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Extraction of Rhodium Chlorocomplexes and Acid through a Supported Liquid Membrane of Kelex 100

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ABSTRACT

The supported liquid membrane (SLM) technique was employed to effect the separation of Rh chlorocomplexes from hydrochloric acid solutions. The liquid membrane consisted of an alkylated 8-hydroxyquinoline extractant (Kelex 100), tridecanol, and kerosene. The nonaquated Rh complexes were transported through the membrane upon ion-pair formation with protonated Kelex 100 molecules. The ion-pair was then dissociated at the strip side of the membrane, releasing the Rh values. The main driving force for this transport process was the acid activity gradient across the membrane. The permeation of acid and water, which were cotransported with the Rh complexes, was partially prevented upon addition of NaCl to the strip phase. However, the accumulation of Cl^- ions in the strip phase, in turn, slowed down the extraction of Rh. Optimum Rh extraction performance was obtained when a feed of 2.5 M HCl and a strip solution of pH 1 were used. Under these conditions the membrane was found to be very stable for at least a period of 72 hours (maximum period tested) while the rate of extraction was found to be 2.8×10^{-6} mol·s^{-1}·m^{-2}.

Key Words. Rhodium; Liquid membrane; Kelex 100; Solvent extraction

INTRODUCTION

The separation and purification of rhodium (Rh) is among the most difficult areas in precious metal refining due to the complex chemistry of

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Rh in chloride-based solutions (1). At McGill University, research has been conducted over the past decade in the area of solvent extraction (SX) of precious metals using 8-hydroxyquinoline derivatives (R-HQ). A part of this continuing research has focused on the factors which hamper the extraction of Rh(III) via conventional solvent extraction contacting (2). Thus Benguerel et al. (3) determined that the extraction of Rh(III) from acidic chloride solutions with alkylated 8-hydroxyquinoline extractants (R-HQ), like the commercially available extractant Kelex 100, occurs to a limited degree ($D = 0.5$) via an ion-pair formation mechanism involving $RhCl_6^{3-}$ and the protonated extractant. However, the aquated Rh(III) chlorocomplexes like $RhCl_5(H_2O)^{2-}$, which is the dominant one in aged aqueous solutions (2), were found not to respond to conventional liquid–liquid extraction. In a recently published detailed study (4) of the interfacial chemistry of the Rh(III)–HCl–Kelex 100 system, the present authors demonstrated that W/O microemulsions form inside the organic phase and "catalyze" the aquation of Rh(III), thus making nonfeasible the development of a conventional solvent extraction system for Rh(III) (i.e., D always remains low, <1). Therefore, alternative approaches have to be found to effect its separation. One possible alternative is to use a liquid membrane technique to permit the continuous transfer of the extractable $RhCl_6^{3-}$ complex from the feed aqueous phase to a receiving phase through an organic membrane of Kelex 100. Of course, this approach implies that upon withdrawal of the nonaquated Rh species the aqueous feed will undergo reequilibration, thus producing more of the nonaquated complexes by shifting the aquation–anation reaction toward anation.

It was indeed the object of the present work to investigate the feasibility and viability of the transport of Rh(III) complexes through a liquid membrane containing Kelex 100 in a kerosene medium. To this end, first, various combinations of available surfactants (5, 6) were applied in order to obtain a suitable emulsion liquid membrane (ELM) system. The results, which are not reported here, consistently showed a lack of satisfactory stability. By contrast, the supported liquid membrane (SLM) system behaved in a very stable and reproducible manner, thus justifying continuation of the investigation which led to this publication. It should be noted, though, that in general the SLM system suffers from having a limited interfacial area in comparison to the ELM system, and consequently a rather low transfer rate (7). However, the advantages of long-term stability, operational simplicity, low solvent and energy consumption, and easy scale-up calculations (8) make it a very promising separation system, in particular in situations where conventional liquid–liquid extraction fails, as is the case of Rh(III). It must be added, nevertheless, that the shortcoming of low interfacial area has been considerably improved in recent years by applying hollow fiber modules as the support. Recent manufacturing developments on this issue along with various technical considerations are discussed in detail by Ho and Sirkar (9).

EXPERIMENTAL

Chemicals

Kelex 100, supplied by WITCO Co., was used as extractant. This reagent has an average molecular weight of 299 and a purity and density in the vicinity of 85% and 1 g/mL, respectively. A more detailed description of this reagent can be found in Reference 10. Kerosene obtained from Fisher Scientific was used as diluent and tridecanol (Harcros Chemicals) was added as phase modifier. The relative percent composition, on a volume basis, of the organic solutions were x, x, and $(100 - 2x)$ v/o, mostly 25, 25, and 50 v/o of Kelex 100, tridecanol, and kerosene, respectively. (The 25, 25 v/o composition corresponds to approximately 0.70 M extractant and 1.0 M tridecanol solution.) The Rh aqueous solutions were prepared using sodium hexachlororhodate(III) hydrate ($Na_3RhCl_6 \cdot xH_2O$) obtained from Aldrich Chemicals. NaOH, HCl, NaCl, and $LaCl_3$, all of reagent grade, were obtained from Canlab. Distilled water, which was deionized to a minimum resistance of 1 MΩ/cm, was used for preparation of aqueous solutions.

