Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Transport of Palladium(II) through Trioctylamine Liquid Membrane

Jianshun Fu[a]; Shigeto Nakamura[a]; Kenichi Akiba[a]
[a] INSTITUTE FOR ADVANCED MATERIALS PROCESSING TOHOKU UNIVERSITY, AOBA-KU, SENDAI, JAPAN

To cite this Article Fu, Jianshun , Nakamura, Shigeto and Akiba, Kenichi(1995) 'Transport of Palladium(II) through Trioctylamine Liquid Membrane', Separation Science and Technology, 30: 5, 793 — 803
To link to this Article: DOI: 10.1080/01496399508013892
URL: http://dx.doi.org/10.1080/01496399508013892

SEPARATION SCIENCE AND TECHNOLOGY, 30(5), pp. 793–803, 1995

Transport of Palladium(II) through Trioctylamine Liquid Membrane

JIANSHUN FU, SHIGETO NAKAMURA, and KENICHI AKIBA
INSTITUTE FOR ADVANCED MATERIALS PROCESSING
TOHOKU UNIVERSITY
KATAHIRA-2, AOBA-KU, SENDAI 980, JAPAN

ABSTRACT

The permeation behavior of palladium(II) through a supported liquid membrane (SLM) impregnated with trioctylamine (TOA) in kerosene has been investigated. By selecting perchloric or nitric acid as a stripping agent, Pd(II) was transported through the SLM containing 0.5 M TOA and 20% 1-octanol without remaining in the liquid membrane. The permeation rate ($k_{f,obs}$) of Pd(II) for HNO_3 was faster than that for $HClO_4$. Palladium(II) was concentrated across the SLM from the 0.5 M HCl solution into the $HClO_4$ or HNO_3 solution.

INTRODUCTION

Solvent extraction is now a well-established process in precious metals refining (1). Although this method has been widely used on an industrial scale, alternative methods have been required to overcome several problems due to limited selectivity, poor kinetics, and many operation steps to accomplish efficient separation. Liquid membrane transport has been anticipated as a potential alternative to conventional liquid–liquid extraction (1) because it simultaneously combines both extraction and stripping in one step and considerably reduces solvent usage.

Palladium(II) extraction has been performed with some appropriate reagents, such as sulfur-containing extractants, from acidic media under conditions where most metals are not extracted. This provides high selectivity in recovery and purification of Pd(II). However, the time required for the achievement of Pd(II) extraction is usually very long, and this is a practical problem (2). Further, some difficulties in stripping Pd(II) species from the organic phase may be a major drawback in the application of liquid–liquid extraction processes to the liquid membrane transport of Pd(II).

In a previous study (3) the transport of platinum(IV) across a supported liquid membrane (SLM) containing trioctylamine (TOA) was examined using perchloric acid as the stripping solution. Platinum(IV) was almost quantitatively transported against its large concentration gradient without accumulation in SLM in the presence of 1-octanol.

The present study deals with the transport behavior of palladium(II) across a TOA liquid membrane supported on a microporous film by selecting appropriate reagents for stripping Pd(II).

EXPERIMENTAL

Reagents

Trioctylamine (TOA > 97% purity, Wako Pure Chemical Ind.) was diluted with kerosene in the presence of 1-octanol. A solution of 2.35×10^{-4} M (M = $\text{mol}\cdot\text{dm}^{-3}$) palladium(II) in 0.5 M HCl was prepared by diluting a standard solution containing 1000 ppm Pd(II) in 1.0 M HCl. All other reagents were of analytical grade. A microporous support for the liquid membrane used here was a polytetrafluoroethylene film (Sumitomo Electric Ind.) with a thickness of 80 μm, a porosity of 74%, and an average pore size of 0.45 μm.

