

	facial zone	$[\text{m} \cdot \text{s}^{-1}]$
k_w	= mass transfer coefficient in aqueous phase	$[\text{m} \cdot \text{s}^{-1}]$
N_s	= saturated concentration at interface	$[\text{m}^{-2}]$
P	= distribution ratio of iron defined by \bar{C}_F/C_F	$[-]$
R	= mass transfer resistance	$[\text{s} \cdot \text{m}^{-1}]$
r	= reaction rate of interfacial reaction	$[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$
T	= temperature	$[\text{K}]$
Γ	= excess surface concentration	$[\text{m}^{-2}]$
θ	= fraction adsorbed	$[-]$
Π	= interfacial pressure	$[\text{N} \cdot \text{m}^{-1}]$
ϕ	= coefficient to relate the concentration of iron in neutral form to the total concentration of iron	$[-]$
<Subscripts>		
b	= bulk phase	
i	= at interface position	
o	= organic phase	
r	= interfacial	

w	= aqueous phase
F	= iron
TH	= R_3NHCl
THF	= $\text{R}_3\text{NHClFeCl}_3$
—	= organic phase

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SOME CHARACTERISTICS OF LIQUID MEMBRANE WITH TRI-*n*-OCTYLAMINE

MAKOTO HARADA, FUMIO YAMAZAKI, MOTONARI ADACHI
AND WATARU EGUCHI

Institute of Atomic Energy, Kyoto University, Uji 611

Key Words: Liquid Membrane, Extraction, Tri-*n*-Octylamine, Enrichment of Iron, Permeation Rate

The characteristics of the liquid membrane with tri-*n*-octylamine were elucidated. This liquid membrane spontaneously concentrates metals without controlling the concentrations of the agent which provides the driving force to the uphill transport of metals. The rate of iron permeation through the liquid membrane is dependent on the diffusional resistances in two aqueous phases, the diffusional resistance in the membrane phase, and the interfacial resistances. When the acid concentration in the aqueous raffinate phase is large, the interfacial resistances are negligibly small, and the diffusional resistance in the membrane phase is also negligibly small at high amine concentration in the membrane phase. In this case, the permeation rate is controlled only by the diffusional resistance in the raffinate phase.

Introduction

Uphill transport by means of liquid membrane is performed with the aid of an agent which provides the driving force to the transport by coupling with a carrier involved in the membrane.^{1,3)} If we use a carrier such as a chelating agent, hydrogen ion controls the uphill transport.⁷⁾ The hydrogen ion permeates through the membrane, causing uphill trans-

port of the solute. Thus the concentrations of hydrogen ion in two aqueous phases must be controlled to requisite values, because the concentrations vary greatly during uphill transport. If, however, an amine of high molecular weight is used as the metal carrier, the concentrations of the agent providing the driving force to the uphill transport would spontaneously be maintained at the initial values during the transport of solute, because the amine acts as a carrier at high concentration of the agent and permeation of the agent by the other mechanism hardly occurs compared to the permeation of solute accompanied with

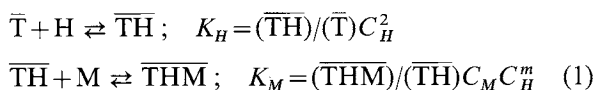
Received October 24, 1983. Correspondence concerning this article should be addressed to M. Harada. F. Yamazaki is now at Nippon Steel Corp., Kimitsu 292, and W. Eguchi is now at Dept. of Chem. Eng., Kyoto Univ., Kyoto 606.

uphill transport.⁴⁾

This work aims at the elucidation of this characteristic of the amine carrier. First, the characteristic of concentrating metals by amine carrier is discussed theoretically. The maximum enrichment factor is introduced to evaluate the enrichment ability of the carrier. Second, the spontaneous enrichment of metal by amine carrier without controlling the agent concentrations is experimentally demonstrated. Finally, the kinetics of iron enrichment through the liquid membrane is discussed by taking into account the interfacial rate process accompanied by iron enrichment.⁶⁾ It will be shown that the permeation resistance in the liquid membrane is negligibly small under appropriate operation conditions.

