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## Facilitated Transport of Gold through a Membrane via Complexation to Thiourea-Based Reagents

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### ABSTRACT

The facilitated transport of Au(III) from hydrochloric acid solutions through double solid supported liquid membranes (SSLMs) is reported. The organic phase consisted of a chloroform solution of thiourea-based extraction reagents, dodecylthiourea (DTH) or nonylthiourea (NTH), physically absorbed onto microporous polypropylene films, Celgard 2500 or Celgard 2400 (Celanese Plastic Inc.). A cell composed of three compartments, including a reservoir of organic solution, with double SSLM was used in this study. Aqueous solutions of thiourea, KSCN, or  $\text{Na}_2\text{S}_2\text{O}_3$  were used for removing Au(III) from the membrane phase. The permeability coefficient,  $P$ , of the SSLM was determined from the slope of  $\log[\text{Au}]/[\text{Au}]_0$  or  $\log A/A_0$  vs time plot. The influences of the stirring rate in aqueous feed and organic solutions, of the stripping reagents and their concentration, of the carrier concentration, and of the concentration of HCl in the aqueous feed on the permeability coefficient were determined. A model describing the transport mechanism consisting of diffusion through a feed aqueous diffusion layer, a fast interfacial chemical reaction, and diffusion through the membranes is reported. The study also demonstrates the suitability of the liquid membrane technique to use reagents with low solubility in organic solutions for the permeation of  $\text{Au}^{3+}$  without problem of solid-phase formation.

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## INTRODUCTION

The extraction of gold from acidic chloride solutions by thiourea-based reagents synthesized in our laboratory has been carried out in a previous study (1). The binding of  $\text{Au}^{3+}$  ions in chloride media by coordinating polymers containing thiourea as the selective functional group has also been characterized (2). The results of these studies showed that these reagents have a good selectivity for gold and silver against several other base-metal ions. The kinetics of the extraction of gold by the "free" ligand dissolved in chloroform is much faster ( $t_{1/2}$  is a fraction of a minute) than coordinating polymers containing the same functional groups ( $t_{1/2}$  is several minutes). A serious limitation of the extraction reagents is their low solubility in organic phases and consequently their low metal loading capacity of these reagents. Liquid membranes, both liquid surfactant membranes (LSMs) and solid supported liquid membranes (SSLMs), have the common feature of coupling extraction and stripping reactions. Liquid membranes have been studied as an efficient selective separation technique (3–8) which is frequently considered as a possible technique to overcome problems with selective reagents having low solubility (9). The amount of reagent required in liquid membranes is much less than in solvent extraction operations. Besides, the coupling of the extraction and backextraction reactions results in a very low loading of metal ions in the membrane phase.

The extraction of gold with various extractants has been extensively studied during the past few years (10–20). However, the study of permeation of  $\text{Au}^{3+}$  through liquid membranes, especially SSLMs, has drawn less attention. Tromp et al. (21) reported the transport of  $\text{Au}^+$  and  $\text{Ag}^+$  from alkaline cyanide solutions through a membrane containing a macrocyclic extractants, Kryptofix 22 DD, in decanol supported by Celgard or Accurel polymer films. They reported that the fluxes are higher for gold than for silver, follow the order of the equilibrium extraction constants, and that the flux is influenced by the characteristics of the supports. Within our group, Salvadó et al. (22) have studied the permeation of  $\text{Au}^{3+}$  from acidic chloride solution through SSLMs using different polymers and triisobutylphosphine sulfide (Cyanex 471x) as carrier with the data analyzed following the model developed by Danesi (8).

SSLMs are usually prepared by impregnating the polymer membrane with an extractant-containing organic solution (23). The SSLM is placed to separate the two compartments containing feed and stripping solutions, respectively. In this case, difficulty is encountered when a volatile diluent is employed because it evaporates from the solid support before the cell can be assembled. This has caused poor reproducibility and a continuous

decrease of the flux during an experiment (24). In the present study of the permeation of  $\text{Au}^{3+}$  from hydrochloric acid solution through solid supported liquid membranes, chloroform was used as diluent in which thiourea-based extraction reagents, dodecylthiourea (DTH) and nonylthiourea (NTH), were dissolved. To overcome problems with the evaporation of chloroform, a cell composed of three compartments separated by double membranes with a reservoir of organic solution was employed. A model describing the permeation of metal ions through a SSLM, developed by Danesi (8) for a two-compartment system, has been used in the treatment of the results obtained in this study.

