

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Permeation of Iridium(IV) and Metal Impurity Chlorocomplexes through a Supported Liquid Membrane Designed for Rhodium Separation

Seyed N. Ashrafizadeh; George P. Demopoulos; Miquel Rovira; Ana M. Sastre

**To cite this Article** Ashrafizadeh, Seyed N. , Demopoulos, George P. , Rovira, Miquel and Sastre, Ana M.(1998) 'Permeation of Iridium(IV) and Metal Impurity Chlorocomplexes through a Supported Liquid Membrane Designed for Rhodium Separation', Separation Science and Technology, 33: 8, 1145 – 1162

**To link to this Article:** DOI: 10.1080/01496399808545246

**URL:** <http://dx.doi.org/10.1080/01496399808545246>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Permeation of Iridium(IV) and Metal Impurity Chlorocomplexes through a Supported Liquid Membrane Designed for Rhodium Separation

SEYED N. ASHRAFIZADEH and GEORGE P. DEMOPOULOS\*

DEPARTMENT OF MINING AND METALLURGICAL ENGINEERING  
MCGILL UNIVERSITY  
MONTREAL, QUEBEC H3A 2A7, CANADA

MIQUEL ROVIRA and ANA M. SASTRE

DEPARTMENT OF CHEMICAL ENGINEERING  
UNIVERSITAT POLITÈCNICA DE CATALUNYA  
E.T.S.E.I.B.  
BARCELONA, CP 08028, SPAIN

### ABSTRACT

A supported liquid membrane (SLM) system previously designed for Rh separation has been examined for its capability to reject the metal impurities which are commonly encountered in industrial Rh chloride solutions. Special attention was paid to Ir(IV) chlorocomplexes and their extraction/transport behavior against both conventional solvent extraction and supported liquid membrane systems of Kelex 100. A lab-scale SLM cell with an effective membrane area of 44 cm<sup>2</sup> was used to conduct the SLM permeation tests. The SLM was composed of a Gore-Tex polymer substrate impregnated with an organic solution of Kelex 100, tridecanol, and kerosene. The impurities tested [in addition to Ir(IV)] were Ag(I), As(V), Bi(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II), Pd(II), Pt(IV), Se(IV), Te(IV), and Zn(II). These impurities, based on their response against the SLM, were classified into three groups, i.e., those permeated through [Zn(II), Pb(II), Cd(II), Bi(III), Te(IV), and Ir(IV)], those nonpermeated at all [Ni(II), Co(II), As(V), Se(IV), Cu(II), and Fe(III)], and those blocking the membrane [Pt(IV), Pd(II), Ag(I), Pb(II), and Bi(III)]. The SLM was not capable of discriminating between Rh(III) and Ir(IV) transport at the optimum operating conditions. Complementary upstream and downstream processes are re-

\* To whom correspondence should be addressed.

quired to separate the impurities from the feed and the product solutions, respectively. Overall, this work revealed the great limitations of SLMs as effective and potentially useful separation media for the extraction of metals from industrial-like multicomponent aqueous feed solutions.

**Key Words.** Supported liquid membrane; Rhodium; Kelex 100; Solvent extraction; Iridium; Platinum group metals; Separation; Impurities; Hydrochloric acid

## INTRODUCTION

Platinum group metals (PGM) are recovered as by-products from sulfide matte leach residue or smelted anode slime residue in Cu/Ni refineries and smelters (1). As a consequence, rhodium (Rh) feed solutions encountered in the precious metal refining industry always contain substantial amounts of various metal species as impurities. In a previous work the promising features of a developed SLM of Kelex 100 (an alkylated 8-hydroxyquinoline) for the separation/refining of Rh was reported (2). As an extension of that project, an investigation was also conducted on the transport behavior of metal impurities through the same SLM. The latter, which is the subject of this communication, is of importance from three main standpoints. First, prior to development of a SLM process flow sheet for Rh recovery, it is necessary to evaluate the potential problems which might be encountered in the operation of the SLM due to the presence of impurities and hence devise appropriate techniques to face those problems. Second, the separation of rhodium from iridium always remains an important issue in the PGM refining industry (3). Third, despite the large number of papers published during the last 10–15 years in the area of SLM separation of metals, hardly any of these have commented or reported on the behavior of impurities. Almost all previous studies involved a single metal (the metal targeted for recovery)—a highly idealized situation from an industrial application point of view. For the above reasons, it was deemed appropriate to investigate the transport behavior of a series of metal impurities, that potentially can be found in industrial Rh feedstocks, against the developed SLM of Kelex 100 for Rh separation (2).

The Rh feed impurities can be readily classified into three groups, i.e., base metals (Cu, Fe, Co, Cd, Ni, Zn, Pb, Sn), metalloids (As, Sb, Bi, Se, Te), and precious (Ag and PGMs) (Ag, Pt, Pd, Ir, Ru, Os). Due to the similarity between the SLM process and the SX process (in effect, SLM is a combination of solvent extraction and solvent stripping), it is worthy to relate the present work to previous works involving SX of these elements with 8-hydroxyquinoline (8-HQ) type extractants. In this regard, the solution chemistry (speciation

and oxidation states) and solvent extraction behavior of most of these elements was critically reviewed recently from the standpoint of PGM refining by Aprahamian and Demopoulos (4). Moreover, the same researchers studied the distribution and scrubbing of these elements from a solvent similar to Kelex 100 used here, i.e., TN 1911 (5). Hence, this previous SX work was used as reference for the design of the SLM experiments and the interpretation of the obtained results.

## EXPERIMENTAL

The chloride-based aqueous solutions of metals were prepared by dissolving analytical grade chloride reagents in HCl solutions of the desired acidity. Platinum and palladium solutions were produced from pure metal powder via aqua-regia digestion followed by evaporation to dryness and redissolution in HCl. Iridium(IV) solutions were prepared by dissolving Ir(IV) chloride hydrate in concentrated chloride solutions while heating the solution at 60°C for 1 hour. In order to maintain the oxidation state of iridium(IV), 5 v/o of 0.3% chlorine water was added and the solution was allowed to cool for about 2 hours. The presence of Ir(IV) species was examined via UV absorption spectroscopy using a UV-240 UV-Visible Spectrometer from Shimadzu. The detection of four absorption bands at about 305, 420, 435, and 485 nm confirmed its existence (6).