1. Characteristic of Liquid Membrane with Amine

Let us first consider the liquid membrane system with an amine as the carrier, where ion pairing is simplified as



In the ion pair system, the amine-metal complex \overline{THM} is formed from the amine-acid complex \overline{TH} , and thus \overline{THM} is formed by consecutive reaction. The formation constants of acid and metal complexes are also given in Eq. (1). The m value is determined by the metal-ion charge and is set at 2 for the sake of simplicity.

A liquid membrane containing the carrier is located between two aqueous phases, 1 and 2. We postulate for the sake of simplicity: 1) the thickness of the liquid membrane L is small so that the holdup of metal in the membrane is negligibly small; 2) a steady concentration profile is formed in the membrane and the reactions between the aqueous and the membrane phases are rapid enough to be equilibrated; and 3) the diffusion coefficients of the species in question have a unique value irrespective of species and the total concentration of the carrier, \bar{C}_N , is kept constant through the membrane.

The concentrations of the species in the membrane are expressed at the two interfaces:

$$\begin{aligned} (\bar{T})_j &= \bar{C}_N / (1 + K_H C_{Hj}^2 + K_j C_{Hj}^m C_{Mj}) \\ (\overline{TH})_j &= K_H C_{Hj}^2 \bar{C}_N / (1 + K_H C_{Hj}^2 + K_j C_{Hj}^m C_{Mj}) \\ (\overline{THM})_j &= K_j C_{Hj}^m C_{Mj} \bar{C}_N / (1 + K_H C_{Hj}^2 + K_j C_{Hj}^m C_{Mj}) \\ &\quad (j=1, 2) \end{aligned} \quad (2)$$

Here, $K_j = K_H K_M C_{Hj}^2$. The fluxes of metal and acid through the membrane are expressed as

$$\begin{aligned} J_M &= k_m [(\overline{THM})_1 - (\overline{THM})_2] \\ J_H &= k_m [\{(\overline{TH})_1 + (\overline{THM})_1\} - \{(\overline{TH})_2 + (\overline{THM})_2\}] \end{aligned} \quad (3)$$

where k_m is the mass transfer coefficient in the membrane. We assume negligible resistances for acid and metal transfer in the two films of the aqueous phases.

Figure 1 shows the equilibrium relation calculated from Eq. (1) and the phase trajectory of metal enrichment, which is calculated for the batch operation with the use of Eqs. (2) and (3) and the balance equations of the acid and the metal species.

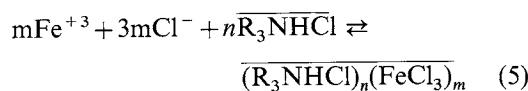
Figure 1(a) shows typical features of the equilibrium relationships in the ion-pairing system, where metal complex is formed by reacting with acid complex without releasing acid. The total concentration of acid in the membrane phase \bar{C}_H increases with C_H , approaching a saturated value, \bar{C}_N . Since mineral acid reacts with free amine to yield stable amine-acid complex, the acid concentration in the membrane is kept nearly constant in a wide range of C_H , with and without metal loading. Thus, the J_H value is kept at a very low value during metal enrichment. Figure 1(b) shows typical features of the phase trajectory. The metal is concentrated towards the aqueous phase 2, accompanied with negligible change of the acid concentrations in both aqueous phases, until the metal concentration reaches the $J_M=0$ curve. Thereafter, the trajectory changes along the curve $J_M=0$, approaching the thermodynamic equilibrium state, Eq. (2). A quasi-equilibrium state is attained after the trajectory changes on the $J_M=0$ curve, because the metal flux is actually maintained at a negligibly small value and the acid flow is fixed at a small value. Thus, it requires a very long period until the concentrations of acid and metal appreciably change. This causes spontaneous enrichment of metal without controlling the acid concentrations in either aqueous phase.

The maximum degree of metal enrichment E is obtained from point M as shown in Fig. 1(b), which is evaluated by postulating a negligible change of acid concentrations in both aqueous phases.

$$E = [C_{M2}^+ / C_{M1}^+]_{C_{H2}=C_{H20}, C_{H1}=C_{H10}} \quad (4)$$

The real degree of enrichment takes a value close to this maximum value.

