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Separation of Precious Metals through a Trioctylamine Liquid Membrane

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ABSTRACT

The extraction behavior of precious metals (PMs) from HCl media has been studied using trioctylamine (TOA) in kerosene. The extraction sequence of PMs was found to be Au(III) > Pd(II), Pt(IV), Ir(IV) > Ir(III), Ru. Transport of PMs was performed through a supported liquid membrane (SLM) impregnated with TOA as a mobile carrier from the HCl feed solution into the $HClO_4$ or HNO_3 product solution. Selective transport ;and recovery of PMs from certain mixtures were accomplished across the TOA-SLM on the basis of differences in extraction equilibria and kinetics.

INTRODUCTION

Liquid membrane transport mediated with a mobile carrier has been proposed as a promising technology for separation and enrichment of various substances such as metal ions, acids, bases, and organic compounds (1–4). A suitable mobile carrier in this technology is of significant importance in order to extract selectively desired substances on one side of liquid membrane and to release readily on the other side. Trioctylamine (TOA) was found to exhibit high extractability for some precious metals (PMs) from a dilute HCl solution while showing low extractability from an HNO_3 or $HClO_4$ solution. Based on these findings, the membrane transport of individual PMs such as Au(III), Pt(IV), Pd(II), and Ir(IV) was

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previously investigated using TOA as a mobile carrier (5–8). These metals were transported across the TOA liquid membrane from the dilute HCl feed solution into the HNO_3 or $HClO_4$ product solution with high enrichment factors.

Supported liquid membrane (SLM) procedures are useful not only for the enrichment of metal species but for their selective separation. Efficient separation is of particular importance in precious metal refining since these metals commonly occur together in nature. This paper describes the feasibility of the separation and recovery of PMs with a TOA-SLM from certain mixtures.

EXPERIMENTAL

Materials

A solution of Ir(IV) was freshly prepared by dissolving $IrCl_4$ (Wako Pure Chemical Ind.) in aqua regia before each experiment, evaporating to dryness, and then dissolving in a 3 M HCl solution. In order to keep the Ir(IV) in an oxidized form, a small amount of chlorine water was added. A stock solution of Ir(III) was obtained by dissolving $IrCl_3 \cdot 3.5H_2O$ (High Purity Chemicals) in a dilute HCl solution.

A feed solution containing several metals was prepared by suitable dilution of the solutions mentioned above and atomic absorption standard solutions for other metals such as Pt(IV) and Pd(II) (Wako) and Ru (Aldrich Chemical Company). Other chemicals employed here were of guaranteed reagent grade. An organic solution was prepared by diluting trioctylamine (TOA, Wako) of a purity of more than 97% in kerosene. The organic solution was generally modified with about 20% (v/v) 1-octanol in the experiments of liquid membrane transport. This was found to be capable of stabilizing the TOA liquid membrane (5). A polytetrafluoroethylene membrane (Fluoropore FP-045, Sumitomo Electric Ind.; 80 μm thick, 74% porous, and 0.45 μm average pore size) was employed as an inert support.

Solvent Extraction

An aqueous phase containing 1.27×10^{-4} M Au(III), 2.56×10^{-4} M Pt(IV), 2.35×10^{-4} M Pd(II), 1.30×10^{-4} M Ir, or 4.95×10^{-4} M Ru was contacted with an equal volume of a TOA-kerosene solution at 25°C. After phase separation by centrifugation, the concentrations of metals in the aqueous phase were determined by ICP-AES, and those in the organic phase were calculated on the basis of mass balance.

Liquid-Membrane Transport

The apparatus was composed of inner and outer polypropylene compartments. A feed solution (100 cm^3) containing precious metals was placed in the outer compartment and an equal volume of product solution was placed in the inner compartment. The SLM (with a geometric surface area of 26 cm^2) impregnating a TOA-kerosene solution modified with 1-octanol was interposed between the two aqueous solutions. The apparatus was shaken at 120 strokes per minute in a water bath kept at 25°C. At time intervals the concentrations of metals in both the feed and product solutions were determined by ICP-AES. The detailed experimental procedures for transport are described elsewhere (9).

