RATE OF FERRIC CHLORIDE EXTRACTION WITH TRI-*n*-OCTYLAMINE

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The rate of iron(III) extraction and stripping by TOA in benzene-hydrochloric acid aqueous solution system is elucidated. Interfacial reaction between iron in neutral form in the aqueous phase and the adsorbed amine-acid complex plays a significant role in the extraction and the stripping rates when the hydrochloric acid concentration is low in the aqueous phase. At high acid concentration, the rates are controlled by the diffusional steps in the aqueous and the organic phases.

Introduction

The major reaction process concerned with metal extraction by an amine of high molecular weight is interfacial in nature, because the amine has very low solubility in the aqueous phase. This reaction process is rapid and the rate of metal extraction from the aqueous phase to the organic phase is usually controlled by diffusion processes of the reactants. By contrast, metal extraction in the reverse direction is not always rapid compared with the rate evaluated on the premise of diffusion control. A kinetic study of metal extraction is, therefore, of particular interest in solvent extraction and liquid membrane operations.

Single drop technique has usually been used for enhancing the diffusional rates of the reactants so that the reaction process plays a significant role in the overall extraction rate. In a recent paper, Inoue *et al.*⁶⁾ presented their kinetic data of experiments using the single drop technique. This technique, however, has significant difficulties which arise from the complicated hydrodynamics of drop motion. The kinetic data may involve some uncertainties because of the difficulty of separating the effect of hydrodynamics from the overall extraction rate.

The interfacial reaction rate depends on the concentration of the metal species in the aqueous phase which directly reacts with the amine. This concentration is strongly affected by the acid concentration, and the interfacial reaction process can be elucidated if the extraction condition is properly selected so that the reaction rate process plays a significant role in the overall extraction rate. In this case, other tech-

niques such as use of the stirred transfer cell with constant interfacial area provides information on a relatively slow reaction process, because the effect of hydrodynamics is well understood.

Danesi *et al.*²⁾ reported kinetic data in iron(III) extraction by tri-laurylamine-hydrochloric acid complex with the use of the stirred transfer cell. However, the interpretation of their data has several weak points, e.g., the evaluation of the diffusional step and the description of reaction rate equations.

This work is to provide kinetic information on iron(III) extraction by tri-*n*-octylamine (TOA) with the aid of the transfer cell of Lewis type. It is shown that the interfacial reaction between iron and TOA-acid complex plays a significant role in the extraction rate at low acid concentration in the aqueous phase.

1. Experimental

1.1 Reagents

TOA supplied by Tokyo Kasei Co. Ltd. was used after purification by usual procedures.¹⁾ Benzene, hydrochloric acid and ferric chloride of guaranteed grade, supplied by Nakarai Chemicals Co. Ltd. were used without further purification. Water was purified by distillation.

1.2 Procedures

Iron(III) was transferred between hydrochloric acid solution and TOA in benzene solution, which had been equilibrated with 1 mol/dm³-hydrochloric acid aqueous solution. In the forward extraction, iron was transferred from the hydrochloric acid solution to the organic phase in a stirred transfer cell, the same as described in the previous report.⁴⁾ Iron concentration in the aqueous phase was measured on-line by circulating the phase through the cell of a spectrophotometer. The organic phase was sample out and was

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fed back to the original organic phase after determining the concentration of iron by a spectrophotometer. The initial flux was measured from the changes of iron concentrations in both phases.

In the reverse extraction, iron was transferred from the organic phase to the aqueous phase, which contained hydrochloric acid (0.50 mol/dm³). The organic phase containing iron was prepared by contacting the TOA–hydrochloric acid complex solution with aqueous solution which contained iron in the requisite amount. The iron flux was measured from the concentration change of iron in the aqueous phase.

Mass transfer coefficients in both phases were determined by the same procedures as in the previous work.⁴⁾ The diffusion coefficients of iron(III), TOA–acid complex, and iron–TOA complex were measured by a Schlieren apparatus⁵⁾ and a position-scanning spectrophotometer⁷⁾ with use of a slide contact cell or flow junction cell.⁷⁾ The interfacial tension of the extraction system was measured by the Wilhelmy's plate or the pendant drop methods. All experiments in this work were performed at 25.0°C.