SLM Apparatus

SLM experiments were carried out in a two-compartment cell schematically shown in Fig. 1. The apparatus was composed of an inner Plexiglass

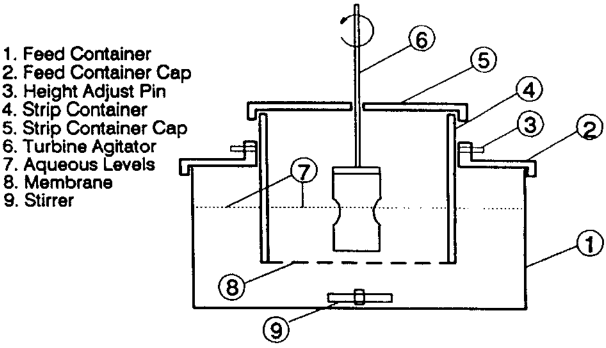

FIG. 1 SLM apparatus.

vessel held vertically in a Pyrex crystallizing dish (125 × 65) as the outer container. A membrane with an effective surface area of 44 cm^2 (7.5 cm in diameter) separated the two parts and was sealed with a Viton (acid-resistant) gasket. Two structurally different hydrophobic microporous polymers [polytetrafluoroethylene (PTFE)], supplied by W. L. Gore & Associates under the commercial name of 4C5 Gore-Tex, were used as the membrane support. One of the polymer materials had a pore size of 0.45 μm, a thickness of 57 μm, and a porosity of 75.9%. The other had a pore size of 0.20 μm, a thickness of 20 μm, and a porosity of 66.8%. Agitation was provided by a magnetic stirrer for the feed and a cylindrical Teflon impeller for the strip solution. The latter had been used previously (11) in a solvent extraction kinetic study as a part of a rotating diffusion cell (RDC).

Procedure

The SLMs were prepared by soaking the polymeric support for 10–15 hours in the liquid membrane solution, then letting it drip for a few minutes before placing it in the cell. The liquid membrane solution containing the carrier (Kelex 100) was treated prior to its use through a procedure that involved contacting it with an equal volume of 4 M HCl aqueous solution for 5 minutes to wash out all of the acid-soluble organic impurities. The acidified organic phase was then subjected to four 5-minute contacts with distilled water at an aqueous-to-organic volume ratio (A/O) of 1, which removed all of the organic-phase acidity. The feed and strip containers were filled by previously prepared feed and strip solutions according to the required specifications, always at a volume ratio of 200 to 20 mL, respectively. Except for the experiments devoted to measuring the extraction of water, the duration of the large majority of tests was 1 hour. For the case of water-extraction experiments, due to the volumetric measurement of the strip phase, it was required to run the experiments for a longer period of time to achieve higher quantities of extracted water and thus decrease the error introduced in the volumetric determination. For this reason a period of 6 hours was chosen for that set of experiments.

The experiments were conducted at constant feed and strip acidity. This was almost satisfied for the feed which contained a high volume and a relatively high acid concentration. However, for the strip solution, the coextracted acid caused the pH of the strip solution (pre-fixed at pH 1) to change. Therefore, a solution of 10 M NaOH was used to neutralize the extracted acid and maintain the pH at 1. This was done every 30 minutes. In this way it was assured that the variation in the pH of the strip solution was almost negligible. For the cases where an accurate measurement of the volume was necessary, the amount of the added NaOH was taken into account. For the Rh content analysis, aliquots of 1 mL were taken from the feed and strip solutions before and after each run. Experiments were carried out at room temperature (23 ± 2°C).

Analysis

The acidity of the strip solutions was determined through a standard acid-base titration. Titrations were performed manually using standard 0.1 M NaOH as the titrant and phenolphthalein as the end-point indicator. pH measurements were performed with a PHM 84 Research pH meter from Radiometer Copenhagen in combination with an ORION ROSS pH electrode. The fast response, stability, accuracy, and reproducibility were of primary importance in performing pH measurements in the region of pH 1–2, and the precision was ±0.01 in that pH scale. The Rh concentrations in the feed and strip solutions were determined by atomic absorption spectroscopy on an spectrophotometer Model 357 from Instrumentation Laboratory Inc. All the samples and the AA standards were diluted to the linear region using 1.4 M HCl. A drop of 100 g/L $LaCl_3$ was added to all samples and standards to minimize the effect of sodium on the Rh determinations. A nitrous oxide-acetylene flame was used rather than the more common air-acetylene flame (12).

The rates of water, acid, and Rh transport through the membrane were determined for the initial stage of the transport process and expressed as moles of transported species per second per unit area (geometric) of the SLM (i.e., $mol \cdot s^{-1} \cdot m^{-2}$). The rate of Rh extraction was determined by monitoring the change in Rh concentration of both aqueous phases, i.e., feed and strip solutions. The reported rate is an average of the two values obtained. The calculations take into account volume changes due to the transport of water. SLM extraction experiments were performed more than once, and reproducibility was always within ±5%.

