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Iridium(IV) Transport across Trioctylamine Supported Liquid Membrane

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ABSTRACT

Transport behavior of iridium through a supported liquid membrane (SLM) was investigated using trioctylamine (TOA) as a mobile carrier. Iridium(IV) was almost quantitatively extracted with TOA in kerosene from a low HCl solution, and extracted Ir(IV) was stripped with an $HClO_4$ or HNO_3 solution. Based on the extraction and stripping data, transport of Ir(IV) through a TOA-SLM was performed. Iridium(IV) in the feed solution with low HCl concentration was effectively transported into the $HClO_4$ or the HNO_3 product solution. Iridium(IV) was recovered and concentrated in the 1 M $HClO_4$ product solution by reducing the volume of strip solution relative to the volume of feed solution, yielding a sufficient enrichment factor.

INTRODUCTION

Liquid–liquid extraction has been successfully utilized for the separation and recovery of iridium from other platinum group metals (PGMs) by employing some effective extractants (1–4). Iridium generally has two oxidation states, Ir(III) and Ir(IV), in an HCl solution. Iridium(IV) can be effectively extracted by some extractants such as aliphatic amines, while Ir(III) is poorly extracted in HCl media. Control of these oxidation states is one of the most important subjects in refining iridium species. Extraction of Ir(IV) and subsequent stripping with reducing media have commonly been applied to industrial separation of Ir from PGMs (5, 6). However, repeating cycles between oxidizing and reducing conditions may lead to fairly rapid degradation of extractants. An investigation of prospective methods for the recovery of Ir seems to be of practical interest.

Liquid membrane transport has been expected to be an effective alternative to conventional solvent extraction because it affords active transport of metal against its concentration gradient with a small amount of a mobile carrier (7). In previous studies (8–11), precious metals such as Au(III), Pt(IV) and Pd(II) were almost quantitatively transported across a supported liquid membrane (SLM) containing a trioctylamine (TOA)-kerosene solution modified with 1-octanol. Separation of Au(III) from Pt(IV) and Pd(II) with a TOA carrier (12) and the mutual separation between Pt(IV) and Pd(II) with a LIX 26 carrier (13) have also been successfully accomplished. On the other hand, little information has been known on the transport of Ir across an SLM.

This paper presents extraction behavior of Ir(III) and Ir(IV) with TOA and variables affecting the transport of Ir(IV) through a TOA-SLM.

EXPERIMENTAL

Materials

A solution of Ir(IV) was prepared by dissolving $IrCl_4$ (Wako Pure Chemical Ind.) in aqua regia, evaporating to dryness, and then dissolving in a 3 M HCl solution. In order to keep Ir(IV) at oxidation conditions, 5% (v/v) of 0.3% chlorine water was added, and the solution was freshly prepared prior to every experiment. A stock solution of Ir(III) was prepared by dissolving $IrCl_3 \cdot 3.5\ H_2O$ (High Purity Chemicals) in a dilute HCl solution.

Trioctylamine (TOA; R_3N, Wako) of a purity of more than 97% was used by diluting with kerosene. Other chemicals employed here were of guaranteed reagent grade.

A polytetrafluoroethylene membrane (FP-045; Sumitomo Electric Ind.) with a thickness of 80 μm, a porosity of 74%, and an average pore size of 0.45 μm was used as an inert support.

Solvent Extraction

An 8 cm^3 portion of an aqueous phase containing 1.30×10^{-4} M Ir was contacted with an equal volume of a kerosene solution of TOA at 25°C. After phase separation by centrifugation, the concentration of metal in the aqueous phase was determined by ICP-AES, and that in the organic phase was determined from a mass balance. A spectrum of Ir(IV) species in the HCl solution was measured with an Hitachi 124 spectrophotometer.

Liquid-Membrane Transport

Transport experiments were carried out in a manner similar to that described previously (14). An apparatus for liquid-membrane transport was composed of inner and outer polypropylene compartments. A membrane (26 cm^2) impregnated with TOA-kerosene solution modified with 1-octanol was fixed in the bottom of the inner compartment. A feed solution (100 cm^3) containing Ir was placed in the outer compartment, and an equal volume of a product solution was placed in the inner compartment unless otherwise noted. The apparatus was shaken at 120 strokes per minute at 25°C, and the concentrations of Ir in the feed and product solutions were measured with ICP-AES.

