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Separation of Palladium and Silver from a Nitric Acid Solution by Liquid Surfactant Membranes

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ABSTRACT

The recovery of palladium from a nitric acid solution containing silver has been conducted by application of liquid surfactant membranes (LSMs) containing LIX 860, a β -hydroxyoxime, as a mobile carrier in a stirred tank. The extraction equilibria of palladium and silver using several different extractants were also studied. Palladium was selectively extracted from a silver-containing liquor with LIX 860 while it was also observed that both palladium and silver were extractable with a sulfur-containing extractant. The recovery of palladium with LIX 860 was selectively achieved by using perchloric acid solution as the LSM internal phase dosed with thiourea. In the LSM operation, the effects of several chemical parameters on the selective recovery of palladium were studied. The use of hydrochloric acid as an internal receiving phase prevented the transport of silver into the emulsion due to the formation of silver chloride in the external feed solution. Commercially available Span 80 was found suitable for the selective extraction of palladium as a surfactant in LSM operation. Under optimum conditions, palladium was successfully separated from silver and concentrated into a receiving phase in W/O emulsions.

INTRODUCTION

Recently, the development of an efficient technique for the recovery of valuable metals contained in industrial wastes has come under serious

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consideration due to resource scarcity and some hazards these metals might cause to the global environment. Of the valuable metals, precious metals are known to possess unique physical and chemical properties that are suitable for manufacturing industrial materials such as catalysts, electrical and corrosion-resistant alloys. In most of the wastes, target metals are often very rare compared to a primary source and thus the separation is very difficult. Therefore, it is necessary to develop an efficient recovery process for such valuable metals.

The solvent extraction process has already been industrially applied to the recovery of precious metals (1). However, the extraction rate of precious metals is understood to be kinetically very slow, and as a result a huge amount of extractant and interfacial area are required to operate the process efficiently.

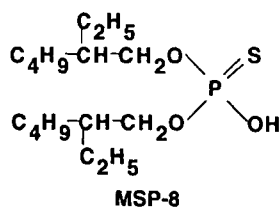
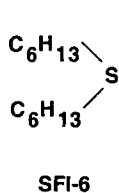
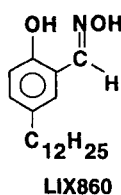
The liquid surfactant membrane (LSM) process is considered to possess the capacity to meet the demands of optimally low extractant levels together with a huge interfacial area. Nakashio et al. (2) reviewed the advantages of the LSM process and indicated that the LSMs are capable of separating selectively and concentrating rapidly metal ions owing to the thin liquid membrane and large interfacial area. Therefore, it has been suggested that an LSM process could be the best process for the recovery of industrial resources. Many investigators have studied the applicability of LSMs to industrial operations since it was invented by Li (3). Studies with respect to capital and operating costs of potential LSM processes have been conducted (4–6). Hayworth et al. (4) economically compared an LSM process with a solvent extraction process for the recovery of uranium ions from a wet process of phosphoric acid. It was concluded that the LSM process is superior to the solvent extraction process from both the capital and operating costs viewpoints because the number of stages constituting a series of mixer-settlers and the loss of organic solution in the LSM process were lower than in the solvent extraction process. Furthermore, Marr et al. (6) estimated the cost of an LSM plant for a zinc recovery process from a viscose effluent and noted that the payback time for the LSM process was positive in contrast to many other environmental protection processes. Therefore, the LSM process will be useful for the recovery of valuable materials such as precious metals. The LSM process has already been applied at an industrial scale for the removal of zinc from waste liquor at a textile plant in Austria (7).

So far, few investigations concerning the recovery of precious metals by LSMs have been conducted due to the difficulties associated with developing an effective carrier and stable LSM system for precious metals. We have successfully conducted test work to permeate palladium through to the internal stripping phase of the LSM by using a sulfur-

containing extractant as a carrier and found that palladium recovery is attainable in a few minutes under optimum conditions (8–10). A sulfur-containing extractant is known to have strong affinity for soft metals such as palladium. Therefore, palladium was completely extracted by the extractant even under acidic conditions. However, the strong complexation affinity toward palladium made stripping difficult. In a previous paper (8) we found that the selection of a suitable stripping agent was a key factor to developing an effective LSM system to recover palladium ions, and the use of thiourea as the stripping agent facilitated the effective transport of palladium from a feed solution to a receiving phase in the LSM system. Furthermore, palladium ions were selectively separated from a large amount of iron ions and enriched rapidly into the receiving phase of the W/O emulsions by using a sulfur-containing carrier (9, 10).

In the present work, the separation of palladium from acidic waste liquor which contains palladium and silver after treating precious metal articles

Carrier



Surfactant

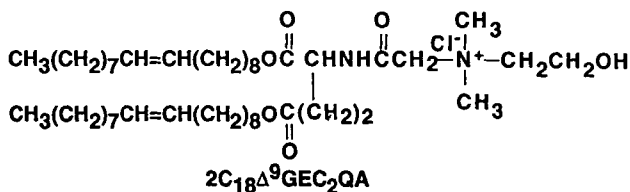
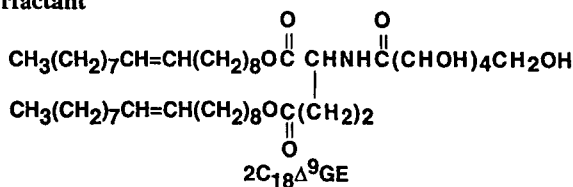


FIG. 1 Molecular structure of carriers and surfactants used in an LSM experiment.

with nitric acid has been performed by LSMs in a batch-type cell. An appropriate carrier for the selective separation of palladium from silver was selected along with a surfactant. Optimum conditions are also discussed for the recovery of palladium from an external feed solution to an internal receiving phase of W/O emulsions.