2. Experimental Results and Discussion

The equilibrium relationships for iron extraction by TOA–acid complex³⁾ are essential to interpret the kinetic data and are summarized in **Table 1**. In this table, the amine–acid complex in monomer form is produced almost irreversibly, as shown in Eq. (1). $(\overline{\text{TH}})_n\text{F}_m$ represents the complex $(\overline{\text{R}_3\text{NHCl}})_n(\text{FeCl}_3)_m$. The overline shows the species in the organic phase. The complexes of the sets $n=1, 2, m=0$, and $n=4, m=1$, involve combined water.³⁾ Water is omitted in the table for the sake of simplicity. (S) represents the concentration of the species S . C_F is the total concentration of iron in the aqueous phase. The ϕ value is a factor for evaluating the activity of iron in FeCl_3 -form in the aqueous phase:

$$[\text{FeCl}_3] \propto [\text{Fe}^{3+}][\text{Cl}^-]^3 \propto \phi C_F$$

Here, $[]$ represents the activity. The ϕ value is a function of chloride concentration, C_c , when $C_c \gg C_F$, and is defined to be unity when $C_c = 0.5 \text{ mol/dm}^3$. When the aqueous phase involves hydrochloric acid, the ϕ value is a function of acid concentration in the aqueous phase, C_H , as shown in **Table 2**.

2.1 Diffusion coefficients

Figure 1 shows the diffusion coefficient of 1:1 amine–acid complex obtained from the Schlieren patterns in an experiment in which the benzene phase was contacted with benzene solution involving amine–acid complex in 0.3 mol/dm³. The diffusion coefficient is strongly dependent on the acid complex concentration.

The diffusion process for iron–amine complex in benzene solution was elucidated by using a position-

Table 1. Mechanism of iron extraction by TOA

$\overline{\text{R}_3\text{N}} + \text{H}^+ + \text{Cl}^- \rightarrow \overline{\text{R}_3\text{NHCl}}$	(1)
$2\overline{\text{R}_3\text{NHCl}} \rightleftharpoons (\overline{\text{R}_3\text{NHCl}})_2; K_H = 35.5$	(2)
$\text{Fe}^{+3} + 3\text{Cl}^- + 4\overline{\text{R}_3\text{NHCl}} \rightleftharpoons (\overline{\text{R}_3\text{NHCl}})_4(\text{FeCl}_3); K_{41} = 1.2 \times 10^6$	(3)
$2\text{Fe}^{+3} + 6\text{Cl}^- + 4\overline{\text{R}_3\text{NHCl}} \rightleftharpoons (\overline{\text{R}_3\text{NHCl}})_4(\text{FeCl}_3)_2; K_{42} = 9.0 \times 10^7$	(4)
$3\text{Fe}^{+3} + 9\text{Cl}^- + 4\overline{\text{R}_3\text{NHCl}} \rightleftharpoons (\overline{\text{R}_3\text{NHCl}})_4(\text{FeCl}_3)_3; K_{43} = 1.4 \times 10^6$	(5)
$4\text{Fe}^{+3} + 12\text{Cl}^- + 4\overline{\text{R}_3\text{NHCl}} \rightleftharpoons (\overline{\text{R}_3\text{NHCl}})_4(\text{FeCl}_3)_4; K_{44} = 4.6 \times 10^2$	(6)
$K_{nm} = ((\overline{\text{R}_3\text{NHCl}})_n(\text{FeCl}_3)_m) / (\overline{\text{R}_3\text{NHCl}})^n (\phi C_F)^m$	(7)
$\text{R}_3\text{N} : \text{T}, \text{R}_3\text{NHCl} : \text{TH}, (\overline{\text{R}_3\text{NHCl}})_n(\text{FeCl}_3)_m : (\overline{\text{TH}})_n\text{F}_m$	

Table 2. ϕ -Value

C_H [mol/dm ³]	0.05	0.1	0.5	1.0	2.0	3.0
ϕ	0.018	0.045	1.0	5.2	36	410

Fig. 1. Mutual diffusion coefficient in benzene–TOA–hydrochloric acid complex as a function of amine–acid complex concentration.

