Transport of Rhodium(III) from Chloride Media across a Polymer Inclusion Membrane Containing an Ionic Liquid Metal Ion Carrier

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Cite This: ACS Omega, 2020, 5, 12989−12995

ABSTRACT: Efficient and selective transport of rhodium(III) across a polymer inclusion membrane (PIM) from a 0.1 mol dm$^{-3}$ HCl feed solution, also containing iron(III), to a receiving solution containing 0.1 mol dm$^{-3}$ HCl and 4.9 mol dm$^{-3}$ NH$_4$Cl was achieved using a phosphonium-type ionic liquid, trioctyl(dodecyl)phosphonium chloride (P$_{88812}$Cl), as the metal ion carrier. The optimum PIM composition for the Rh(III) transport was 50 wt % poly(vinylidene-co-hexafluoropropylene) (PVDF-HFP), 30 wt % P$_{88812}$Cl, and 20 wt % plasticizer 2-nitrophenyl octyl ether (2NPOE). The driving force for the Rh(III) transport was suggested to be the concentration difference of the chloride ion between the feed and the receiving solutions. More than 70% rhodium(III) could be recovered from the receiving solution, and no transport of iron(III) was observed; however, the two metal ions cannot be separated by liquid−liquid extraction. This is the first report of selective transport of rhodium(III) across a polymer inclusion membrane.

1. INTRODUCTION

Platinum group metals (PGMs), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), play an important role as key elements in various industrial applications owing to their excellent catalytic and mechanical properties. However, the corresponding ores are scarce and unevenly distributed. For the stable supply of these metals, efficient separation and recovery techniques are required. Solvent extraction has conventionally been used for metal separation because it allows for the highly selective recovery of target metals. The key to the successful extraction and separation is the performance of the extractant used. Recently, various extractants for PGMs, including Rh, have been developed. However, the extraction of Rh has been a big challenge to date because its ligand exchange is well known to be inert and the chloro-complex species in the aqueous chloride media change drastically depending on the chloride ion concentration.

The price of Rh has been increasing significantly in recent years because most of Rh is produced as a by-product of platinum refining in South Africa. It is recovered from the final raffinate in the refining process after the separation of the other PGMs. Membrane separation is a very promising separation method, allowing simultaneous extraction and back-extraction of the target species at the membrane/feed solution and membrane/receiving solution interfaces, respectively. It has received much attention as an environmentally friendly alternative to solvent extraction, which uses large amounts of volatile, flammable, and toxic organic solvents. Polymer inclusion membranes (PIMs) are homogeneous liquid membranes comprising a base polymer, a carrier, and, in some cases, a plasticizer. PIMs have better stability compared to that of other liquid membranes, such as supported liquid membranes, which have been the mainstream of liquid membrane research. A PIM-based recovery of PGMs has been reported by several researchers, using various types of polymers, carriers, and plasticizers. Recently, ionic liquids (ILs) have been used not only as solvents but also as extractants. Various types of ionic liquids such as phosphonium, imidazolium, and ammonium ionic liquids have been applied to the extraction of PGMs and it has been confirmed that they have high extraction ability for PGMs. In particular, phosphonium-based ionic liquids, used undiluted as the

Received: February 27, 2020
Accepted: April 7, 2020
Published: May 27, 2020
Ionic liquids, which exhibit excellent ability for the recovery and separation of PGMs, have also been used as metal ion carriers for the transport of PGMs such as Pd and Pt. Regel-Rosocka et al. reported the transport of Pd(II) through a cellulose triacetate-based PIM using a series of commercially available phosphonium-type ionic liquids such as Cyphos 101 (triethyl(tetradecyl)phosphonium chloride, C66414Cl), Cyphos 102 (triethyl(tetradecyl) phosphonium bromide), and Cyphos 104 (triethyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)-phosphinate) as the carriers. Pospiech et al. used 102 (trihexyl(tetradecyl) phosphonium bromide), and Cyphos 104 (trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)-phosphinate) as the carriers. Pospiech et al. used tricapryl-methylammonium thiosalicylate for the Pd(II) transport. To the best of our knowledge, PIM-based recovery and separation of Rh have not yet been achieved.

Recently, we have reported that a novel phosphonium-type ionic liquid, trioctyl(dodecyl)phosphonium chloride (P88812Cl), could be applied to the extraction of PGMs as an extractant without dilution and that Pt, Pd, and even Rh have been effectively extracted into this ionic liquid. P88812Cl has shown a similar extraction behavior for PGMs to that of a commercial reagent, P66614Cl, analogous to P88812Cl. However, P88812Cl has been shown to have a much higher hydrophobicity than the commercially available P66614Cl, thus suggesting that the use of P88812Cl would produce more stable PIMs.