## EXPERIMENTAL

### Reagents and Solutions

Aqueous feed solutions of gold were prepared from a 5-mM stock solution. The ionic strength in the feed solution was kept constant at 1.0 M HCl, except for the experiments where the dependence of the permeability coefficient on HCl concentration in the feed solution was studied. In those experiments the HCl concentration in the feed solution was varied from 0.5 to 3.0 M. Dodecylthiourea (DTH) and nonylthiourea (NTH) synthesized in our laboratory (1) (listed in Table 1) were employed as the carrier. The organic solutions were prepared by dissolving an exactly weighed amount of reagent into a given volume of chloroform. [The solubilities of the reagents have been tested in a variety of diluents (1). In our modeling study we used a diluent with a well-defined composition. Chloroform has a high enough solubility for this purpose. For application purposes, commercial solvents of a less harmful nature could be applied.] The concentration of DTH and NTH was kept at 10–15 mM except for the investigation of the influence of the carrier concentration on the permeation. In these experiments, the concentrations of the reagents were varied in the range of 1.0–15 mM. Thiourea and KSCN, used as stripping reagents, were prepared at various concentrations in 1.0% HCl, while  $\text{Na}_2\text{S}_2\text{O}_3$  aqueous solutions (also used for stripping) were prepared by dissolving the solute in deionized water.

TABLE 1  
Thiourea-Based Reagents

Reagent	Structure
Nonylthiourea (NTH)	$\text{CH}_3-(\text{CH}_2)_8-\text{NH}-\text{CS}-\text{NH}_2$
Dodecylthiourea (DTH)	$\text{CH}_3-(\text{CH}_2)_{11}-\text{NH}-\text{CS}-\text{NH}_2$

### Analytical Techniques

The  $\text{Au}^{3+}$  concentration in the feed solutions was measured at given time intervals without disturbing the experiments. This was carried out by pumping the solution continually through a flow cuvette by a peristaltic pump. The measurements were carried out on a Cary-3 UV-visible spectrophotometer. The absorption of gold was measured at 311.4 nm for solutions with gold concentrations lower than 0.50 mM and at a wavelength of 331.0 nm for solutions with a higher concentration ( $>0.50$  mM).

### Solid Support

Two polymeric supports were used in this study. They were Celgard 2500 (Celanese Plastic), a microporous polypropylene flat-sheet film having 45% porosity and a thickness of 25  $\mu\text{m}$ , and Celgard 2400 (Celanese Plastic), a microporous polypropylene flat-sheet film having a porosity of 38% and a thickness of 25  $\mu\text{m}$ .

### Apparatus

An attempt to use a two-compartment cell similar to that described in Ref. 22 was unsuccessful because chloroform evaporates from the polymeric support before the cell can be assembled. This results in poor reproducibility of the data and difficulties in obtaining steady-state conditions. Instead, the experiments were performed with a three-compartment cell as shown in Fig. 1, where one membrane (*a*) is placed between the feed and carrier solutions, and another membrane (*b*) separates the carrier and stripping solutions. The three compartments are made of plastic cylinders with an inner diameter of 4.1 cm. The effective lengths of the feed and stripping compartments are 6.0 cm each, while the compartment for the organic solution is 2.4 cm in length. The volumes of the feed and stripping compartments are 80 mL each, while the volume of the organic compartment is 32 mL. The propellers take the shape of vertical plate in size of  $1 \times 1$  cm. The geometrical area of the membrane is 13.2  $\text{cm}^2$ . The stirring speed of the feed solution was kept at 1200 rpm except for experiments to investigate the influence of the stirring speed on the permeability coefficients. The stirring speed of the reservoir of the organic solution was kept at 250 rpm in all the experiments except for a set of experiments where the stirring speed was varied.

The measurement started when the stirrer's motors were simultaneously switched on; that time was taken as zero. All the experiments were carried out at 25°C.

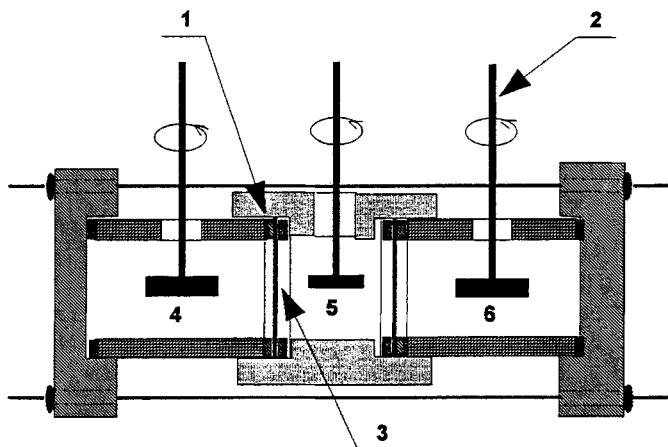


FIG. 1 A cross section of the SSLM cell with three compartments used in this study: (1) O-ring, (2) stirrer, (3) membrane, (4) feed solution, (5) organic solution, (6) stripping solution.

## THEORETICAL CONSIDERATION

A theoretical treatment of the extraction of metal ions by solid supported liquid membranes is described in the literature (see, e.g., Refs. 8, 22, 24). In the following, we outline the basis of the permeation process adapted to the system used in the present investigation.

