Platinum(IV) Extraction with Supported Liquid Membrane Containing Trioctylamine Carrier

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In the practical application of liquid membranes to the selective separation and concentration of metals, it is important to elucidate the mass transfer mechanism for permeation through the liquid membranes. Most of the studies reported to date relate to the extraction of copper and uranium. The purpose of the present study is to examine the possibility of applying a supported liquid membrane to concentrate platinum from dilute solution and to clarify the permeation mechanism of platinum through the membrane. The experiments were carried out using a supported liquid membrane impregnated with trioctylamine (TOA) as a mobile carrier. TOA has been used to extract platinum chloride anion (Cleare et al., 1979). The effects of the concentration of TOA carrier and that of platinum in the aqueous solutions on the permeation rate of platinum were examined. The transport mechanism through the liquid membrane is discussed on the basis of a simple model for platinum permeation.

TRANSPORT MECHANISM OF PLATINUM ACROSS A TOA LIQUID MEMBRANE

The liquid membrane system consists of a feed solution, a TOA-xylene liquid membrane, and a stripping solution, and is schematically shown in Figure 1a. Platinum chloride anion in the feed solution diffuses toward the interface at $x = 0$, where platinum is extracted by TOA through the overall interfacial reaction denoted by the following equation (Cleare et al., 1979):

$$2\,\overline{R_3N} + 2\,H^+ + PtCl_6^{2-} \rightleftarrows \overline{(R_3NH)_2PtCl_6} \tag{1}$$

where the overbar refers to the membrane phase. The platinum-TOA complex diffuses to the right interface at $x = l$, where the stripping agents in the right cell react with the complex and platinum chloride anion and protons are stripped from the membrane. TOA reformed at the right interface then diffuses back to the left side of the membrane and the entire process is repeated. Thus, platinum can be pumped from a low concentration solution into a higher concentration solution through the TOA liquid membrane because its flow is coupled to a flow of hydrogen ion in the same direction.

Figure 1b shows the schematic concentration profile of diffusing species. The transport rate of platinum through the liquid membrane is influenced by the diffusion rate of platinum chloride anion in the aqueous films at the feed and stripping sides of the membrane and that of platinum-TOA complex through the membrane if the effects of interfacial reaction rates are assumed to be negligible. The fluxes of platinum in the aqueous films and the membrane phase are given by

$$J_M^L = (D_M/\delta)(C_M^L - C_M^O) = k_M(C_M^L) - C_M^O) \tag{2}$$

$$\bar{J}_M = (\bar{D}_M/\tau' l)(\bar{C}_M^O - \bar{C}_M^l) \tag{3}$$

$$J_M^R = (D_M/\delta)(C_M^l - C_M^R) = k_M(C_M^l - C_M^R) \tag{4}$$

where τ' is a constant factor that allows for the diffusion of species through the tortuous pore within the membrane.

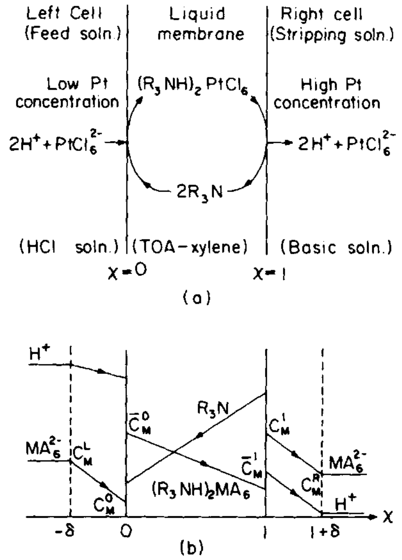

Figure 1. Schematic diagrams: (*a*) permeation mechanism; (*b*) concentration profile.

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The change of platinum concentration with time in the feed solution can be calculated from the following equation:

$$dC_M^L/dt = -(S/V)(J_M^L) = -(S/V)(\bar{J}_M) \qquad (5)$$

Here S and V are the membrane area and the volume of the solution in each cell compartment.