RESULTS AND DISCUSSION

Membrane Selection

As has been published previously (3, 4), Kelex 100 tends to extract a certain fraction of Rh(III) (the nonaquated complex $RhCl_6^{3-}$) in a reversible manner from chloride solutions ($D < 0.5$) via protonation (step 1) and ion-pair formation (step 2):

Step 1: Protonation

$$\overline{R{-}HQ} + H^+ + Cl^- \leftrightarrow \overline{R{-}H_2Q^+Cl^-} \qquad (1)$$

Step 2: Ion-pair formation

$$RhCl_6^{3-} + 3\overline{R{-}H_2Q^+Cl^-} \leftrightarrow \overline{RhCl_6^{3-}(R{-}H_2Q^+)_3} + 3Cl^- \qquad (2)$$

The extraction reaction (Eq. 2) can be easily reversed upon contact of the loaded Kelex 100 with a dilute acid solution of pH ≥ 1. It was thought, therefore, that upon combining extraction and stripping in the form of an SLM system, quantitative transfer of rhodium from an impure dilute solution into a purified concentrated strip solution could be achieved. This was thought so because the aquation–anation reaction of Rh(III) (Reaction 3) is relatively fast (4):

$$RhCl_6^{3-} + H_2O \leftrightarrow RhCl_5(H_2O)^{2-} + Cl^- \qquad (3)$$

To this end a Kelex 100-based SLM system was designed and tested. During the first stage of the work the concentration of Kelex 100 (in mixture with tridecanol and kerosene), the type of support, and the agitation regime were selected by measuring the acid permeation rates. During this part of the work the stability of the membrane was studied as well.

Agitation

The effect of agitation on the rate of acid extraction was first examined through a set of experiments using a 0.45-μm Gore-Tex membrane as support and a LM of 25 v/o of Kelex 100. The results, which are summarized in Table 1, exhibit an increase in the rate of acid extraction upon increasing the agitation speed from the low to the intermediate agitation range. However, an almost negligible increase was observed upon any further increase of the agitation speed. Moreover, it can be seen that an increase in the agitation speed of the strip side has a more pronounced effect than that of the feed side. In other words, the rate of acid extraction

TABLE 1
Effect of Agitation Speed on Rate of Acid Permeation[a]

Feed agitation speed (rpm)	Strip agitation speed (rpm)	J_{acid} (mol/s·m^2)
50	50	1.68×10^{-4}
100	100	1.85×10^{-4}
150	150	1.90×10^{-4}
50	100	1.83×10^{-4}
100	50	1.71×10^{-4}

[a] Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 2.5 M HCl. Strip: 20 mL (initial) water/HCl at pH 1.

seems to be controlled by the strip-phase boundary layer resistance rather than that of the feed phase. As a precaution against loss of membrane stability, the intermediate range of agitation speed (100 rpm) was chosen eventually for the rest of the experimental work.

Support Structure

To investigate the effect of support pore size on the performance of the SLM system, two Gore-Tex polymer sheets were tested at different LM concentrations of Kelex 100. The results from these tests, summarized in Table 2, show identical performance of the two supports (0.2 and 0.45 μm pore size). It must be mentioned here that the membrane with the smaller pore size had a smaller thickness and this perhaps had compensated any decrease in permeation rate as a result of the pore size. For the subsequent series of tests, the 0.45 μm pore size membrane was retained and used since it possesses a higher durability and thus a higher mechanical strength.

Kelex 100 Concentration

The rate of acid extraction was found to increase with Kelex 100 concentration and eventually to reach a plateau at about 0.7 M (25 v/o) Kelex 100 (Fig. 2). This concentration of Kelex 100 was chosen to conduct the remaining SLM experiments. Higher concentrations apparently result in a very viscous liquid membrane which imposes resistance to the transport process. Another interesting observation which is worthwhile to mention is the behavior of the SLM when LM does not contain the carrier (i.e., zero v/o Kelex 100). In this case the support was soaked in a pure kerosene solution. The impermeability of the SLM shows that even if all the Kelex

TABLE 2
Effect of Support Pore Size on Rate of Acid Permeation[a]

Kelex 100 (v/o)	J_{acid} (mol/s·m^2)	
	0.2 μm pore size	0.45 μm pore size
15	1.392×10^{-4}	1.396×10^{-4}
20	1.790×10^{-4}	1.786×10^{-4}
25	1.831×10^{-4}	1.850×10^{-4}

[a] Support: Gore-Tex. LM: x v/o Kelex 100, x v/o tridecanol, $(100 - 2x)$ v/o kerosene. Feed: 200 mL 2.5 M HCl. Strip: 20 mL (initial) water/HCl at pH 1.

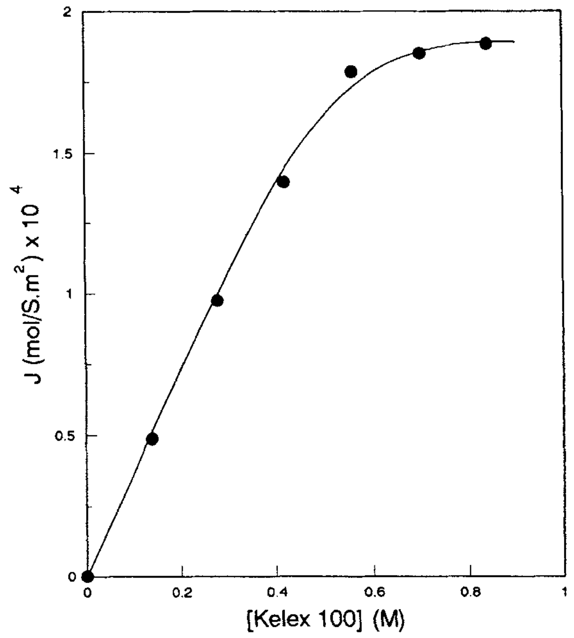

FIG. 2 Effect of carrier concentration on rate of acid permeation. Support: 0.45 μm Gore-Tex. LM: x v/o Kelex 100, x v/o tridecanol, (100 − 2x) v/o kerosene. Feed: 200 mL 2.5 M HCl. Strip: 20 mL water/HCl at pH 1.