The equilibrium of gold extraction by the extractants DTH and NTH has been studied previously. The results of the analysis of the distribution data suggest that the extraction of gold could be explained by the formation of a single 1:3 species in the organic phase, as given by



where L refers to the extractant, DTH or NTH. The stability constants  $\log \beta_{13}$  of the 1:3 species, i.e.,  $\text{AuCl}_3(\text{DTH})_3$  or  $\text{AuCl}_3(\text{NTH})_3$ , have been determined to be 43.64 and 48.74, respectively (1, 25).

In this three-compartment cell with a double membrane, the organic phase is in contact with two aqueous solutions. The feed solution, organic phase, and the stripping solution contained in the three different compartments are stirred independently. The chemical reactions are most likely to take place at the organic-aqueous film interfaces,  $f_a$  (feed/organic) and  $f_b$  (organic/stripping). Previous studies suggest that the chemical reactions can be considered to occur instantaneously relative to the diffusion pro-

cesses (8, 24b). The gold ions are transported to the organic solution by reaction between  $\text{Au}^{3+}$  and the extractant at the feed/organic interface  $f_a$ . At both sides of the membrane there exists a stagnant liquid film (organic and aqueous) through which a diffusion resistance may occur. The thicknesses of these films are dependent of the hydrodynamic conditions in the different compartments as determined mainly by the stirring speed. The concentrations of the different species in the bulk of the solutions are assumed to be uniform if adequate stirring is applied. The concentration gradient in the diffusion layers at the organic side adjacent to the membranes are neglected (8, 24b). Thus, the two membranes are treated as a single membrane with twice the geometrical thickness of the polymer support. The diffusion resistance of the stagnant aqueous film on the stripping side of membrane  $b$  can be neglected compared to that of the diffusion layer on the feed side of membrane  $a$  (8, 24). The extracted  $\text{Au}^{3+}$  species are removed from the organic phase by reaction with the stripping reagents/solution at the interface  $f_b$ . The distribution ratio  $K_d$  of  $\text{Au}^{3+}$  ions at the interfaces is defined by

$$K_d = \frac{[\overline{\text{AuCl}_3\text{L}_3}]}{[\text{Au}^{3+}]_i} \quad (2)$$

where  $[\overline{\text{AuCl}_3\text{L}_3}]$  and  $[\text{Au}]_i$  denote the concentration of  $\text{Au}^{3+}$  in the organic phase and the concentration of  $\text{Au}^{3+}$  ions in the aqueous phase, respectively. (The bar indicates that the species exists in the organic phase.) When  $K_{da}$  at the interface  $f_a$  is much higher than  $K_{db}$  at the interface  $f_b$ , the overall flux equation can be obtained by applying Fick's first diffusion law to the diffusion layer in the feed side of membrane  $a$  and to the membrane itself. The equations describing the flux through the membrane,  $J_0$ , and the flux of the aqueous diffusion layer,  $J_a$ , are presented as

$$J_0 = \frac{D_0}{d_0} [\overline{\text{AuCl}_3\text{L}_3}] \quad (3)$$

$$J_a = \frac{D_a}{d_a} ([\text{Au}^{3+}] - [\text{Au}^{3+}]_i) \quad (4)$$

where the  $D_0$  and  $D_a$  are the diffusion coefficient of  $\text{AuCl}_3\text{L}_3$  species in the membrane and the aqueous diffusion coefficient of  $\text{Au}^{3+}$  species, respectively;  $d_0$  denotes the thickness of the membrane; and  $d_a$  represents the thickness of the aqueous diffusion film on the feed side of membrane  $a$  and is a function of the hydrodynamics of the aqueous solution. At the steady state,  $J_a = J_0$ , and Eqs. (2)–(4) can be solved to result in

$$\begin{aligned}
 J &= K_d \frac{[\text{Au}^{3+}]}{K_d \frac{d_a}{D_a} + \frac{d_0}{D_0}} \\
 &= K_d \frac{[\text{Au}^{3+}]}{K_d \Delta_a + \Delta_0}
 \end{aligned} \tag{5}$$

where  $\Delta_a$  and  $\Delta_0$ , defined by  $\Delta_a = d_a/D_a$  and  $\Delta_0 = d_0/D_0$ , denote the diffusion resistance of the feed aqueous diffusion layer and the membrane, respectively.

Thus the permeability coefficient,  $P$ , defined as  $J/[\text{Au}^{3+}]$ , can be expressed as

$$P = \frac{K_d}{K_d \Delta_a + \Delta_0} \tag{6}$$

where the flux is defined as

$$J = -\frac{d[\text{Au}^{3+}]}{dt} \frac{V}{Q_e} \tag{7}$$

and  $V$  denotes the aqueous feed volume and  $Q_e$  is the effective membrane area which was calculated by multiplying the geometrical area and the porosity of the polymer support. For all the experiments in this study, the initial concentration of  $\text{Au}^{3+}$  in the feed solution was chosen to be sufficiently low that only a small fraction of mobile carrier at the interface was converted to  $\text{Au}^{3+}$ -carrier species,  $\text{AuCl}_3(\text{DTH})_3$ , and  $D_0$  is time independent (8). The integrated equation can be derived from Eqs. (6) and (7):

$$\int_{[\text{Au}^{3+}]_0}^{[\text{Au}^{3+}]} \frac{d[\text{Au}^{3+}]}{[\text{Au}^{3+}]} = -\frac{Q_e}{V} P \int_0^t dt \tag{8}$$

$$\log\left(\frac{[\text{Au}^{3+}]}{[\text{Au}^{3+}]_0}\right) = -0.434 \frac{Q_e}{V} P t \tag{9}$$