MATERIALS

Figure 1 shows the structures of carriers (extractants) and surfactants used in this LSM study. Span 80 and PX 100 were purchased from Kishida Chemical Co., Ltd. (Japan) and Exxon Chemical Japan Co., respectively. MSP-8 and SFI-6 were supplied by Daihachi Chemical Industry Co., Ltd. (Japan). CYANEX 301 and CYANEX 471X were supplied by Mitsui Cytec Co., Ltd. (Japan). LIX 860 was supplied by Henkel Co., TBP and D2EHPA were purchased from Kishida Chemical Co., Ltd. (Japan) and Tokyo Chemical Industry Co., Ltd. (Japan), respectively. Kelex 100 was purchased from Dojindo Laboratories (Japan). All commercial extractants and surfactants were used without further purification. $2C_{18}\Delta^9GE$ and $2C_{18}\Delta^9GEC_2QA$ were synthesized in our laboratory according to the procedures described in previous papers (11, 12). *n*-Heptane was employed as an organic solvent in all the experiments. All other reagents used were of guaranteed reagent grade and were used as received.

EXPERIMENTAL

Extraction of Palladium and Silver

The preparation of the external aqueous solution was carried out by dissolving palladium nitrate, silver nitrate, and nitric acid into deionized water. On the other hand, the organic solution was prepared by weighing an extractant into *n*-heptane.

The experimental procedure of extraction equilibrium was the same as that described in a previous paper (13). Equal volumes of the aqueous and organic solutions prepared as mentioned above were contacted in a glass vessel and shaken vigorously for approximately 24 hours to attain extraction equilibrium. After that, the samples were further shaken in a thermostated water bath maintained at 303 K for 24 hours. The metal concentration in aqueous solution was determined by atomic absorption spectrophotometry (Seiko, Model SAS-760).

Stripping of Palladium and Silver

The internal electrolyte solution was prepared by dissolving thiourea and hydrochloric acid into deionized water. The organic solution to be

used in the stripping experiment was loaded with an appropriate amount of palladium or silver in advance. The experimental method for the stripping equilibrium is similar to that of the extraction equilibrium operation.

Separation of Palladium and Silver by LSMs

The experimental apparatus used for the LSM experiment was a stirred tank equipped with four glass baffles. The inner diameter and the depth of the glass cell are 9.2 and 9.5 cm, respectively. Stirring was conducted with a turbine impeller having six flat blades and a speed controller.

The external feed solution was a pseudowaste liquor, similar to that obtained after treating precious metal articles with nitric acid, and the concentration ratio of palladium to silver corresponded to that in actual waste liquor. An internal aqueous solution was prepared by dissolving thiourea and an acid into deionized water. Nickel nitrate was added as a break-up tracer to the internal electrolyte solution of W/O emulsions. The organic phase was prepared by dissolving an extractant and a surfactant into *n*-heptane. The W/O emulsion was made from equal volumes of the organic and electrolyte phases mixed at 13,500 rpm using a homogenizer (Ika, Model T25).

The detailed experimental procedure is as described in previous papers (8–10). A measured volume of the emulsion was added to the stirred cell containing the external aqueous solution of palladium and silver, and was stirred at 300 rpm. The cell was placed in a thermostated water bath maintained at 303 K. Nickel nitrate in the internal electrolyte solution of the

TABLE I
Experimental Conditions for the LSM Operations

| | |
|---------------------------|--|
| External aqueous phase: | |
| Pd ²⁺ : | 0.1 mol/m ³ |
| Ag ⁺ : | 0.4 mol/m ³ |
| HNO ₃ : | 1000 mol/m ³ |
| Organic phase: | |
| Solvent: | <i>n</i> -Heptane |
| Carrier: | LIX 860, SF1-6, MSP-8; 0, 20–100 mol/m ³ |
| Surfactant: | Span 80, PX 100, 2C ₁₈ Δ ⁹ GE, 2C ₁₈ Δ ⁹ GEC ₂ QA; 20–100 mol/m ³ |
| Internal receiving phase: | |
| Thiourea: | 1–100 mol/m ³ |
| Acid: | HCl, HClO ₄ , HNO ₃ , H ₂ SO ₄ ; 1000 mol/m ³ |
| Stirring speed | 300 rpm |
| Temperature | 303 K |

emulsion was employed as an indicator to measure the degree of breakup of the emulsions. Samples of about 3–4 cm³ were taken at intervals. The sample phase in each test tube was allowed to disengage in a few minutes and later separated. The metal concentration in the aqueous phase was determined by atomic absorption spectrophotometry. The detailed experimental conditions for the LSM are listed in Table 1.