Kelex 100 supplied by Witco, kerosene from Fluka, and tridecanol from Rhone-Poulenc were used as extractant, diluent, and modifier, respectively, throughout this work to prepare the organic solutions for both SX and SLM experiments. Details on extractant characterization and purification, the SX and SLM experimental procedures adopted, and the SLM apparatus were reported in previous publications (2, 7). The membrane support (Gore-Tex) used had an effective area of 44 cm<sup>2</sup>, a pore size of 0.45 μm, a thickness of 57 μm, and a porosity of 75.9%. In most of the SLM experiments the feed and strip solutions were 2.5 M HCl and 0.1 M HCl, respectively (the optimum conditions for the permeation of rhodium) (2). The volume ratio of the feed to the strip solution was 200 mL:20 mL respectively. The SLM experiments were carried out with single metal solutions, and the initial metal concentration was  $3.89 \times 10^{-3}$  M except for copper for which higher metal concentrations were used. Silver concentration was lower than the norm due to the low solubility of this metal in aqueous chloride media. The duration of each SLM experiment was 2 hours.

The metal concentration in the feed and product (strip) solutions was measured using standard atomic absorption spectroscopy (AA) with a spectrophotometer Model 357 from Instrumental Laboratory Inc. The iridium concentration, however, was measured by induced coupled plasma (ICP) spectroscopy

using a spectroflame from Spectro Analytical Instruments. The iridium was detected at 224.268 nm using argon of 99.99 purity with an incident plasma of 1200 W.

## SPECIATION OF METAL IMPURITIES AND EXTRACTION WITH 8-HQ

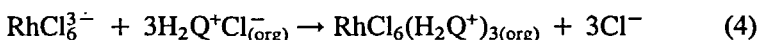
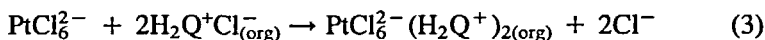
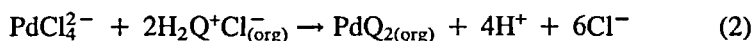
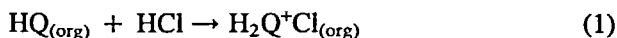
Many of the metal elements readily form chlorocomplexes in chloride solutions. Therefore, good knowledge of the aqueous chlorochemistry of the various impurity elements under investigation is of vital importance. Regarding the optimum conditions for the feed and strip solutions in the SLM system of Rh [i.e., 2–3 M HCl feed and 0.1–0.3 M HCl strip, respectively (2)], it was deemed appropriate to list the most probable complexes of these elements in Table 1 for quick reference.

8-Hydroxyquinolines derivatives like Kelex 100 may extract metal species via either compound formation (chelates) or via ion-pair formation involving the protonated form of 8-HQ. Thus it has been found, for example, that 8-hydroxyquinoline derivatives undergo protonation in HCl media (Reaction

TABLE 1  
Summary of Most Probable Metal Complexes Expected in HCl SCM  
Feed and Strip Solutions [most data extracted from Aprahamian  
and Demopoulos (4)]

| $M_{aq}$ | 1.0–3.0 M HCl<br>(analogous to feed)    | 0.1–1.0 M HCl<br>(analogous to strip)   |
|----------|---|---|
| Fe(III)  | $FeCl_2^+$ , $FeCl_3^0$                 | $Fe^{3+}$ , $FeCl^{2+}$ , $FeCl_2^+$    |
| Cu(II)   | $CuCl^+$ , $CuCl_2^0$ , $CuCl_3^-$      | $Cu^{2+}$ , $CuCl^+$                    |
| Ni(II)   | $NiCl^+$                                | $Ni^{2+}$                               |
| Zn(II)   | $ZnCl_2^0$ , $ZnCl_3^-$ , $ZnCl_4^{2-}$ | $Zn^{2+}$                               |
| Pb(II)   | $PbCl_2^0$ , $PbCl_3^-$ , $PbCl_4^{2-}$ | $Pb^{2+}$ , $PbCl^+$                    |
| Co(II)   | $CoCl_2^0$                              | $Co^{2+}$ , $CoCl^+$                    |
| Cd(II)   | $CdCl_3^-$                              | $CdCl^+$ , $CdCl_2^0$                   |
| As(V)    | $H_3AsO_4$                              | $H_3AsO_4$                              |
| Bi(III)  | $BiCl_6^{3-}$                           | $BiCl_3^0$ , $BiCl_4^-$ , $BiCl_5^{2-}$ |
| Se(IV)   | $H_2SeO_3$                              | $H_2SeO_3$                              |
| Te(IV)   | $TeOCl_2$ , $TeOCl_3^-$                 | $TeO^{2+}$ , $TeOCl_2^0$                |
| Ag(I)    | $AgCl_2^+$                              | $AgCl_2^+$                              |
| Pt(IV)   | $PtCl_6^{2-}$                           | $PtCl_6^{2-}$                           |
| Pd(II)   | $PdCl_4^{2-}$                           | $PdCl_4^{2-}$                           |
| Ir(IV)   | $IrCl_6^{2-}$                           | $IrCl_6^{2-}$                           |

1) (8) and extract Pd(II) via chelation (Reaction 2) (9) and Pt(IV) (Reaction 3) (10) and Rh(III) (Reaction 4) (11) via ion-pair formation:



Hence, those elements which form anionic chlorocomplexes (see Table 1) or chelates may potentially permeate through the SLM of Kelex 100.

The distribution of the various metals in the system HCl-8-HQ is given in Figs. 1 to 3. These distribution data can aid in interpreting the subsequent SLM permeation results reported in this paper.