100 contents are lost, the support is capable of partitioning the two aqueous phases due to its inherent hydrophobicity, and thus diffusion in an unwanted direction can be prevented.

SLM Stability

To examine the stability of the SLM system and also to determine whether its performance is reproducible under the fixed experimental conditions (i.e., 0.45 μm Gore-Tex, 25 v/o Kelex 100, 100 rpm agitation speed), two sets of experiments were conducted in which the change of Rh concentration in two similar feed solutions was measured as a function of time. In the first experiment the SLM was periodically (every 3 hours) replaced with a fresh one, while in the second experiment the same SLM was used throughout its whole duration. The results, which are shown in Fig. 3, indicate a very similar trend for both systems, an observation which suggests that the SLM remained stable throughout the whole duration of the test (70 hours). The same figure serves to demonstrate the separation

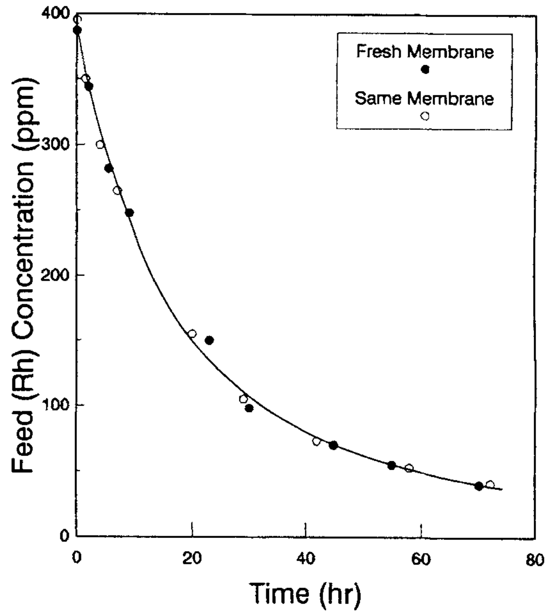

FIG. 3 Stability of SLM vs operation time. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 2.5 M HCl, 400 ppm Rh, 2-week aged. Strip: 20 mL 1.5 M NaCl at pH 1.

capability of the present SLM process as it achieves more than 90% Rh extraction and subsequent concentration of the extracted Rh values in the low volume (feed volume/strip volume = 10) strip solution.

Permeation of Acid and Water through SLM

Acid Permeation

As discussed previously (4), acid (HCl) and water are coextracted along with Rh(III) with Kelex 100. Acid is extracted via the protonation of Kelex 100 (Eq. 1) while water is extracted through hydration at the low acid region and through the formation of W/O microemulsions in the loaded organic phase at elevated acid concentrations (≥0.7 M HCl) (4). Both of these coextracted components have negative consequences on the SLM process of Rh. Permeation of acid causes two kind of problems. First, it increases the acidity of the strip phase and thus causes a decrease in the HCl concentration gradient. This results in a loss of driving force and stoppage of metal transfer unless the extracted acid is neutralized. Second, it produces a buildup of chloride ion concentration in the strip phase. As a result, this further complicates the Rh extraction process, as will be shown below.

In Fig. 4 the rate of acid extraction is plotted against feed acidity. The rate increases sharply with the feed acidity up to about 2 M HCl, followed by a plateau region up to 4 M HCl. Beyond that acidity, the rate again increases with feed acidity. This behavior is quite similar to that of the solvent extraction process (4) and it might be interpreted as follows. The sharp increase at lower acidities is due to an increase in the protonation of the extractant molecules (Eq. 1). However, since the protonation of the extractant is supposed to be completed at 2.5–3 M HCl (4, 13), any further increase in the feed acidity at the plateau region does not significantly promote the extraction. At higher acidities the mechanism of acid extraction changes and W/O microemulsions are believed to be responsible for this extra acid uptake (4). The effect of the strip phase acid concentration on the rate of acid extraction is depicted in Fig. 5. As shown, the

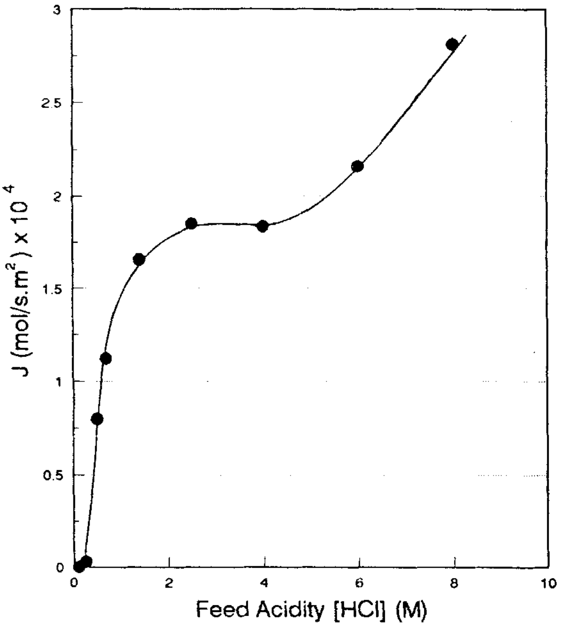

FIG. 4 Effect of feed acidity on rate of acid permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL different [HCl]. Strip: 20 mL water/HCl at pH 1.