RESULTS AND DISCUSSION

Extraction of Iridium

Extraction behavior of Ir with TOA in kerosene was examined in order to choose optimum conditions for the SLM transport. Figure 1 shows the distribution ratios (*D*) of Ir from the aqueous solutions prepared in differ-

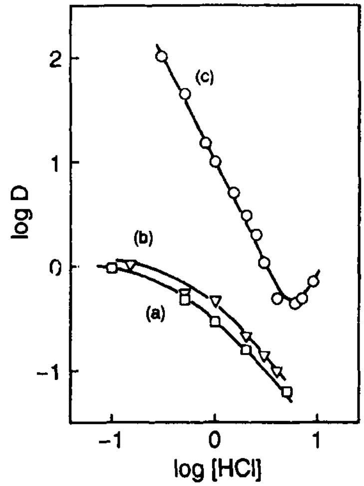

FIG. 1 Effect of HCl concentration on the extraction of iridium. Organic phase: 0.05 M TOA in kerosene; aqueous phase: (a) prepared by dissolving $IrCl_3$ in the HCl solution, (b) prepared by dissolving $IrCl_4$ in the HCl solution, (c) prepared by dissolving $IrCl_4$ in aqua regia.

ent ways as a function of HCl concentration. In the extraction of Ir(III), the *D* value decreased along with increasing HCl concentration, and it was at a very low level over a wide concentration region of HCl [Curve (a)]; this may be due to the instability of the Ir(III)–chloro complex in the HCl solution (6). Extraction of Ir from the solution prepared by dissolving $IrCl_4$ in dilute HCl is also indicated [Curve (b)]. The extraction profile was similar to that of Ir(III), though the *D* value was slightly higher, indicating that Ir(IV) dissolving in the HCl media was unstable and a large amount of Ir(IV) was converted into Ir(III). This was also suggested by the fact that the red-brown color corresponding to Ir(IV) disappeared after extraction. In order to avoid the reduction of Ir(IV), the Ir(IV) solution was prepared by dissolving $IrCl_4$ in aqua regia and kept at the oxidizing condition. The UV spectra of the solution exhibit absorption peaks at 305, 420, 440, and 490 nm, and these peaks are in agreement with those for $IrCl_6^{2-}$ (15). The distribution ratio of Ir(IV) varied inversely with the HCl concentration below 4 M with a slope of −2, as illustrated by Curve (c) in Fig. 1. The *D* value increased along with a further increase in the HCl concentration; this may be attributed to a salting-out effect accompanying the reduction of the activity of water. Figure 2 illustrates the effect of TOA concentration on the distribution ratio of Ir(IV). A plot of log *D* against log [TOA] in a low concentration region was approximately linear with a slope of 1.8. The extraction process for Ir(IV) with TOA (R_3N) can be expressed by

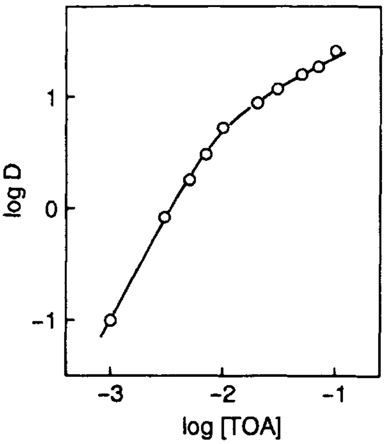

FIG. 2 Effect of TOA concentration on the extraction of iridium(IV) from 1 M HCl solution.

$$R_3N_{org} + HCl_{aq} \rightleftharpoons R_3NH^+Cl^-_{org} \tag{1}$$

$$IrCl^{2-}_{6,aq} + 2R_3NH^+Cl^-_{org} \rightleftharpoons (R_3NH)_2IrCl_{6,org} + 2Cl^-_{aq} \tag{2}$$

TOA is first protonated in contact with HCl solution and then serves as an ion exchanger for Ir(IV) chloride anionic complex. The extraction equilibrium can be reached in a short time, and this is preferable for the transport of Ir(IV) through a liquid membrane.

Stripping Behavior of Ir(IV)

Effective stripping is essential for the recovery of metals in SLM transport. The stripping of Ir(IV) with a high concentration of HCl would be insufficient, as illustrated in Fig. 1. In previous studies (8–10), perchloric acid or nitric acid was found to be efficient for stripping precious metals such as Au(III), Pt(IV), and Pd(II) from loaded TOA-kerosene solutions. Figure 3 shows the stripping behavior of Ir(IV) as a function of acid concentration. The *D* value of Ir(IV) decreased with an increase in the $HClO_4$ concentration, and similar stripping behavior was found in the HNO_3 solution although the stripping ability of HNO_3 was lower than that of $HClO_4$.

In the extraction and stripping processes, a third phase was sometimes observed between the organic and aqueous phases at high concentrations of mineral acids. It was found that this problem could be solved by the addition of an alcohol such as 1-octanol, which was also favorable for a stable liquid membrane (8).