As the limiting cases, the maximum fluxes of platinum in the aqueous phase and the membrane phase are obtained from Eqs. 2 and 3 as follows:

$$J_{M,\max}^L = k_M C_M^L \qquad (6)$$

$$\bar{J}_{M,\max} = (\bar{D}_M/\tau' l)\,\bar{C}_M^0 = (\bar{D}_M/\tau' l)(\bar{C}_R^T/2) \qquad (7)$$

where $\bar{C}_R{}^T$ is the total concentration of TOA. When the platinum concentration in the feed solution is low, the transport rate of platinum is controlled by the aqueous film diffusion in the left cell and the flux of platinum is evaluated from Eq. 6. The time-dependent concentration of platinum in the feed solution is therefore expressed by Eq. 8 obtained from Eqs. 5 and 6:

$$\frac{C_M^L}{C_{MO}^L} = \exp\left(-\frac{S}{V} k_M t\right) \qquad (8)$$

where $C_{MO}{}^L$ is the initial platinum concentration of the feed solution. If the flux calculated from Eq. 6 is larger than the flux from Eq. 7, both diffusion processes in the aqueous and membrane phases will affect the transport rate of platinum. In this case, it is necessary to obtain the inferfacial concentrations to evaluate the flux of platinum.

EXPERIMENTAL

The solid support membrane (thickness:127 μm, porosity:65%, pore size:5–10 μm) and the experimental apparatus for measuring the permeation rates of platinum used in this study and the experimental procedures were the same as described in the previous paper (Nishiki and Bautista, 1983). The membrane was clamped between two glass half-cells of 8.9 cm I.D. The turbine impellers of 3.9 cm dia. with six flatblades were driven at a stirring speed of 82 rpm in both cells. The volume of the solution in each cell was 400 cm^3 and the membrane area was 31.7 cm^2. The membrane solution was prepared by diluting trioctylamine (TOA; Eastman Kodak Co.) with xylene. The feed solution was prepared by dissolving platinum (IV) chloride (Alfa Products), which had a purity of 99.98% in aqueous hydrochloric acid solution. The concentration of platinum was determined by a spectrophotometric method based on the platinum(IV)-tin(II) chloride color system (Ayres and Meyer, 1951). Sodium carbonate solutions of 0.5 and 1.0 kmol/m^3 and 0.98 kmol/^{3} sodium hydroxide solution were used as a stripping solution. All aqueous solutions were saturated with xylene.

All experiments were carried out at 298 K.

PERMEATION RATE

The permeation rates of platinum were measured by varying TOA carrier concentration $\bar{C}_R{}^T$ at initial platinum concentration of $C_{MO}{}^L = 1.01 \times 10^{-3}$ kmol/m^3 and hydrochloric acid concentration of $C_{HO}{}^L = 0.505$ kmol/m^3 in the left cell and initial sodium carbonate concentration of $C_{SO}{}^R = 0.500$ kmol/m^3 in the right cell. The results are presented in Figure 2, which shows a semilog plot of the dimensionless concentration $C_M{}^L/C_{MO}{}^L$ of platinum in the left cell against time t. There is no difference in the $C_M{}^L/C_{MO}{}^L$ value obtained for all $\bar{C}_R{}^T$ and a linear relationship between $C_M{}^L/C_{MO}{}^L$ and t holds. This is satisfied by a relation such as Eq. 8, which was derived for the aqueous film diffusion control. The mass transfer coefficient $k_M = 1.3 \times 10^{-5}$ m/s could therefore be obtained from the slope of the solid line in the figure and Eq. 8.