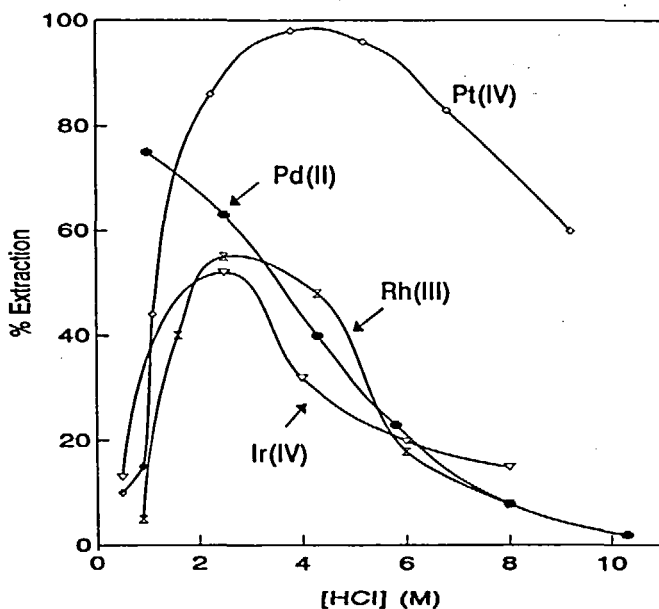


FIG. 1 The distribution of PGM in 8-hydroxyquinoline extractants as a function of feed acidity (O: 5 v/o TN 1911 (Pt(IV) and Pd(II)) or 5 v/o Kelex 100 (Rh(III) and Ir(IV)), 10 v/o tridecanol, Solvesso 150 (Pt(IV) and Pd(II)) or kerosene (Rh(III) and Ir(IV))  $[M]_{\text{initial}} = 500 \pm 100$  ppm; except  $[\text{Ir}] = 250$  applied solutions and single metal loading; A/O = 1, 3 minutes contact time; Rh(III) data from Ref. 7).

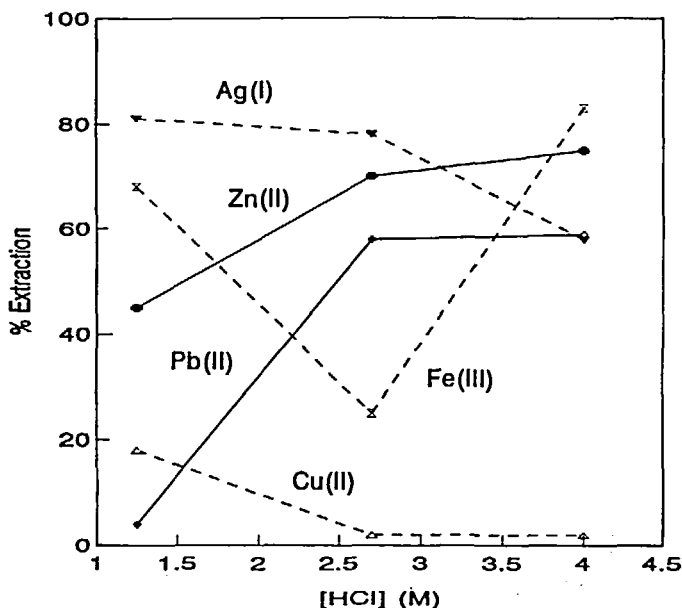


FIG. 2 The distribution of silver and base metals in 8-hydroxyquinoline extractants as a function of feed acidity (O: 5 v/o TN 1911, 10 v/o isodecanol, Solvesso 150;  $[M]_{\text{initial}} = 1000 \pm 200$  ppm; except  $[Ag]_{\text{initial}} = 100 + 50$  ppm single metal loading, 3 minutes contact time; A/O = 1) (data from Ref. 4).

## RESULTS AND DISCUSSION

### Solvent Extraction of Iridium(IV) with Kelex 100

The extraction behavior of Ir(IV) vis-a-vis 8-hydroxyquinolines reagents, like Kelex 100, has not been examined before. Hence, the need to examine the conventional SX system before an SLM study of it is attempted.

Aging is known to play a critical role in the extraction of Rh(III) chlorocomplexes (7). Thus, the effect of aging on Ir(IV) extraction was first studied. To this end, aqueous solutions of variable age (up to 2 weeks) containing 3 M HCl and 50 ppm Ir(IV) were contacted with organic solutions of Kelex 100 (1 v/o Kelex 100, 4 v/o tridecanol, kerosene). The results (which are not presented here for reasons of space economy) were found to exhibit only a minor decrease in terms of % extraction with solution age. (Percent extraction dropped from 45 to 40% after 1 day of aging with no further decrease thereafter). Apparently the oxidation state of iridium had not been altered under

the applied conditions (3M HCl), and hence significant aquation/aging, such as is encountered with the chlorocomplexes of iridium(III) (12) or rhodium(III) (7), did not occur. The latter notion was further verified with the recording of UV-Visible spectroscopy which showed similar absorption bands (305, 420, 435, and 485 nm) for the aged solutions as reported previously for fresh Ir(IV) solutions (6).

The extraction of Ir(IV) from aged chloride solutions versus feed acidity (HCl) is depicted in Fig. 1. As shown, a trend very similar with that of rhodium chlorocomplexes is obtained (7). In other words, at low acidities the extraction is very low, reaches a maximum at about 2.5 M of acidity, and subsequently decreases with the acidity of the feed solution. The low extraction at the lower range of acidity may be attributed mainly to the incomplete protonation of the extractant (see Reaction 1). An additional contributing factor, but less likely, may be the reduction of Ir(IV) to Ir(III) due to low chloride concentration. On the other hand, the decrease in extraction at higher acidities is due to a shift of the ion-pair extraction Reaction (5) to the left with an increasing concentration of chloride ions (10, 11):