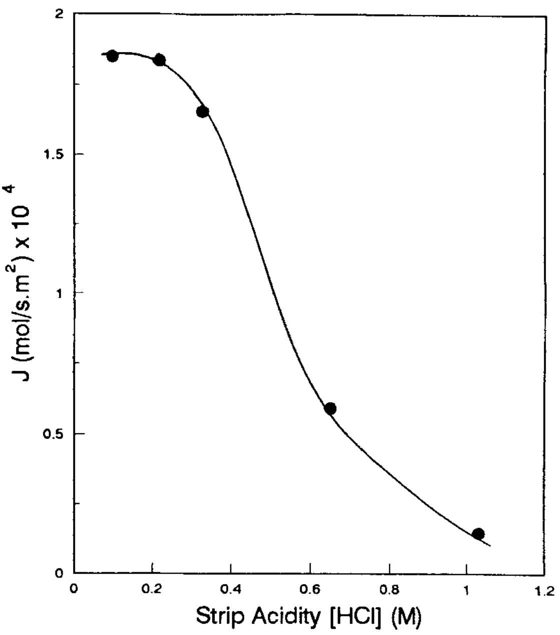

FIG. 5 Effect of strip acidity on rate of acid permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 2.5 M HCl. Strip: 20 mL different [HCl].

rate of extraction is not sensitive to small increases in the strip acidity (0.1 to 0.2 M HCl). However, at higher acidities it sharply decreases with the acidity of the strip phase.

One of the variables that had to be considered in the SLM system under investigation was the amount of salt in the feed and strip solutions. The salt (NaCl) is accumulated in the strip solution as a result of the neutralization of the coextracted acid with NaOH. On the other hand, NaCl may be present in the feed solution either as a component of the original industrial solution or again as a result of the adjustment of acid with NaOH. The effect of NaCl accumulation in the strip solution on acid extraction is shown in Fig. 6. It can be clearly seen that as the salinity of the strip solution increases, the rate of acid extraction drops drastically. This negative effect of strip solution salinity on acid extraction is attributed to the effect [Cl$^-$] has on the activity of HCl (α_{HCl})* as well as on the individual

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* The activity of HCl is defined as $\alpha_{HCl} = \alpha^2_{\pm(HCl)} = \alpha_{H^+}\alpha_{Cl^-}$, where $\alpha_{\pm(HCl)}$ is the mean activity and α_{H^+} and α_{Cl^-} are the individual ion activities.

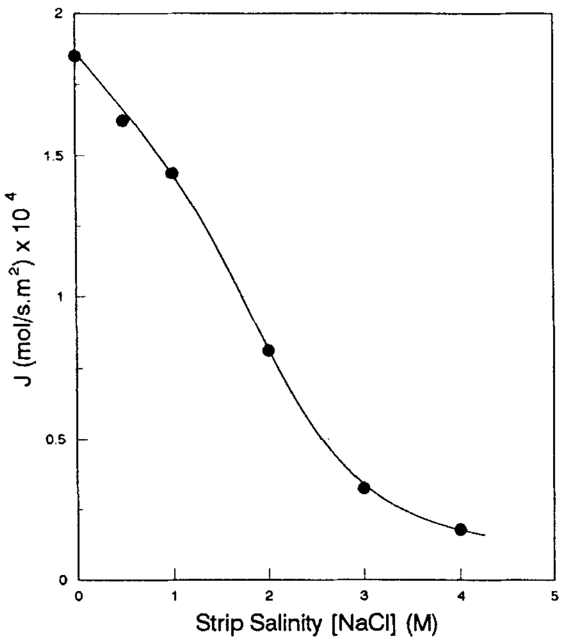

FIG. 6 Effect of strip salinity on rate of acid permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 2.5 M HCl. Strip: 20 mL water/HCl/NaCl at pH 1.

H^+ ion activity (14). As a result of the increasing α_{HCl} of the strip solution with increasing [NaCl], the acid activity gradient decreases or equivalently the driving force for acid extraction decreases. For exactly the same reasons an increase in the salinity of the feed solution is observed to increase the rate of acid extraction, as can be seen in Fig. 7.

To further demonstrate the significance of acid activity (as opposed to simple acid concentration) as the true driving force for the transport of acid across the membrane, the following evidence is presented. Figure 8 depicts the transfer of acid from a feed solution with low acid concentration (0.7 M HCl/3.3 M NaCl; the acid concentration was kept constant throughout the whole experiment) toward a strip solution whose acidity progressively increased from 0.1 to 2.2 M, at which point equilibrium was reached. In other words, in this case acid was transferred from the feed phase to the receiving phase against the apparent acid concentration gradient. This is so because a positive acid activity ($\alpha_{HCl} = \alpha_{H^+}\alpha_{Cl^-}$) gradient was operating due to the high salt (3.3 M NaCl) concentration of the