scanning spectrophotometer. The benzene phase was contacted in a diffusion cell with a benzene solution with iron and TOA content of 0.15 and 0.30 mol/dm³, respectively. In this case, the iron was in the form $(\overline{\text{TH}})_4\text{F}_2$ and the mutual diffusion coefficient of $(\overline{\text{TH}})_4\text{F}_2$ and benzene system could be measured. The resultant value was found to be nearly constant irrespective of the iron concentration, $2.11 \times 10^{-10} \text{ m}^2/\text{s}$. The diffusion coefficient of $(\overline{\text{TH}})_4\text{F}_2$ increased at low iron concentration. To ensure this, the benzene phase was contacted with a benzene solution with iron and TOA content of 0.0083 and 0.0223 mol/dm³, respectively. The diffusion coefficient of iron observed under this condition was $3.5 \times 10^{-10} \text{ m}^2/\text{s}$, a little larger than that in the higher iron concentration range.

When iron is extracted, an iron–amine complex is formed and diffuses in TOA–acid complex solution,

accompanied by association reactions. The diffusion of iron species in this situation is different from the mutual diffusion process mentioned previously. To investigate this difference, two benzene solutions were contacted with each other, one containing 0.116 mol/dm^3 of $(\text{TH})_4\text{F}_2$ and the other containing 0.462 mol/dm^3 of iron-free amine-acid complex. The diffusion coefficient of the iron species, obtained from the concentration profiles of iron, was nearly constant irrespective of iron concentration, at $1.8 \times 10^{-10} \text{ m}^2/\text{s}$. This value is a little smaller than the mutual diffusion coefficient for $(\text{TH})_4\text{F}_2$ -benzene solution at high iron concentration, $2.1 \times 10^{-10} \text{ m}^2/\text{s}$.

The diffusion coefficients of iron in the aqueous phase, which contained $0.5\text{--}3 \text{ mol/dm}^3$ of hydrochloric acid, were measured. The observed values were insensitive to iron concentration and were nearly $5 \times 10^{-10} \text{ m}^2/\text{s}$.

2.2 Mass transfer coefficients

The mass transfer coefficients in both phases were determined by the method mentioned in the previous report.⁴⁾ The results can be correlated by the following equations for a stirring speed of 100 rpm.

$$k_w = 0.64D^{0.53}, \quad k_o = 0.50\bar{D}^{0.53} \quad (8)$$

Here, D and $\bar{D}$ represent the diffusion coefficients in the aqueous and the organic phases, respectively.

2.3 Initial flux of iron in forward direction

The initial iron fluxes were determined from the gradients of the iron concentration changes in both phases, which were measured at the conditions $\bar{C}_N = 0.0223$ and 0.121 mol/dm^3 , $\bar{C}_N$ being the total concentration of amine. Fluxes obtained from the concentration changes in the aqueous and the organic phases agreed with each other. Figure 2 shows the results of the initial flux, J_F .

The measured fluxes at $C_H = 3.0 \text{ mol/dm}^3$ were proportional to the total concentration of iron in the aqueous bulk phase, C_{Fb} , and fell approximately on a single line irrespective of $\bar{C}_N$ in the low C_{Fb} range. As C_{Fb} increased, the flux branched into separate curves depending on the values of $\bar{C}_N$, and the changes of the flux became insensitive to C_{Fb} . The above single line can be fitted to $J_F = k_w C_{Fb}$. This shows that the extraction of iron is controlled by the diffusion step of iron in the aqueous phase. The dotted lines are calculated from $J_F = k_o \bar{C}_N/2$. In evaluating the k_o value, we used the diffusion coefficient for the amine-acid complex shown in Fig. 1. The observed fluxes are close to the dotted lines when C_{Fb} is large. In this case, it can be deduced from the equilibrium relationships that $(\text{TH})_4\text{F}_2$ is formed near the interface almost irreversibly and thus the rate of extraction is controlled by the diffusion step of the amine-acid complex in the organic phase.