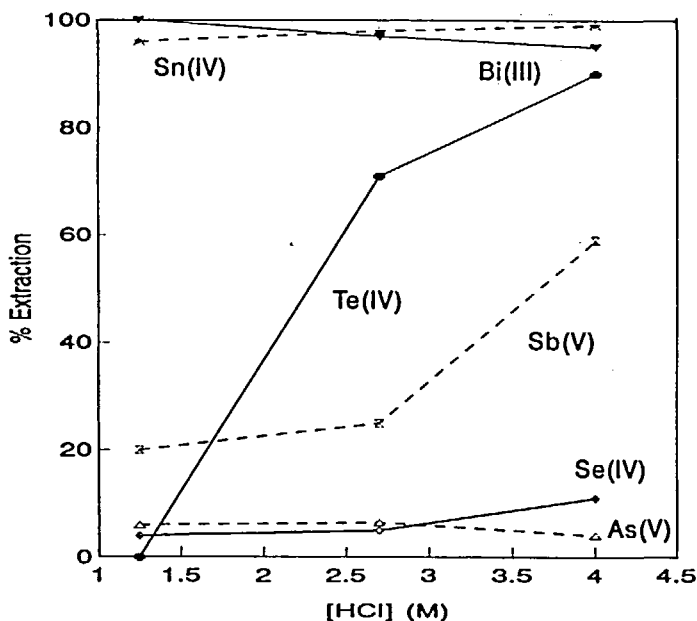


FIG. 3 The distribution of metalloids in 8-hydroxyquinoline extractants as a function of feed acidity (O: 5 v/o TN 1911, 10 v/o isodecanol, Solvesso 150;  $[M]_{\text{initial}} = 1000 \pm 200$  ppm; single metal loading; A/O = 4; 3 minutes contact time) (data from Ref. 4).



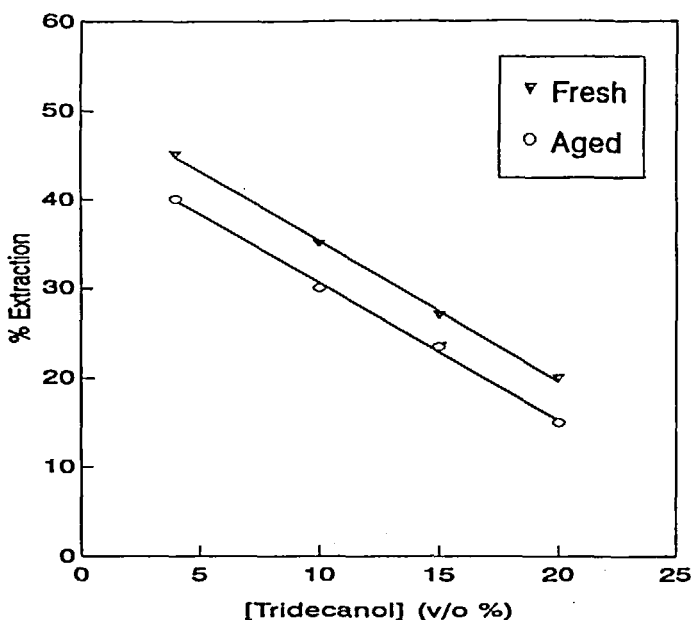
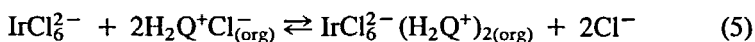


FIG. 4 Effect of alcohol concentration on extraction of Ir(IV) (O: 1 v/o Kelex 100  $\times$  v/o tridecanol, kerosene;  $[M]_{\text{initial}} = 50$  ppm, 3.1 M HCl; single metal loading; 3 minutes contact time; A/O = 1).



The effects of alcohol (Fig. 4) and extractant concentrations (data not shown) on the extraction of Ir(IV) were also investigated. While extraction increased with increased extractant concentration, as would be expected [the same happened with Rh(III)], the dramatic negative effect of alcohol was distinctly different from that (only a modest one) registered with the rhodium extraction system (7). This might have to do (in addition to interfacial factors) with possible catalysis of the reduction of Ir(IV) to Ir(III). Further work is needed to elaborate these phenomena.

### Permeation Behavior of Impurities through SLM

The permeation behavior of various impurities (single metal solutions of  $3.9 \times 10^{-3}$  M initial concentration) was investigated at the optimum conditions for Rh permeation that had been established earlier (2), i.e., support 0.45  $\mu\text{m}$  Gore-Tex; LM: 25 v/o Kelex 100; feed: 2.5 M HCl, strip: 0.1 HCl. The elements studied were found either not to extract at all or to permeate

(partially or completely) through the membrane and contaminate the receiving phase. On the other hand, some of the impurities were found to "accumulate" or form a precipitate on the membrane, resulting in blockage of the latter.

The percent extraction (defined as the percentage of metal concentration drop in the feed solution after 2 hours operation of the SLM), percent stripping (defined as the percentage of the metal initially in the feed solution that reports in the strip solution), and percent loading [defined as the percentage of the initial metal retained ("locked") on the membrane] results are presented in Figs. 5 to 7. Finally, the ratios of the rate of transport of each impurity (defined as the number of moles of metal reported to the receiving phase per  $\text{m}^2$  of membrane per second) in comparison to that of rhodium are summarized in Fig. 8. These ratios serve as a measure of the contamination of the Rh strip solution by each impurity element. The SLM behavior of all these elements is discussed next according to the following groupings: base metals, metalloids, and precious metals.

### Base Metals

Cobalt and nickel were found not to permeate to any measurable degree through the SLM, apparently because of their low tendency to form anionic complexes at 2.5 M HCl (see Table 1).

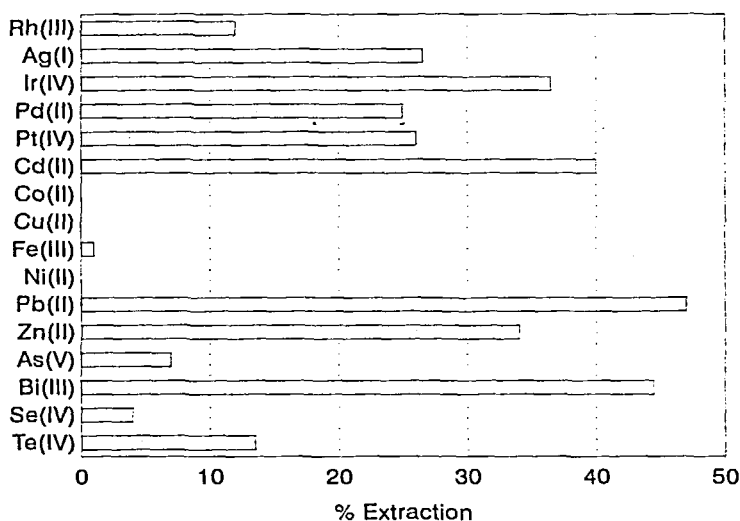


FIG. 5 Percent extraction of metals from the SLM feed solution Feed (Conditions: 2.5 M HCl,  $3.8 \times 10^{-3} \pm 6 \times 10^{-4}$  M of metal except  $6.55 \times 10^{-3}$  M for Cu(II) and  $2.8 \times 10^{-4}$  M for Ag(I); Strip: 0.1 M HCl; SLM: 25 v/o Kelex 100; 2 hours operation).