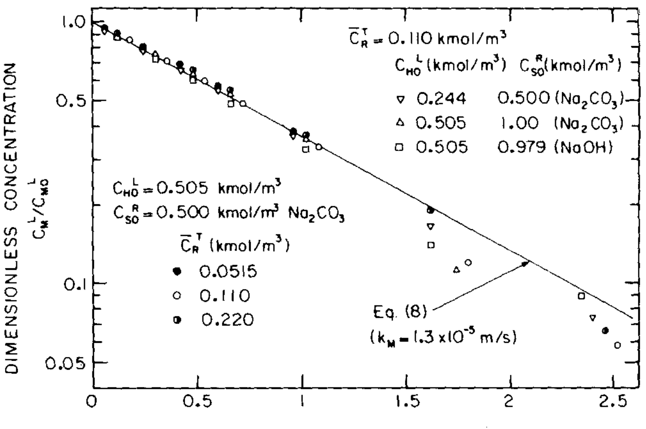

Figure 2. Effects of TOA carrier concentration and initial concentrations of HCl and the stripping agents on the permeation rate. $C_{MO}{}^L = 1.01 \times 10^{-3}$ kmol/m^3.

The effects of $C_{HO}{}^L$ and $C_{SO}{}^R$ on the permeation rate of platinum were investigated. The results are also shown in Figure 2. In the present experimental condition, the permeation rate of platinum is not affected by $C_{HO}{}^L$, $C_{SO}{}^R$, and the stripping agents and can be expressed by Eq. 8 with $k_M = 1.3 \times 10^{-5}$ m/s.

Permeation experiments were carried out to investigate the effect of initial platinum concentration in the feed solution on the permeation rate of platinum. Figure 3 shows the variations of Pt concentration with time in the left cell at TOA carrier concentration $\bar{C}_R{}^T = 0.0515$ kmol/m^3. The solid line in the figure represents Eq. 8 with $k_M = 1.3 \times 10^{-5}$ m/s. The observed results for $C_{MO}{}^L = 1.01 \times 10^{-3}$ kmol/m^3 are in very close agreement with the calculated results, but the observed values for $C_{MO}{}^L = 2.08 \times 10^{-3}$ and 3.06×10^{-3} kmol/m^3 deviate above the line generated by Eq. 8. In this case, the value of $\bar{J}_M$, max calculated from Eq. 7 using the same τ' value of 7.0 and the diffusion coefficient $\bar{D}_M$ of 5.10×10^{-10} m^2/s estimated in the same way as in the previous paper (Nishiki and Bautista, 1983) is 1.5×10^{-5} mol/m^2·s. On the other hand, the value of $J_M{}^L$ max obtained from Eq. 6 for $C_{MO}{}^L = 2.08 \times 10^{-3}$ kmol/m^3 is 2.6×10^{-5} mol/m^2·s and larger than the above $\bar{J}_M$,max value. Therefore, the permeation rate of platinum at $C_{MO}{}^L = 2.08 \times 10^{-3}$ kmol/m^3 may be affected by both the diffusion processes in the aqueous and membrane phases as mentioned above. It is considered that this effect results in the

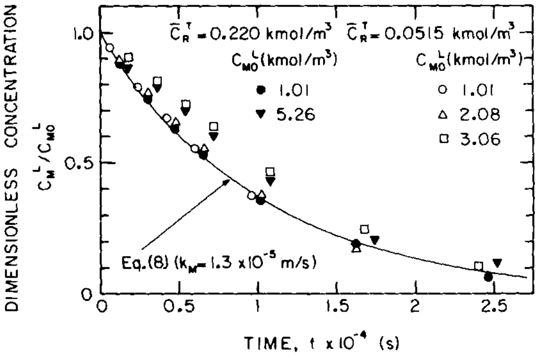

Figure 3. Effect of initial Pt concentration in the field solution on the permeation rate. $C_{HO}{}^L = 0.505$ kmol/m^3; $C_{SO}{}^R = 0.500$ kmol/m^3.