Let us next consider the application of metal enrichment by amine membrane to the ferric ion system. The distribution of iron(III) between the hydrochloric acid aqueous solution and tri-*n*-octylamine in benzene solution is described as⁵⁾



$$\bar{C}_F = f(\bar{C}_N, \phi C_F) \quad (6)$$

ϕ is the function of acid concentration in the aqueous phase, which is a catch-all coefficient for grasping the effects of the aqueous-phase activity coefficients and activity of chloride ion. A typical example of the

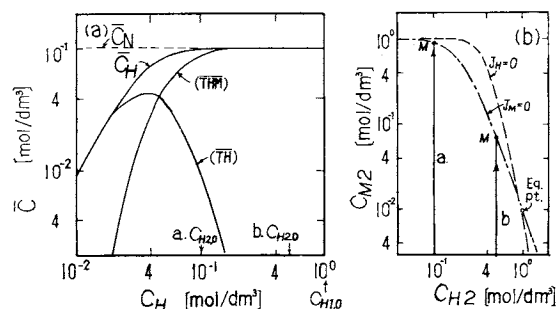


Fig. 1. Characteristics of amine-ion pairing extraction and trajectories of metal enrichment by liquid membrane in batch operation.

(a) Equilibrium relationship, $K_H = 10^3$, $K_M = 10^6$, $\bar{C}_N = 0.1$, $C_M = 0.01$, in mol/dm³ units.
(b) Trajectories of metal enrichment, $C_{M10} = 10^{-2}$, $C_{M20} = 10^{-3}$, $C_{H10} = 1.0$, $C_{H20} = 0.1$ for a, $C_{H20} = 0.5$ for b, $\bar{C}_N = 0.1$, in mol/dm³ units, $V_1/V_2 = 100$.

distribution of iron(III) is demonstrated in **Fig. 2**. The distribution can be described by Eq. (6), as is clear from Fig. 2. The ϕ -value is strongly dependent on the acid concentration, as shown in the previous report.⁶⁾

A quasi-equilibrium state of the liquid membrane operation is described as

$$\bar{C}_{F1} = \bar{C}_{F2} \quad (7)$$

The maximum degree of enrichment is expressed by use of Eqs. (7) and (6):

$$E = \phi_1/\phi_2 \quad (8)$$

In Fig. 2, the total concentration of acid in the organic phase is also shown. It attains a saturated value which is equal to \bar{C}_N in a wide range of acid concentration. Since the acid transport through the membrane is expected to be negligibly small, Eq. (8) can be used for evaluating maximum degree of enrichment. The E value is about 10^4 if $C_{H1} = 3$ and $C_{H2} = 0.1$ mol/dm³, and one can expect very effective enrichment with the help of a liquid membrane containing the amine as the metal carrier.

The following experiments were performed to ensure that spontaneous enrichment is realized in the iron-TOA system and to elucidate the rate of iron permeation through the liquid membrane.

2. Experimental

All reagents used in this work were the same as reported elsewhere.⁵⁾

Ferric chloride was concentrated with the use of a liquid membrane, supported by a porous filter made of Teflon (fluoro milipore filter, Sumitomo Electric Company, mean pore size $0.65 \mu\text{m}$, thickness $50 \mu\text{m}$ and void fraction 0.75). The liquid membrane consisted of tri-*n*-octylamine (TOA)-acid complex in benzene solution.

The experimental set-up is shown in **Fig. 3**. The

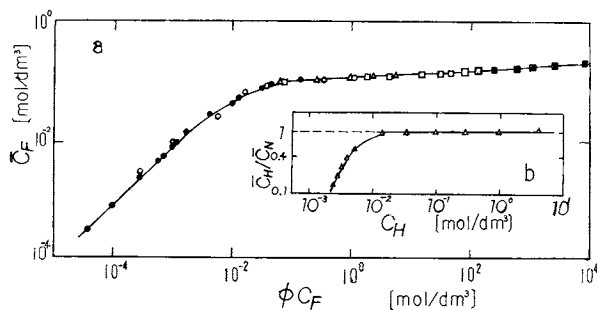


Fig. 2. Distribution equilibrium of iron extraction by TOA in benzene and equilibrium in acid extraction.

(a) Distribution of iron(III) by TOA-acid complex in benzene $\bar{C}_N = 0.236$ mol/dm³. The several types of keys correspond to the experimental results for various acid concentrations in aqueous phase.