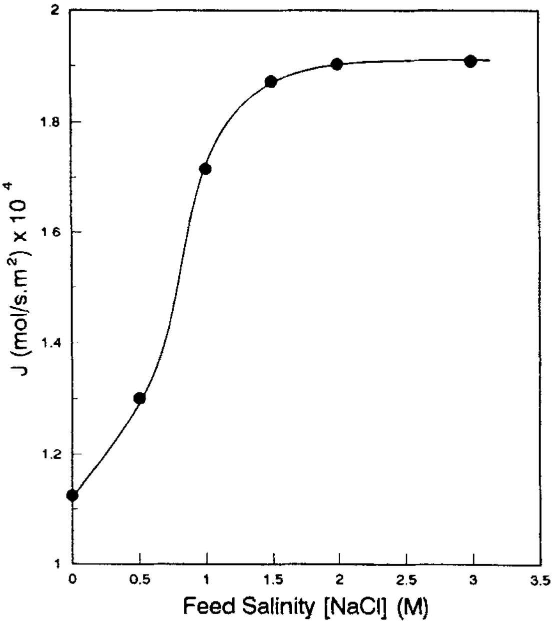

FIG. 7 Effect of feed salinity on rate of acid permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 0.7 M HCl and different [NaCl]. Strip: 20 mL water/HCl at pH 1.

feed phase. This was confirmed by estimating the activities of acid at the equilibrium point (0.7 M HCl/3.3 M NaCl feed vs 2.2 M HCl strip). The estimated activity values are given in Table 3.

Water Permeation

The permeation of water through the membrane imposes problems on obtaining a concentrated Rh strip solution due to the dilution brought about. It has been shown in a previous publication that in a conventional solvent extraction system Kelex 100 extracts water along with acid (4). The coextraction of water with acid has been confirmed in the present SLM system as well. Some measured water transport rates* are given along with the corresponding acid transport rates in Table 4. The permea-

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* It must be stated here that due to difficulties with the measurement of water transport rates, the reported data should be viewed as approximate with a relative rather than absolute value.

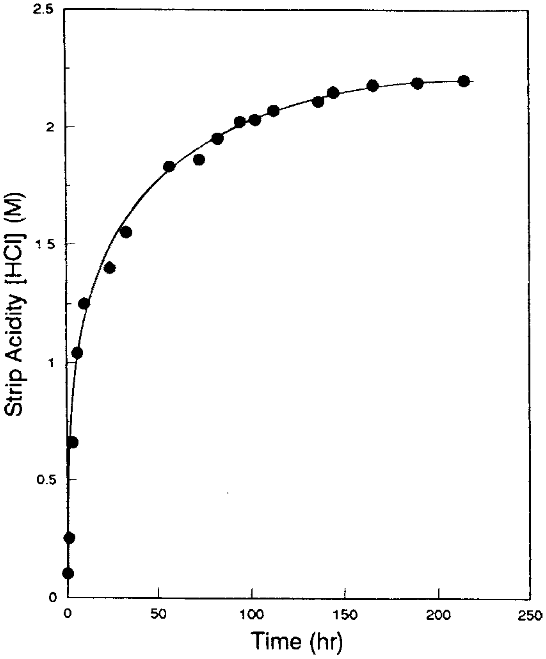

FIG. 8 Build-up of strip acid concentration with time. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 0.7 M HCl and 3.3 M NaCl. Strip: 20 mL water/HCl.

TABLE 3
Estimations of Acid Activities

Feed, 0.7 M HCl and 3.3 M NaCl	Strip	
	[HCl] (M)	$\alpha_{H^+} \times \alpha_{Cl^-}$
α_{H^+} = 1.867[b]	1.0	0.80[a]
α_{Cl^-} = 3.633[b]	1.5	2.27[a]
$\alpha_{H^+} \times \alpha_{Cl^-}$ = 6.816[b]	2	5.15[a]
	2.2	6.82[a]
	2.5	10.31[a]

[a] Tables 2 and 3, Ref. 14.
[b] Figures 7 and 8, Ref. 14.

TABLE 4
Rates of Water and Acid Permeation through SLM[a]

	Feed		Strip				
Expt.	HCl (M)	NaCl (M)	HCl (M)	NaCl (M)	J_{water} (mol/s·m^2)	J_{acid} (mol/s·m^2)	$J_{\text{water}}/J_{\text{acid}}$
1	0.7	0.0	0.1	0.0	1.30×10^{-4}	1.15×10^{-4}	1.13
2	0.7	3.0	0.1	0.0	1.38×10^{-4}	1.90×10^{-4}	0.73
3	0.7	0.0	0.1	0.5	1.35×10^{-4}	—	—
4	2.5	0.0	0.1	0.0	2.92×10^{-4}	1.85×10^{-4}	1.60
5	2.5	2.0	0.1	0.0	2.70×10^{-4}	—	—
6	2.5	0.0	0.1	2.0	3.20×10^{-4}	0.80×10^{-4}	4.00

[a] Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL different *M* HCl and NaCl. Strip: 20 mL (initial) at different *M* HCl and NaCl.

tion of water is seen to be low when the feed acidity is low (0.7 M). However, higher water transport rates are observed with the 2.5 M HCl feed. This drastic increase in water transport seems to relate to the mechanism of water extraction (4). Thus, at low acid concentration (0.7 M) water is extracted through partial hydration of the protonated Kelex 100 molecules. On the other hand, at acidities above 0.7 M HCl, W/O microemulsions form which make possible the transport of high quantities of water through the organic phase. Finally, the variable ratio $J_{\text{water}}/J_{\text{acid}}$ at the high feed acid range (expt 4 vs expt 6) can be at least partly explained on the basis of a higher water activity gradient as a result of the higher level of salinity in the strip phase.

