Selective Separation and Recovery of Pt(IV) from Pd(II) through an Imidazolium-ionic-liquid-based Supported Liquid Membrane

Wataru YOSHIDA,* Fukiko KUBOTA,* Riho KONO,* and Masahiro GOTO*,**†

**Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motoooka, Fukuoka 819-0395, Japan*

***Center for Future Chemistry, Kyushu University, 744 Motoooka, Fukuoka 819-0395, Japan*

A supported liquid membrane (SLM) system for the selective separation of platinum(IV) from palladium(II) has been developed. The SLM was prepared using imidazolium-based IL 1-octy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. The initial flux and separation factor of Pt(IV) from Pd(II) were found to significantly depend on the composition of the receiving solution. Based on the performance, a 0.1 mol dm⁻³ NaClO₄ solution was selected as a suitable receiving solution. Membrane transport experiments showed that 93% of Pt(IV) can be selectively transported into the receiving solution, whereas most Pd(II) remains in the feed solution.

Keywords Supported liquid membrane (SLM), separation, platinum, imidazolium ionic liquid

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Introduction

Platinum group metals (PGMs) are essential elements for high-tech industries, such as the electronic, chemical, and automobile industries.¹ The separation and recovery of PGMs from secondary resources and liquid waste from factories has attracted attention for a stable supply of PGMs as well as the prevention of environmental pollution.² However, the separation and sensitive determination of PGMs are generally difficult because of similarities of the chemical and physical properties of PGMs.³

Solvent extraction is one of the most effective techniques for the analysis and separation of metal ion(s).⁴ Platinum (Pt) and/or palladium (Pd) extraction using a variety of extractants has been reported.^{5–10} However, the separation of Pt from Pd is still a difficult issue, and more effective analytical methods are required. In addition, solvent extraction causes serious environmental and health issues associated with using toxic organic diluents.¹¹

Supported liquid membranes (SLMs) have attracted attention as an efficient method for the separation and preconcentration of target metals.^{12,13} Organic diluents have also been used for SLMs as membrane phases. Several researchers have reported effective SLMs based on ionic liquids (ILs), which are salts with a melting point below 100°C.^{14–18} ILs have unique properties, such as high thermal stability, negligible vapor pressure and flame resistance; therefore, they have gained tremendous attention from researchers of separation science.^{19–23} Separation using IL-based SLMs is an attractive green alternative to traditional solvent extraction because an organic solvent is not required. However, Pt transport with IL-based SLMs has not been reported.

PGM extraction using ILs has recently been reported.^{24–30} Moreover, in our previous studies, we reported on the selective extraction of Pt(IV) over Pd(II) using undiluted imidazolium-based ILs as the extracting phase.^{31–33} We investigated the effects of the alkyl chain length of the IL cation and the type of partner anion on the extraction performance. 1-Octy-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₈mim][Tf₂N]) was selected as an optimal IL for the separation of Pt(IV) from Pd(II).

In this study, we investigated the selective transport of Pt(IV) through a SLM with [C₈mim][Tf₂N] as the membrane phase. This is the first report of concerning the efficient and selective separation of Pt(IV) from Pd(II) through a SLM.

Results and Discussion

A liquid-liquid extraction experiment using [C₈mim][Tf₂N] as the extracting phase was performed to determine the optimal HCl concentration in the aqueous feed solution for the selective extraction of Pt(IV). Figure S1 (Supporting Information) shows the extraction behavior of Pt(IV) and Pd(II) with [C₈mim][Tf₂N] from their HCl solutions. The degree of extraction (*E*) of Pt(IV) increases with increasing HCl concentration in the concentration range of <1 mol dm⁻³; it decreases with increasing HCl concentration for >1 mol dm⁻³ owing to competitive extraction of the Cl⁻ anion.³ The maximum *E* for Pt(IV) (about 68%) occurs at around 1 mol dm⁻³ HCl. Conversely, *E* of Pd(II) decreases with increasing HCl concentration until no Pd(II) extraction is observed in the range of 1–2 mol dm⁻³ HCl. Based on the results, 1 mol dm⁻³ was selected as the optimal HCl concentration in terms of the extraction performance of Pt(IV) and the selectivity for Pt(IV) over Pd(II). As shown in the speciation graphs of Pt(IV) and Pd(II) in aqueous HCl solutions, calculated using the