$[\text{Au}^{3+}]_0$  is the initial  $\text{Au}^{3+}$  concentration in the feed solution. In this study, UV-Visible spectrophotometry was used to determine the  $\text{Au}^{3+}$  concentration of the feed solution. In this case the absorption  $A$  at a given wavelength is proportional to  $[\text{Au}^{3+}]$ , and Eq. (9) is rewritten as

$$\log\left(\frac{A}{A_0}\right) = -0.434 \frac{Q_e}{V} P t \tag{10}$$



The permeability coefficient  $P$  can thus be obtained from the slope of a plot of  $\log(A/A_0)$  versus time.

## RESULTS AND DISCUSSIONS

### Evaluation of Permeability Coefficient

One of the main assumptions on which the model described earlier is based is that  $K_{da}$  is much higher than  $K_{db}$ . There are no available equilibrium data on the distribution of  $Au^{3+}$  between the organic phase and the stripping reagents employed in this work. However, it is possible to estimate  $K_{db}$  from the extraction of  $Au^{3+}$  by DTH and NTH as well as the data from stripping the extracted species with thiourea solutions.  $K_{db}$  is found to be very small ( $\approx$  zero). The value of  $K_{da}$  can be calculated from the results of the previous study, e.g.,  $K_{da}$  of  $AuCl_3(DTH)_3$  (1).

The equilibrium constant of the extraction of  $Au^{3+}$  from acidic chloride solutions by DTH (or NTH) represented by Eq. (1) can be described as

$$\beta_{13} = \frac{[AuCl_3(DTH)_3]}{[Au^{3+}][Cl^-]^3[DTH]^3} \quad (11)$$

where  $\beta_{13}$  represents the conditional stability constant (26). For DTH,  $\log \beta_{13} = 43.64$  (1). By combining Eq. (2) and (11), we obtain

$$K_{da} = \frac{\beta_{13}[Cl^-]^3[DTH]^3}{1 + \sum \beta_i [Cl^-]^i} \quad (12)$$

Since  $\sum \beta_i [Cl^-]^i \gg 1$  and  $\beta_4 = 29.63 \gg \beta_3 \gg \beta_2 \gg \beta_1$  (27–29), then

$$(1 + \sum \beta_i [Cl^-]^i) \approx \beta_4 [Cl^-]^4$$

The value of  $\log K_{da}$  can be computed from

$$\log K_{da} = \log \beta_{13} + 3 \log [DTH] + (3 - 4) \log [Cl^-] - \log \beta_4 \quad (13)$$

A value of  $K_{da}$  as high as  $10^8$  is obtained. This confirms the validity of Eq. (10) which can thus be used for evaluation of the permeability coefficient.

Figure 2 shows a typical linear relationship of  $\log(A/A_0)$  and time under the experimental conditions of an initial concentration of  $Au^{3+}$  in the aqueous feed of 0.25 mM at 1.0 M HCl, 1.10 mM DTH in the organic phase, a stripping solution containing 5% thiourea and 1% HCl, and stirring speed of 250 rpm in the organic solution and 1200 rpm in the feed solution. This is in a good agreement with Eq. (10). During the extraction, no solid phase was seen to be formed in the organic solution or the mem-

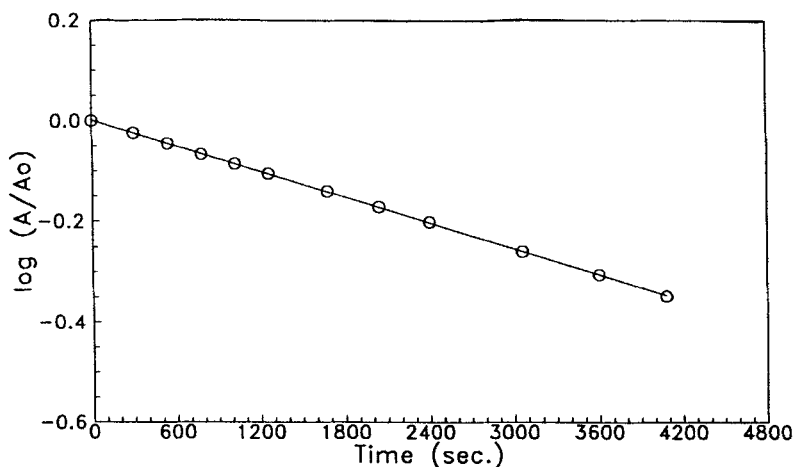


FIG. 2  $\log(A/A_0)$  vs time for the transport of  $\text{Au}^{3+}$  through SSLM system. Feed solution:  $[\text{Au}^{3+}] = 0.25 \text{ mM}$ ,  $[\text{HCl}] = 1.0 \text{ M}$ . Organic phase:  $[\text{DTH}] = 1.10 \text{ mM}$  in chloroform. Stripping solution: 5% thiourea in 1% HCl. Stirring rate: Organic solution 250 rpm, feed solution 1200 rpm. Support: Celgard 2500.

brane phase. The straight line obtained in Fig. 2 also confirms that there is no formation of a solid phase.