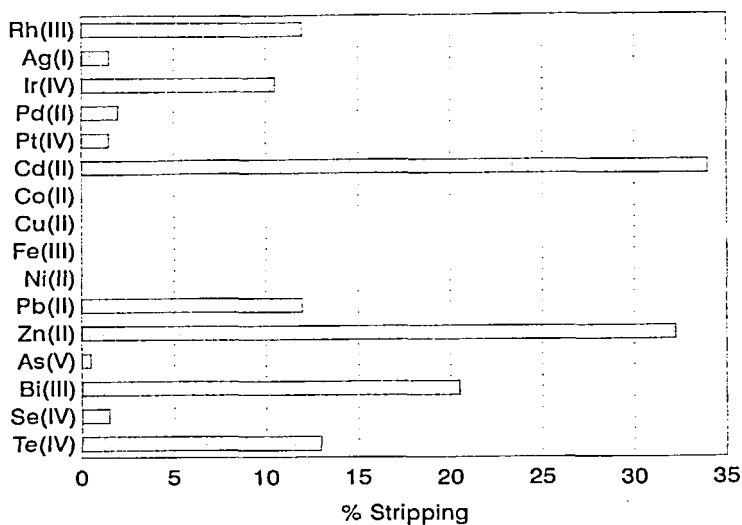


FIG. 6 Percent of metals reported to the SLM strip solution. (Conditions: same as in Fig. 5.)

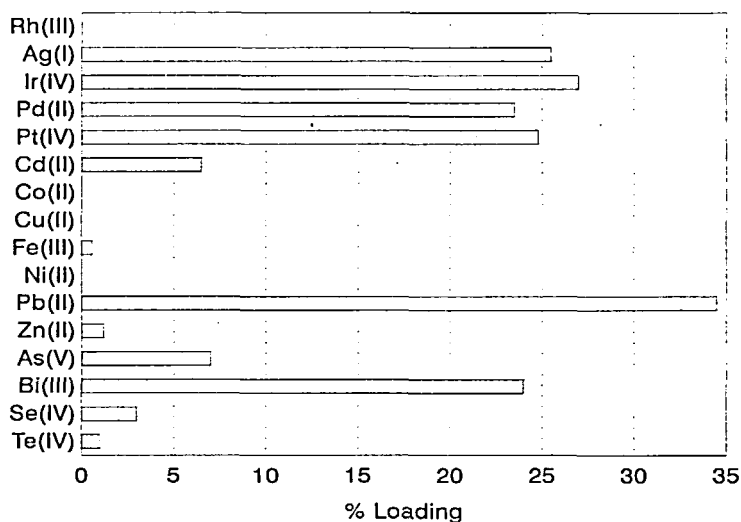


FIG. 7 Percent of metals reported (Loaded) on the SLM. (Conditions: same as in Fig. 5.)

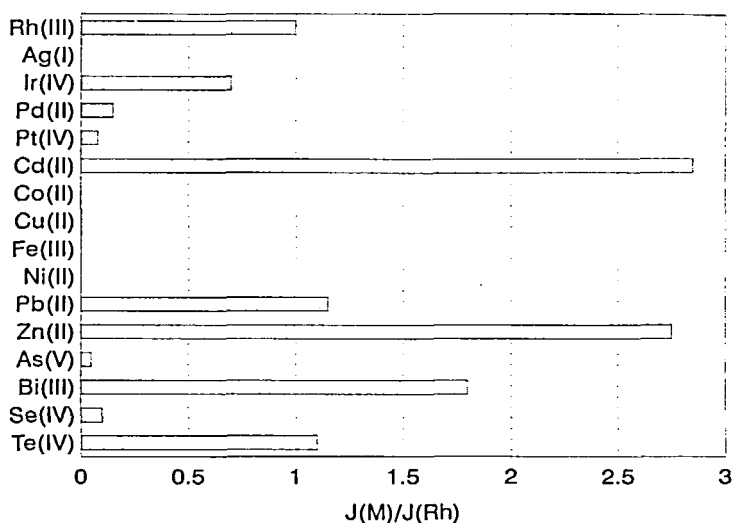


FIG. 8 Comparison of the net rate of transport (fraction of metal reporting to the receiving phase) of the various elements to that of Rh where  $J(Rh) = 1$  corresponds to 12% stripping in 2 hours or in absolute values is  $1.5 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ .

Cadmium and zinc were found to permeate substantially through the SLM and become extracted into the receiving phase (Fig. 5 and 6). It may be postulated that the extracted species are  $\text{CdCl}_3^-$  and  $\text{ZnCl}_3^- / \text{ZnCl}_4^{2-}$  according to the data of Table 1. Due to the favorable conditions in both feed and receiving phases, the metal anionic complexes form ion-pairs at the feed–SLM interface while at the strip–SLM interface the ion-pairs become dissociated and release the permeated metal species. The rate of transport for these metals is about two to three times faster than that for rhodium (Fig. 8).

Lead, similar to Cd(II) and Zn(II), was found to substantially permeate through the membrane (see Figs. 5 and 6), but this time a large amount of it was found to accumulate on the membrane (Fig. 7). The permeation of Pb(II) apparently involves the extraction of the anionic species  $\text{PbCl}_3^- / \text{PbCl}_4^{2-}$  (see Table 1) via ion-pair formation. On the other hand, the accumulation of Pb(II) on the membrane is attributed to the limited solubility of  $\text{PbCl}_2$ , especially at the membrane/strip interface where the chloride ion concentration is low.

The permeation of Cu(II) and Fe(III) at the fixed conditions tested was very low—about 100 times lower than that of rhodium. Copper(II) [and to a lesser extent Fe(III)] is known to be extracted with Kelex 100 via chelation from low acid solutions ( $<0.2 \text{ M HCl}$ ) and to be stripped with strong acid

solutions. Therefore, the applied conditions in the present SLM system (high acid as feed and low acid as strip) did not favor the extraction of copper. Nevertheless, the slowly extracted copper values [and Fe(III)] with time may lead to accumulation on the SLM (due to lack of stripping power to permit their transfer into the receiving phase), thus potentially resulting in membrane blockage.