Permeation of Rh through SLM

In this section the effects of different variables on the rate of Rh permeation through the Kelex 100-based SLM are discussed. First, the effect of feed acidity on the rate of Rh permeation is presented. As can be seen in Fig. 9, the rate of permeation increases with feed acidity up to about 2 to 2.5 M HCl where it reaches a plateau, thereafter decreasing with any further increase in the feed acidity. The initial increase is attributed primarily to the increased protonation, Eq. (1), of Kelex 100, and secondarily to an increase of the relative ratio $RhCl_6^{3-}/RhCl_5(H_2O)^{2-}$ via the suppression of aquation (Eq. 3). On the other hand, the decrease in the latter stage is attributed to the suppression of the ion-pair formation reaction (Eq. 2) at high chloride concentrations. A similar observation can be made with the effect the NaCl content of the feed (1.4 M HCl) had on the rate

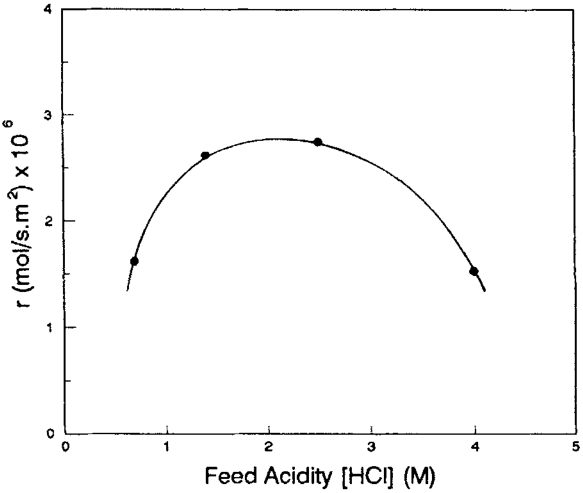

FIG. 9 Effect of feed acidity on rate of Rh permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL different [HCl], 400 ppm Rh, 2-week aged. Strip: 20 mL at pH 1.

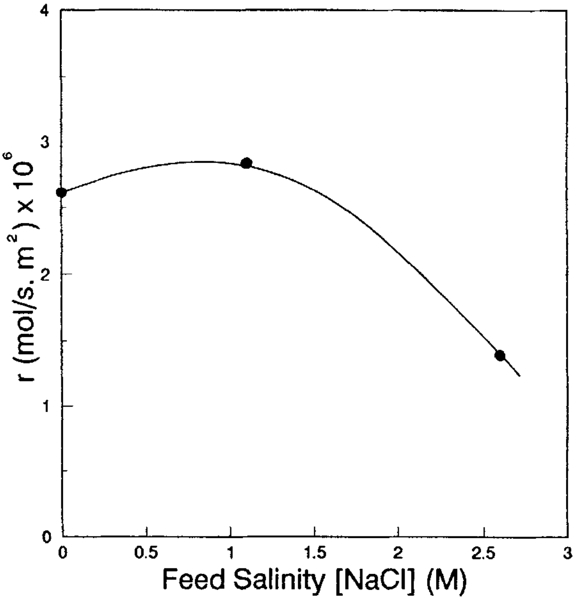

FIG. 10 Effect of feed salinity on rate of Rh permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 1.4 M HCl, 400 ppm Rh, 2-week aged, different [NaCl]. Strip: 20 mL water/HCl at pH 1.

of Rh extraction (Fig. 10). Again, the plateau is reached in almost the same region, 2 to 2.5 M Cl^-, followed by a decrease at higher chloride concentrations.

The effect of strip solution salinity on the transport of rhodium is depicted in Fig. 11. No effect is observed up to 1 M NaCl concentration, but at higher Cl^- concentrations the rate of rhodium transport is negatively affected. This might be interpreted in terms of the possible effect [NaCl] has on the activity of acid ($\alpha_{HCl} = \alpha_{H^+}\alpha_{Cl^-}$), which in turn effects the rate of acid permeation and eventually the dependent rate of Rh extraction. Alternatively, NaCl may be seen as effecting the relative ratio of $RhCl_6^{3-}/RhCl_5(H_2O)^{2-}$ in the strip solution by favoring the formation of $RhCl_6^{3-}$ as opposed of $RhCl_5(H_2O)^{2-}$, and in this way results in partial backextraction of rhodium.

Finally, the effect of Rh concentration (both in the feed and the strip phases) was determined. As can be seen in Fig. 12, the Rh extraction rate

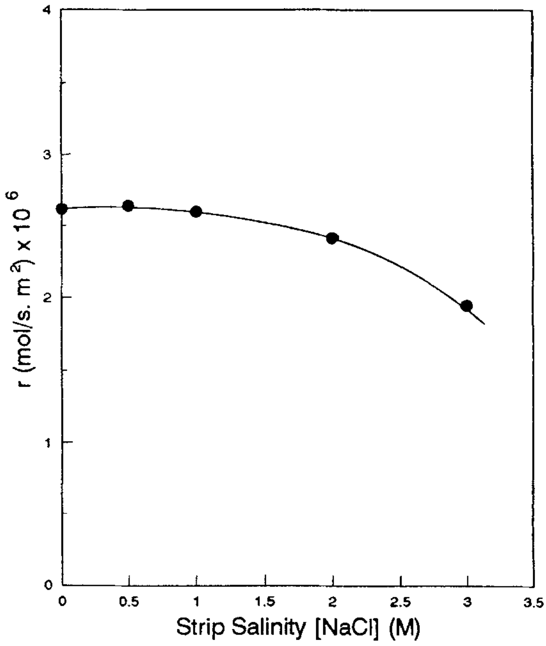

FIG. 11 Effect of strip salinity on rate of Rh permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 1.4 M HCl, 400 ppm Rh, 2-week aged. Strip: 20 mL water/HCl/NaCl at pH 1, different [NaCl].