RESULTS AND DISCUSSION

Liquid–Liquid Extraction of PMs

In an HCl solution, TOA (R_3N) accepts a proton to form a cationic species. Extraction of PMs generally proceeds via an anion-exchange reaction which can be represented as (10–13)

$$R_3N_{org} + HCl_{aq} \rightleftarrows R_3NH^+Cl^-_{org} \quad (1)$$

and

$$MCl^n_{z\,aq}^- + nR_3NH^+Cl^-_{org} \rightleftarrows (R_3NH^+)_nMCl^n_{z\,org}^- + nCl^-_{aq} \quad (2)$$

where $MCl^n_{z\,aq}^-$ species corresponds to $AuCl_4^-$, $PtCl_6^{2-}$, $PdCl_4^{2-}$, $IrCl_6^{2-}$, $IrCl_6^{3-}$, and Ru chloro complexes.

Extraction profiles of PMs with TOA at different concentrations of HCl are shown in Fig. 1. Gold(III), Pt(IV), and Pd(II) were quantitatively extracted in the region of low HCl concentration. The extraction of Ir greatly depended on its oxidation states; Ir(III) was slightly extracted while Ir(IV) was efficiently extracted with TOA in kerosene. Here, the extraction of Ir(IV) was observed to remain unaltered within 5 hours after the preparation of Ir(IV) solution. The extraction behavior of Ru appears to be complicated due to its various chloro species and oxidation states which relate to the redox potential and the chloride concentration in the aqueous phase (12, 14, 15). As seen in Fig. 2, the extractability of PMs increased along with the TOA concentration in the sequence Au(III) > Pd(II), Pt(IV), Ir(IV) > Ir(III), Ru.

Considerable difficulties arise in stripping of Au, Pt, Pd, and Ir(IV) because of their high extractability. Several prospective reagents, such as another anion (acids and salts) to competition, alkaline solutions to deprotonation, and some strong coordinating ligands like thiourea, were

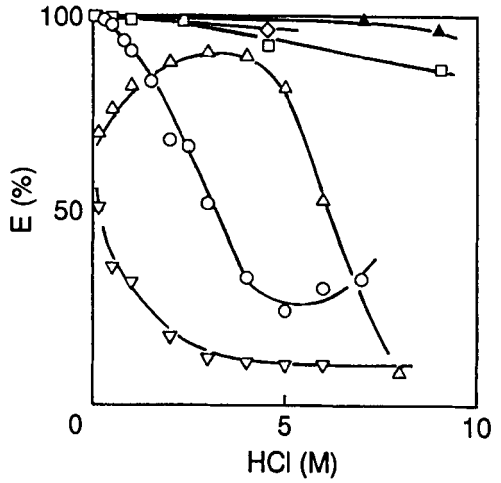

FIG. 1 Effect of HCl concentration on extraction of precious metals. Organic phase: 0.1 M [0.05 M for Ir(IV)] TOA in kerosene. (▲) Au(III), (○) Ir(IV), (◇) Pd(III), (□) Pt(IV), (▽) Ir(III), (△) Ru.

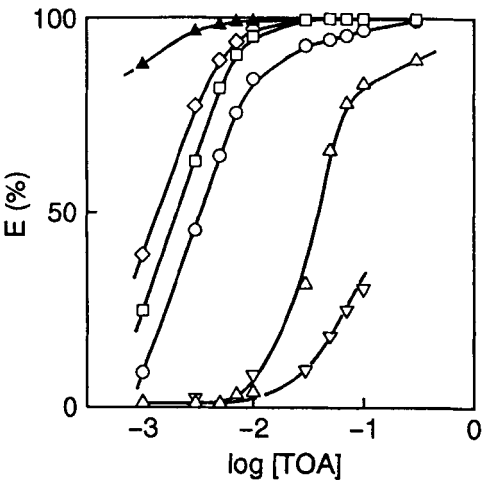

FIG. 2 Effect of TOA concentration on extraction of precious metals. Aqueous phase: (▲) Au(III), (○) Ir(IV), (◇) Pd(II), (□) Pt(IV), (▽) Ir(III), (△) Ru in 1 M HCl. A third phase was observed at [TOA] > 0.3 M.

then tested as stripping agents from the loaded TOA solution. Perchloric and nitric acids, which have a very strong affinity for TOA, were found to be effective for stripping of Pt(IV), Pd(II) and Ir(IV) even from an organic solution with a relatively high TOA concentration (5, 6, 8). The stripping ability of Au(III) is related to the TOA concentration, and Au(III) was instantaneously stripped from the loaded organic solution with very low TOA concentration (7).