### Influence of Stirring Speed

The dependence of the gold permeability coefficient on the stirring rate of the feed solution is shown in Fig. 3 for Celgards 2500 and 2400. The conditions used are  $0.28 \text{ mM Au}^{3+}$  and  $1.0 \text{ M HCl}$  in the feed solution,  $10 \text{ mM DTH}$  in the organic phase, and a stirring speed of the organic solution of 250 rpm. Earlier studies (24) showed that the rate of stirring applied to the stripping solution does not significantly influence permeation. In our experiments we applied the same stirring speed to both the feed and the stripping solutions. As seen, for both Celgard 2500 and 2400 polymer supports, the permeability coefficient increases with increasing stirring speed until a plateau is reached. By using a stirring speed in the 1000–2000 rpm range, the permeability coefficient does not seem to depend on the stirring rate. It is also observed that the permeability coefficient is not affected by the different supports used in this study. The flux for Celgard 2500 and Celgard 2400 is the same when their effective area used is the same. For all other experiments, Celgard 2500 was used as

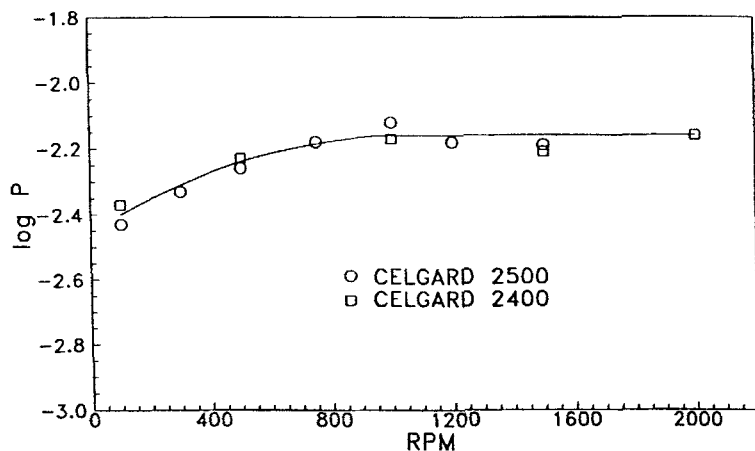


FIG. 3 Influence of stirring speed of feed solution on permeation of  $\text{Au}^{3+}$ . Other experimental conditions are similar to those for Fig. 2.

the membrane support and the stirring speed of the aqueous feed was kept at 1200 rpm unless otherwise stated.

The influence of the stirring speed of the organic solution on the permeability coefficient is shown in Fig. 4. The experiments were carried out by varying the stirring speed of the organic phase while maintaining a

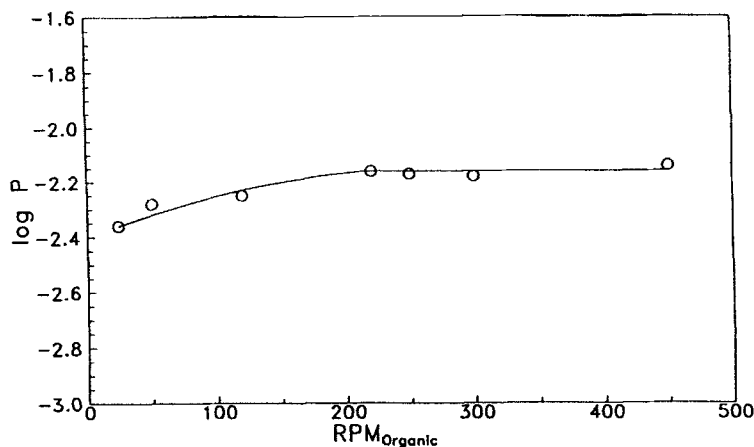


FIG. 4 Influence of stirring speed of organic solution on permeation of  $\text{Au}^{3+}$ . Stirring rate of feed solution 1200 rpm. Other experimental conditions are similar to those for Fig. 2.

constant stirring speed of 1200 rpm in the feed and stripping solutions. The data suggest that the permeability coefficient is dependent on the stirring speed of the organic solution in the lower rpm range (rpm < 220). At higher stirring speeds (rpm > 220) the permeability is independent of the rate of stirring. Increasing the stirring speed decreases the diffusion film thickness on both membrane *a* and membrane *b* to a minimum constant value. In the model used in this study, the organic diffusion layers were neglected since the stirring speed used in the rest of the experiments was kept at 250 rpm.