### ***Metalloids***

Arsenic(V) and selenium(IV) exhibited very low rates of permeation, perhaps due to negligible dissociation of  $\text{H}_3\text{AsO}_4$  and  $\text{H}_2\text{SeO}_3$  acids.

On the other hand, Bi(III) and Te(IV) exhibited very high rates of permeations (Figs. 5 and 6). Similar to the previous cases, the mechanism of extraction is presumably through ion-pair formation between the protonated Kelex 100 molecules and the anionic  $\text{BiCl}_6^{3-}$  and  $\text{TeOCl}_3^-$  species (see Table 1). In addition to high permeation, Bi(III) exhibited a tendency for accumulation on the membrane (see Fig. 7). This may be partly due to hydrolysis of  $\text{BiCl}_{3(\text{aq})}$  to  $\text{BiOCl}_{(\text{s})}$  at the membrane/strip interface due to the low acidity of the latter phase (13).

### ***Precious Metals***

Due to low solubility of Ag(I) in chloride media, the permeation of this element was studied at much lower concentrations than the other metals,  $[\text{Ag}] = 2.8 \times 10^{-4}$  M. Silver(I) forms anionic chlorocomplexes (Table 1) which are extracted by 8-hydroxyquinoline reagents via ion-pair formation in conventional SX systems (Fig. 2). The same behavior was exhibited with the SLM system (Fig. 7). However, most of the extracted silver was found to accumulate on the membrane (Fig. 8) due to the apparent precipitation of  $\text{AgCl}$  at the membrane/strip interface.

The net rate of transport of palladium was low in comparison to that of rhodium (Fig. 8). However, what happened in this case was that the membrane became saturated with the metal (Fig. 7) due to good extraction (Fig. 5) and bad stripping (Fig. 6). This is so because palladium(II) is extracted via chelation (9) (see Reaction 2) from HCl solutions. Due to the low acid strength of the receiving phase, stripping was not effective, hence the accumulation of Pd(II) on the SLM. Replacement of the 0.1 M HCl strip phase with more concentrated HCl solutions did indeed allow for the uninhibited permeation of Pd(II) (Fig. 9).

Platinum, despite the favorable extraction and stripping conditions (see Reaction 3) (10), did not register a high permeation rate (Fig. 8) due to the formation of a precipitate on the membrane. Increasing the platinum concentration in the feed solution resulted in worsening the problem with the forma-

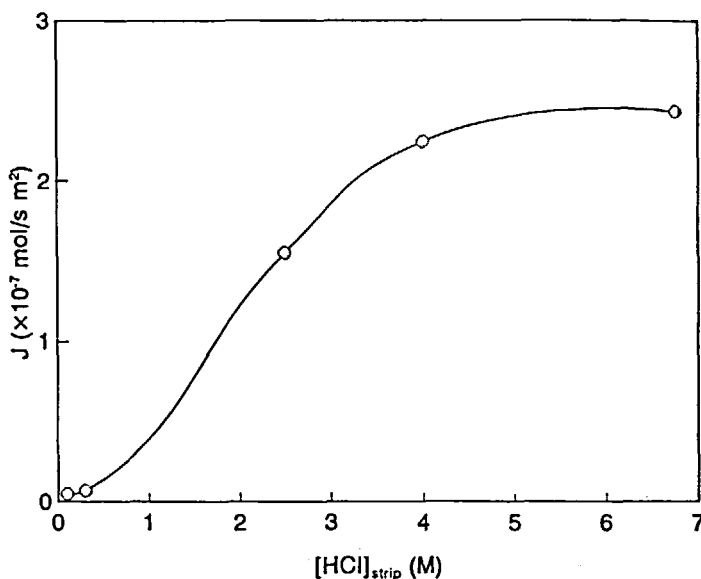


FIG. 9 Effect of strip acidity on rate of Pd(II) permeation. (Conditions: same as in Fig. 5 with exception of metal concentration:  $4.42 \times 10^{-4}$  M Pd.)

tion of a large amount of precipitate on the membrane that was clearly visible. The formation of such a precipitate was observed previously in conventional SX tests by Pouskouleli and Demopoulos (14). The use of other than Kelex 100 8-hydroxyquinoline derivatives, like Lix 26 (15) or TN 1911 (10, 16), is needed to overcome this problem. From the standpoint of Rh(III) recovery with a Kelex 100 SLM, however, Pt(IV) and Pd(II) are expected to cause problems due to membrane blockage.

The permeation behavior of Ir(IV) was found to be very similar to that of Rh(III) (2). Figures 10 and 11 show the rate of Ir(IV) permeation versus feed and strip acidity, respectively. As shown, the permeation rate exhibited a plateau at about 2.5 M HCl in the feed solution (Fig. 10) while the rate decreased sharply with increasing strip acidity (Fig. 11). Similar to Rh (2), the rate of iridium permeation is also a direct function of the metal feed concentration and linearly increases with the Ir concentration in the feed solution (Fig. 12). The observed SLM behavior of Ir(IV) is consistent with the postulated ion-pair extraction mechanism (Reaction 15). Similar behavior was reported by Fu and coworkers (6) for the  $\text{IrCl}_6^{2-}$ -HCl-trioctylamine SLM system. Hence, separation of Rh(III) from Ir(IV) is not possible with the Kelex 100 SLM system, and it may be extrapolated to be the same with

