaded IL phase was prepared by extraction from a feed aqueous solution containing 1 mM Pt and Pd (1 M HCl) at $V_{aq}/V_{IL} = 2$. It was observed that the Pt stripping degree increased with increasing acid concentration. HNO$_3$ gave a higher stripping efficiency than that of HCl. When the IL phase that was subjected to stripping by HCl was reused as the extraction phase, the extraction efficiency declined compared with that of the fresh IL phase. When we reused the IL phase, recovered after stripping with HCl with a concentration greater than 3 M, the extraction degree of Pt decreased to less than 60% of that of the fresh IL phase. Chloride ion remaining in the IL phase in high concentration is considered to prevent the anion exchange of Cl$^-$ with PtCl$_4^-$ in the ionic liquids, for example, by anion exchange of Tf$_2$N with Cl$^-$. Figure 5(b) shows the stripping of the metal ions by HNO$_3$ at $V_{str}/V_{IL} = 2$. Stripping of Pt and Pd was possible, as shown in Figure 5(b). The extraction
ability of the IL phase recovered with HNO₃ showed efficiency as good as or better than that during the first extraction. Thus, nitric acid was effective in regenerating the IL phase, likely through anion exchange of nitrate with the metal chloro-anion. The Cl⁻ in the IL phase was likely replaced with NO₃⁻ at a constant rate according to the concentration of HNO₃ used. When the IL phase was regenerated with HNO₃ at a high concentration, the Pd extraction efficiency increased; more than 30% Pd extraction was observed, when the IL phase recovered with 5 M HNO₃ was used. The extraction phase recovered with 2 M HNO₃ maintained a similar Pt extraction ability and the selectivity for Pd was the same as that of a fresh IL mixture.

3.3 Recycling of the IL phase

To examine the reusability of the mixed IL extraction phase, five cycles of the extraction and stripping tests were performed as follows: Extraction was performed from 1 M HCl solution containing 1 mM of each metal ion (Pt 200 ppm and Pd 100 ppm), in the same manner as described previously. After phase separation, the IL phase was washed with 2 M HNO₃ to recover the metal ions. The IL phase was reused for the second extraction in the same manner as the first extraction. The volume ratios of the aqueous to the IL phases for extraction and stripping, \( V_{\text{aq}}/V_{\text{IL}} \) and \( V_{\text{str}}/V_{\text{IL}} \), were maintained at 2. As shown in Figure 6, the extraction ability slightly declined for the 5th extraction cycle but the selectivity between Pt and Pd was

![Figure 5. Effect of acid type and concentration on the stripping ability of Pt and Pd.](image)

(a) \( C_{\text{MIL,0}} \) Pt 376 ppm, Pd 3.6 ppm, \( V_{\text{str}}/V_{\text{IL}} = 4 \), HNO₃, HCl (b) \( C_{\text{MIL}} \) Pt 376 ppm, Pd 23 ppm, \( V_{\text{str}}/V_{\text{IL}} = 2 \), HNO₃, IL mixture (10 wt% addition of \([P_{6,6,6,14}][\text{Cl}]\) to \([\text{C}_8\text{mim}][\text{Tf}_2\text{N}]\))

![Figure 6. Reuse of the IL phase.](image)

\( C_{\text{Mag,0}} \) Pt 200 ppm, Pd 100 ppm, 1 M HCl, \( V_{\text{str}}/V_{\text{IL}} = 2 \), IL mixture (10 wt% addition of \([P_{6,6,6,14}][\text{Cl}]\) to \([\text{C}_8\text{mim}][\text{Tf}_2\text{N}]\)), Stripping 2 M HNO₃, \( V_{\text{str}}/V_{\text{IL}} = 2 \)
maintained. Although Cl\(^-\) in the IL phase was replaced with NO\(_3^-\) in the stripping step, as described above, it is thought that [P\(_{6,6,6,14}\)][NO\(_3^-\)] was regenerated to [P\(_{6,6,6,14}\)][Cl\(^-\)] by exchange of NO\(_3^-\) with Cl\(^-\) during the extraction step. Under the experimental conditions, the stripping degree of Pt from the IL phase is around 60\%, therefore some amounts of Pt and a small amount of Pd still remained in the IL phase. However, as the loading capacity of the IL is high enough for the IL phase for the next extraction operation, the IL phase can be reused repeatedly. In fact, the IL mixture showed a similar tendency in the five extraction cycles.

4. Conclusions

An imidazolium-based ionic liquid, [C\(_8\)mim][Tf\(_2\)N] showed the ability to extract Pt chloro-anions and showed selectivity against Pd. The extraction was considered to proceed via anion exchange between the IL anions and the Pt chloro-anion. In this study, an IL mixture system of [C\(_8\)mim][Tf\(_2\)N] with a phosphonium type IL, [P\(_{6,6,6,14}\)][Cl\(^-\)] was examined as the extraction phase to improve Pt extraction. Compared with the [C\(_8\)mim][Tf\(_2\)N] single IL system, Pt extraction increased for the mixed IL system. The selectivity between Pt and Pd was also improved. Nitric acid was effective for stripping the Pt and Pd from the IL phase. It was shown that the IL systems have good potential for use in extraction and separation of Pt without the need for any organic solvents.

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