Precious metals such as Au(III), Pt(IV), Pd(II), and Ir(IV) are therefore effectively transported across a stable TOA-SLM modified with 1-octanol because of large differences in the distribution ratios between the HCl feed and the $HClO_4$ or HNO_3 product sides. The differences in the extractability of PMs shown in Figs. 1 and 2 is significant for the selective transport of metal species from mixtures.

Transport Behavior of Pt(IV), Pd(II), and Ir Mixtures

The membrane transport system was comprised of the HCl feed solution containing Pt(IV), Pd(II), and Ir, the TOA-SLM, and the HNO_3 product solution on the basis of extraction and stripping behavior. Transport of Ir(IV), Pt(IV), and Pd(II) was performed across the SLM impregnated with 0.1 M TOA in kerosene modified with 20% 1-octanol from the 0.2 M HCl feed to the 4 M HNO_3 product solutions. Figure 3 illustrates the time-dependent fractions of Ir(IV), Pt(IV), and Pd(II) in the feed and the product solutions. The fractions of the three metals on the feed side gradu-

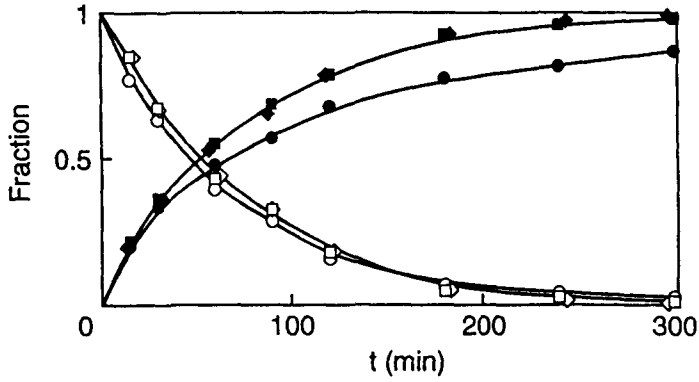

FIG. 3 Transport behavior of Ir(IV), Pd(II), and Pt(IV) through TOA-SLM. Feed: 0.2 M HCl; SLM: 0.1 M TOA and 20% 1-octanol in kerosene; product: 4 M HNO_3. (○, ●) Ir(IV), (◇, ◆) Pd(II), (□, ■) Pt(IV). Open symbols: feed; filled symbols: product.

ally decreased with shaking time in the same manner, and were reduced to zero after 6 hours. Increments in fractions on the product side are close to decrements in those on the feed side, and their fractions attained a value close to unity for Pt(IV) and Pd(II) and more than 0.9 for Ir(IV). It is evident that Ir(IV) can be readily transported together with Pt(IV) and Pd(II) across the TOA-SLM into the HNO_3 product solution. This transport behavior was little affected by variation in the concentrations of HCl in the feed solution and of TOA in the SLM. Moreover, reasonable enrichment factors for all three metals corresponding to the feed-to-product volume ratios were obtained, yielding relatively high recovery of metals in the product solution within the volume ratio of 20 as listed in Table 1.

On the other hand, the transport of Ir(III) wqs less effective and only a small portioin of Ir(III) was transported, as seen in Fig. 4. The transport behavior of Pt(IV) and Pd(II) was not affected by changing the oxidation states of Ir, and hence considerable difference in the transport rates was observed between Pt(IV), Pd(II), and Ir(III).