In a previous study, we have demonstrated the possibility of selectively extracting Pt and Pd from spent automotive catalyst leachate containing 5 mol dm$^{-3}$ HCl in undiluted P66614Cl, thus separating them from Rh and base metals such as Fe, Zn, and Cu. However, the separation of Rh from the raffinate using the same approach but at a lower HCl concentration in the aqueous phase has resulted in significant coextraction of Fe. Hence, a subsequent scrubbing process is required for the removal of Fe from the ionic liquid.

Therefore, the present study is aimed at simplifying the separation of Rh from the raffinate containing Fe by the application of a PIM containing P88812Cl as its carrier. The membrane composition and the operating conditions have been investigated for determining the optimal conditions for the successful transport of Rh(III) across the PIM. This is the first report of efficient and selective transport of Rh through a PIM.

2. RESULTS AND DISCUSSION

2.1. Characterization of the PIM. The PIMs prepared in this study were soft, transparent, and self-standing. The morphology of the PIM composed of 50 wt % polyvinylidene-co-hexafluoropropylene (PVDF-HFP), 30 wt % P88812Cl, and 20 wt % 2-nitrophenyl octyl ether (2NPOE) was investigated by scanning electron microscopy (SEM) and scanning probe microscopy (SPM). The SEM micrograph of the cross-section of the PIM shows that the PIM is dense and nonporous (Figure 1a). The surface of the PIM is rough at the submicron scale, contributing to efficient extraction and overall trans-membrane transport of solutes (Figure 1b). The contact angle of the PIM was measured to be 66.9 ± 0.5°, indicating that the membrane surface was hydrophilic even when the hydrophobic base polymer was used. The image of the water droplet on the PIM is shown in Figure 1d.
In the case of all stripping reagents, nearly 80% of Rh(III) recovery from the metal-loading PIM was achieved.

2.3. Membrane Transport Experiments. 2.3.1. Optimization of the Solution Conditions. Since both Rh(III) and Fe(III) can be extracted individually into the PIM studied (Figure 2), it was of interest to investigate the effect of the feed HCl concentration on the transport of Rh(III) in the presence of Fe(III). The receiving solution in these experiments contained 4.9 mol dm$^{-3}$ NH$_4$Cl and 0.1 mol dm$^{-3}$ HCl. Table 1 shows the initial flux ($J_0$) and the recovery factor (% RF) of Rh(III) and Fe(III) for each HCl concentration tested. Rh(III) was transported to the receiving solution without being accumulated in the membrane at any of the HCl concentrations studied, and the transport efficiency increased at lower HCl concentrations. The %E of Fe(III) was 2.7% at a feed HCl concentration of 0.1 mol dm$^{-3}$. However, as high as 34% of Fe(III) were accumulated in the membrane when the feed HCl concentration was increased to 1.0 mol dm$^{-3}$. Therefore, 0.1 mol dm$^{-3}$ was selected as the optimal HCl feed solution concentration since it provided the highest initial flux and recovery factor values for Rh(III) and the lowest for Fe(III) with no PIM accumulation of either metal ions.

Rh(III) forms different chloro-complex anionic species represented as [RhCl$_{3-n}$(H$_2$O)$_n$]$^{3-n-}$ depending on the Cl$^-$ ion concentration in the feed solution. Under the present experimental conditions, RhCl$_4$(H$_2$O)$_2$ is the dominant species; however, RhCl$_4$(H$_2$O)$_2$ can also be formed in the lower Cl$^-$ concentration range and the formation of RhCl$_6$ increases at high Cl$^-$ concentrations. Each of these complexes can hardly be extracted because of its high charge density and the difficulty in the coordination of three cation ligands around this anionic species. RhCl$_4$ and/or RhCl$_5$ are most likely extracted with P$_{88812}$Cl into the membrane according to the following equations:

$$\text{P}_{88812}\text{Cl} + \text{RhCl}_4 = \text{P}_{88812}\text{RhCl}_4 + \text{Cl}^-$$  (1)
$$2\text{P}_{88812}\text{Cl} + \text{RhCl}_5 = \left(\text{P}_{88812}\right)_2\text{RhCl}_5 + 2\text{Cl}^-$$  (2)

where the horizontal bars indicate species in the PIM phase. The proposed facilitated transport mechanism is shown in Figure 3. It involves ion-exchange reactions between the Rh(III) chloro-complex and the Cl$^-$ ions of P$_{88812}$ and the stripping reagents at the PIM feed and receiving solution interfaces, respectively. The transport is driven by the difference in Cl$^-$ concentrations in the two aqueous solutions.