Procedure

Liquid–liquid extraction and stripping were performed by contacting equal volumes of an aqueous and an organic phases for 5 minutes at 25°C. Transport experiments were carried out in the same manner described previously (4). A feed solution (100 cm^3) of 0.5 M HCl containing 2.35×10^{-4} M Pd(II) and a product solution (100 cm^3) of a stripping agent were placed, respectively, in the outer and the inner compartments separated by SLM impregnated with a TOA–kerosene solution modified with 1-octanol. These transport compartments were usually shaken at 120 strokes per minute (spm) at 25°C, and the concentrations of Pd(II) in the feed and the product solutions were periodically measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

RESULTS AND DISCUSSION

Extraction and Stripping of Palladium(II)

Palladium(II) is effectively extracted by trioctylamine (TOA) from dilute hydrochloric acid solutions (5–7). Extraction of Pd(II) with TOA(R_3N)

proceeds through an anion-exchange reaction:

$$R_3N_{org} + HCl_{aq} \rightleftharpoons R_3NHCl_{org} \quad (1)$$

$$2R_3NHCl_{org} + PdCl_{4,aq}^{2-} \rightleftharpoons (R_3NH)_2PdCl_{4,org} + 2Cl_{aq}^{-} \quad (2)$$

Experimental data show that Pd(II) was quantitatively extracted with 0.1 M TOA in kerosene from 0.1–2.0 M HCl solution. The distribution ratio of Pd(II) decreased with increasing HCl concentration; however, Pd(II) was only partially stripped even by a high concentration of HCl (12 M). Both extraction conditions and stripping conditions are essential to accomplish liquid membrane transport.

The possibility of stripping Pd(II) from a loaded organic phase was tested by using some mineral acids and coordinating ligands such as thiourea (tu). The distribution ratios (*D*) as determined by backward extraction are plotted against the stripping reagent concentrations in Fig. 1. The *D* values decreased with increasing concentrations of stripping acids, and the distribution behavior for the $NaClO_4$ solution was found to be similar to that for $HClO_4$. The distribution ratios of Pd(II) were in the order HCl > HNO_3 > $HClO_4$ >> tu. In the case of strongly complexing tu, Pd(II) can

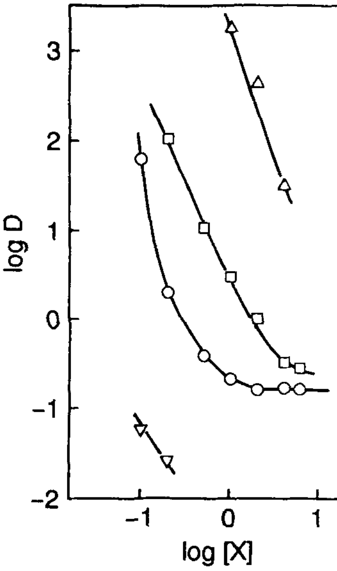

FIG. 1 Effect of the concentrations of stripping agents on the distribution ratio of palladium(II). Organic phase: 0.1 M TOA in kerosene containing palladium(II); aqueous phase: (△) HCl, (□) HNO_3, (○) $HClO_4$, (▽) 0.5 M tu/0.5 M HCl.

be almost quantitatively stripped owing to the formation of unextractable cationic complexes of Pd(II) with tu (8).

$$(R_3NH)_2PdCl_{4,org} + 4tu_{aq} \rightleftharpoons 2R_3NHCl_{org} + Pd(tu)_{4,aq}^{2+} + 2Cl_{aq}^{-} \qquad (3)$$

In the experimental procedure, a third phase accumulating Pd(II) species was sometimes observed between the organic and aqueous phases. However, this practical difficulty was overcome by the addition of a modifier, 1-octanol.

Liquid Membrane Transport of Palladium(II)

On the basis of extraction and stripping behavior, the transport of Pd(II) across a TOA liquid membrane was tested by adopting three stripping reagents, tu, $HClO_4$, and HNO_3, as product solutions. Figure 2 illustrates the time-dependent fractions of Pd(II) in the feed and the product solutions for transport through an SLM containing 0.5 M TOA.

In the tu case, Pd(II) was only partially transported because of the formation of an orange precipitate on the feed side of the SLM; such a phenomenon implies that a small amount of tu moves through the liquid membrane to the feed side of the SLM, and this leads to a substitution reaction in which cationic Pd(II) thiourea complexes are formed. Some of the Pd-tu species produced have a limited solubility and deposit on the SLM (9).

