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Takahiko Kakoi[a]; Naoki Horinouchi[a]; Masahiro Goto[a]; Fumiyuki Nakashio[a]
[a] DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY FACULTY OF ENGINEERING, KYUSHU UNIVERSITY, FUKUOKA, JAPAN

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Recovery of Palladium from an Industrial Wastewater Using Liquid Surfactant Membranes

TAKAHIKO KAKOI, NAOKI HORINOUCHI, MASAHIRO GOTO, and FUMIYUKI NAKASHIO*
DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY
FACULTY OF ENGINEERING
KYUSHU UNIVERSITY
HAKOZAKI, FUKUOKA 812, JAPAN

ABSTRACT

Selective recovery of palladium from an industrial wastewater including a large amount of iron was studied by liquid surfactant membranes (LSMs) prepared with a sulfur-containing extractant as a carrier in a stirred cell. The extraction behavior of palladium and iron ions in liquid–liquid extraction was also investigated in order to choose an appropriate carrier for the LSM operations. Palladium ions were found to be extracted selectively over iron ions by using the sulfur-containing extractant from an acidic aqueous solution. The effects of several chemical species and operation factors on the recovery of palladium by LSMs were systematically examined with several kinds of sulfur-containing carriers and thiourea as a stripping reagent. The selection of carrier is a key factor for designing an efficient recovery process of palladium with an LSM technique. Di-2-ethylhexyl monothiophosphoric acid (commercial name MSP-8) appears to be one of the best carriers currently available for palladium recovery using the LSM technique. Recovery of more than 95% palladium from a pseudoindustrial wastewater could be attained in a few minutes under optimum conditions.

INTRODUCTION

Noble metals are well-known as precious materials, and they have been used for coins, jewelry, in teeth, and recently they have also been utilized as industrial catalysts and electrical and corrosion-resistant materials

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* To whom correspondence should be addressed.

based on their specific physical and chemical properties. Because the resources of noble metals are limited, their worth has increased in recent years. Thus, a recycling technique for noble metals from secondary resources such as industrial and nuclear wastes is desirable. In such waste resources, however, the concentration of noble metals is often low and many kinds of metals coexist.

The liquid surfactant membrane (LSM) process is a novel separation process for ordinary solvent extraction. The LSM process with its very thin liquid membrane and large interfacial area has many advantages for the rapid separation and concentration of metal ions compared to a conventional solvent extraction process. Based on the above advantages, the practical application of the LSM process is considered to be suitable for the recycling of industrial resources or energy conservation.

Many investigators have studied the separation of metals by LSMs, since it was invented by Li in 1968 (1). By 1986 the LSM process was used in an industrial process for the removal of zinc from wastewater at a textile plant in Austria (2). However, only three papers on the extraction of noble metals by LSMs have been published (3–5); the extraction rate of noble metals is very slow and the stripping of extracted noble metals is often difficult. Izatt et al. (3) investigated the transport of silver, palladium, and gold by LSMs containing K^+-dicyclohexano-18-crown-6 as a carrier and reported that the transport of more than 90% with respect to palladium and gold was achieved in about 15 minutes. For our previous papers (4, 5) we studied the transport of palladium by LSMs containing didodecylmonothiophosphoric acid or dihexyl sulfide (commercial name SFI-6) as a carrier and reported that extraction of more than 95% palladium could be attained in a few minutes under optimum conditions. Further, we made clear that the selection of the stripping reagent is one of the most important factors for effective operation of a LSM system. Thiourea was found to be the best stripping reagent in an LSM system for the extraction of palladium.

In the present study we focus attention on an industrial wastewater which includes a small amount of palladium (about 60 ppm) and a large amount of iron (about 25,000 ppm) after treating the iron steel with an acid. We apply the LSM technique for the selective recovery of palladium from the wastewater. Because the carrier has a crucial effect on the separation and extraction efficiency of metals in the LSM process, it is very important to choose an appropriate carrier for a target metal ion, and the selection of the carrier often decides the success of the LSM process.

In this study we used four kinds of carriers which have a sulfur atom. It is well known that an extractant containing the sulfur atom has a high affinity for noble metals such as palladium.

The aim of the present study was twofold. One purpose was to select an appropriate carrier in an LSM operation for the recovery of palladium from a wastewater solution with a high iron concentration. The other purpose was to determine the optimum conditions in the LSM process when using the best carrier.