The decreasing rate of metal fractions on the feed side in the early period is approximated by

$$\ln([M]_{f,t}/[M]_{f,0}) = -k_f t \quad (3)$$

where $[M]_{f,t}$ and $[M]_{f,0}$ denote the concentration at time t and the initial state, respectively. $k_f(s^{-1})$ can be regarded as the apparent rate constant for the overall transport of the desired metal species when approximately symmetrical fraction curves are obtained between the feed and product sides. The separation factor (α) is defined as the ratio of the k_f values (16):

TABLE 1
Effect of V_p on Transport of Pt(IV), Pd(II), and Ir(IV)[a]

V_p (mL)	V_f/V_p	$[M]_p/[M]_{f,0}$ after 6 hours			Recovery after 6 hours (%)		
		Pt(IV)	Ir(IV)	Pd(II)	Ir(IV)	Pt(IV)	Pd(II)
100	1	0.98	0.92	0.99	92.4	98.3	98.4
50	2	1.97	1.82	1.98	91.0	98.5	98.1
30	3.3	3.29	3.00	3.30	90.9	97.9	98.2
20	5	4.90	4.45	4.85	89.0	98.0	97.0
10	10	9.72	9.02	9.50	90.2	97.2	95.0
5	20	18.90	17.60	18.30	88.0	94.7	91.3

[a] Feed: Pt(IV), Pd(II), and Ir(IV) in 0.2 M HCl (100 cm^3). SLM: 0.1 M TOA and 20% 1-octanol in kerosene. Product: 4 M HNO_3.

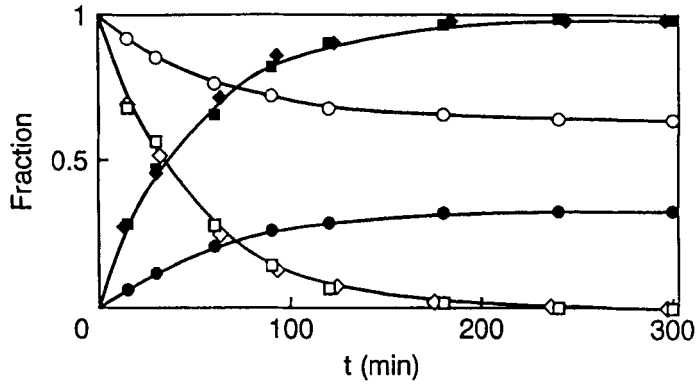

FIG. 4 Transport behavior of Ir(III), Pd(II), and Pt(IV) through TOA-SLM. Feed: 0.1 M HCl; SLM: 0.1 M TOA and 20% 1-octanol in kerosene; product: 4 M HNO_3. (○, ●) Ir(III), (◇, ◆) Pd(II), (□, ■) Pt(IV). Open symbols: feed; filled symbols: product.

$$\alpha = k_{f,M1}/k_{f,M2} \tag{4}$$

Transport behavior of the metals was further examined by varying the HCl concentration in the feed solution and the TOA concentration in the SLM in order to select optimal conditions for separation. Since very similar transport behaviors for Pt(IV) and Pd(II) were found in this TOA-SLM system, the transport behavior of only two metals, Pd(II) and Ir(III), was investigated here. Figure 5 shows the effect of HCl concentration in the

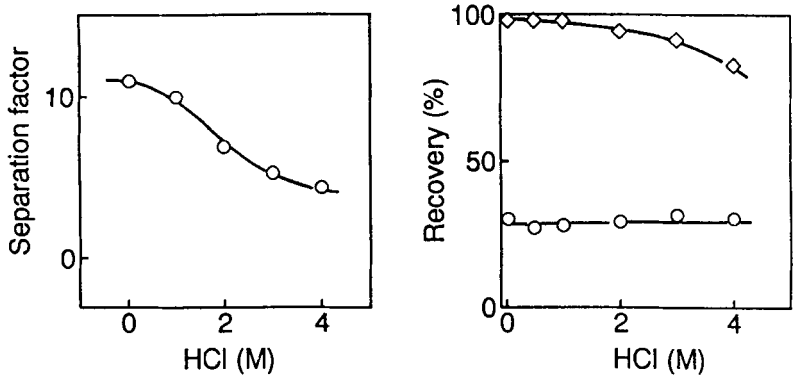

FIG. 5 Effect of HCl concentration in the feed solution on the separation factor and recovery of Pd(II) and Ir(III). SLM: 0.1 M TOA and 20% 1-octanol in kerosene; product: 4 M HNO_3. Right figure: (○) Ir(III), (◇) Pd(II).