The iron flux is described by Eq. (9), if we postulate

Fig. 2. Initial iron fluxes in iron extraction from aqueous phase to organic phase. Keys: solid curves, calculated by taking into account the resistances in aqueous and organic phases and interfacial resistance; dotted lines, calculated from $J_F = k_o \bar{C}_N/2$; broken-dotted curves, calculated by taking into account the diffusional resistances; symbol, experimental results.

that (1) the association reactions in the organic phase are in local equilibrium, and (2) the diffusion coefficients of both reactants and products are assumed to be equal with each other in the organic phase for the sake of simplicity.

$$J_F = k_w(C_{Fb} - C_{Fi}) = k_o(\bar{C}_{Fi} - \bar{C}_{Fb}) \quad (9)$$

Here, the subscript i represents the value at the interface position. $\bar{C}_{Fb}$ was zero because the organic phase was initially free from iron. The k_o value is assumed to be unique irrespective of species and is evaluated from Eq. (8) with the help of the diffusion coefficient for the amine-acid complex at $\bar{C}_{Hb}$, because the diffusion of the amine-acid complexes plays a key role in the extraction rate. The total TOA concentration, $\bar{C}_N$, is constant throughout the stagnant layer in the organic phase because of postulation (2). Finally, we make another postulation: (3) The interfacial reaction process is fast and the equilibrium state is attained at the interfacial zone.

The broken-dotted curves a and b in Fig. 2 for $C_H = 3.0 \text{ mol/dm}^3$ are calculated from Eq. (9) with postulation (3). These curves can well interpret the trend of the experimental results. The weak dependency of the experimental J_F -value on C_{Fb} in the high C_{Fb} range arises from the formation of the species $(\text{TH})_4\text{F}_3$ in small amount. The agreement of the experimental results with the calculated ones ensures that the reactions involved in this extraction system are rapid enough to be equilibrated at the interfacial zone when $C_H = 3.0 \text{ mol/dm}^3$.

The experimental fluxes obtained at $C_H = 1.0$ and 0.05 mol/dm^3 took much lower values than that at $C_H = 3.0 \text{ mol/dm}^3$. The fluxes at $C_H = 1.0$ and 0.05 mol/dm^3 calculated from Eq. (9) with postulation (3)

are shown as broken-dotted lines, and they cannot interpret low experimental fluxes. Thus, it can be deduced that postulation (3) is not satisfied at lower acid concentrations.

2.4 Initial flux of iron reverse extraction

The initial fluxes obtained in iron extraction in the reverse direction are shown in Fig. 3 together with the experimental conditions. The experimental fluxes at $\bar{C}_N = 0.0223$ and 0.0033 mol/dm³ are proportional to $\bar{C}_{Fb}$ and the difference in the fluxes at these $\bar{C}_N$ values is small. By contrast, the iron fluxes at $\bar{C}_N = 0.121$ mol/dm³ are much smaller than the above results.

The flux is described on the same postulations (1) and (2) mentioned previously:

$$J_F = k_w(C_{Fi} - C_{Fb}) = k_o(\bar{C}_{Fb} - \bar{C}_{Fi}) \quad (10)$$

C_{Fb} is zero in this experiment. The k_o value can be evaluated from Eq. (8) by assuming that $\bar{D} = 1.8 \times 10^{-10}$ m²/s for $\bar{C}_N = 0.121$ mol/dm³ and $\bar{D} = 3.5 \times 10^{-10}$ m²/s for $\bar{C}_N = 0.0223$ mol/dm³, which corresponds to the diffusion coefficient of iron complex in benzene solution. The broken curves in Fig. 3 are calculated from Eq. (10) with the help of postulation (3). The calculated values agree closely with the value estimated from $J_F = k_o \bar{C}_{Fb}$ and fits well the experimental results at $\bar{C}_N = 0.0223$ mol/dm³. Thus, the extraction rate at this condition is controlled by the diffusion process of iron-amine complex in the organic phase. The fluxes at $\bar{C}_N = 0.0033$ mol/dm³ are slightly larger than the result at $\bar{C}_N = 0.0223$ mol/dm³. This arises from the difference in the diffusion coefficient of iron-amine complex. The broken line for $\bar{C}_N = 0.12$ mol/dm³ is also calculated from Eq. (10) with postulation (3). This line is about half the calculated values for $\bar{C}_N = 0.0223$ mol/dm³, and the mass transfer resistance in the aqueous phase comes into play at $\bar{C}_N = 0.12$ mol/dm³. However, the calculated value at this condition (broken line) still cannot interpret the low experimental flux. This disagreement suggests that postulation (3) is not usable at high concentrations of TOA.