† To whom correspondence should be addressed.
E-mail: m-goto@mail.cstm.kyushu-u.ac.jp

Fig. 1 Kinetic plots of the transport of (a) Pt(IV) and (b) Pd(II) across a $[C_8mim][Tf_2N]$ -based SLM. Experimental conditions: feed solution volume and composition, 50 mL and 50 mg dm^{-3} each of Pt(IV) and Pd(II) in 1 mol dm^{-3} HCl; receiving solution volume and composition, = 50 mL and 0.1 mol dm^{-3} thiourea, 5 mol dm^{-3} HNO_3 , or 0.1 mol dm^{-3} $NaClO_4$.

corresponding stability constants^{34,35} (Fig. S2), Pt(IV) and Pd(II) mainly form anionic chloride complexes in >0.01 mol dm^{-3} HCl solution. Therefore, the extraction of Pt(IV) and Pd(II) from 1 mol dm^{-3} HCl with $[C_8mim][Tf_2N]$ is assumed to proceed by the anion exchange mechanism.^{24–26}

The transport experiments were carried out using the transport apparatus shown in Fig. S3 (Supporting Information). The transport of Pt(IV) and Pd(II) from the feed solution through a $[C_8mim][Tf_2N]$ -based SLM was investigated using three different receiving solutions: 0.1 mol dm^{-3} thiourea (pH 6.0), 5 mol dm^{-3} HNO_3 , and 0.1 mol dm^{-3} $NaClO_4$ (pH 5.5). These solutions are often used for the efficient stripping of Pt(IV).^{3,13,30,36} The kinetic rate constant, k (h^{-1}), permeability coefficient, P ($m\ h^{-1}$), initial flux, J_0 ($mol\ m^{-2}\ s^{-1}$), separation factor, β (–), and recovery factor, RF (%), were calculated using the following equations:

$$\ln\left(\frac{C_{M,t}^f}{C_{M,t=0}^f}\right) = -kt, \quad (1)$$

$$P = \left(\frac{V}{A}\right)k, \quad (2)$$

$$J_0 = PC_{M,t=0}^f, \quad (3)$$

Fig. 2 Effect of the $NaClO_4$ concentration in the receiving solution on the transport of Pt(IV) and Pd(II) across the $[C_8mim][Tf_2N]$ -based SLM. Experimental conditions: feed solution volume and composition, 50 mL and 50 mg dm^{-3} of both Pt(IV) and Pd(II) in 1 mol dm^{-3} HCl; receiving solution volume and composition, 50 mL and 0.05 – 1 mol dm^{-3} $NaClO_4$.

$$\beta = \frac{J_{0,Pt}}{J_{0,Pd}}, \quad (4)$$

$$RF = \frac{C_{M,t}^f}{C_{M,t=0}^f} \times 100, \quad (5)$$

where t is time (h); $C_{M,t=0}$ and $C_{M,t}$ are the concentrations of the metal ion ($mol\ m^{-3}$) at $t = 0$ (original solution) and t (extraction time), respectively. V (m^3) is the volume of the feed solution and A (m^2) is the effective membrane area. Superscripts f and r denote the feed and receiving solution, and subscripts Pt and Pd refer to platinum and palladium. The k value was obtained as the slope of $\ln(C_{M,t}^f / C_{M,t=0}^f)$ versus t .