RESULTS AND DISCUSSION

Extraction Equilibrium of Palladium and Silver

The extraction equilibrium tests of palladium and silver were carried out in nitric acid media using different commercial extractants in order to choose a suitable extractant for the selective separation of palladium and silver in the LSM process. Trial runs were made for several extractants such as MSP-8 and CYANEX 301 which are acidic and contain ligand sulfur atom, SFI-6 and CYANEX 471X which are neutral and contain sulfur, D2EHPA which is acidic, TBP which is neutral, and LIX 860 and Kelex 100 which are typical chelating extractants.

Figure 2 shows the effect of nitric acid concentration on the extraction of palladium and silver with different extractants. The symbol "E" denotes the degree of metal extraction. Using a sulfur-containing extractant MSP-8, CYANEX 301, or CYANEX 471X, both palladium and silver ions were unselectively extracted under the present experimental conditions (data not shown). However, by using SFI-6, which has an alkyl sulfide

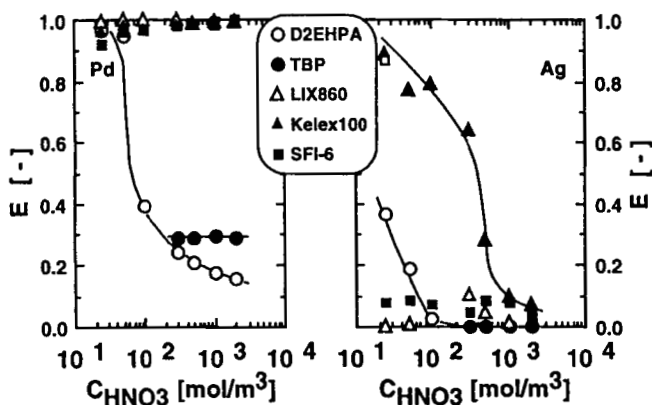
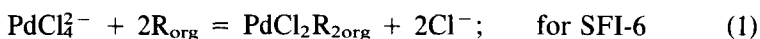


FIG. 2 Relationship between the degree of metal extraction and nitric acid concentration for several different extractants.

ligand, palladium ions were selectively extracted from a silver component liquor. Both palladium and silver ions are soft metals and as such interact strongly with an extractant possessing a soft sulfur atom. Therefore, the separation of palladium and silver ions was considered to be difficult with a sulfur-containing extractant. In the case of SFI-6, silver extraction was observed to increase with the concentration of the extractant (14). The extractant D2EHPA, well known for its effectiveness for recovering various metal ions, has been widely used in industrial solvent extraction processes. Results showed that the extracted ratio of palladium and silver with D2EHPA increased with a decreasing concentration of nitric acid. However, the extraction capacity of D2EHPA was relatively low by comparison. Palladium ions were preferred over silver ions by TBP, although a higher concentration was required for the complete recovery of palladium ions. Using the chelating extractants Kelex 100 and LIX 860, the separation of palladium and silver ions was achieved with a satisfactory yield of palladium under the present experimental conditions. For Kelex 100, the degree of silver extraction tends to increase with a decreasing concentration of nitric acid due to the promotion of acid dissociation. However, at a high nitric acid concentration range a small amount of precipitate was observed at the interface. In addition, an increase in the concentration of Kelex 100 resulted in the extraction of both palladium and silver ions. On the other hand, for LIX 860, palladium ions were selectively extracted while silver ions were hardly extracted under the concentration ranges of nitric acid used in this study. Therefore, the best separation was achieved through the LIX 860 option. Hence the use of a chelate-type of extractant was found to be very useful for the separation of palladium and silver. Further, the effect of extractant concentration on the separation process of palladium from silver using either SFI-6 or LIX 860 was investigated. Results in Fig. 3 show that the degree of palladium extraction increases with an increase in extractant concentration, and the best selective extraction was observed in the extractant concentration range higher than 1 mol/m^3 , in which case silver ions remained in the external solution.

The complex formation of palladium with alkylsulfide (R) (1, 15) (Eq. 1) or hydroxyoxime (HR) (16) (Eq. 2) under a high hydrochloric acid concentration is



where the subscript "org" denotes the organic species. Palladium ions have a large stability constant with chloride ions and exist as tetrachlo-

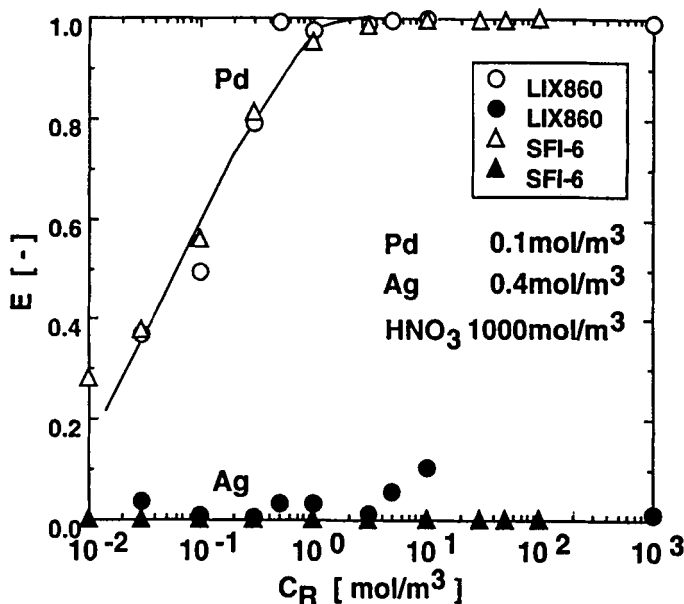


FIG. 3 Relationship between the degree of metal extraction and extractant concentration of LIX 860 and SFI-6.