feed solution on the α value and on the recovery of metals. The transport of HCl itself seems to be negligibly small, since the affinity of Cl^- for amine is lower than that of NO_3^- in the product solution (10). The transport of HCl might not affect the transport and the separation of PMs. The α value decreased as the HCl concentration increased. The recovery of Pd(II) was nearly quantitative in a low concentration region of HCl and slightly decreased with increasing HCl concentration, while that of Ir(III) was rather low and remained almost unaltered. Transport parameters at different TOA concentrations in the SLM are illustrated in Figure 6. The α value increased with TOA concentration up to 0.05 M and approached a constant value at higher TOA concentrations. Relatively high TOA concentration in the SLM was suitable for the recovery of Pd(II), but a concentration of more than 0.1 M TOA is not recommended because a third phase tends to be formed onto the SLM phase.

Table 2 summarizes the transport parameters of Pd(II) and Ir(III) with the variation of HNO_3 concentration in the product solution. The HNO_3 concentration had little influence on the α value, while low HNO_3 concentration (< 1 M) resulted in a lowering of recovery due to insufficient stripping on the product side of the SLM.

Lower concentrations of HCl in the feed solution and considerably higher concentrations of TOA in the SLM were found to be favorable for both the separation of Pt(IV), Pd(II) over Ir(III), and the recovery of metals in the product solution. Almost quantitative transport of Pt(IV) and Pd(II) was accomplished across 0.1 M TOA-SLM from the 0.1 M HCl

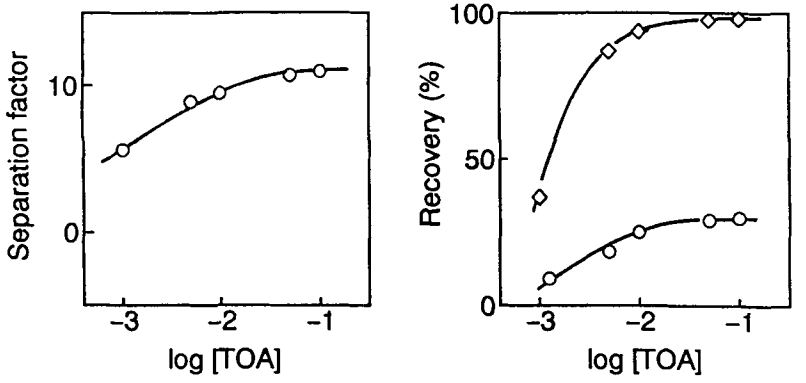

FIG. 6 Effect of TOA concentration in the SLM on the separation factor and recovery of Pd(II) and Ir(III). Feed: 0.1 M HCl; SLM: TOA and 20% 1-octanol in kerosene; product: 4 M HNO_3. Right figure: (○) Ir(III), (◇) Pd(II).

TABLE 2
Effect of HNO_3 Concentration in the Product Solution on the Separation Factor and Recovery[a]

$[HNO_3]_p$ (M)	$k_{f,obs}$ (s^{-1})		α	Recovery after 5 hours (%)	
	Pd(II)	Ir(III)	Pd(II)/Ir(III)	Pd(II)	Ir(III)
0.1	2.17×10^{-4}	2.95×10^{-5}	10.6	71.3	12.2
0.5	3.37×10^{-4}	2.70×10^{-5}	12.4	94.1	29.1
1.0	3.46×10^{-4}	2.82×10^{-5}	12.2	98.0	31.2
2.0	3.61×10^{-4}	2.88×10^{-5}	12.5	98.2	32.8
4.0	3.36×10^{-4}	2.85×10^{-5}	11.8	98.4	31.5

[a] Feed: 0.1 M HCl. SLM: 0.1 M TOA and 20% 1-octanol in kerosene.

feed side into the 4 M HNO_3 product side, yielding an α value of more than 10 for Pt(IV)/Pd(II) to Ir(III).