The effect of three receiving solution compositions, all containing 5 mol dm$^{-3}$ Cl$^-$, on the transport of Rh(III) and Fe(III) is illustrated in Figure 4. The transport efficiency of Rh(III) increased as the concentration of NH$_4$Cl in the receiving solution was increased (Figure 4a); however, this trend was less pronounced for the stripping efficiency in the batchwise experiments described above. When a high concentration of HCl was used as the receiving solution, transport of HCl from the receiving solution to the feed solution was observed, whereas this process was inhibited when a mixture of HCl and NH$_4$Cl was used instead. When the receiving solution contained only HCl, the permeation of Cl$^-$ into the feed solution associated with the permeation of acids increased the concentrations of the Rh(III) chloro-complexes, which were difficult to be extracted into the PIM. At the same time, the concentrations of extractable Fe species in the feed solution increased too. Furthermore, the increase in the Cl$^-$ concentration in the feed solution and its decrease in the receiving solution reduce the Cl$^-$ concentration difference between the two aqueous solutions, which drives the Rh(III) transport. The sharp reduction in Cl$^-$ transport across the PIM when NH$_4$Cl was used as the main Cl$^-$ source in the receiving solution can be explained by the much larger molecular size of the ammonium ion compared to that of the hydrogen ion, resulting in the high membrane permeability for Rh(III). The recovery efficiency (%RF) values for Rh(III) and Fe(III) in the case of the 4.9 mol dm$^{-3}$ NH$_4$Cl and 0.1 mol dm$^{-3}$ HCl receiving solution (Figure 4b) showed excellent Rh(III) recovery and no accumulation of either Rh(III) or Fe(III) within the PIM.

2.3.2. Effect of the Composition of PIM. The concentrations of the base polymer, carrier, and plasticizer in a PIM affect its transport performance. The effect of the PIM composition on the transport parameters of Rh(III) such as initial flux ($J_0$) and recovery factor (%RF) is illustrated in Figure 5. It should be noted that the transport of Fe(III) was...
almost negligible for the PIM composition studied under the experimental conditions described earlier, and the corresponding data are not included in Figure 5. As expected, \( J_0 \) for Rh(III) increased with the increase in the concentration of P88812Cl from 10 to 30 wt %, and no further increase was observed with the further increase in the P88812Cl concentration. Thus, the P88812Cl concentration of 30 wt % was selected as the optimal concentration for the transport of Rh(III). The results for the effect of the PIM composition on %RF showed that %RF increased with the increase in the concentration of P88812Cl from 10 to 30 wt %, and then it decreased upon further increasing the P88812Cl concentration. This decrease was most likely due to the decrease in the plasticizer concentration, on the one hand, and, on the other hand, due to the fact that higher concentration of the extractant will favor the extraction rather than stripping of Rh(III) according to the Le Chatelier’s principle applied to eq 1. Generally, plasticizers with a bulky molecular structure play an important role in the diffusion of metallic species across PIMs because they reduce the size of the crystalline base polymer regions in the PIMs.\(^{18}\)

Compared to liquid–liquid extraction, the selectivity of Rh(III) separation was improved in the newly developed PIM-based system. In PIM-based separation, the target species are extracted into the PIM liquid phase comprising a carrier and a plasticizer and located in nanometer-size channels.\(^{33}\) Therefore, the effect of the plasticizer on the metal selectivity in liquid–liquid extraction was examined using undiluted P88812Cl containing 40 wt % 2NPOE. There was no significant change in the metal extraction efficiency in the presence of 2NPOE compared to that using only undiluted IL as the extraction phase, which demonstrated that 2NPOE were not involved in the metal extraction. Therefore, the improvement in the PIM selectivity for Rh(III) was attributed to the characteristics of the PIM itself. One of these characteristics is the concentration of P88812Cl in the PIM, which is very low compared to that in the extraction phase in liquid–liquid extraction where undiluted P88812Cl is used. This low extractant concentration enhances the competitive extraction of metals into the PIM.

2.3.3. Effect of the Membrane Thickness. The transport behavior of Rh(III) and Fe(III) using PIMs with different thicknesses under the optimized conditions is shown in Figure 6, where no permeation of Fe(III) was observed regardless of the membrane thickness. As expected, the transport kinetics and its efficiency for Rh(III) were improved using thinner PIMs. The kinetic parameters for the transport of Rh(III) across membranes of different thicknesses are shown in Table 2.

The stability of a PIM with a composition (40 wt % P88812Cl, 50 wt % PFDV-HFP and 10 wt % 2NPOE) similar to that of the PIMs investigated in the present study and thickness (55.6 \( \mu \)m) similar to that of the thinner PIM studied (66.5 \( \mu \)m, Table 2) was examined by us in a previous study, where it was found that it could be reused at least seven times without performance degradation.\(^{34}\) However, it was observed that the 16.2 \( \mu \)m thick PIM stretched to the receiving solution due to the osmotic pressure caused by the high salt concentration of this solution.