(b) Distribution of hydrochloric acid at $\bar{C}_N = 0.236$ mol/dm³.

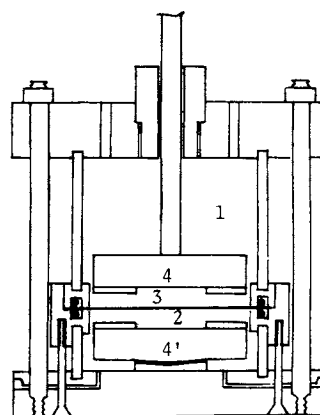


Fig. 3. Experimental apparatus of liquid membrane. 1, 2, aqueous phase compartment; 3, liquid membrane; 4, 4', stirrers.

liquid membrane was supported between two hydrochloric acid solutions. Both aqueous phases were stirred by impellers, one being driven magnetically and the other driven by the usual agitator. Two stirrers were located at symmetrical positions from the membrane. The start-up of the membrane operation was performed as follows: First, the aqueous phase was fed to the lower compartment. Then the teflon filter was set and filled with the amine solution. Finally, the other aqueous phase was fed to the upper compartment and stirring was started. Concentrations of ferric ion were measured on-line by circulating both aqueous phases through the cells of spectrophotometers with pumps. The pH meter was located at the circulating line of the aqueous phase of lower acid concentration. The interfacial area A of the membrane was 19.6 cm^2 and the volumes of the aqueous phases were $30\text{--}50 \text{ cm}^3$.

The resistances existing in the two aqueous films and in the membrane were determined by transferring phenol and acetone between the two aqueous phases. In this case, the membrane contained benzene only.

The stirring speed was changed to evaluate separately the resistances in the aqueous films and in the membrane. All experiments were performed at 25°C.

3. Results and Discussion

3.1 Iron enrichment

The course of enrichment of iron is demonstrated in Fig. 4. The experimental condition is shown in the figure. The time course of the concentration changes of iron shows that iron was concentrated from aqueous phase 1 ($C_{H1}=1.0$ mol/dm³) to phase 2 ($C_{H2}=0.05$ mol/dm³). The phase trajectory of the enrichment is shown in Fig. 5. The initial states for the two aqueous phases were located at I_1 and I_2 . During enrichment, the acid concentrations were kept to their initial values and effective enrichment was realized in this system. After reaching the curve $J_F=0$, the concentrations of acid and iron changed on the curve $J_F=0$. The feature of the trajectory is the same as mentioned in the preceding section. The closed circles represent the quasi-equilibrium points, which are estimated by assuming immobility of the acid. The experimental results (open circles) approaches the closed circles. The maximum degree of enrichment is calculated from Eq. (8) to be 410 at this experimental condition, while the corresponding value obtained experimentally was 110. This difference arises from acid permeation during enrichment due to partial rupture of the liquid membrane and to the formation of a small amount of excess acid-amine complex, TH_{1+n} , at the interface contacting with higher-acidity aqueous phase.

3.2 Kinetics of iron permeation

The transport of solutes through carrier-free membrane is described as

$$\begin{aligned} J_S &= k_w(C_{S1} - C_{S1i}) = k_m(\bar{C}_{S1i} - \bar{C}_{S2i}) \\ &= k_w(C_{S2i} - C_{S2}) \end{aligned} \quad (9a)$$

where the subscript i represents the value at the boundary between aqueous and membrane phases. The mass transfer coefficients in both aqueous phases agree with each other, because agitation in both phases was performed under almost the same conditions. Thus the overall mass transfer coefficient K_{ov} is given by

$$1/K_{ov} = 2/k_w + 1/Pk_m, \quad (10)$$

where P is the distribution coefficient of the solute between the aqueous phase and the membrane. In deriving Eqs. (9) and (10), we assume steady transport in the membrane phase, because the time delay to approach steady transport is about 120 s.