Transport Behavior of Au(III), Pt(IV), and Pd(II) Mixtures

It is known that the extraction power of TOA for Au(III) is stronger than that for Pt(IV) or Pd(II) (12). At a very low concentration of TOA, Au(III) can be readily extracted while Pt(IV) and Pd(II) are poorly extracted as shown in Fig. 2; this provides the possibility of separating Au(III) from Pt(IV) or Pd(II). Figure 7 represents the transport profiles of Au(III) and Pd(II) across an SLM containing a low concentration of TOA. Au(III) was nearly quantitatively transported after 7 hours because of its high extractability, whereas about 25% of Pd(II) was transported during the same period. Table 3 lists the separation factor and recovery of these two metals at different TOA concentrations in the SLM. Low carrier concentration seems to be appropriate for separation performance. The recovery of Au(III) was depressed with increasing TOA concentration, while that of Pd(II) was enhanced. High carrier concentration caused difficulties in the recovery of Au(III) into the product solution due to low stripping ability, and a large portion of Au(III) was retained in the SLM. Low TOA concentration in the SLM was desirable for the selective transport of Au(III) from Pt(IV) or Pd(II), while moderate TOA concentration was suitable for the recovery of all these metals into the product solution.

The effect of HCl concentration in the feed solution on the transport of Au(III) and Pd(II) across the 10^{-3} M TOA-SLM is also summarized in Table 3. Separation factors for Au(III) to Pd(II) were strongly enhanced with increasing HCl concentration from 0.1 to 4.0 M HCl. A high α value,

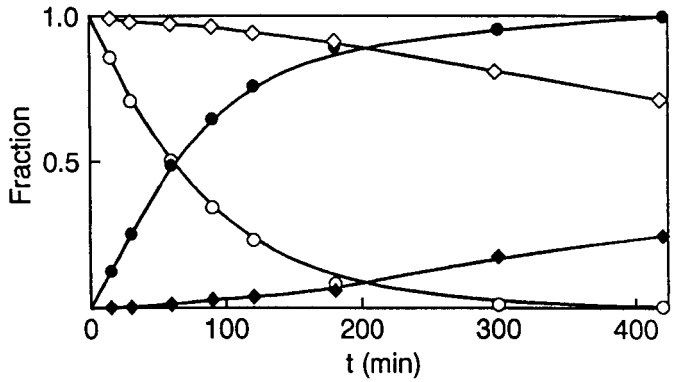

FIG. 7 Transport behavior of Au(III) and Pd(II) through TOA-SLM. Feed: 0.1 M HCl; SLM: 10^{-3} M TOA and 20% 1-octanol in kerosene; product: 1 M $HClO_4$. (○, ●) Au(III), (◇, ◆) Pd(II). Open symbols: feed; filled symbols: product.

over 300, was obtained at 4.0 M HCl in which more than 95% of the initial Au(III) was selectively recovered in the product solution, leaving almost all Pd(II) in the feed solution after 7 hours.

Selective Transport of PMs from Ru

As presented in Figs. 1 and 2, an SLM containing a high concentration of carrier is preferable for the transport of Ru from a feed solution of 1–5

TABLE 3
Effect of Concentrations of TOA in SLM and of HCl in the Feed Solution on the Separation Factor and Recovery[a]

$[TOA]_{SLM}$ (M)	$[HCl]_f$ (M)	α Au(III)/Pd(II)	Recovery after 7 hours (%)	
			Au(III)	Pd(II)
10^{-3}	0.1	17	100	23.9
5×10^{-3}	0.1	7.2	99.6	74.6
10^{-2}	0.1	5.3	98.6	85.3
10^{-1}	0.1	2.2	68.0	98.8
10^{0}	0.1	1.4	46.2	97.4
10^{-3}	0.4	32	99.5	25.7
10^{-3}	0.7	75	99.8	17.9
10^{-3}	1.0	108	96.7	2.6
10^{-3}	4.0	340	95.7	1.0

[a] SLM: TOA and 20% 1-octanol in kerosene. Product: 1 M $HClO_4$.

M HCl. Unfortunately, transport was found to be very slow across the 0.5 M HCl. TOA-SLM from the 3 M HCl feed solution, and only about 20% of Ru was recovered in the product solution after 7 hours. Moreover, a large decrease in the transport rate was observed with a decrease in the concentrations of both TOA and HCl. Such a low transport rate is expected to provide a practical method for the separation of PMs from Ru under optimum conditions. Figure 8 illustrates the transport profiles of two metals, Ir(IV) and Ru, across a 0.1 M TOA-SLM from 0.2 M HCl feed solution to the 1 M $HClO_4$ product solution. Iridium(IV) was selectively transported, and a large portion of Ir(IV) was recovered into the product solution while almost no Ru was transported.