3. CONCLUSIONS

This study demonstrated, for the first time, the possibility of conducting facilitated transport of Rh(III) across a PIM. The PFDV-HFP-based PIM using P88812Cl as a carrier and 2NPOE as a plasticizer showed excellent transport performance for Rh(III). Under the optimum conditions, Rh(III) was transported from the feed to the receiving solution against its apparent concentration gradient, while the transport of Fe(III), co-existing in the feed solution, was negligible. The carrier P88812Cl could be continuously regenerated during operation because the membrane was constantly in contact with the Cl\(^-\) ions in both solutions. Transport performance was found to be enhanced by decreasing the membrane thickness. The use of undiluted ionic liquids is one way to construct an ecofriendly liquid–liquid extraction system with high extraction efficiency for Rh(III), but the separation of other metal ions, co-extracted with Rh(III), such as Fe(III), requires an additional process like scrubbing. The newly developed PIM provides a simple and efficient method for the separation of Rh(III) from Fe(III), which are difficult to separate by other methods. Based on the prices of the reagents used, 1 m\(^2\) of this membrane costs approximately $60; however, if the membrane is mass-produced on the industrial scale, this cost is expected to decrease significantly.

4. EXPERIMENTAL SECTION

4.1. Reagents. We designed the ionic liquid P88812Cl, and it was synthesized by Nippon Chemical Industrial Co. Ltd. The...
Table 2. Kinetic Parameters of the Transport of Rh(III) across PIMs with Different Thicknesses and Compositions of 50 wt % PVDF-HFP, 30 wt % P88812Cl, and 20 wt % 2NPOE

| thickness [μm] | k [h⁻¹] | V [m²] | A [m²] | C<sub>0</sub>[Rh,init] [mol dm⁻³] | P [m h⁻¹] | J<sub>0</sub> [mol m⁻² s⁻¹] |
|---------------|---------|-------|-------|---------------------------|---------|-----------------|
| 66.5          | 0.043   | 5 × 10⁻⁵ | 4.9 × 10⁻⁴ | 2 × 10⁻⁴         | 4.4 × 10⁻⁵ | 2.3 × 10⁻⁷     |
| 16.2          | 0.070   | 5 × 10⁻⁵ | 4.9 × 10⁻⁴ | 2 × 10⁻⁴         | 7.1 × 10⁻⁵ | 3.8 × 10⁻⁷     |

“The solution conditions were the optimized conditions, as described in Figure 5.

The membrane transport experiments were carried out by sandwiching a PIM between two jacketed glass compartments that are identical in size. The effective membrane area exposed to each solution was 4.9 × 10⁻⁴ m². The feed and the receiving solutions (50 cm³) were poured into the corresponding glass compartments, separated by the PIM, and stirred with stirring bars using magnetic stirrers (HK-55D, Vidrex). Both glass compartments were kept at 298 K by continuous water circulation through their glass jackets from a water bath using a thermost regulator (RCB-1200, EYELA). Samples from both solutions were periodically collected from each glass compartment and measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to quantify the metal concentrations.

The liquid–liquid extraction experiments were carried out by contacting the feed solution and P<sub>88812Cl</sub> without dilution at an aqueous/organic volume ratio of 2:1 and shaken at 160 rpm for 3 h after being vigorously mixed for 60 s by a vortex mixer (VORTEX-GENIE 2, Scientific Industries).

The transport kinetics was assumed to be of first-order (eq 4). Therefore, the permeability coefficient P (m h⁻¹), the initial flux J<sub>0</sub> (mol m⁻² s⁻¹), and the recovery factor %RF are described using eqs 5–7, respectively.

\[ \ln \left( \frac{C_{M,t}}{C_{M,init}} \right) = -kt \]  

\[ P = \left( \frac{V}{A} \right)^k \]  

\[ J_0 = PC_{M,init}^f \]  

\[ \%RF = \frac{C_{M,t}}{C_{M,init}} \times 100 \]
area (m²), and superscripts f and r refer to the feed and the receiving solutions, respectively.

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**Author Contributions**

This manuscript was written through contributions of all authors. All authors have given approval to the submission of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Environment Research and Technology Development Fund (ERTDF, 3-1710) from the Ministry of the Environment of Japan, and JSPS KAKENHI Grant Number JP19K05126. The authors are grateful to the Center of Advanced Instrumental Analysis, Kyushu University, for help with the SEM measurements.

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