MATERIALS

Figure 1 shows the structures of the carriers (extractants) and surfactants used in this study. Span 80 and PX 100 were purchased from Kishida

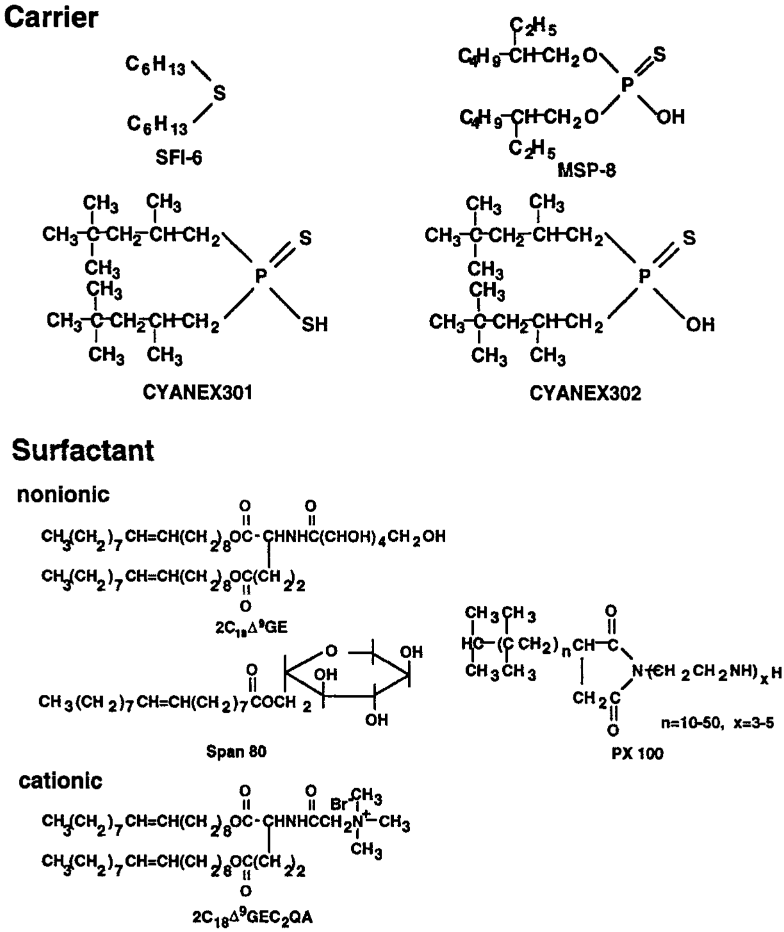

FIG. 1 Molecular structure of carriers and surfactants used.

Chemical Co., Ltd. (Japan) and Exxon Chemical Japan Co., Ltd., respectively. SFI-6 and di-2-ethylhexyl monothiophosphoric acid (commercial name MSP-8) were supplied by Daihachi Chemical Industry Co., Ltd. (Japan). Bis(2,4,4-trimethylpentyl) dithiophosphinic acid (commercial name CYANEX 301) and bis(2,4,4-trimethylpentyl) monothiophosphinic acid (commercial name CYANEX 302) were supplied by Mitsui CYTEC Co., Ltd. (Japan). All commercial extractants and surfactants were used without further purification. The two surfactants ($2C_{18}\Delta^9GE$ and $2C_{18}\Delta^9GEC_2QA$) in Fig. 1 were synthesized according to a procedure described in previous papers (6, 7). *n*-Heptane was used as an organic solvent in all experiments. All other reagents used were of guaranteed reagent grade and were used as received.

EXPERIMENTAL

Extraction of Palladium and Iron

An aqueous solution was prepared by dissolving palladium chloride, iron(III) chloride 6-hydrate, and hydrochloric acid in deionized water. The organic solution was prepared by placing the weighted extractants in *n*-heptane. The experimental procedure for extraction equilibrium was the same as that described in a previous paper (8).

LSM Experiment for the Recovery of Palladium from Iron

The experimental apparatus is a batch-type stirred cell equipped with four glass baffles. The inner diameter and the depth of the glass cell are

TABLE 1
Experimental Conditions for Metal Extraction by LSM.

External aqueous phase:	
Pd^{2+}:	63 ppm
Fe^{3+}:	25,000 ppm
HCl:	1,000 mol/m^3
Organic phase:	
Solvent:	*n*-Heptane
Carrier:	MSP-8, CYANEX 301, CYANEX 302, SFI-6; 5–500 mol/m^3
Surfactant:	Span 80, PX 100, $2C_{18}\Delta^9GE$, $2C_{18}\Delta^9GEC_2QA$; 5–50 mol/m^3
Internal aqueous phase:	
Thiourea:	20–200 mol/m^3
Acid:	HCl, $HClO_4$, HNO_3, H_2SO_4; 100–2000 mol/m^3
Stirring speed 300 rpm	
Temperature 303 K	

7.0 and 11.5 cm, respectively. Stirring was carried out with a turbine impeller having six flat blades and a speed controller.

As the external feed solution is a pseudoindustrial wastewater after treating for iron steel, the concentrations of palladium and iron correspond to those in the actual industrial wastewater. The internal aqueous solution was prepared by dissolving thiourea and an acid in deionized water. Nickel nitrate was added to the internal aqueous solution as a break-up tracer. The organic solution was prepared by dissolving extractants and surfactants in *n*-heptane. A W/O emulsion was made from equal volumes of the organic and aqueous solutions by mixing at 13,500 rpm using a homogenizer. The experimental procedure was the same as in a previous paper (4). The detailed conditions for the LSM experiments are listed in Table 1.