Equation (10) can be rewritten by use of diffusion coefficients:

$$1/K_{ov} = 2L_w/D + L\chi/P\bar{D}\varepsilon \quad (11)$$

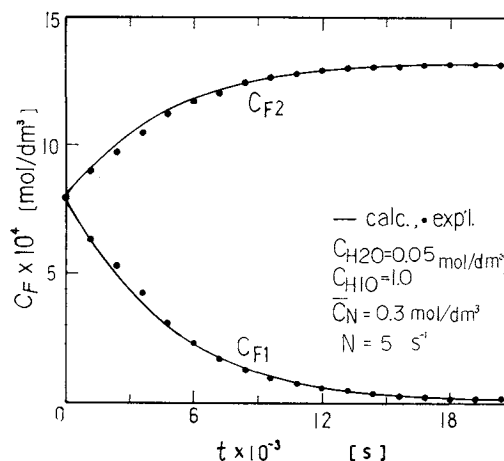


Fig. 4. Time course of enrichment in batch operation.

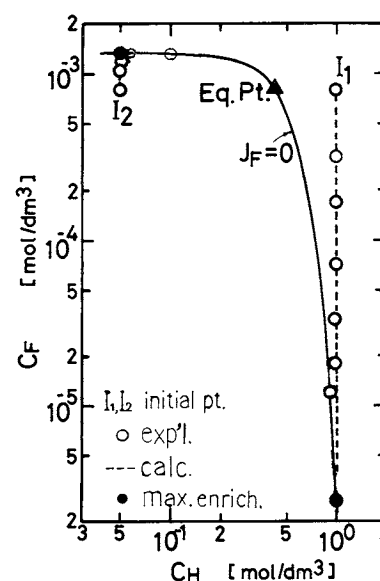


Fig. 5. Trajectory of enrichment of iron obtained in the experiment shown in Fig. 4.

Here, D is the diffusion coefficient of the solute. ε and χ represent the porosity and the tortuosity of the membrane filter. In deriving Eq. (11), film theory is assumed for the sake of simplicity. The thickness of the aqueous phase film L_w and the membrane thickness L are separately evaluated from the observed values of K_{ov} for different solutes, acetone and phenol, with the help of the diffusion coefficients in the aqueous and organic phases. The resultant value is

$$\chi L/\varepsilon = 1.3 \times 10^{-4} \text{ m} \quad (12)$$

The L_w value can be correlated with the stirring speed as

$$L_w = 1.02 \times 10^{-4} N^{-0.67} \text{ m} \quad (13)$$

N is the stirring speed in r.p.s.

Permeation of iron through the liquid membrane was carried out at 5 r.p.s. The initial fluxes measured are shown in Fig. 6. The open circles are the experi-

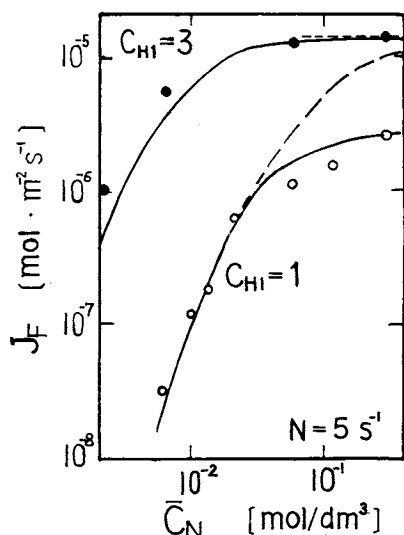


Fig. 6. Initial flux of iron permeation through membrane. $C_{F1} = C_{F2} = 1.0 \times 10^{-3}$, $C_{H2} = 0.05$ mol/dm³. Keys: solid curves, calc. by taking into account all resistances; broken curve, calc. by assuming diffusional resistances; dotted line, calc. by assuming diffusional resistance in aqueous phase 1.

mental results at $C_{H1} = 1.0$ mol/dm³ and $C_{H2} = 0.05$ mol/dm³. The broken curve represents the result of calculation from Eq. (9b).

$$J_F = k_w(C_{F1} - C_{F1i}) = k_m(\bar{C}_{F1i} - \bar{C}_{F2i}) \\ = k_w(C_{F2i} - C_{F2}) \quad (9b)$$

We assumed equilibrium between aqueous and membrane phases. D and \bar{D} were taken as 5×10^{-10} m²/s and the average of the diffusion coefficients for the amine-acid complex and the amine-iron complex, respectively.⁶⁾ The experimental results at low TOA concentrations agree well with the broken curve but take much lower values at high TOA concentrations when $C_{H1} = 1.0$ mol/dm³. This disagreement arises from the resistances due to the interfacial processes at the phase boundaries between the aqueous phases and the membrane.