As for the product solution of 3 M $HClO_4$, the fraction in the feed side decreased smoothly but that in the product side increased somewhat slowly. It is desirable to shorten the time lag between the feed and the

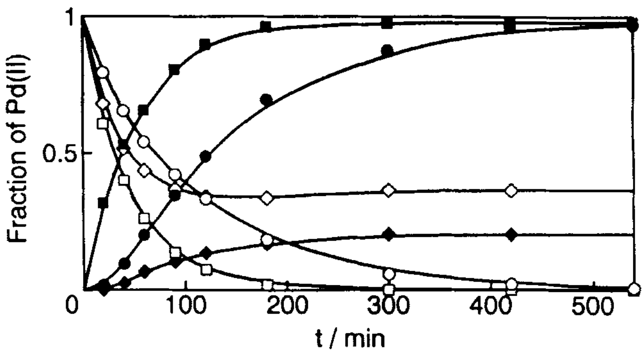

FIG. 2 Transport of palladium(II) through an SLM into different product solutions. SLM: 0.5 M TOA in kerosene; feed: 0.5 M HCl; product: (○, ●) 3 M $HClO_4$, (□, ■) 4 M HNO_3, (◇, ◆) 0.5 M tu/0.5 M HCl. Open: feed; closed: product.

product fractions to perform fast transport. In the case of the 4 M HNO_3 product solution, the fraction in the feed solution decreased with time and that in the product solution increased almost symmetrically. Nearly quantitative transport of Pd(II) was accomplished after 9 hours into a product solution of perchloric or nitric acid.

In a previous study (3) the stripping process was found to be considerably promoted by the addition of 1-octanol to the liquid membrane phase. Figure 3 illustrates a comparison of the transport of Pd(II) in the presence and the absence of 1-octanol. The decreasing rate of Pd(II) in the feed solution was slightly dependent on the presence of 1-octanol, while the increasing rate in the $HClO_4$ product solution was improved by the addition of 1-octanol in the SLM. Approximately symmetrical plots of Pd(II) fractions in the feed and the product solutions were obtained in the presence of 20% 1-octanol.

The transport of Pd(II) with TOA proceeds as follows. TOA is present in the membrane phase as an amine salt with a mineral acid HX:

$$R_3N_{SLM} + HX_{aq} \rightleftharpoons R_3NHX_{SLM} \tag{4}$$

The affinity of TOA for mineral acids is in the order (10) $HClO_4 > HNO_3 > HCl$. The complex $PdCl_4^{2-}$ is incorporated in the SLM through an anion-exchange reaction:

$$2R_3NHX_{SLM} + PdCl_{4,aq}^{2-} \underset{\text{product side}}{\overset{\text{feed side}}{\rightleftharpoons}} (R_3NH)_2PdCl_{4,SLM} + 2X_{aq}^{-} \tag{5}$$

and Pd(II) is released from the SLM by the reverse reaction. As is seen

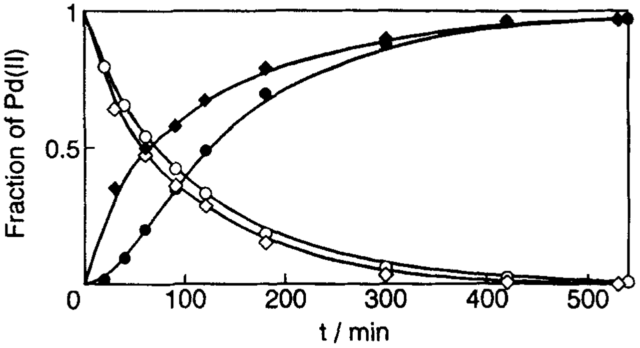

FIG. 3 Transport of palladium(II) through an SLM. Feed: 0.5 M HCl; product: 3 M $HClO_4$; SLM: 0.5 M TOA and (○, ●) no 1-octanol, (◇, ◆) 20% 1-octanol in kerosene. Open: feed; closed: product.

in Fig. 1, the distribution ratios were too high to strip Pd(II) even at high concentrations of HCl. However, the distribution ratios of Pd(II) in the $HClO_4$ or HNO_3 system were relatively low, and it is feasible to strip Pd(II) at increasing acid concentrations. The transport of Pd(II) across an SLM would be accomplished by the large difference in the distribution ratios between the feed and product sides of the SLM.