### Effect of Stripping Reagents

Three different reagents that form strong complexes with  $\text{Au}^{3+}$  (thiourea, KSCN, and  $\text{Na}_2\text{S}_2\text{O}_3$ ) were tested as stripping reagents. A set of experiments was carried out using different concentrations of the reagents. Thiourea and KSCN were dissolved in 1% HCl while  $\text{Na}_2\text{S}_2\text{O}_3$  was dissolved in water. The results are presented in Fig. 5 as  $\log P$  vs the concentration of the reagents. For all three reagents the permeability coefficient increases with increasing reagent concentration and then reaches a plateau. However, different permeability coefficients are obtained for the different reagents used, and they are in the order  $\text{Na}_2\text{S}_2\text{O}_3$

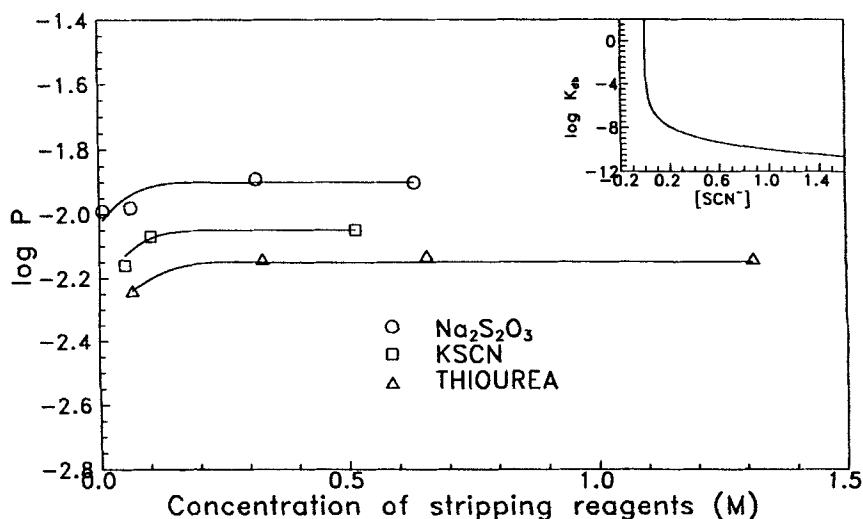


FIG. 5 Effect of stripping reagents on the permeability coefficient. Stirring rates: Feed solution 1200 rpm, organic solution 250 rpm. Other experimental conditions are similar to those for Fig. 2. Inset: Calculated  $K_{ab}$  versus  $[\text{SCN}^-]$ .

$> \text{KSCN} > \text{thiourea}$ . The differences in the permeability coefficients may be explained by different  $\text{Au}^{3+}$  complexations with the reagents. Different permeability coefficients for different stripping reagents have been obtained under similar experimental conditions, which reflects the effect of the chemical reaction taking place at interface  $f_b$  between the extracted species and the different stripping reagents on the membrane permeability coefficient. The available data on the complexation of  $\text{Au}^+$  and  $\text{Au}^{3+}$  to the different reagents are given in Table 2.

$\text{Au}^+$  forms 1:2 complexes while  $\text{Au}^{3+}$  has a higher number of ligands (1:3). Since data on the complexation of  $\text{Au}^{3+}$  are not complete,  $\text{Au}^+$  complexation data may be used as an indication for the order of the complexation of  $\text{Au}^{3+}$  to the different ligands, i.e., assuming that the stability of the  $\text{Au}^{3+}$  complexation to these ligands follows the same order of that of  $\text{Au}^+$ . It is expected that the higher stability of the complexes of  $\text{Au}^{3+}$  with stripping reagent results in lower distribution ratio,  $K_{db}$ , at the interface  $f_b$ , and consequently the higher membrane permeability coefficient which is observed in Fig. 5. The results shown in Fig. 5 also indicate a dependence of the permeability coefficient on the concentration of stripping reagent at  $[\text{L}] < 0.2 \text{ M}$ . In this concentration range,  $K_{db}$  is too high to allow a driving force for removing  $\text{Au}^{3+}$  from the membrane phase. The inset in Fig. 5 shows  $K_{db}$  calculated using the corresponding equation to Eq. (13) species and the equilibrium constants for  $\text{Au}^{3+}$ -DTH and  $\text{Au}^{3+}$ - $\text{SCN}^-$  species as a function of  $[\text{SCN}^-]$ . As seen, at  $[\text{SCN}^-] \cong 0.2 \text{ M}$ ,  $K_{db} \cong 10^{-8} \cong (K_{da})^{-1}$ . As  $[\text{SCN}^-]$  increases further,  $K_{db}$  decreases ( $10^{-9}$ - $10^{-10}$ ), which allows a suitable driving force for  $\text{Au}^{3+}$  permeation.