The concentration of Pt(IV) in the feed solution decreased with time, and that in the receiving phase increased simultaneously, although it was only slightly transported during the operation time (6 h) in the case using thiourea. Pd(II) is hardly transported during the same period in each case. Plots of $\ln(C_{M,t}^f / C_{M,t=0}^f)$ versus time are shown in Fig. 1, and the corresponding rate constants (k) obtained from the slopes of the plots are given in Fig. 1. For Pt(IV), the highest k was obtained using $NaClO_4$ solution, and the effect of the $NaClO_4$ concentration in the receiving solution was investigated.

The initial flux of each metal (J_0) and the separation factor (β) for different $NaClO_4$ concentrations in the receiving solution are shown in Fig. 2. The initial flux of Pt(IV) increases with increasing concentration of $NaClO_4$ in the range of 0.05 – 1 mol dm^{-3} . A higher concentration of $NaClO_4$ in the receiving solution facilitates the transport of Pt(IV). The initial flux of Pd(II) is nearly zero in the range of 0.05 – 0.1 mol dm^{-3} $NaClO_4$, and then increases with increasing $NaClO_4$ concentration above 0.1 mol dm^{-3} because of an increase in the stripping efficiency for Pd(II). A high concentration of ClO_4^- may lead to anion exchange with the ionic liquid anion. Owing to this trend, the separation factor between Pt(IV) and Pd(II) is highest at 0.1 mol dm^{-3} $NaClO_4$. Based on the performance,

Fig. 3 Transport of Pt(IV) and Pd(II) across the $[C_8mim][Tf_2N]$ -based SLM. Experimental conditions: feed solution volume and composition, 50 mL and 50 mg dm⁻³ of both Pt(IV) and Pd(II) in 1 mol dm⁻³ HCl; receiving solution volume and composition, 50 mL and 0.1 mol dm⁻³ NaClO₄.

Table 1 Kinetic parameters for the transport of Pt(IV) and Pd(II) across the $[C_8mim][Tf_2N]$ -based SLM (thickness 125 μm) (experimental conditions same as in Fig. 3).

Metal ion	k/h^{-1}	$P/m\ h^{-1}$	$C_{M,t=0}^f/mol\ m^{-3}$	$J_0/mol\ m^{-2}\ s^{-1}$
Pt(IV)	5.6×10^{-2}	5.7×10^{-3}	0.262	4.1×10^{-7}
Pd(II)	9.0×10^{-4}	9.2×10^{-5}	0.492	1.3×10^{-8}

0.1 mol dm⁻³ was selected as the optimal NaClO₄ concentration in the receiving solution.

Figure 3 shows the transport behavior of Pt(IV) and Pd(II) from the feed to the receiving solution using the $[C_8mim][Tf_2N]$ -based SLM. Pt(IV) is selectively transported from the feed to the receiving solution, contrary to its apparent concentration gradient, whereas Pd(II) is only slightly transported during the same period. The recovery factors of Pt(IV) and Pd(II) using the SLM are 93 and 4% at 48 h, respectively. Based on the plot of $\ln(C_{M,t}^f/C_{M,t=0}^f)$ versus time shown in Fig. 1, the kinetic parameters for Pt(IV) and Pd(II) were calculated, and are summarized in Table 1. These results show the potential of the SLM for the selective separation of Pt(IV) from an aqueous solution also containing Pd(II).

Conclusions

We have reported an IL-based SLM for the selective separation of Pt(IV) from Pd(II) in a HCl solution. The SLM with $[C_8mim][Tf_2N]$ as the membrane phase allows the selective transfer of Pt(IV) from a feed solution to a 0.1 mol dm⁻³ NaClO₄ receiving solution against the concentration gradient, whereas most of the Pd(II) is remains in the feed solution. The results show that the developed a SLM system is effective for the separation of Pt(IV) from a mixture also containing Pd(II) in such applications as industrial and analytical fields.

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Supporting Information

Experimental details, extraction behavior of metals using $[C_8mim][Tf_2N]$, speciation graphs of the chloride complexes and schematic diagram of the SLM transport system are in Supporting Information. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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