Effect of TOA Concentration in SLM

Figure 4 illustrates the time-dependent fractions of Pd(II) with different TOA concentrations in the presence of 20% 1-octanol in SLM. The fraction curves for both sides are almost symmetrical, indicating that the amount of Pd(II) accumulating in the SLM is practically negligible. Thus, the decreasing rate of Pd(II) fraction in the feed solution can be considered to be the transport rate of Pd(II) through the SLM. The apparent rate constant, $k_{f,obs}$, was evaluated from the following equation:

$$\ln[Pd]_{f,t}/[Pd]_{f,0} = -k_{f,obs}t \tag{6}$$

where $[Pd]_{f,t}$ and $[Pd]_{f,0}$ are the concentrations of Pd(II) in the feed solution at time t and the initial concentration, respectively. As Fig. 5 shows, the $k_{f,obs}$ value in the $HClO_4$ system increased gradually with TOA concentration; this may be due to an increase in extractability into the liquid membrane. The $k_{f,obs}$ values obtained for 4 M HNO_3 as a product solution increased with increasing TOA concentration from 0.01 to 0.1 M and reached a plateau at high TOA concentrations. The transport rate of Pd(II) into 4 M HNO_3 was faster than that into 3 M $HClO_4$ throughout all TOA

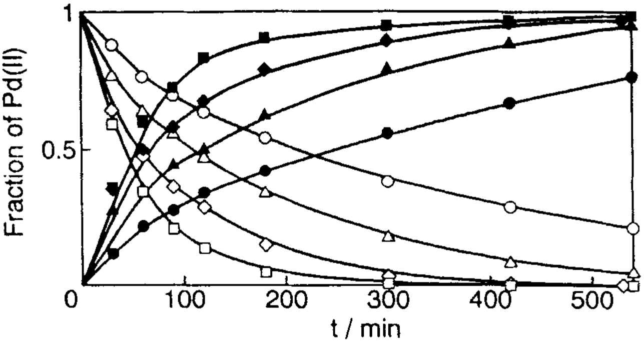

FIG. 4 Effect of TOA concentration in an SLM on the transport of palladium(II). Feed: 0.5 M HCl; product: 3 M $HClO_4$; SLM: (○, ●) 0.01 M, (△, ▲) 0.1 M, (◇, ◆) 0.5 M, (□, ■) 0.8 M TOA and 20% 1-octanol in kerosene. Open: feed; closed: product.

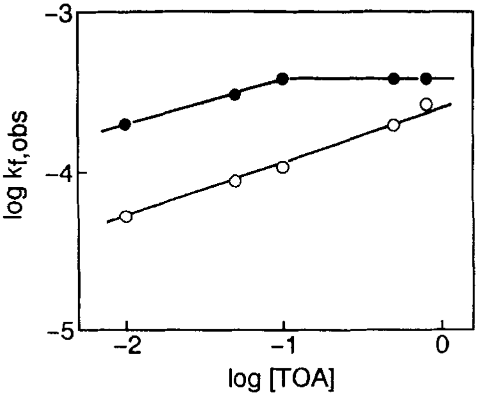

FIG. 5 Effect of TOA concentration on $k_{f,obs}$ value. SLM: TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: (○) 3 M $HClO_4$, (●) 4 M HNO_3.

concentration regions. The extraction of $PdCl_4^{2-}$ from the feed side might be depressed owing to the high stability of R_3NHClO_4 compared with that of R_3NHNO_3 (11).