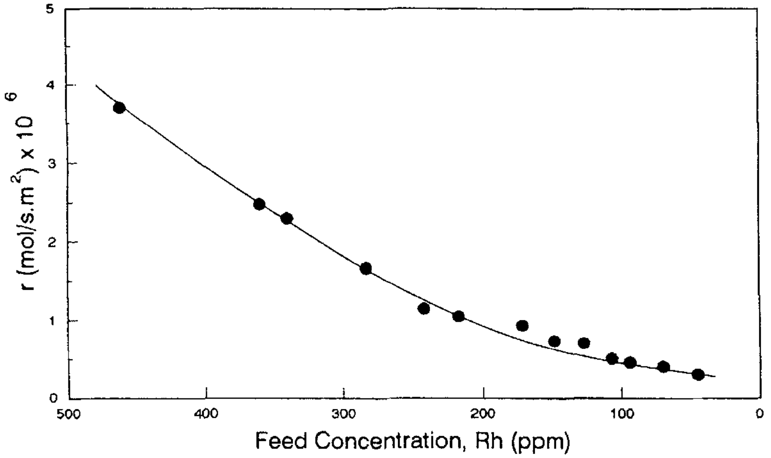

FIG. 12 Effect of feed Rh concentration on rate of Rh permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 2.5 M HCl, different [Rh], 2-week aged. Strip: 20 mL water/HCl at pH 1.

increases with increasing Rh concentration in the feed. On the other hand, the concentration of Rh in the strip phase was not found to have any effect on the rate of Rh permeation (Fig. 13).

Comparison of the relative magnitude of the rates of acid (and water) extraction with the rate of rhodium permeation shows the former to be 100 times higher than the latter. The rates of Rh extraction (in the order of 10^{-6} mol·s^{-1}·m^{-2}) compare very well with other reported rates of similar SLM systems, i.e., 1.50×10^{-8} for Pu(IV) (15), 1.75×10^{-6} for Cd(II) (16), and 4.90×10^{-11} for Zn(II) (17). Nevertheless, the extraction of acid is of concern (due to the dilution* brought to the strip phase on one hand and the reduction it brings to the rate of Rh extraction as a result of Cl^- build-up in the strip phase on the other hand). Interfacing the SLM system with an acid recycling process is an option presently under investigation in our laboratory as a way of overcoming this undesirable side-effect of the Rh recovery process.

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* For example, after operating the SLM system for 70 hours with an initial 10/1 aqueous feed (400 ppm Rh/2.5 M HCl) to strip solution (pH 1) relative ratio, a strip solution containing 2100 ppm Rh was produced while the raffinate concentration of Rh was 40 ppm. This gives a concentration ratio of about 5 compared to the expected one of 10 if no acid and water coextraction had taken place.

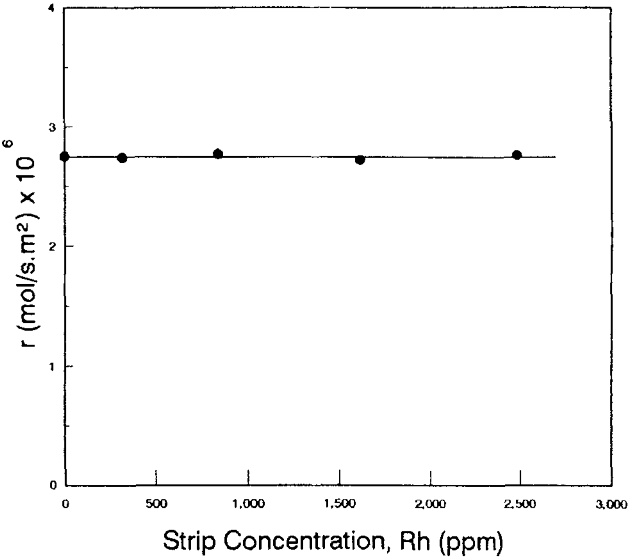

FIG. 13 Effect of strip Rh concentration on rate of Rh permeation. Support: 0.45 μm Gore-Tex. LM: 25 v/o Kelex 100, 25 v/o tridecanol, 50 v/o kerosene. Feed: 200 mL 2.5 M HCl, 400 ppm Rh, 2-week aged. Strip: 20 mL water/HCl at pH 1.

CONCLUSIONS

A supported liquid membrane technique utilizing Kelex 100 as the carrier has been successfully applied to the separation of Rh from a hydrochloric acid solution. The non-aquated chlorocomplexes of Rh(III) are transported through the membrane via the formation of ion-pairs with protonated extractant molecules. The main driving force for this extraction process is the acid activity gradient across the membrane. Acid and water are cotransported along with the Rh species via protonation of the extractant and the formation of W/O microemulsions. The rate of acid and water extraction is about 100 times that for Rh. The rate of acid extraction can be substantially reduced by using a strip solution containing a high salt (NaCl) concentration. However, this may slow down the Rh extraction rate. At optimum conditions, i.e., a feed solution of 2.5 M HCl and a strip solution of essentially zero salt concentration and pH 1, the rate of Rh extraction is on the order of 10^{-6} mol·s^{-1}·m^{-2}, which compares very well with analogous systems described in literature.

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