ropalladate ions in hydrochloric acid solution. The exchange reaction of chlorides with a ligand is well known to be significantly slow because the complex is very stable in aqueous solution. In nitric acid medium the extraction rate of palladium is improved because palladium exists as a free ion. The extraction process of palladium with a hydroxyoxime in HCl medium follows the proton exchange reaction, while with an alkylsulfide, two nitric ions are required as counterions in order to neutralize the positive charge of palladium ions.

Stripping Equilibrium of Palladium and Silver

In order to prepare an efficient LSM system, the metal ions extracted into a liquid membrane phase by a mobile carrier should be effectively transferred into a receiving phase of the W/O emulsion. The stripping of palladium extracted by the alkylsulfide and hydroxyoxime is often very difficult due to the high stability of the complex in organic media. An ammonia solution has been industrially employed in a solvent extraction process as a stripping reagent for palladium extracted by an alkylsulfide

(1), however, in an LSM process the ammonia solution may not be employed as an internal receiving phase because it readily dissolves in the liquid membrane phase and immediately permeates to the external solution. In a liquid-liquid system with a hydroxyoxime, the stripping behavior of palladium was investigated with sodium thiosulfate and satisfactory results were reported (16). In previous papers (8-10) we investigated the extraction characteristics of palladium using the LSM process with a sulfur-containing carrier and accomplished satisfactory permeation rates of palladium into the receiving phase using thiourea as a stripping reagent. Because the stability constant of palladium and silver in thiourea is extremely high, thiourea reagent proved to be a better alternative for stripping palladium in combination with other carrier systems. Table 2 summarizes the results of the stripping process with an electrolyte solution containing both thiourea and HCl at 1 kmol/m³ for various extractants. In the case of LIX 860, Kelex 100, or SFI-6, the degree of silver stripping could not be evaluated because silver ions were scarcely recovered. Palladium ions can be completely stripped by using a thiourea solution as a stripping reagent. In the case of CYANEX 471X, CYANEX 301, or MSP-8, silver ions were also stripped. Palladium extracted by MSP-8 was readily stripped unlike by CYANEX 301 in which palladium stripping was difficult owing to the strong interaction with two sulfur atoms in the extractant. In CYANEX 471X, palladium ions were not detected in the stripping solution due to formation of a precipitate at the interface which appears to be a palladium complex. The acidic thiourea solution was found to be very effective as a receiving phase for palladium extracted in the

TABLE 2
Effect of Extractants on the Degree of Metal Stripping

| Extractant | Stripping ratio (%) | |
|-------------|---------------------|--------------|
| | Pd | Ag |
| LIX 860 | 100 | ^a |
| Kelex 100 | 100 | ^a |
| SFI-6 | 100 | ^a |
| CYANEX 471X | ^a | 100 |
| CYANEX 301 | 0 | 100 |
| MSP-8 | 100 | 100 |

^a Metal ions were not extracted by the extractant in the organic solution.

LSM process. On the basis of the results obtained, three extractants (SFI-6, LIX 860 and MSP-8) were adopted as potential mobile carriers for the selective separation of palladium and silver ions in the LSM process.

Separation of Palladium and Silver by LSMs

To evaluate the stability of emulsions as well as the extraction behavior of metal ions, it is necessary to make an assessment of the efficiency of the whole LSM system in terms of: metal ions in raffinate solution, $1 - E$ (—); the recovered metal ions in internal receiving phase, R (—); and the degree of emulsion break-up, ϵ (—). These parameter were defined by the following equations according to the previous paper (8):

$$1 - E = C_{M,e}/C_{M,e,0} \quad (3)$$

$$R = 1 - (C_{M,e}V_e + C_{M,org}V_{org})/C_{M,e,0}V_e \quad (4)$$

$$\epsilon = (C_{Ni,e}V_e)/(C_{Ni,i,0}V_i) \quad (5)$$

where the subscripts "e," "org," and "i" denote the external, organic, and internal phase, and ϵ was estimated by determining the amount of break-up tracer released from the internal receiving phase through the emulsion globules to the external aqueous solution.

Selection of Electrolyte as a Receiving Phase for Palladium

Figures 4 (a) and (b) show the time profile of the extraction behavior of metals and break-up of emulsions. Using LIX 860 as a carrier, the liquid membranes were stabilized by the addition of the surfactant Span 80 or $2C_{18}\Delta^9GE$. The liquid membranes formed by dosing the organic phase with the surfactant $2C_{18}\Delta^9GE$ were more stable than those formed with Span 80. Based on the results of metal extraction by LSMs with surfactant Span 80 or $2C_{18}\Delta^9GE$, it was observed that silver ions were transferable without the carrier, while palladium ions depended on the interaction with LIX 860 for permeation in the emulsion. These results suggest that the surfactants have extraction capacity for silver ions, although the reason for this is not clearly understood.