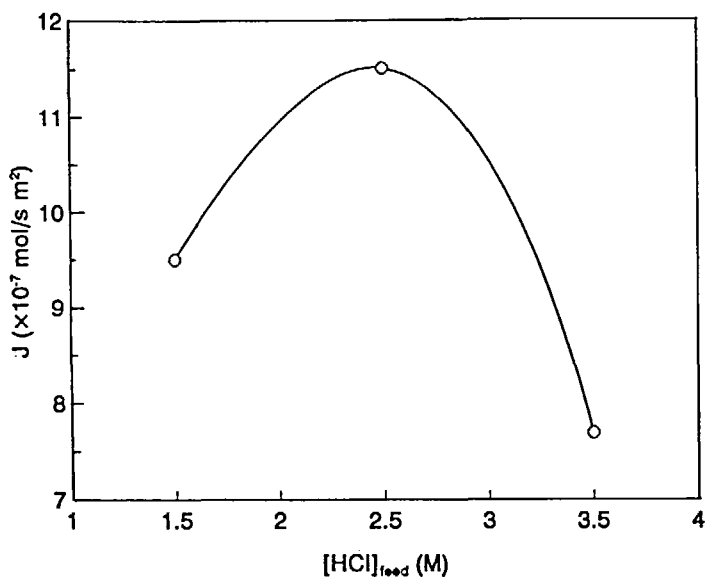


FIG. 10 Effect of feed acidity on rate of Ir(IV) permeation. (Conditions: Feed:  $1.04 \times 10^{-3}$  M Ir(IV); other conditions as in Fig. 5.)

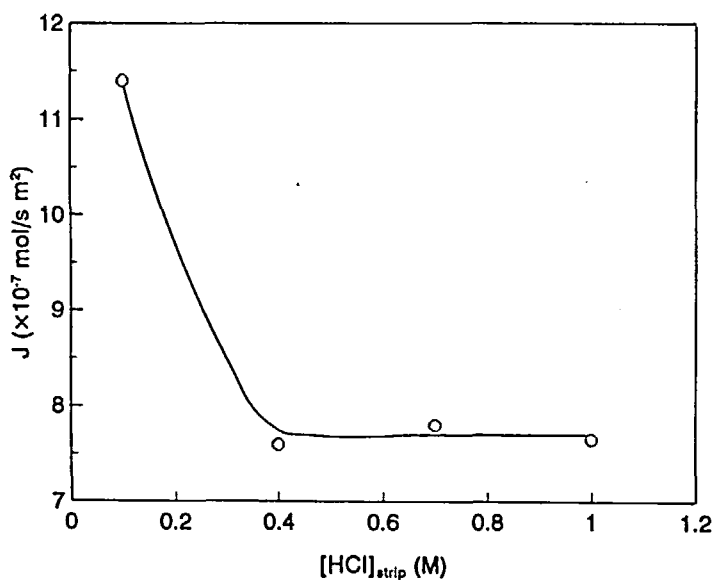


FIG. 11 Effect of strip acidity on rate of Ir(IV) permeation. (Conditions: same as in Fig. 10.)

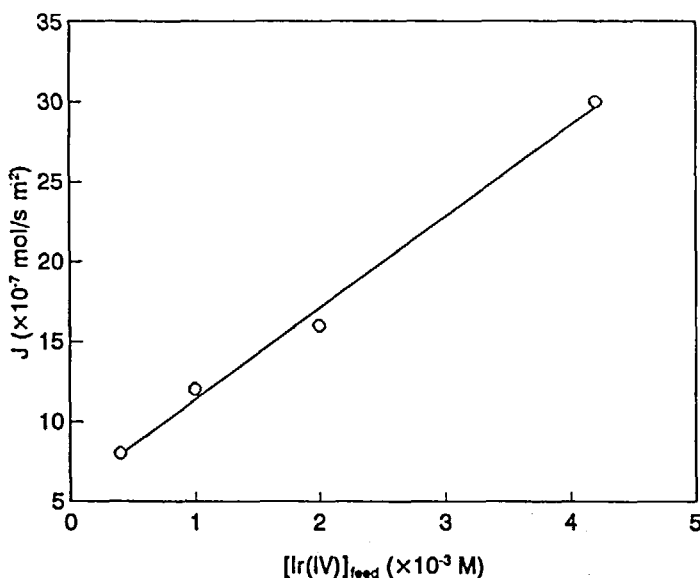


FIG. 12 Effect of feed Ir(IV) concentration on rate of Ir(IV) permeation. (Conditions: same as in Fig. 10.)

the trioctylamine system (6, 17). It remains to be seen if prior reduction of Ir(IV) to Ir(III) as practiced in the refining industry (3) can facilitate separation of the two metals. The origin of the observed accumulation of Ir(IV) on the membrane (Fig. 7) and the implications this may have on rhodium permeation was not clarified or studied further.

### Practical Implications

The various impurity elements tested in this work can be classified into three groups (Table 2) according to their particular behaviour vis-à-vis the Kelex 100 SLM system previously designed for rhodium(III) recovery from chloride solutions. In Group 1 the elements that are expected to be the least extracted or to interfere with the operation of the SLM system are listed. In Group 2 the elements which end-up loading up partially or completely on the membrane are listed. These elements either form unstrippable complexes or precipitates and block the membrane. In Group 3 the elements that permeate considerably through the SLM and reach a significant level in the receiving phase are listed. These elements are expected to follow rhodium and hence to lower the purity of the final rhodium product.



TABLE 2  
Classification of Impurity Elements According to Their Permeation Behavior through a  
Kelex 100 SLM Designed for Rhodium Separation

| $M_{aq}$ | Group 1 <sup>a</sup> | Group 2 <sup>b</sup> | Group 3 <sup>c</sup> | Comments   |
|----------|----------------------|----------------------|----------------------|--|
| Fe(III)  | X                    |                      |                      | Potential for long-term<br>"poisoning" of the membrane |
| Cu(II)   | X                    |                      |                      |  |
| Ni(II)   | X                    |                      |                      |  |
| Zn(II)   |                      |                      | X                    | Formation of PbCl <sub>2</sub> precipitate             |
| Pb(II)   |                      | X                    | X                    |  |
| Co(II)   | X                    |                      |                      |  |
| Cd(II)   |                      |                      | X                    |  |
| As(V)    | X                    |                      |                      |  |
| Bi(III)  |                      | X                    | X                    |  |
| Se(IV)   | X                    |                      |                      |  |
| Te(IV)   |                      |                      | X                    |  |
| Ag(I)    |                      | X                    |                      | AgCl precipitate on the<br>membrane                    |
| Pt(IV)   |                      | X                    |                      | Pt(IV)-Kelex 100 complex<br>insoluble                  |
| Pd(II)   |                      | X                    |                      | Pd-Kelex chelate forms                                 |
| Ir(IV)   |                      | X?                   | X                    | Origin of Ir(IV) accumulation<br>not verified          |

<sup>a</sup> Impurities with little or nil permeation capacity.