2.5 Interfacial processes

The experimental results for forward and reverse extractions assert that the reaction rate at the interface plays a significant role in the extraction of iron. In this section we discuss the interfacial processes concerned with iron extraction.

Amine-acid complex is strongly surface-active, and the change of interfacial tension as amine-acid complex is added to the benzene-water system provides important information about the interfacial processes. It would be natural to consider that monomeric complex, $\overline{\text{TH}}$, can adsorb on the interface. The concentration of the monomeric complex is easily evaluated from Eq. (2).

The Gibbs equation in the isothermal case is ex-

Fig. 3. Initial iron fluxes in iron extraction from organic phase to aqueous phase $C_H = 0.5$ mol/dm³. Keys: solid lines, calculated by taking into account the resistances in aqueous and organic phases and the interfacial resistance; broken lines, calculated by taking into account the diffusional resistances in aqueous and organic phases; symbols, experimental results.

pressed by Eq. (11) when $\overline{\text{TH}}$ only adsorbs.

$$\partial \Pi = \Gamma_{\text{TH}} \partial \bar{\mu}_{\text{TH}} \quad (11)$$

Here, Π is the interfacial pressure and Γ_{TH} is the excess surface concentration of $\overline{\text{TH}}$. $\bar{\mu}_{\text{TH}}$ is the chemical potential of $\overline{\text{TH}}$. We assume the Langmuir isotherm from the kinetic viewpoint, for the sake of simplicity.

$$\theta_{\text{TH}} = K_{\text{TH}}(\overline{\text{TH}}) / [1 + K_{\text{TH}}(\overline{\text{TH}})], \quad K_{\text{TH}} = k_{a\text{TH}} / k_{d\text{TH}} \quad (12)$$

$k_{a\text{TH}}$ and $k_{d\text{TH}}$ are the rate constants of adsorption and desorption, respectively. θ_{TH} represents the surface fraction covered by $\overline{\text{TH}}$. Combining Eq. (11) with Eq. (12), Szyszkowski's equation can be derived:

$$\Pi = N_s k_b T \ln [1 + K_{\text{TH}}(\overline{\text{TH}})] \quad (13)$$

In the above derivation, we assumed that $\overline{\text{TH}}$ behaves ideally in the organic phase. N_s is the saturated concentration of $\overline{\text{TH}}$ at the interface. k_b and T are the Boltzmann constant and the temperature.

Plots of Π against $(1 + K_{\text{TH}}(\overline{\text{TH}}))$ on semi-log scale are shown in Fig. 4. The K_{TH} value can be determined so that the experimental values give a good fit to a straight line. The K_{TH} and N_s values obtained from Fig. 4 are

$$K_{\text{TH}} = 1.4 \times 10^4 \text{ dm}^3/\text{mol}, \\ N_s = 6.0 \times 10^{18} \text{ molecule/m}^2 \quad (15)$$

The interfacial pressures were also measured between the benzene-amine solution containing iron in $\bar{C}_F \cong \bar{C}_N/2$ and 3 mol/dm³-hydrochloric acid aqueous

Fig. 4. Interfacial pressure against concentration of amine-acid complex in monomer form in benzene.

solution in equilibrium with the organic phase. The pressure was insensitive to $\bar{C}_F$ in the range $0.0055 < \bar{C}_F < 0.15$ mol/dm³. The closed keys in Fig. 4 are the pressures measured in this experiment. The concentration $(\overline{\text{TH}})$ in Fig. 4 was calculated from the equilibrium relationships shown in Table 1. The interfacial pressures of the system with iron are close to the open keys, which correspond to the iron-free system. This fact asserts that iron complex is much less surface-active than $\overline{\text{TH}}$, even when the iron complex exists in large amount.