When HCl solution is used as an internal electrolyte solution, silver chloride forms in the external phase; this is mainly due to the permeation of hydrochloric acid from the internal receiving phase to the external solution through the liquid membrane. Furthermore, the effect on silver extraction by various acid reagents, which are likely to be used as the internal phase liquor, was investigated. Based on the results in Fig. 5 it was found that silver ions are not extracted with perchloric, nitric, and

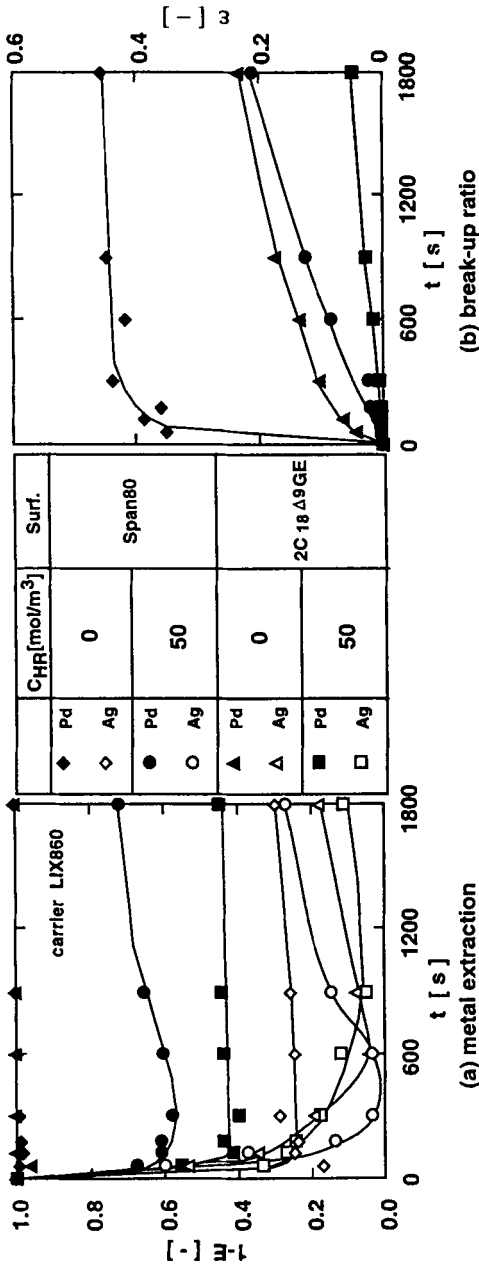


FIG. 4 Effect of surfactants on metal extraction and emulsion stability in a hydrochloric acid system (surfactant concentration: 10 mol/m^3 ; thiourea concentration: 50 mol/m^3).

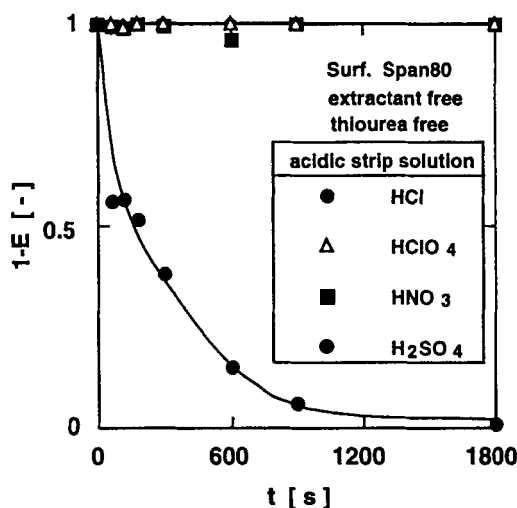


FIG. 5 Effect of internal acid solution on silver extraction by LSMs [surfactant concentration: 50 mol/m³; inner acid concentration: 1000 mol/m³ (HCl, HClO₄, HNO₃), 500 mol/m³ (H₂SO₄)].

sulfuric acids working as stripping reagents. In the case of stripping with HCl acid solution, AgCl forms in the external phase. This is mainly due to the ionic transport of chloride ions through the thin membrane to the external phase containing silver ions. Based on these results, the use of hydrochloric acid does not appear to be suitable for the effective recovery of silver by the LSM process under the present conditions. Further investigations have shown that palladium ions can be effectively separated from silver ions by using perchloric acid solution as an internal receiving phase. Hence, perchloric acid was chosen as an internal acid solution in the subsequent experiments.