In solvent extraction separation, a simple comparison of distribution ratios is often sufficient to predict the extent of separation. However, the transport rate of respective metal species across SLMs is based not only on thermodynamic equilibria but also on kinetics. Figure 9 shows the extraction of Ir(IV) and Ru at different shaking times. Ir(IV) can be instantaneously extracted, similarly to other PMs, while the extractability of Ru increased along with shaking time up to 30 minutes and then reached equilibrium. It is obvious that the selectivity of Ir(IV) over Ru by TOA-SLM depends on kinetic behavior rather than thermodynamic considerations. In view of this point, the separation of other PMs such as Au(III), Pt(IV), and Pd(II) from Ru would be possible because their transport behavior is similar to that of Ir(IV).

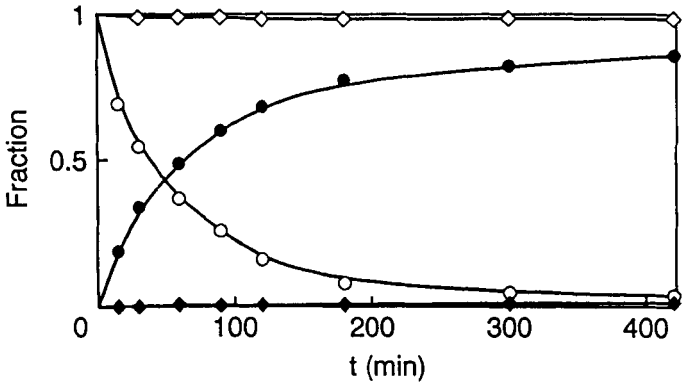

FIG. 8 Selective transport of Ir(IV) from Ru through TOA-SLM. Feed: 0.2 M HCl; SLM: 0.1 M TOA and 20% 1-octanol in kerosene; product: 1 M $HClO_4$. (○, ●) Ir(IV), (◇, ◆) Ru. Open symbols: feed; filled symbols: product.

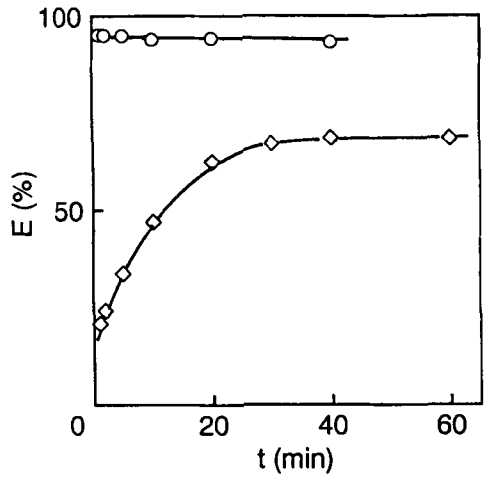

FIG. 9 Effect of contact time on extraction of Ir(IV) and Ru. Organic phase: 0.05 M TOA in kerosene; aqueous phase: 1 M HCl. (○) Ir(IV); (◇) Ru.

In conclusion, in the Pt(IV)–Pd(II)–Ir mixture the transport behavior of Ir depended on its oxidation state. Ir(IV) was well transported together with Pt(IV) and Pd(II), while only a small portion of Ir(III) was moved, yielding a relatively high separation factor of Pt(IV) and Pd(II) over Ir(III). As for the Au(III)–Pt(IV)–Pd(II) mixture, separation and recovery were related to the concentrations of both TOA in SLM and HCl in the feed solution. All these metals can be transported with a moderate concentration of TOA liquid membrane and recovered into the product solution. However, quantitative separation of Au(III) over Pt(IV) and Pd(II) was accomplished from the 4 M HCl feed solution across the SLM only with a low concentration of TOA. Separation of such PMs as Au(III), Pt(IV), Pd(II), and Ir(IV) from Ru seems to be feasible by large differences not only in the extraction equilibria but also in the kinetics.

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