The interfacial process concerned with iron extraction by TOA was elucidated in the previous report. The rate of interfacial process can be expressed by⁶⁾

$$J_F = k_{rj}(C_{Fji} - C_{Fji}^*), \\ k_{rj} = k(\overline{\text{TH}})_{ji} \phi_j / [1 + K_{\text{TH}}(\overline{\text{TH}})_{ji}] \\ j = 1, 2 \quad (14)$$

where C_{Fi}^* represents the concentration in equilibrium with \bar{C}_{Fi} . K_{TH} is the adsorption constant of $\overline{\text{TH}}$.

$$K_{\text{TH}} = 14000 \text{ dm}^3/\text{mol} \quad (15a)$$

and k is given as

$$k = 2.1 \times 10^{-5} \text{ m}^4/\text{mol} \cdot \text{s} \quad (15b)$$

In this case, the iron flux given by Eq. (14) is balanced

with Eq. (9b). $(\overline{\text{TH}})_i$ can be evaluated from the equilibrium relationships reported previously.⁵⁾ Combination of Eq. (9b) with Eq. (14) yields

$$J_F = (1/R_{ov})(C_{F1} - C_{F2}P_2/P_1) \quad (16a)$$

where R_{ov} is the overall resistance and is related with

$$R_{ov} = 1/k_w + 1/k_{r1} + 1/k_m P_1 + P_2/P_1 k_{r2} + P_2/P_1 k_w \\ \equiv R_{w1} + R_{r1} + R_m + R_{r2} + R_{w2} \quad (16b)$$

where P_j is the distribution coefficient of iron:

$$P_j = \bar{C}_{Fj}/C_{Fj}^*, \quad j = 1, 2$$

The iron flux calculated from Eq. (16) by use of the diffusion coefficients mentioned previously is shown in Fig. 6 as the solid curve. The curve well interprets the trend of the experimental results.

The contributions of all resistances to the overall total are shown in Fig. 7. The open circles are the results for $C_{H1} = 1.0$ mol/dm³ and $C_{H2} = 0.05$ mol/dm³. In this case, the interfacial resistances R_{r1} and R_{r2} play a major role in the overall value at higher \bar{C}_N value. On the contrary, at lower concentrations of \bar{C}_N , the dominant resistance is the resistance in the membrane, R_m .

The experiment shown in Fig. 5 was performed at the same condition for the acid concentrations as in Fig. 6 (open keys). The time course of the concentration changes as shown in Fig. 4 can be calculated by Eqs. (9), (14) and (15), (16), and is shown in the same figure as the solid curves. The trajectory calculated is also shown as the solid curve in Fig. 5. The agreement of the calculated value with the experimental one is satisfactory.

The methods of decreasing permeation resistance can be estimated from the relation, Eq. (16b). One is to increase the P_1 value and the other is to increase the ϕ_1 -value. Both conditions are satisfied by increasing the C_{H1} value. To ensure this, iron was transferred from the aqueous phase 1, ($C_{H1} = 3.0$ mol/dm³) to the other aqueous phase 2 ($C_{H2} = 0.05$ mol/dm³). The experimental fluxes are shown in Fig. 6 as the closed keys. The flux in this case is much higher than that at $C_{H1} = 1.0$ mol/dm³ and $C_{H2} = 0.05$ mol/dm³. The overall resistance and the contributions of each resistance to the overall total are shown in Fig. 7. The overall resistance is controlled by the R_m at lower \bar{C}_N values, but approaches the R_{w1} value as \bar{C}_N increases. When \bar{C}_N is large, iron transport is controlled only by the diffusion step in the aqueous film of phase 1. The amine carrier in this case gives full play to the facilitated transport of metal.