Effect of Acid Concentration in the Product Solution

Figure 6 represents the effect of the stripping acid concentration on the transport rate of Pd(II) through an SLM containing 0.5 M TOA and 20%

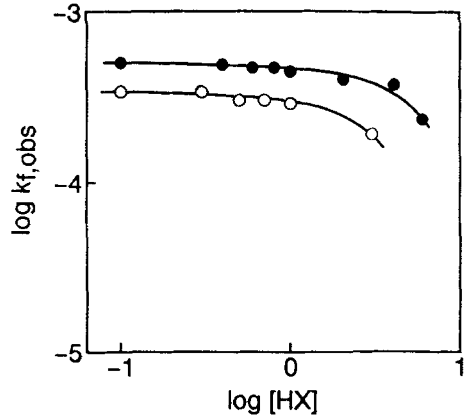

FIG. 6 Effect of acid concentration in product solution. SLM: 0.5 M TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: (○) $HClO_4$, (●) HNO_3.

1-octanol. In the $HClO_4$ system, the $k_{f,obs}$ value was little affected below 1.0 M $HClO_4$ and slightly decreased with a further increase in $HClO_4$ concentration. It appears that a small amount of perchlorate ion permeates through the SLM to the feed side and reduces the distribution ratio of Pd(II).

In the case of HNO_3, the $k_{f,obs}$ value was approximately constant from 0.1 to 4.0 M HNO_3 and declined at high concentrations. At concentrations below 1 M a third phase containing Pd(II) species was detected at the product side of the SLM, and small amounts of this deposit were further observed at 0.1 M HNO_3. When 30% 1-octanol was added to the SLM containing 0.1 M TOA, no third phase was produced in the region from 0.1 to 4.0 M HNO_3. An increase in 1-octanol content and a decrease in TOA concentration led to a lower distribution ratio and served to release Pd(II) rapidly from the TOA-SLM (3).

It is obvious that both $HClO_4$ and HNO_3 can be employed as product solutions. The optimum conditions may lie up to 1.0–3.0 M $HClO_4$ and 2.0–4.0 M HNO_3, where Pd(II) can be almost quantitatively transported across an SLM containing 0.5 M TOA and 20% 1-octanol.

Permeation Behavior through SLM

Permeation processes for Pd(II) transport are approximately those described in a previous study (12). The $k_{f,obs}$ for Pd(II) transport through an SLM can be expressed by

$$k_{f,obs} = \frac{1}{\dfrac{\delta_a}{D_a} + \dfrac{1}{k_1} + \dfrac{\delta_0}{D_0}\dfrac{1}{D}} \frac{S}{V} \tag{7}$$

where k_1 is the apparent rate constant of the forward extraction; δ_a and D_a are the thickness of the feed–SLM boundary layer and the diffusion coefficient of Pd(II), respectively; and δ_0 and D_0 are the thickness of the SLM and the diffusion coefficient of the Pd(II)–TOA complex, respectively.

In order to examine the rate-determining step of the transport processes, the effect of shaking speed was investigated. As seen in Fig. 7, the $k_{f,obs}$ value increased with increasing shaking speed; this appears to be attributable to a decrease in the thickness of the aqueous boundary layer. The term of δ_a/D_a in Eq. (7) is derived from the diffusion process in the aqueous boundary layer, and this may be the main resistance in the transport rate of Pd(II) through an SLM.

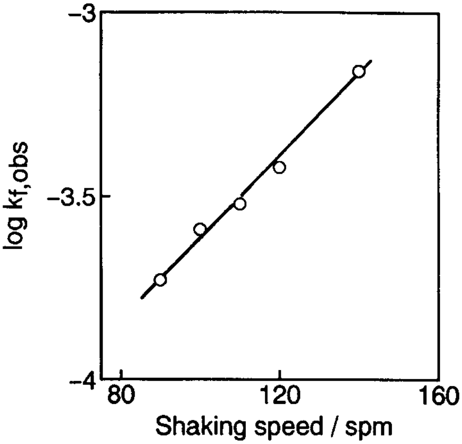

FIG. 7 Effect of shaking speed on $k_{f,obs}$ value. SLM: 0.5 M TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: 4 M HNO_3.