<sup>b</sup> Impurities which accumulate on the membrane or form precipitates.

<sup>c</sup> Impurities which permeate through the membrane at a rate comparable or higher than that of rhodium.

These results demonstrate the serious limitations of supported liquid membranes as effective separation means for metals from multicomponent solutions such as the PGM refining liquors. Hence there is a need for researchers to consider more than one metal in their studies on one hand and to pursue novel engineering approaches for the design and operation of SLM systems on the other.

The impurities of Group 3 may in principle be rejected via the interfacing of a downstream solvent extraction system incorporating scrubbing to effect the separation of rhodium. Such an interfacing of a SX system to a SLM system was proposed in a recent paper in connection to the SLM separation of Rh(III) with Kelex 100 (17). The SX system involved the use of trioctylamine to extract rhodium and acid from the SLM receiving phase. Such a system will not be able to separate rhodium from irridium.

As far as the present system is concerned, the following suggestions are made to remove the problems imposed by the impurities of Groups 2 and 3.

For the impurities of Group 2, modified SLM contactors will have to be employed or designed such as liquid film pertraction (18) or 3-stream (feed/organic/strip) (as opposed to two streams) solvent extraction with immobilized interfaces (19).

## CONCLUSIONS

The permeation behavior of a number of potential impurity elements in an SLM system (Kelex 100) previously proposed for the separation of rhodium was studied, and the impurities were classified into three groups. Group 1 impurities [Ni(II), Co(II), As(V), Se(IV), Cu(II), and Fe(III)] do not permeate through the SLM, hence impose no problem on rhodium separation. Group 2 impurities [Pt(IV), Pd(II), Ag(I), Pb(II), and Bi(III)] do not permeate through the SLM but introduce serious problems in the operation of SLM such as fouling and blocking. Group 3 impurities [Zn(II), Pb(II), Cd(II), Bi(III), Te(IV), and Ir(IV)] permeate through the SLM along with Rh and accumulate in the SLM receiving phase. From the latter, the permeation of Ir(IV) occurs at comparable rates to that of Rh(III). That makes a Kelex 100-based SLM unsuitable as a means for separating Rh and Ir. On the other hand, this work revealed the great limitations of the SLM method when it comes to the selective extraction of metals from multicomponent aqueous feed solutions as is the case for industrial PGM refining liquors.

## ACKNOWLEDGMENTS

Financial support received by S.N.A. from the Ministry of Culture and Higher Education of Iran and by M.R. from the Ministry of Science and Culture of Spain is gratefully acknowledged. This research has been partially supported through a Natural Sciences and Engineering Research Council of Canada research grant.

## REFERENCES

1. G. P. Demopoulos, *CIM Bull.*, 82(923), 165 (1989).
2. S. N. Ashrafizadeh and G. P. Demopoulos, *Sep. Sci. Technol.*, 31(7), 895 (1996).
3. R. A. Grant, R. F. Burnham, and S. Collard, "The High Efficiency Separation of Iridium from Rhodium by Solvent Extraction Using a Mono *N*-Substituted Amide, in *Solvent Extraction 1990, Part A* (Proceedings ISEC'90, T. Sekine, Ed.), Elsevier, Amsterdam, 1992, pp. 961-966.
4. V. H. Aprahamian and G. P. Demopoulos, *Miner. Processing Extract. Metall. Rev.*, 14, 143 (1995).
5. V. H. Aprahamian, G. P. Demopoulos, and G. B. Harris, "The Behaviour of Impurities during the Solvent Extraction of Platinum Metals with TN 1911," in *Precious Metals 1991* (L. Manziak, Ed.), IPMI, Allentown, PA, 1991, pp. 143-157.

6. J. Fu, S. Nakamura, and K. Akiba, *Sep. Sci. Technol.*, **30**(20), 3821 (1995).
7. S. N. Ashrafizadeh and G. P. Demopoulos, *J. Colloid Interface Sci.*, **173**, 448 (1995).
8. B. Côté and G. P. Demopoulos, *Solv. Extr. Ion Exch.*, **11**, 349 (1993).
9. B. Côté and G. P. Demopoulos, *Ibid.*, **12**(2), 393 (1994).
10. B. Côté and G. P. Demopoulos, *Ibid.*, **12**(3), 517 (1994).
11. E. Benguerel, G. P. Demopoulos, G. Côte, and D. Bauer, *Ibid.*, **12**(3), 497 (1994).
12. D. A. Fine, *J. Inorg. Nucl. Chem.*, **32**, 2731 (1970).
13. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, NY, 1980, p. 448.
14. G. Pouskoupleli and G. P. Demopoulos, "Direct Recovery of Precious Metals by Integration of Solvent Extraction and Hydrogen Reduction Techniques," in *Precious Metals 1984* (T. P. Mohide, Ed.), IPMI, Allentown, PA, 1985, pp. 189–207.
15. G. Pouskoupleli, S. Kelebek, G. P. Demopoulos, "Recovery and Separation of Platinum and Palladium by Co-extraction and Selective Stripping," in *Separation Processes in Hydrometallurgy* (G.A. Davies, Ed.), Ellis Horwood, Chichester, UK, 1987, pp. 174–188.
16. G. P. Demopoulos, N. Kuyucak, D. L. Gefvert, and M. H. Richler, "TN 1911: A New Hydroxyquinoline Extractant for the Refining of Platinum Metals," in *Precious Metals 1989* (B. Harris, Ed.), IPMI, Allentown, PA, 1989, pp. 201–215.
17. S. N. Ashrafizadeh and G. P. Demopoulos, *J. Chem. Tech. Biotechnol.*, **67**, 367 (1996).
18. L. Boyadzhiev, *Sep. Sci. Technol.*, **25**(3), 187 (1990).
19. R. Prasad, A. Kiani, R. R. Bhavé, and K. K. Sirkar, *J. Membr. Sci.*, **26**, 79 (1986).

*Received by editor June 20, 1997*

*Revision received September 1997*