### Influence of Carrier Concentration

The results of the experiments for studying the influence of the concentration of extraction reagents in the organic phase on gold permeation are presented in Fig. 6. As seen,  $\log P$  increases by increasing the carrier concentration up to 9 mM, after which the permeability of gold becomes independent of the carrier concentration. The dependence of  $\log P$  on the

TABLE 2  
Stability Constants of Gold Species

Ligand (L)	Log $\beta$ of $\text{Au}^{(I)}\text{L}_2$	Log $\beta$ of $\text{Au}^{(III)}\text{L}_3$
$\text{S}_2\text{O}_3^{2-}$	26 (Ref. 28)	—
$\text{SCN}^-$	25 (Ref. 28)	42 (Ref. 31)
$\text{CS}(\text{NH}_2)_2$	23.3 (Ref. 30)	—

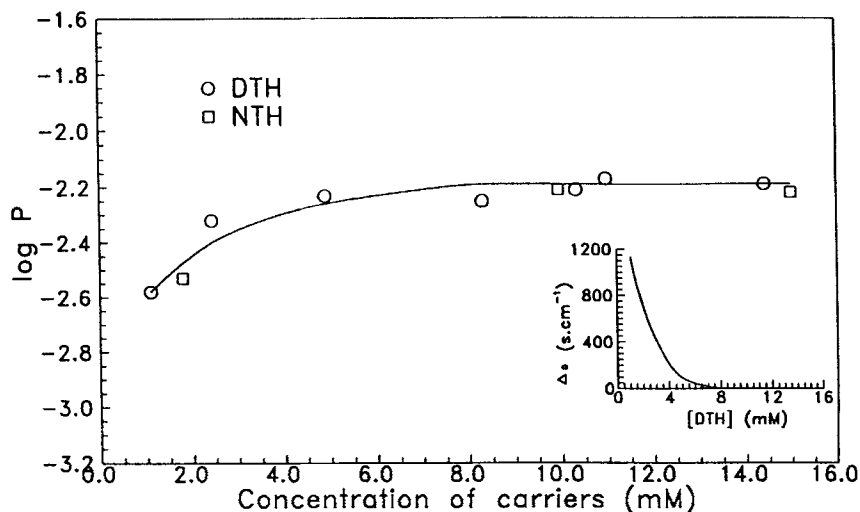


FIG. 6 Log  $P$  vs carrier's concentration. Experimental conditions are similar to those for Fig. 2. Inset: Plot of the calculated  $D_0$  against the concentration of DTH.

carrier concentration (DTH or NTH) can be explained by the increase of the membrane diffusion resistance,  $\Delta_0$ , as the carrier concentration decreases. In the low concentration range ( $< 9$  mM),  $\Delta_0$  is not small enough to be neglected compared to  $K_d \Delta_a$  in Eq. (6). This is demonstrated in the following.

First we consider the region where log  $P$  is not dependent on the carrier concentration. In this region the permeation process is controlled by diffusion in the aqueous feed layer and the term  $K_d \Delta_a \gg \Delta_0$  in Eq. (6), which then reduces to

$$P = 1/\Delta_a \quad (14a)$$

An average value for  $\Delta_a = 154.8 \text{ s}\cdot\text{cm}^{-1}$  is then computed out, and it is in good agreement with the results obtained by Salvadó (22). Using this value of  $\Delta_a$  as well as the  $K_d$  of  $\text{AuCl}_3(\text{DTH})_3$  evaluated from Eq. (13) for the experimental conditions where a low reagent concentration was used, we can calculate a value of  $\Delta_0$  for each [DTH] (or [NTH]) concentration. The results are plotted in the Fig. 6 inset. As seen, in the lower DTH concentration range the membrane diffusion resistance decreases rapidly with increasing concentration of DTH until it reaches a minimum constant at  $[\text{DTH}] > 9 \text{ mM}$ . At this concentration the permeation is completely controlled by the diffusion of the aqueous layer adjacent to membrane  $a$ .

When the concentration of carrier is less than 0.1 mM, the permeation is a membrane diffusion-controlled process, where  $K_d\Delta_a \ll \Delta_0$ , and Eq. (6) can thus be rewritten as

$$P = K_d/\Delta_0 \quad (14b)$$

The membrane diffusion coefficient is calculated as  $D_0 < 4.4 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$  through  $\Delta_0 = d_0/D_0$ . It is in a good agreement with the value reported by Danesi et al. (8).

### Effect of HCl Concentration in Feed Solution

A set of experiments was carried out to investigate the dependence of the permeability coefficient on the concentration of HCl in an aqueous feed solution under conditions of initial  $[\text{Au}^{3+}] = 0.27 \text{ mM}$  at 1.0 M HCl,  $[\text{DTH}] = 14.4 \text{ mM}$ , and 5% thiourea in 1% HCl as the stripping solution. The results, shown in Fig. 7, indicate that there is no influence of HCl concentration in the feed solution on the membrane permeability coefficients. This is in agreement with the results reported in Ref. 22. From our experimental data, a value of  $K_{da}$  is calculated by Eq. (13). The membrane permeability coefficient  $P$  is then computed using Eq. (6) to give a value of  $\Delta_a$  and a minimum constant value of  $\Delta_0$  ( $0.65 \text{ s} \cdot \text{cm}^{-1}$ ). The results are plotted as a straight line in Fig. 7; the estimates of  $\log P$  fit the experimental data well.