Effect of Thiourea Concentration in LSM Operations

Figure 6 exhibits the effect of thiourea concentration on the extraction behavior of palladium and silver ions. Under the present experimental conditions, the liquid membranes were very stable, and only palladium ions were selectively recovered into the internal aqueous phase. When the thiourea concentration was relatively low at 1 mol/m³, palladium recovery was equally low. The degree of palladium recovery increased with the increase in the concentration of thiourea from 1 to 10 mol/m³. How-

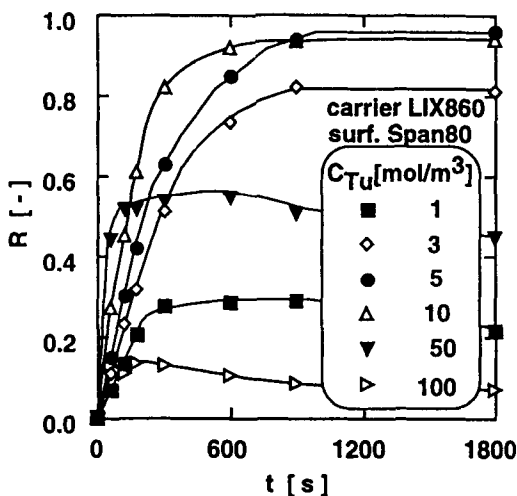


FIG. 6 Effect of thiourea concentration on emulsion stability and metal recovery by LSMs (carrier concentration: 100 mol/m³; surfactant concentration: 50 mol/m³).

ever, a further increase in the thiourea concentration over 10 mol/m³ resulted in a decrease in the extraction efficiency because the permeated thiourea from an internal receiving phase forms a stable complex with palladium ions in the external feed solution; the complex was not extracted by the carrier (8–10). An optimum concentration exists for thiourea as a stripping reagent, and the optimum value in the present study appears to be around 10 mol/m³ in which a rapid rate and a high degree of palladium recovery are achievable.

Selection of a Carrier for the LSM Operations

The effects of several carriers on the recovery of palladium and the stability of liquid membranes were investigated as shown in Fig. 7. The degree of emulsion breakup was found to be in the order LIX 860 < SFI-6 < MSP-8. For LIX 860 and SFI-6, the degree of breakup was less than 5% at 1800 seconds and the liquid membranes were relatively stable. For MSP-8, the value of breakup attained was 10% at 600 seconds and consequently the stable liquid membranes were not formed. MSP-8 has two octyl groups in the hydrophobic part, and the molecular structure is similar to that of a surfactant. Therefore, it is deduced that MSP-8 is surface active and the orientation of surfactants at the interface might be disordered by

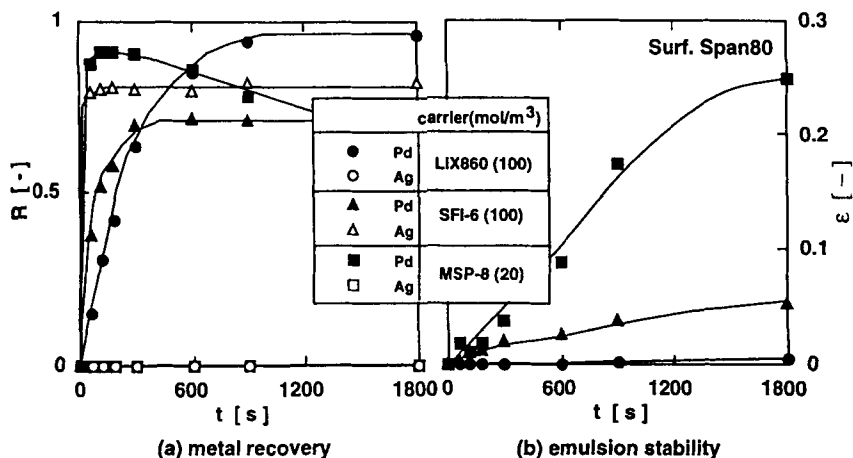


FIG. 7 Effect of carriers on metal recovery and emulsion stability by LSMs [surfactant concentration: 50 mol/m³; thiourea concentration: 5 mol/m³ (in LIX 860 system), 50 mol/m³ (in SFI-6 and MSP-8 systems)].

the adsorption of the carrier. A similar behavior was observed in the previous study (10). The efficiency of palladium recovery increased in the order LIX 860 < SFI-6 < MSP-8 in the initial state; however, the degree of final palladium recovery was in the order SFI-6 = MSP-8 < LIX 860. Silver ions were not recovered in the case of using LIX 860 or MSP-8 for the LSM process. However, MSP-8 readily extracts palladium ions in the LSM process. The degree of palladium recovery in this case decreased with time due to the large breakup of W/O emulsions. For the extractant SFI-6, the initial extraction rate of palladium was fast, although a high degree of palladium recovery was not observed. Owing to the high concentration of the SFI-6 carrier, intended to improve the extraction rate of palladium, the stripping became difficult. In addition, by applying sulfur-containing carriers such as CYANEX 301 and CYANEX 471X, silver ions were co-extracted with palladium, thus rendering the separation poor. In contrast, for LIX 860, palladium ions were selectively recovered from the solution containing silver ions.