RESULTS AND DISCUSSION

Extraction Equilibrium of Palladium and Iron

The LSM technique involves the extraction and stripping unit in liquid–liquid extraction. Therefore, the extraction equilibrium of palladium and iron was first examined using four kinds of extractants in order to select the best carrier available for the separation of palladium from a large amount of iron. Figure 2 shows the extraction behavior of palladium and iron as a function of extractant concentration with 1000 mol/m^3 hydrochloric acid. All the extractants tested did not show an extraction ability for iron ions under the acidic conditions used. However, the degree of

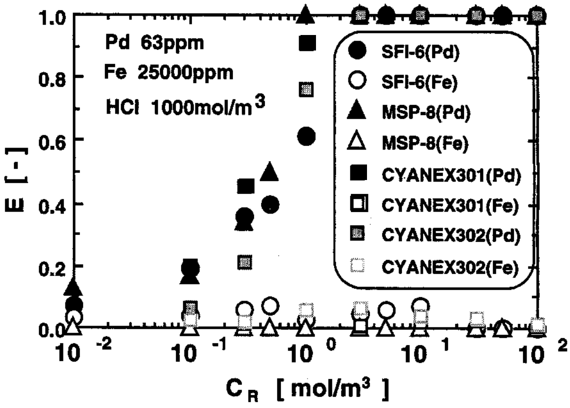

FIG. 2 Relation between extraction ratio of metals and extractant concentration.

palladium extraction was found to increase with an increasing concentration of each extractant, and palladium ions were quantitatively extracted in the high concentration range of more than 3 mol/m^3. These results mean that sulfur-containing extractants have a high selectivity for palladium over iron ions in acidic solution. The complex formations of palladium and these extractants have been elucidated as follows (8–10):

$$PdCl_4^{2-} + 2R_{org} = PdCl_2R_{2org} + 2Cl^- \quad \text{(SFI-6)} \tag{1}$$

$$PdCl_4^{2-} + 2HR_{org} = PdCl_2(HR)_{2org} + 2Cl^- \quad \text{(MSP-8, CYANEX302)} \tag{2}$$

$$2PdCl_4^{2-} + 2HR_{org} = Cl(HR)PdCl_2PdCl(HR)_{org} + 4Cl^- \quad \text{(CYANEX301)} \tag{3}$$

where HR and R denote the acidic and neutral extractants, respectively, and the subscript org denotes organic species. On the basis of the data in Fig. 2, these four extractants are considered to be suitable for the separation of palladium from iron from the viewpoint of the extraction equilibrium. However, when we actually applied these extractants to the carrier in LSM operations, the kind of extractant was found to have a strong effect on the extraction rate and efficiency of palladium recovery by LSMs. The result suggests that the selection of a carrier for the LSM technique is difficult to make if it is based only on the results of extraction equilibrium because the adsorption property of a carrier appears to influence the extraction efficiency.

Recovery of Palladium Using Liquid Surfactant Membranes

Permeation Mechanism of Palladium by LSMs

Figure 3 exhibits the permeation mechanism of palladium through an LSM containing MSP-8 as the carrier. The palladium ion in the feed solution was mainly $PdCl_4^{2-}$ under the present experimental conditions (11, 12). As shown in Fig. 3, palladium ions are separated and concentrated from the external feed solution to the internal recovery phase of W/O emulsions by the following mechanism: 1) diffusion of the palladium–chloro complex and iron ions to the outer surface of emulsion globules; 2) complex formation between metal ions and the carrier by an interfacial reaction at the external interface; 3) diffusion of the palladium–carrier complex in the liquid membrane phase; and 4) the stripping reaction of the palladium–carrier complex by thiourea at the interface of internal water droplets in W/O emulsions. Selective separation of pal-

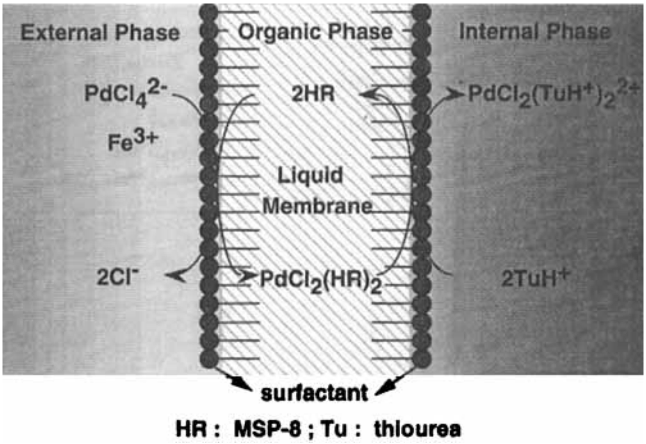

FIG. 3 Permeation mechanism of palladium by LSM.

ladium is considered to be accomplished in Step 2). If a carrier with a high affinity for palladium is employed, palladium ions are permeated selectively into the internal recovery phase against its concentration gradient. In the following sections the effects of operation parameters on the selective recovery of palladium by LSMs are discussed.