We next consider the interfacial reaction process. Since TOA and its complex have very low solubilities in the aqueous phase, the iron in the aqueous phase would react with $\overline{\text{TH}}$ at the interface between the two phases. Taking this into account, we make a postulation on the interfacial process as follows:

$()_s$ represents the species existing in the interfacial zone. $\overline{\text{THF}}$ is less stable in the organic phase and associates with amine-acid complex to yield aggregates.

We assume that the rate-determining step of the interfacial processes is the direct reaction of iron in neutral form with the adsorbed $\overline{\text{TH}}$.

The reaction rate at the interface is described as

$$r = \bar{k}(\text{FeCl}_3)_i \theta_{\overline{\text{TH}}} - \bar{k} \theta_{\overline{\text{THF}}} \quad (18)$$

In the above equation, $\theta_{\overline{\text{THF}}}$ is expressed by

$$\theta_{\overline{\text{THF}}} = K_{\overline{\text{THF}}}(\overline{\text{THF}})_i / [1 + K_{\overline{\text{TH}}}(\overline{\text{TH}})_i] \quad (19)$$

$$K_{\overline{\text{THF}}} = k_{a\overline{\text{THF}}} / k_{d\overline{\text{THF}}}$$

because $K_{\overline{\text{THF}}}(\overline{\text{THF}})_i \ll K_{\overline{\text{TH}}}(\overline{\text{TH}})_i$.

$(\overline{\text{THF}})_i$ can be related to $((\overline{\text{TH}})_4\text{F})_i$:

$$(\overline{\text{THF}})_i = ((\overline{\text{TH}})_4\text{F})_i / (\overline{\text{TH}})_i^3 / K'_{41} \quad (20)$$

K'_{41} is the equilibrium constant of the reaction Eq. (17).

Equation (18) can be rewritten with the help of Eq. (12):

$$\begin{aligned} r &= [\bar{k} / \{1 + K_{\overline{\text{TH}}}(\overline{\text{TH}})_i\}] \\ &\times [K_{\overline{\text{TH}}}(\overline{\text{TH}})_i(\text{FeCl}_3)_i - (\bar{k} K_{\overline{\text{THF}}} / \bar{k} K'_{41}) \\ &\times ((\overline{\text{TH}})_4\text{F})_i / (\overline{\text{TH}})_i^3] \end{aligned} \quad (21)$$

Using the equilibrium relation concerned with $(\overline{\text{TH}})_i$, $((\overline{\text{TH}})_4\text{F})_i$ and ferric chloride, i.e., Eq. (3), and taking into account $(\text{FeCl}_3) \propto \phi C_F$, the rate, r , is simplified as

$$\begin{aligned} r &= k_r(C_{Fi} - C_{Fi}^*) \\ k_r &= (K_{41} K_{\overline{\text{THF}}} \bar{k} / K'_{41}) \phi_i (\overline{\text{TH}})_i / [1 + K_{\overline{\text{TH}}}(\overline{\text{TH}})_i] \\ &\equiv k \phi_i (\overline{\text{TH}})_i / [1 + K_{\overline{\text{TH}}}(\overline{\text{TH}})_i] \end{aligned} \quad (22)$$

where C_{Fi}^* represents the aqueous-phase concentration of iron which is in equilibrium with $((\overline{\text{TH}})_4\text{F})_i$ and $(\overline{\text{TH}})_i$.

$$\phi_i C_{Fi}^* = ((\overline{\text{TH}})_4\text{F})_i / K_{41} (\overline{\text{TH}})_i^4$$

The interfacial process can be expressed in terms of the interfacial resistance, $1/k_r$.