Figure 8 shows the effect of carrier concentration on the palladium recovery and the emulsion stability. The liquid membranes were found to be stabilized by the increase in the concentration of the carrier. It is assumed that the surfactant interacts strongly with the carrier in the liquid membrane phase. The rate of palladium extraction increased with increas-

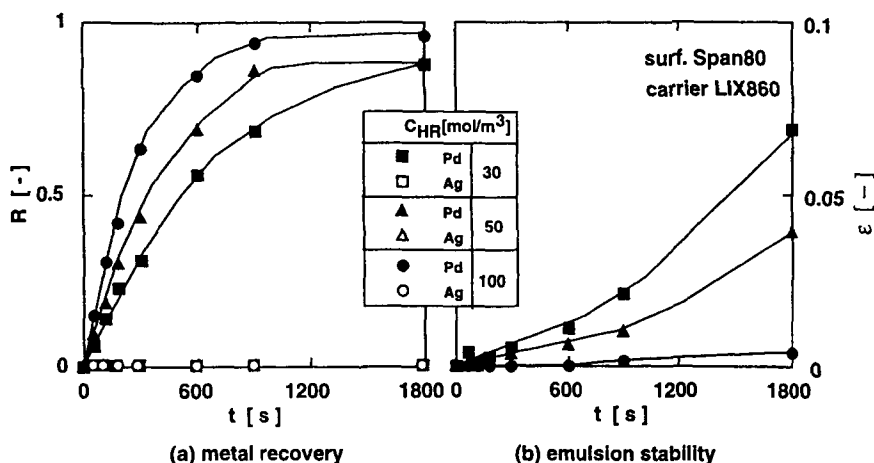


FIG. 8 Effect of carrier concentration on metal recovery and emulsion stability by LSMs (surfactant concentration: 50 mol/m³; thiourea concentration: 5 mol/m³).

ing concentration of the mobile carrier; silver ions were not extracted under the present experimental conditions. The stripping reaction of palladium was confirmed to have been satisfactorily performed because palladium in the membrane phase was not detected after analysis.

Selection of a Surfactant for the LSM Operations

Figure 9 shows the effect of surfactants on the separation of palladium and silver and the emulsion stability. From the viewpoint of the emulsion stability, PX 100 appears to be the best surfactant among the surfactants used, although the recovery of palladium ions was satisfactorily performed in every surfactant and the rate of recovery did not show dependence on the surfactants. However, a surfactant having an amine or ammonium group in the structure, such as PX 100 or 2C₁₈Δ⁹GEC₂QA, appears to have an affinity for palladium and silver ions because palladium and silver ions are known to be extracted by basic extractants having such groups. Silver ions were not extracted by using the surfactants Span 80 or 2C₁₈Δ⁹GE. However, in PX 100 or 2C₁₈Δ⁹GEC₂QA small amounts of silver ions were allowed to permeate through the emulsion and consequently the separation efficiency between palladium and silver decreased. As shown in Fig. 3, in the liquid–liquid extraction equilibrium experiment, LIX 860 hardly extracted silver ions, although silver ions showed some

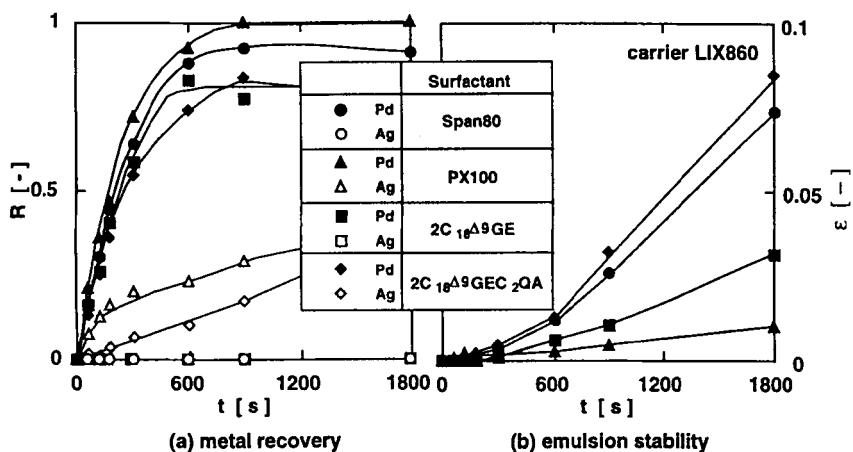


FIG. 9 Effect of surfactants on metal recovery and emulsion stability by LSMs [carrier concentration: 100 mol/m^3 ; surfactant concentration: 30 mol/m^3 (Span 80, PX 100), 20 mol/m^3 ($2C_{18}\Delta^9GE$, $2C_{18}\Delta^9GEC_2QA$); thiourea concentration: 5 mol/m^3].

degree of permeation through the emulsion by using PX 100 as a surfactant in the LSM operation. Furthermore, both palladium and silver ions were found to be extractable by PX 100 in the absence of the carrier. This result means that PX 100, too, has some extraction capacity for palladium and silver ions. Considering both the stability of liquid membranes and the separation efficiency of metals, Span 80 appears to be the best surfactant among the surfactants used in the present LSM systems.