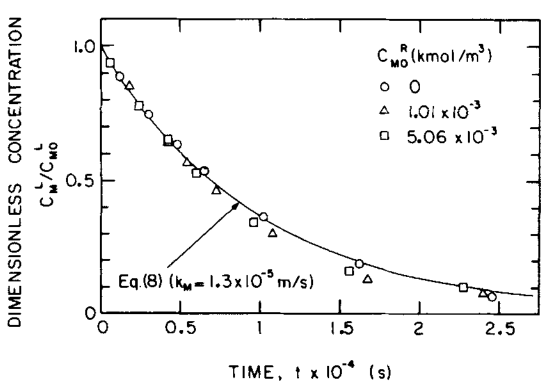

Figure 4. Effect of initial Pt concentration in the stripping solution on the permeation rate. C_{MO}^L = 1.01 × 10^{-3} kmol/m^3; C_{HO}^L = 0.505 kmol/m^3; $\bar{C}_R^T$ = 0.220 kmol/m^3; C_{SO}^R = 0.500 kmol/m^3.

deviation between the observed values of C_M^L/C_{MO}^L for C_{MO}^L = 2.08 × 10^{-3} kmol/m^3 and Eq. 8 for the aqueous film diffusion control.

The similar results at $\bar{C}_R^T$ = 0.220 kmol/m^3 are also shown in Figure 3. The observed values for C_{MO}^L = 1.01 × 10^{-3} kmol/m^3 are in good agreement with Eq. 8, but those for C_{MO}^L = 5.26 × 10^{-3} kmol/m^3 deviate positively from Eq. 8. This deviation is due to the same reason as in the case of $\bar{C}_R^T$ = 0.0515 kmol/m^3 because the J_M^L max value of 6.7 × 10^{-5} mol/m^2·s for C_{MO}^L = 5.26 × 10^{-3} kmol/m^3 is larger than the $\bar{J}_{M,\max}$ value of 5.4 × 10^{-5} mol/m^2·s calculated with $\bar{D}_M$ = 4.35 × 10^{-10} m^2/s.

Permeation experiments in which the stripping solution initially contained platinum at C_{MO}^R = 1.01 × 10^{-3} and 5.06 × 10^{-3} kmol/m^3 were carried out to investigate the extent to which platinum can be concentrated across the liquid membrane. Figure 4 shows the time-dependent concentrations of platinum in the left cell. All the experimental data are in good agreement with Eq. 8, which is represented by the solid line. The permeation rate of platinum can be expressed by Eq. 8, which was derived for the aqueous film diffusion control under the conditions in which the stripping solution initially contains platinum up to 5 × 10^{-3} kmol/m^3.

The concentration factor C_M^R/C_M^L, i.e. the ratio of Pt concentration in the stripping solution to that in the feed solution, attains a high value of 60 in the experiment where C_{MO}^R = 5.06 × 10^{-3} kmol/m^3. This result indicates that the TOA supported liquid membranes can be successfully used in the separation and concentration of platinum from dilute solutions.

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NOTATION

C_{HO} = initial hydrochloric acid concentration, kmol/m^3
C_M = aqueous platinum concentration, kmol/m^3
C_{MO} = initial aqueous platinum concentration, kmol/m^3
$\bar{C}_M$ = platinum complex concentration in the membrane phase, kmol/m^3
$\bar{C}_R^T$ = total concentration of TOA in the membrane phase, kmol/m^3
C_{SO} = initial concentration of stripping agents, kmol/m^3
D_M = diffusion coefficient of platinum in the aqueous phase, m^2/s
$\bar{D}_M$ = diffusion coefficient of the platinum-TOA complex in the membrane phase, m^2/s
J_M = flux of platinum in the aqueous phase, mol/m^2·s
$\bar{J}_M$ = flux of the platinum-TOA complex in the membrane phase, mol/m^2·s
k_M = mass transfer coefficient in the aqueous film, m/s
l = thickness of the supporting membrane, m
S = membrane area, m^2
t = time, s
V = volume of the solution in each cell compartment, m^3
x = distance from the left interface, m
δ = aqueous film thickness, m
τ' = membrane constant

Superscripts

0 = interface, $x = 0$
l = interface, $x = l$
L = left cell compartment
R = right cell compartment

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