Stability of LSMs

Emulsion globules are stabilized in LSMs by surfactants at the interface of emulsion globules, and the degree of enrichment for a target metal into a recovery phase is known to be affected by the stability of the emulsions. Therefore, the stability of emulsions was investigated by using the degree of break-up, ϵ [—], defined by the following equation (4):

$$\epsilon = (C_{\mathrm{Ni,e}} V_{\mathrm{e}})/(C_{\mathrm{Ni,i,0}} V_{\mathrm{i}}) \tag{4}$$

where the subscripts e and i denote the external and internal phases and ϵ is obtained by the amount of break-up tracer released from the internal aqueous solution of the emulsion globules to the external aqueous solution.

The stability of emulsion is also affected by a surface-active carrier. The effects of surfactants, carriers, and their concentrations on the stability of emulsions were studied. Figures 4a and 4b show the effects of several kinds of surfactants and the concentration of surfactant Span 80 on the

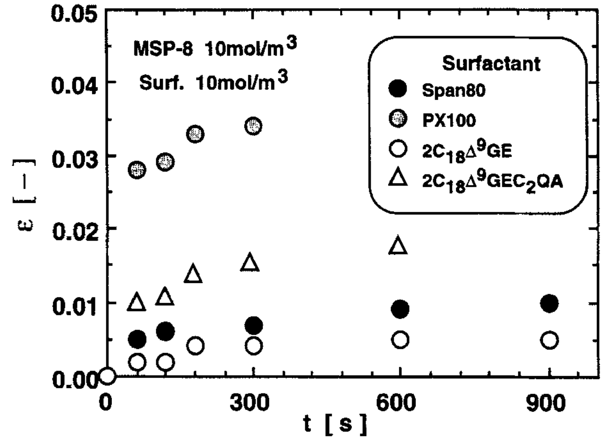

FIG. 4a Effect of several kinds of surfactants on the stability of emulsion.

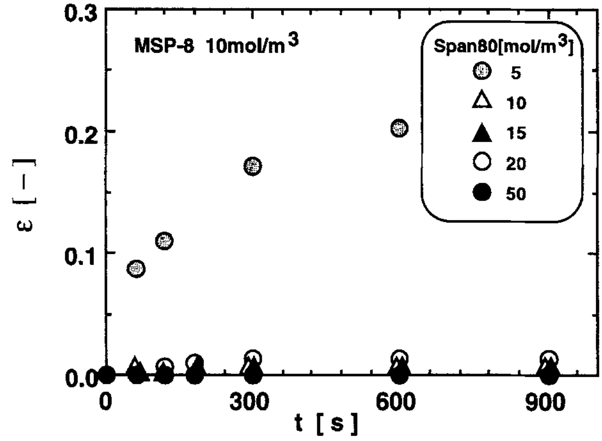

FIG. 4b Effect of surfactant concentration on the stability of emulsion.

stability of emulsions, respectively. At a surfactant concentration of 10 mol/m^3 the emulsions are relatively stable except for the surfactant PX 100 because the break-up ratio is less than several percent. Furthermore, although the emulsions were expected to be stabilized with increasing surfactant concentration, the degree of break-up beyond a critical surfactant concentration (6) becomes approximately constant due to the saturation of surfactants at the oil–water interface.

The effect of a surfactant on the stability of LSMs is often investigated. However, little attention has been paid to the effect of a carrier. Figures 5a and 5b show the effects of carriers and the concentration of carrier MSP-8 on the stability of emulsions. Using SFI-6 or MSP-8, the emulsion was found to be more stable in comparison with the other carriers used in this study. The stability of emulsions might be influenced by the property of adsorption as well as by the molecular structure of the carrier.

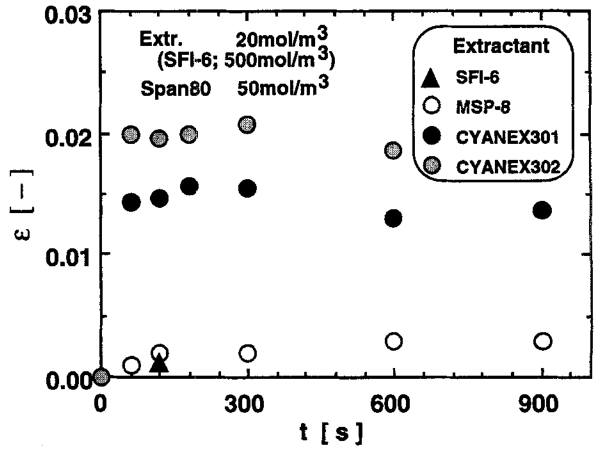

FIG. 5a Effect of several kinds of carriers on the stability of emulsion.

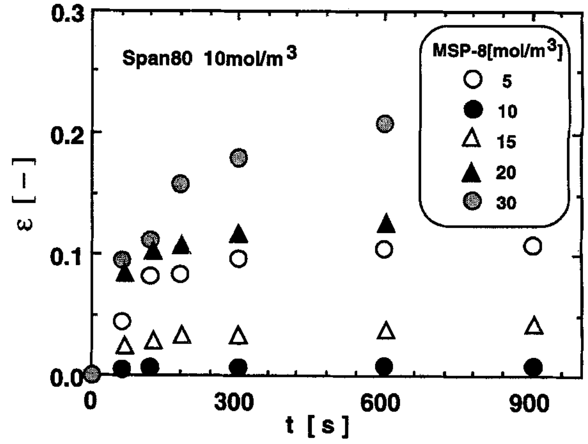

FIG. 5b Effect of carrier concentration on the stability of emulsion.