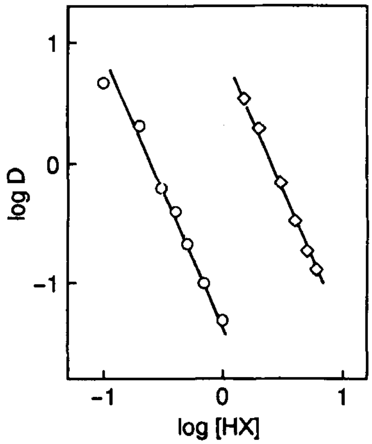

FIG. 3 Effect of acid concentration on the stripping of iridium(IV). Loaded organic phase: 0.05 M TOA in kerosene; aqueous phase: (○) $HClO_4$, (◇) HNO_3.

Transport of Iridium through SLM

On the basis of the data on the extraction and stripping processes, the transport of Ir was performed through an SLM containing 0.1 M TOA and 20% 1-octanol in kerosene. Figure 4 shows the time-dependent fractions of Ir in the feed and product solutions. The increase in the Ir fraction in the 1 M $HClO_4$ product solution was close to the decrease of it in the 0.15 M HCl feed solution. About 94% of Ir(IV) was recovered into the product solution after 7 hours. A similar transport profile of Ir(IV) was also observed across the SLM to the 4 M HNO_3 product solution. On the other hand, only a small portion of Ir(III) was transported into the 1 M $HClO_4$ product solution due to its low extractability. Transport of Ir thus greatly depended on its oxidation states, and Ir(IV) was then adopted in the following experiments.

Effect of TOA Concentration in SLM

The transport of Ir(IV) through the SLM containing TOA with different concentrations is represented in Fig. 5. The fraction curves for the feed and the product sides were found to be almost symmetrical, implying that little Ir(IV) was accumulated in the TOA-SLM. The plot of $\ln[\mathrm{Ir}]_{f,t}/[\mathrm{Ir}]_{f,0}$ against time t gave a straight line, and the rate equation is then given by (16):

$$\ln[\mathrm{Ir}]_{f,t}/[\mathrm{Ir}]_{f,0} = -k_{f,\mathrm{obs}}t \tag{3}$$

where $k_{f,\mathrm{obs}}$ denotes the apparent rate constant, and $[\mathrm{Ir}]_{f,t}$ and $[\mathrm{Ir}]_{f,0}$ are the concentration of Ir(IV) at time t and the initial concentration, respectively.

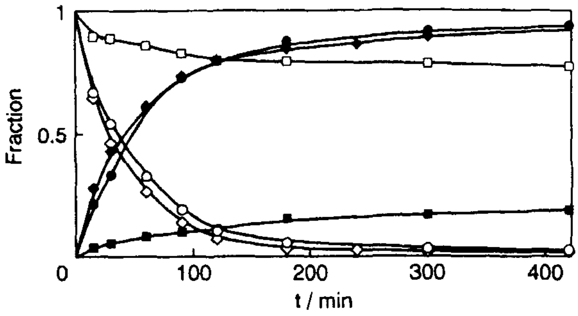

FIG. 4 Transport of iridium(III) and iridium(IV) through SLM containing 0.1 M TOA and 20% 1-octanol in kerosene. (○, ●) Feed: Ir(IV) in 0.15 M HCl; product: 1 M $HClO_4$. (◇, ◆) Feed: Ir(IV) in 0.15 M HCl; product: 4 M HNO_3. (□, ■) Feed: Ir(III) in 0.15 M HCl; product: 1 M $HClO_4$. Open symbols: feed; filled symbols: product.

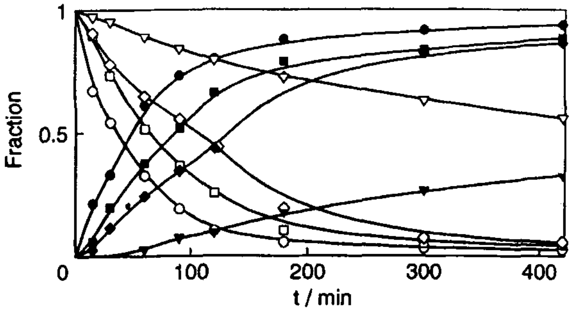

FIG. 5 Transport of iridium(IV) with different concentrations of TOA in the SLM. Feed: 0.15 M HCl; product: 1 M $HClO_4$; SLM: (○, ●) 0.1 M, (□, ■) 0.01 M, (◇, ◆) 0.005 M, (▽, ▼) 0.001 M TOA and 20% 1-octanol in kerosene. Open symbols: feed; filled symbols: product.