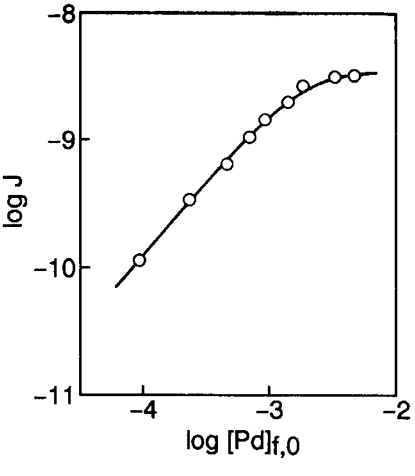

FIG. 8 Effect of initial concentration of palladium(II) on the flux. SLM: 0.5 M TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: 4 M HNO_3.

TABLE 1
Effect of the Volume Ratio of the Feed and Product Solutions[a]

V_p (cm^3)	V_f/V_p	$[Pd]_{p,t}/[Pd]_{f,0}$ at 9 hours	Recovery at 9 hours (%)
100	1	0.966	96.6
50	2	1.94	96.8
25	4	3.84	96.1
10	10	9.57	95.7
5	20	19.2	95.9

[a] SLM: 0.5 M TOA in kerosene. Feed: 0.5 M HCl, 100 cm^3. Product: 3 M $HClO_4$.

Effect of Pd(II) Initial Concentration and Concentration Factor

Figure 8 shows the plot of the initial flux, J (mol·cm^{-2}·s^{-1}), through an SLM against the initial concentration of Pd(II). The Pd(II) flux was proportional to the initial concentration of Pd(II) up to 10^{-3} M. It approached steady-state with further increases in concentration and began to produce the third phase on the feed side of the SLM; higher Pd(II) concentrations resulted in a more serious third phase.

The concentration factor ($[Pd]_{p,t}/[Pd]_{p,0}$) was examined by reducing the volume in the $HClO_4$ solution, and the values obtained are listed in Table 1. Reasonable concentration factors corresponding to the feed-to-product volume ratios employed can be attained. The recovery of Pd(II) is also listed in Table 1. Almost all the Pd(II) in the feed solution was extracted into the SLM, and 96% of Pd(II) was recovered in the product solution after 9 hours even if the volume ratio of the feed to the product solution was fairly high.

REFERENCES

1. M. Cox, in *Developments in Solvent Extraction*, Ellis Horwood Press, Chichester, 1988, p. 177.
2. S. J. Al-Bazi and H. Freiser, *Solv. Extr. Ion Exch.*, *5*, 265 (1987).
3. J. Fu, S. Nakamura, and K. Akiba, *Sep. Sci. Technol.*, *30*, 000 (1995).
4. K. Akiba and T. Kanno, *Ibid.*, *18*, 831 (1983).
5. M. Y. Mirza, *Talanta*, *27*, 101 (1979).
6. M. Y. Mirza, F. Ik. Nwabue, and R. T. Bailey, *J. Inorg. Nucl. Chem.*, *40*, 1945 (1978).
7. S. C. Dhara, *Precious Metals Mining, Extracting and Processing*, Metallurgical Society, AIME, Warrendale, New Jersey, 1984, p. 199.
8. A. Warshawsky, "Integrated Ion Exchange and Liquid–Liquid Extraction Process for

the Separation of Platinum Group Metals," in *Third International Hydrometallurgy Symposium, Atlanta*, 1983, p. 517.
9. A. Warshawsky, *Sep. Purif. Methods*, *9*, 209 (1980).
10. C. F. Coleman et al., *Ind. Eng. Chem.*, *50*, 1756 (1958).
11. E. Högfeldt, in *Developments in Solvent Extraction*, Ellis Horwood Press, Chichester, 1988, p. 36.
12. S. Nakamura, S. Ohashi, and K. Akiba, *Sep. Sci. Technol.*, *27*, 741 (1992).

Received by editor March 25, 1994