Therefore, CYANEX 301 and CYANEX 302, which have two bulky hydrophobic chains, are considered to interrupt the close packing of surfactants at the interface, which SFI-6 and MSP-8 do not. Based on the results in Fig. 5b, while the emulsion is stabilized by increasing the carrier concentration up to 10 mol/m^3, it becomes unstable again by the addition of more carrier. It is deduced that MSP-8 has an interfacial activity as do dioctylmonothiophosphoric acid and didodecylmonothiophosphoric acid (10–12). The addition of excess carrier to the membrane phase causes an interruption of surfactant adsorption at the interface and results in destabilization of the emulsions. We found that the optimum concentration of carrier MSP-8 was around 10 mol/m^3. Preparation of a stable emulsion is relatively easy in the present experimental systems.

Selection of Carrier for the Recovery of Palladium

Figures 6a and 6b exhibit the effects of several kinds of carriers and the concentration of carrier MSP-8 on the selective separation of palladium from iron. In this investigation the concentration of SFI-6 was set at 500 mol/m^3 because the carrier could not extract palladium effectively at a lower concentration [5]. Different carriers having similar extracting capacities can have significantly different behaviors in LSM operations because the extraction efficiency appears to be affected by the nature of the surface-active property of a carrier. Palladium ions are found to be extracted selectively over a large amount of iron ions. However, several percent iron was also extracted into the emulsion phase by the LSM operation, although iron was not extracted for all the carriers in liquid–liquid extraction. The phenomenon called "entrainment of membrane" is well known in LSMs, and a small part of the external aqueous solution containing metal ions is entrapped into the liquid membrane phase nonselectively. The decrease of iron ions in the external feed solution is considered to be due to the entrainment of membranes because iron cannot be extracted by the carriers used under the present acidic conditions. Based on the data in Fig. 6a, we found that the degree of palladium extraction by LSMs increases in the order SFI-6 $\ll$ CYANEX 301 < CYANEX 302 < MSP-8.

Furthermore, on the basis of the results in Fig. 6b, an increase of MSP-8 concentration from 5 to 10 mol/m^3 is found to be effective for the enhancement of the extraction rate of palladium. However, a greater increase of the carrier has a negative effect on the recovery of palladium. As described above, the stability of emulsions greatly depends on the concentration of carrier as shown in Fig. 5b. When the emulsion is unstable during LSM operations, palladium concentrated in the internal phase of emulsions and thiourea as a stripping reagent will leak to the

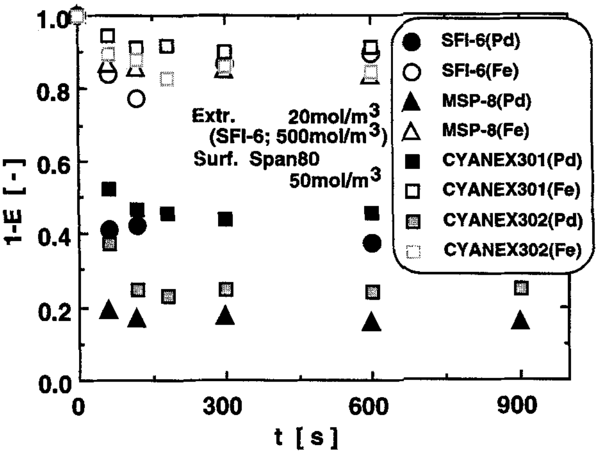

FIG. 6a Effect of several kinds of carriers on the separation of metals.

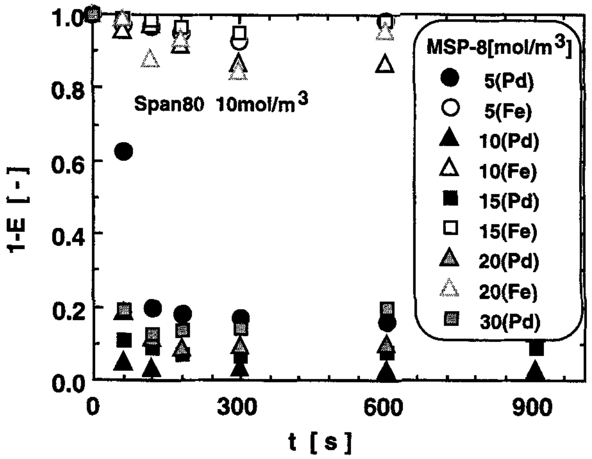

FIG. 6b Effect of carrier concentration on the separation of metals.

external feed solution. Therefore, the efficiency of palladium recovery is decreased by an excess amount of carrier.