Figure 6 presents the effect of TOA concentration in SLM on the $k_{f,obs}$ value for the transport of Ir(IV) into 4 M HNO_3 and 1 M $HClO_4$ product solutions. The $k_{f,obs}$ values in both systems increased along with TOA concentration up to 0.05 M due to an increase in extractability on the feed side of SLM and became a plateau at high TOA concentrations. Any further increase in TOA concentration above 0.4 M was liable to form a third phase on the SLM. The SLM impregnated with around 0.1 M TOA was found to be appropriate to transport Ir(IV) from the HCl solution to the $HClO_4$ or HNO_3 product solution.

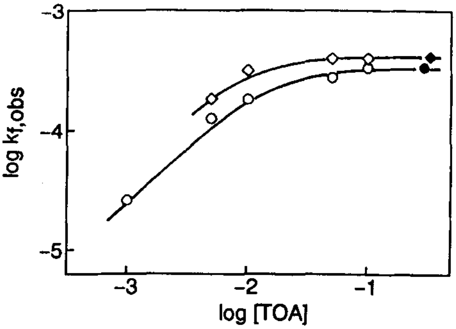

FIG. 6 Effect of TOA concentration on the $k_{f,obs}$ value. Feed: 0.15 M HCl; SLM: TOA and 20% 1-octanol in kerosene; product: (○) 1 M $HClO_4$, (◇) 4 M HNO_3. Filled symbols: the third phase was observed on the SLM.

Effect of Acid Concentrations in the Feed and Product Solutions

Figure 7 shows the $k_{f,obs}$ value for the transport of Ir(IV) across 0.1 M TOA-SLM from the feed solution of different HCl concentrations into the 1 M $HClO_4$ product solution. The $k_{f,obs}$ value was little affected below 0.5 M HCl and decreased with a further increase in HCl concentration owing to a lowering of extractability in the feed side. Recovery of Ir(IV) in the product side at 7 hours slightly declined along with the HCl concentration, as also illustrated in Fig. 7. Lower HCl concentrations were favorable to the transport of Ir(IV) across the TOA-SLM.

The $k_{f,obs}$ value was found to be independent of the product $HClO_4$ concentration, and the recovery of Ir(IV) was approximately constant at concentrations above 1 M. A third phase was formed at low concentrations of $HClO_4$ due to insufficient stripping on the product side of SLM, and a small amount of deposit was observed at concentrations as low as 0.01 M. The suitable concentration of $HClO_4$ is more than 1 M, where most Ir(IV) can be stripped into the product solution.

Enrichment Factor

A concentration parameter is one of the most important factors in the recovery of PGMs which generally exist at low content in feed solutions. The transport of Ir(IV) was carried out by reducing the product volume (V_p) relative to the feed volume (V_f) to sufficiently concentrate Ir(IV).

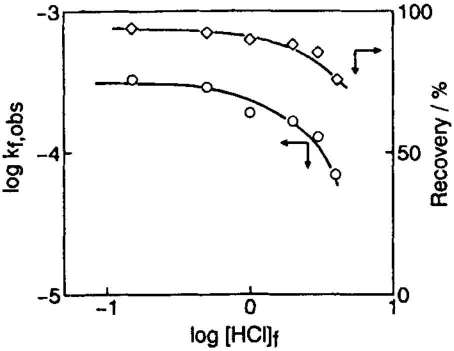

FIG. 7 Effect of HCl concentration in the feed solution on the $k_{f,obs}$ value and the recovery of iridium(IV) at 7 h. SLM: 0.1 M TOA and 20% 1-octanol in kerosene; product: 1 M $HClO_4$. (○) $k_{f,obs}$; (◇) recovery.

TABLE 1
Enrichment Factor and Recovery of Ir(IV)[a]

V_f (cm^3)	V_p (cm^3)	V_f/V_p	$[Ir]_p/[Ir]_{f,0}$ at 7 hours	Recovery (%) at 7 hours
100	100	1	0.94	94.1
	50	2	1.8	92.5
	30	3.3	3.0	92.2
	20	5	4.5	92.0
	10	10	9.1	92.8
	5	20	17.9	90.8

[a] Feed: 0.15 M HCl (100 cm^3); SLM: 0.1 M TOA and 20% 1-octanol in kerosene; product: 1 M $HClO_4$.

As illustrated in Table 1, the enrichment factor, $[Ir]_{p,t}/[Ir]_{f,0}$, was close to that of corresponding volume ratio, V_f/V_p, even if the volume ratio was high. The recovery of Ir(IV) was little affected by increasing the volume ratio, and more than 90% of Ir(IV) was recovered into the product solution within the volume ratio of 20.

It was concluded that the transport of Ir(IV) was accomplished through an SLM containing TOA as the mobile carrier from the HCl feed side to the $HClO_4$ and HNO_3 sides. Iridium(IV) was effectively concentrated in the product solution with relatively high recovery and a reasonable enrichment factor.

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