Conclusion

Characteristics amine-facilitated transport through liquid membrane were elucidated. The liquid mem-

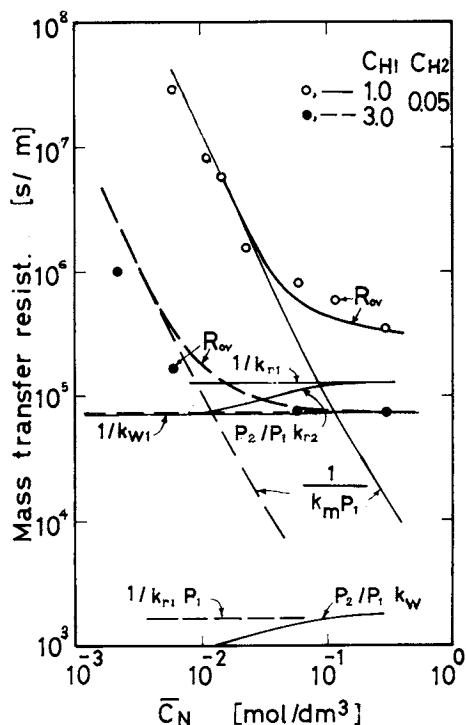


Fig. 7. Overall resistance and contributions of individual resistances thereto. Keys: curves, calculated resistances; conditions of experiment, $C_{F1} = C_{F2} = 1.0 \times 10^{-3}$ mol/dm³. For $C_{H1} = 3.0$ mol/dm³, R_{r2} and R_{w2} are less than 10^3 s/m.

brane with amine carrier can concentrate metals spontaneously without controlling the concentrations of the agent which provides driving force to the uphill transport. The resistance to metal transport in the membrane can be reduced to a negligible order of magnitude under appropriate conditions. This result shows that a liquid membrane of hollow-fiber type is effective in practice.

Acknowledgment

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Nomenclature

C_F, \bar{C}_F	= concentrations of iron in aqueous and organic phases	[mol/dm ³ , or mol/m ³]
C_H	= concentration of acid in aqueous phase	[mol/dm ³ , or mol/m ³]
C_M	= concentration of metal	[mol/dm ³ , or mol/m ³]
\bar{C}_N	= concentration of amine in membrane phase	[mol/dm ³ , or mol/m ³]
C_s	= concentration of solute	[mol/dm ³ , or mol/m ³]
D	= diffusion coefficient	[m ² /s]
E	= maximum degree of enrichment	[—]
J_F	= flux of iron	[mol m ⁻² s ⁻¹]
J_H	= flux of acid	[mol m ⁻² s ⁻¹]
J_M	= flux of metal	[mol m ⁻² s ⁻¹]

J_S	= flux of solute	[mol m ⁻² s ⁻¹]
K_H, K_M	= equilibrium constants defined by Eq. (1)	[in mol, dm ³]
K_{ov}	= overall mass transfer coefficient	[m/s]
k	= interfacial reaction rate coefficient	[mol ⁻¹ m ⁴ s ⁻¹]
k_m	= mass transfer coefficient in membrane	[m/s]
k_r	= mass transfer coefficient for interfacial process	[m/s]
k_w	= mass transfer coefficient of aqueous phase	[m/s]
L	= thickness of membrane	[m]
L_w	= thickness of stagnant layer in aqueous phase	[m]
N	= agitation speed	[s ⁻¹]
P	= distribution ratio	[—]
R_m	= resistance in membrane	[s/m]
R_{ov}	= overall resistance	[s/m]
R_r	= resistance due to interfacial reaction	[s/m]
R_w	= resistance in aqueous phase	[s/m]
V	= volume of aqueous phase	[m ³]
ε	= porosity	[—]
ϕ	= a coefficient to relate concentration of iron in neutral form to total concentration of iron in aqueous phase	[—]
χ	= tortuosity	[—]
()	= concentration	[mol/dm ³]

<Subscripts>

0	= initial state
1, 2	= aqueous phases 1 and 2, and values in membrane adjacent to aqueous phases 1 and 2
i	= value at interface
j	= aqueous phase j
F	= iron
N	= amine
H	= acid
S	= solute

<Subscripts>

*	= value in equilibrium with membrane phase
+	= value at condition $\bar{C}_{M1} = \bar{C}_{M2}$
—	= value in organic phase

<Chemical species>

T	= free amine
TH	= amine-acid complex
H	= acid
THM	= amine-metal complex

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