Another important point in the LSM process is to perform the stripping reaction effectively because the carrier has to be regenerated in the liquid membrane phase. From the viewpoint of membrane regeneration, we have confirmed that the palladium extracted by MSP-8 was completely stripped by measuring the residual concentration of palladium in the organic phase of emulsions as shown in Fig. 7. Also, Figs. 8a and 8b show the recovery ratio of palladium into the internal phase of emulsions at 300 seconds for the four carriers used and as a function of the carrier concentration of MSP-8, respectively. The stripping reaction in the case of SFI-6 or CYANEX 302 was considerably slow, and that of CYANEX 301 did not proceed at all due to the strong interaction between the two sulfur atoms in the carrier and palladium ions. As the results, the effective enrichment of palladium into the internal aqueous phase of emulsions was achieved by using MSP-8 as the carrier of LSMs.

Effect of Surfactants on the Recovery of Palladium by LSMs

It is well known that a surfactant significantly affects the efficiency of metal extraction by LSMs because a complex formation between a carrier and a metal ion takes place at the surface of emulsion globules where the surfactants adsorb (7, 12–16). Figures 9a and 9b exhibit the effects of several kinds of surfactants and the concentration of surfactant Span 80 on the recovery ratio of palladium at 300 seconds. The magnitude of the recovery ratio of palladium increases in the order $2C_{18}\Delta^9GE$ < $2C_{18}\Delta^9GEC_2QA$ < PX 100 < Span 80. This order, however, does not correspond to the order of emulsion stability as evaluated in the previous

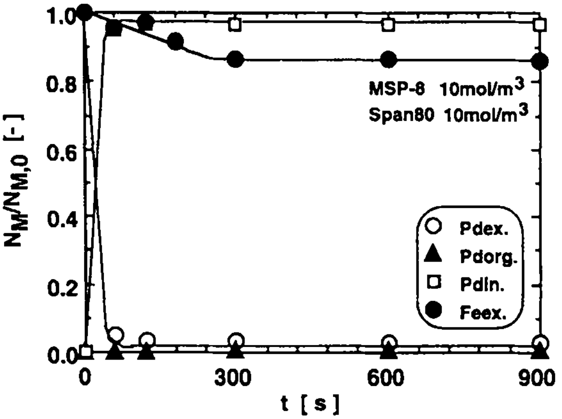

FIG. 7 Typical fraction change of palladium and iron ions in LSM operations.

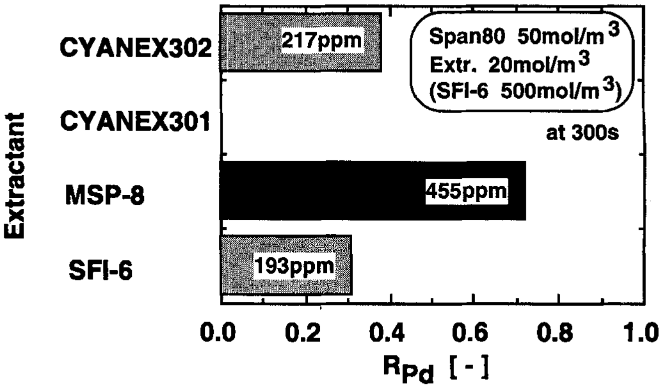

FIG. 8a Relation between recovery ratio of palladium and the kinds of carriers.

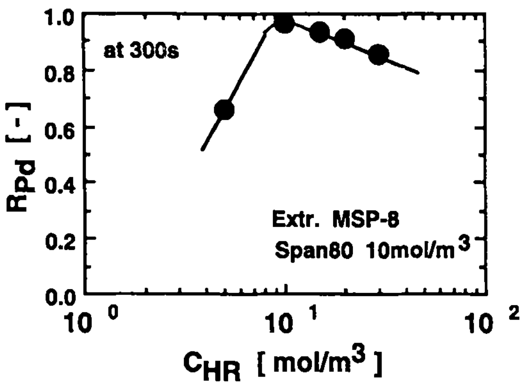

FIG. 8b Relation between recovery ratio of palladium and carrier concentration.

section. In a previous paper (12) we studied the extraction kinetics of palladium using didodecylmonothiophosphoric acid, which has a structure similar to MSP-8, in liquid–liquid extraction, and the extraction rate of palladium was elucidated to decrease with an increase in surfactant concentration such as for $2C_{18}\Delta^9GE$ and $2C_{18}\Delta^9GEC_2QA$ due to strong adsorption of the surfactant at the interface. The magnitude of the shielding effect at the interface was evaluated by the adsorption equilibrium constant, and the order of the adsorption equilibrium constant for the four surfactants was found to increase in the order PX 100 $\leq$ Span 80 $\ll$ $2C_{18}\Delta^9GE < 2C_{18}\Delta^9GEC_2QA$ (15). Except for $2C_{18}\Delta^9GEC_2QA$, the order