The effect of Span 80 surfactant concentration on the recovery of palladium and the emulsion stability is illustrated in Fig. 10. The stability of emulsions was improved with increasing concentration of the surfactant. Therefore, the efficiency of metal enrichment into the receiving phase is greatly enhanced with an increase in the surfactant concentration (17). The liquid membranes were unstable at the surfactant concentration of 20 or 30 mol/m^3 ; however, they were stabilized at the concentration of 50 mol/m^3 . Silver ions were not extracted under the present concentration range of Span 80 and only palladium ions were selectively permeated. The extraction rate of palladium increased with decreasing concentration of the surfactant due to the reduction of shielding effect of surfactants at the reaction interface. However, at low surfactant concentration the degree of palladium recovery becomes low due to the large break-up ratio

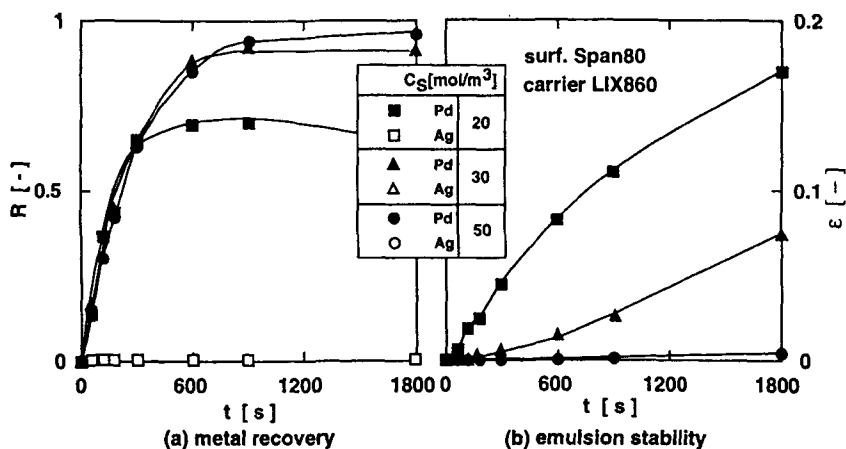


FIG. 10 Effect of surfactant concentration on metal recovery and emulsion stability (carrier concentration: 100 mol/m³; thiourea concentration: 5 mol/m³).

of liquid membrane globules. The surfactant concentration at more than 50 mol/m³ for Span 80 was found to be optimum for the effective recovery of palladium.

CONCLUSIONS

Using several different extractants, the separation of palladium and silver from an acidic pseudoindustrial waste liquor has been performed. Sulfur-containing extractants have been shown to be nonselective mobile carriers in the separation process of palladium and silver because they extract silver ions as well as palladium ions. A chelate extractant, LIX 860, has been demonstrated to be the most suitable extractant among the extractants used in this study. Accordingly, palladium has been efficiently recovered from a dual-component solution containing silver by LSMs with LIX 860 as a mobile carrier. In the LSM operations the recovery of palladium was significantly influenced by the carrier and the surfactant in the liquid membrane phase. Using Span 80 as a surfactant, palladium ions were preferably extracted over silver ions from nitric acid media and subsequently permeated through the thin liquid membrane phase and concentrated into the internal receiving phase under optimum conditions.

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REFERENCES

1. J. E. Barnes and J. D. Edwards, *Chem. Ind.*, **5**, 151 (1982).
2. F. Nakashio, M. Goto, and T. Kakoi, *Solv. Extr. Res. Dev., Jpn.*, **1**, 53 (1994).
3. N. N. Li, US Patent 3,410,794 (1968).
4. H. C. Hayworth, W. S. Ho, W. A. Burns Jr., and N. N. Li, *Sep. Sci. Technol.*, **18**, 493 (1983).
5. J. W. Frankenfeld, R. P. Cahn, and N. N. Li, *Ibid.*, **16**, 385 (1981).
6. R. J. Marr and J. Draxler, "Capital and Operating Costs," in *Membrane Handbook* (W. S. W. Ho and K. K. Sirkar, Eds.), Van Nostrand Reinhold, New York, NY, 1992, p. 718.
7. W. Fürst, J. Draxler, and R. J. Marr, *Proc. 3rd World Congr. Chem. Eng., Tokyo, Jpn.*, **3**, 331 (1986).
8. T. Kakoi, M. Goto, K. Kondo, and F. Nakashio, *J. Membr. Sci.*, **84**, 249 (1993).
9. T. Kakoi, M. Goto and F. Nakashio, *Solv. Extr. Res. Dev., Jpn.*, **2**, 149 (1995).
10. T. Kakoi, N. Horinouchi, M. Goto, and F. Nakashio, *Sep. Sci. Technol.*, **31**, 381 (1996).
11. M. Goto, M. Matsumoto, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn.*, **20**, 157 (1987).
12. M. Goto, H. Yamamoto, K. Kondo, and F. Nakashio, *J. Membr. Sci.*, **57**, 161 (1991).
13. T. Kakoi, M. Goto, and F. Nakashio, *Solv. Extr. Ion Exch.*, **12**, 541 (1994).
14. T. Sato, I. Ishikawa, and T. Nakamura, *Proc. Symp. Solv. Extr., Hamamatsu, Jpn.*, p. 105 (1982).
15. Y. Baba, T. Eguchi, and K. Inoue, *J. Chem. Eng. Jpn.*, **19**, 361 (1986).
16. Y. C. Hoh, W. S. Chuang, and P. S. Yueh, *J. Chem. Tech. Biotechnol.*, **34A**, 97 (1984).
17. F. Nakashio, *J. Chem. Eng. Jpn.*, **26**, 123 (1993).

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