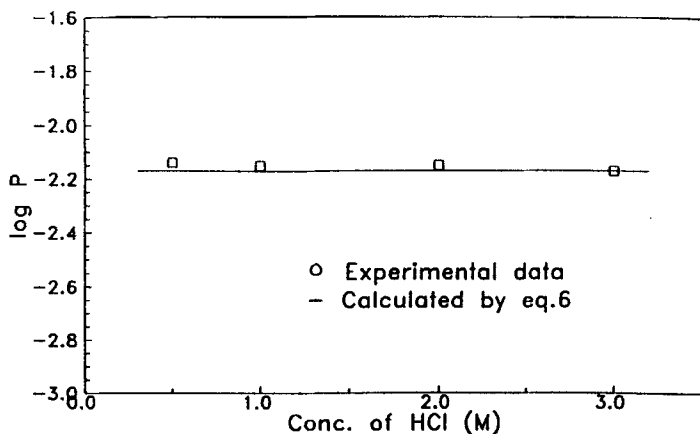


FIG. 7 Influence of HCl concentration of feed solution on  $P$ . Other experimental conditions are similar to those for Fig. 2.

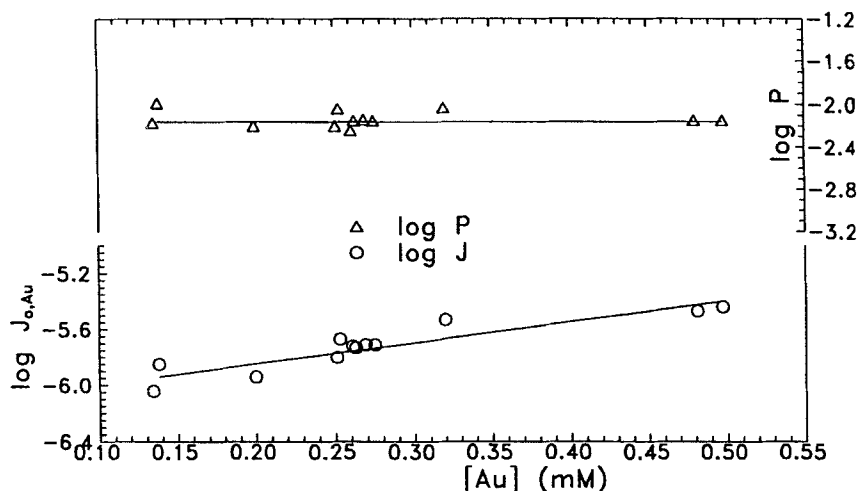


FIG. 8 Effect of initial  $\text{Au}^{3+}$  concentration on  $\log P$  and  $\log J$ . Feed solution: various  $[\text{Au}^{3+}]$ ,  $[\text{HCl}] = 1.0 \text{ M}$ . Other experimental conditions are similar to those for Fig. 2.

### Influence of Initial Concentration of $\text{Au}^{3+}$ in Feed Solution

To investigate the effects of the initial concentration of gold on the permeability coefficient, a set of experiments was carried out for Celgard 2500. The results presented in Fig. 8 show that the permeability coefficient is independent of the  $[\text{Au}^{3+}]$  of the aqueous feed solution. This is consistent with the results of the study of the permeation of gold(III) through Cyanex 471  $\times$  SSLM (22). The flux, as shown, increases with increasing initial  $[\text{Au}^{3+}]$  in the aqueous feed solution, as expected.

## CONCLUSIONS

Reproducible experimental data on the permeation of gold by SSLM have been obtained by using a three-compartment membrane cell. The permeation of  $\text{Au}^{3+}$  through a DTH/chloroform supported membrane could be explained by a model based on a diffusion controlled process. The experimental data of permeation of  $\text{Au}^{3+}$  through the liquid membrane could be fully explained by equilibrium considerations and diffusion control in the proposed model. Under the conditions studied, no diffusion resistance through the organic solutions was considered. The diffusion of  $\text{Au}^{3+}$  species through the aqueous film adjacent to membrane *a*, located



between the feed and carrier solutions, controls the rate of the mass transport process when the carrier concentration is high enough. When the concentration of the carrier is below 10 mM, the mass transfer process is controlled by diffusion through the aqueous layer and by the membrane itself. Diffusion resistances under different experimental conditions were evaluated.

This study demonstrates the usefulness of the liquid membrane technique for making it possible to use reagents with low solubility in organic diluents for the permeation (separation) of metal ions, a procedure which may not be practical in conventional liquid/liquid extraction.

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