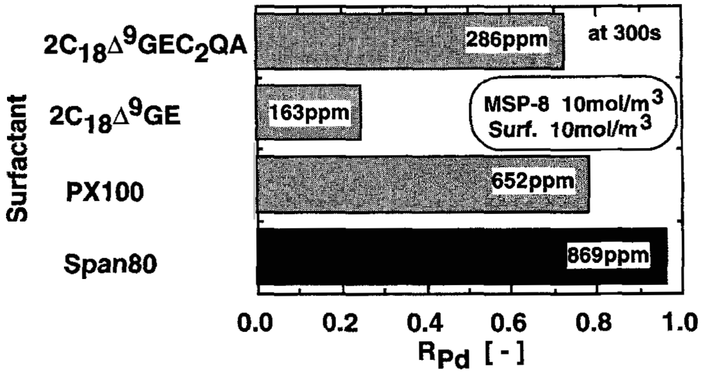

FIG. 9a Relation between recovery ratio of palladium and the kinds of surfactants.

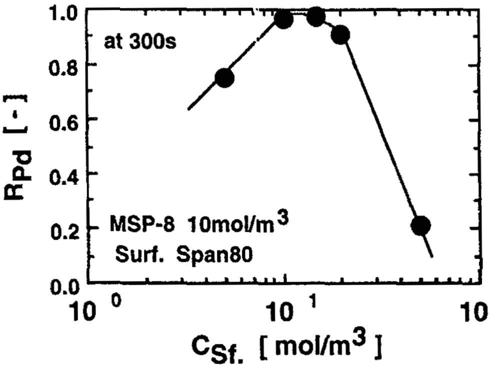

FIG. 9b Relation between recovery ratio of palladium and surfactant concentration.

of recovery efficiency of palladium in Fig. 9 approximately agrees with that of the adsorption ability of surfactants. The permeation rate of palladium in $2C_{18}\Delta^9GEC_2QA$ might be accelerated by an electrostatic interaction between chloro–palladium complex anions and the quaternary ammonium group of the cationic surfactant (7, 15). In the present study, Span 80, which has a relatively small adsorption equilibrium constant, appears to be one of the most effective surfactants for palladium recovery from the viewpoint of the permeation rate of palladium. Furthermore, based on the results in Fig. 9b, we find that there is an optimum surfactant concentration for palladium recovery using LSMs. Although the recovery efficiency of palladium was expected to increase with increasing surfactant concentration, the permeation rate of palladium decreased with an increase in the surfactant concentration due to the shielding effect of excess surfactants at the interface. In conclusion, after the degree of palladium recovery attained a maximum value, it decreased again with an increase in the surfactant concentration as shown in Fig. 9b. Under the present recovery conditions, the optimum surfactant concentration of Span 80 was around 10 mol/m^3.

Effect of Thiourea as a Stripping Reagent for LSMs

Figure 10 shows the effect of thiourea concentration on the degree of palladium recovery at 300 seconds. An optimum concentration of thiourea existed for the effective recovery of palladium by LSMs, although the stripping reaction of palladium was expected to be promoted by increasing the thiourea concentration. These results suggest that thiourea permeates through the liquid membrane from the internal phase to the external feed solution because thiourea has little solubility even in aliphatic solvents such as *n*-heptane. Moreover, thiourea is known to form a stable complex with palladium in an aqueous solution. The palladium–thiourea complex could not be extracted into the membrane phases in a high concentration of thiourea, while a small amount of thiourea accelerates the permeation rate of palladium by a trans-effect (17). In order to prevent the permeation of thiourea from the internal phase, we considered ionizing thiourea by adding an acid, which would depress the permeation of thiourea through the liquid membrane. Under the present conditions, one of the best combi-

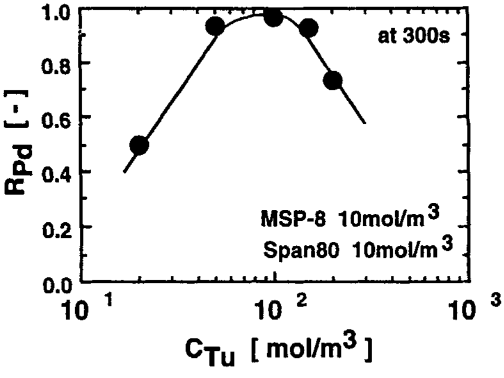

FIG. 10 Relation between recovery ratio of palladium and thiourea concentration.

nations of acid and thiourea was 1000 mol/m^3 hydrochloric acid and 100 mol/m^3 thiourea for the prevention of thiourea leakage.

Effect of Acid as an Internal Recovery Solution for LSMs

Figures 11a and 11b exhibit the effects of several kinds of acid added to the internal aqueous solution and the concentration of hydrochloric acid on the recovery ratio of palladium at 300 seconds. Using hydrochloric acid as the internal acid, palladium ions were recovered most effectively from the external aqueous solution into the internal phase in emulsions. Palladium forms a highly stable chloro complex in a chloride solution and

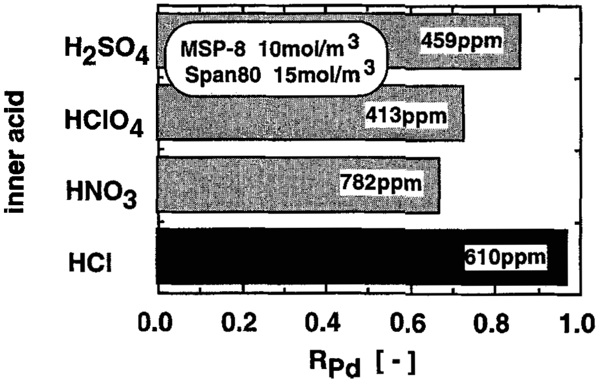

FIG. 11a Relation between recovery ratio of palladium and the kinds of internal acids.

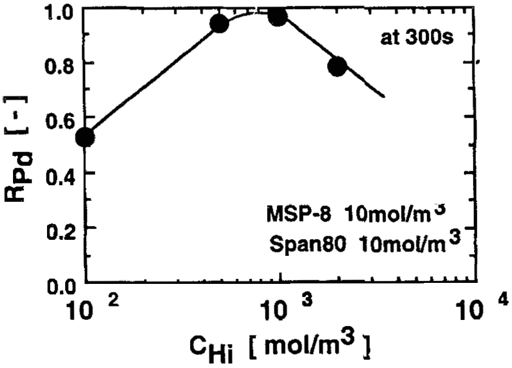

FIG. 11b Relation between recovery ratio of palladium and internal acid concentration.

presents as several palladium–chloro complexes in the aqueous solution (11, 12). In the external aqueous solution of 1000 mol/m^3 hydrochloric acid, the palladium ions mainly exists as $PdCl_4^{2-}$. On the other hand, except for hydrochloric acid, palladium is consider to exist as a free ion because palladium ion does not form a complex with the other anions. The existence of chloride ions in the stripping solution containing thiourea appears to be favorable for the effective recovery of palladium (8). On the basis of the results in Fig. 11a, the concentration of palladium in the recovery solution was found to be considerably high in spite of the low degree of palladium permeation for nitric acid, because the internal aqueous volume of emulsions was reduced to about a half of the initial volume by the leakage of nitric acid. Such a phenomenon was not observed for the other acids. Hydrochloric acid does not permeate through the liquid membrane because the same concentration of hydrochloric acid is contained in the feed solution. Such a leakage of an acid is caused by the concentration difference between the internal and external phases. Therefore, hydrochloric acid seems to be the most suitable acid as the internal aqueous solution. Based on the data in Fig. 11b, the degree of palladium recovery is found to increase as the concentration of hydrochloric acid in the internal aqueous solution increases up to 1000 mol/m^3, but decreases at higher concentrations. In a low concentration of hydrochloric acid, the permeation of thiourea through the liquid membranes could not be depressed because the amount of proton was not enough to produce protonated thiourea. On the other hand, when the concentration of hydrochloric acid in the internal solution is high, the degree of break-up increases because the surfactant Span 80 is unstable in such a highly acidic aqueous solution (18). From the viewpoint of membrane stability, hydrochloric acid of 1000 mol/m^3 was suitable as an internal acid of emulsions.

Under the present optimum conditions of 10 mol/m^3 MSP-8 and Span 80, 100 mol/m^3 thiourea, and 1000 mol/m^3 hydrochloric acid, more than 95% of the palladium was selectively recovered from the pseudowastewater, including a large amount of iron, and concentrated more than ten times. Continuous operation for the recovery of palladium using LSMs has not been discussed here because the focus has been on searching for the optimum conditions in an LSM system. Issues regarding continuous operation by LSMs will be discussed in a broader context in a subsequent communication.

CONCLUSION

Selection of a suitable carrier is a key factor in establishing the recovery process of palladium from a wastewater with a high iron concentration by LSMs. In this study, using four kinds of sulfur-containing extractants as a carrier, the recovery of palladium from a pseudoindustrial wastewater containing a large amount of iron was systematically investigated with an LSM technique.

It is clear that the surface-active property of the carrier strongly affects the degree of palladium recovery by LSMs, and, in particular, the adjustment of carrier concentration is one of key factors in ensuring a high recovery ratio. In the transport of palladium from the feed to the internal aqueous phase, the stability of emulsions has a crucial effect, and the surfactant as well as the carrier significantly affect the liquid membrane stability. A suitable carrier for palladium extraction by LSMs must have a sulfur atom. It should also have a branched hydrophobic group to give it high solubility in an aliphatic solvent, which is considered to be the best liquid membrane for an LSM operation. Another important factor is to make up the best combination of thiourea and acid as an internal recovery phase, taking into account the emulsion stability and the permeation rate of the palladium ion. The internal phase in the emulsion has to be acidic in order to depress the permeation of thiourea from the internal phase to the external phase. Based on the results obtained to date, the commercial extractant MSP-8 appears to be one of the best carriers currently available for palladium recovery by LSMs. Under the optimum conditions, more than 95% of the palladium could be recovered selectively over a large amount of iron in a few minutes and concentrated by more than ten times into the recovery phase in W/O emulsions.

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