The rate of iron extraction in the forward and reverse directions is described as

$$\begin{aligned} J_F &= k_w(C_{Fb} - C_{Fi}) = k_r(C_{Fi} - C_{Fi}^*) \\ &= k_o(\bar{C}_{Fi} - \bar{C}_{Fb}) = K_{ov}(C_{Fb} - \bar{C}_{Fb}/P) \end{aligned} \quad (23)$$

Here,

$$1/K_{ov} = 1/k_w + 1/k_r + 1/Pk_o \quad \text{or}$$

$$R_{ov} = R_w + R_r + R_o$$

and P is the distribution coefficient of iron:

$$P = \bar{C}_{Fi} / C_{Fi}^*$$

The $(\overline{\text{TH}})_i$ value is evaluated from the equilibrium relations in the organic phase at given $\bar{C}_N$ and $\bar{C}_{Fi}$. The k value is evaluated so that the calculated values from Eq. (23) fit well the results obtained in the experiments of iron extraction in the reverse and forward directions.

$$k = 2.1 \times 10^{-5} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1} \quad (24)$$

The solid curves in Figs. 2 and 3 represent the results of calculation with the aid of Eqs. (22) and (23). As is clear from Eq. (22), the interfacial resistance increases as $(\overline{\text{TH}})_i$ and ϕ decrease. Since $K_{\overline{\text{TH}}}(\overline{\text{TH}})_i \gg 1$ in the usual case, the resistance is approximately given by

$$1/k_r = K_{\overline{\text{TH}}} / \phi k \quad (25)$$

and the interfacial resistance, R_r , is dependent upon ϕ only. The ϕ value is a coefficient which relates C_F to (FeCl_3) . Then the interfacial resistance plays a significant role in iron transfer when the concentration

of acid becomes low.

Figure 5 shows the overall resistances in the forward extraction. Iron transfer is controlled by the mass transfer resistance in the aqueous phase, $R_w = 1/k_w$, at $C_H = 3 \text{ mol/dm}^3$, because the ϕ value is large. As C_H decreases, the ϕ value becomes small and interfacial resistance has a strong effect on iron transfer, even in the case of forward extraction.

The experimental results given in Fig. 3 can be converted to an expression in terms of resistance. Figure 6 shows the overall mass transfer resistance based on the organic phase, $\bar{R}_{ov} = P/K_{ov}$, and the contribution of individual resistances $\bar{R}_w = P/k_w$, $\bar{R}_r = P/k_r$, and $\bar{R}_o = 1/k_o$ to the overall resistance. Iron transfer is controlled by the mass transfer resistance in the organic phase, $\bar{R}_o$ in the low $\bar{C}_N$ -range. When $\bar{C}_N$ increases, the distribution ratio P increases and interfacial resistance determines iron transfer.

Conclusion

Extraction and stripping rates of iron(III) were measured for TOA in the benzene-hydrochloric acid aqueous solution system, by using a transfer cell with constant interfacial area. The rate is dependent on the diffusional steps in the organic and the aqueous phases, and the interfacial reaction process. The interfacial reaction is strongly dependent on the acid concentration in the aqueous phase. The rate-determining step in the interfacial processes was estimated to be

The rate of reaction is determined. The interfacial resistance due to this interfacial reaction plays a significant role in the rate of extraction and stripping of iron at low concentration of acid in the aqueous phase.

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Nomenclature

C_F	= total concentration of iron(III)
	[mol·dm ⁻³ or mol·m ⁻³]
C_F^*	= total concentration of iron in the aqueous phase in equilibrium with the iron concentration in the organic phase
	[mol·dm ⁻³ or mol·m ⁻³]
C_C	= total concentration of chloride
	[mol·dm ⁻³ or mol·m ⁻³]
C_H	= total concentration of acid
	[mol·dm ⁻³ or mol·m ⁻³]
$\bar{C}_H$	= total concentration of acid in organic

Fig. 5. Individual resistances and overall resistance in iron extraction in forward direction. Keys: solid lines, calc., $\bar{C}_N = 0.12 \text{ mol/dm}^3$, $C_F = 1 \times 10^{-3} \text{ mol/dm}^3$; symbols, experimental results.

Fig. 6. Individual resistances and overall resistance in iron extraction in reverse direction. Keys: solid lines, calc., $C_H = 0.05 \text{ mol/dm}^3$; symbols, experimental results.

$\bar{C}_N$	phase	[mol·dm ⁻³ or mol·m ⁻³]
	= total concentration of amine in organic phase	[mol·dm ⁻³ or mol·m ⁻³]
D	= diffusion coefficient	[m²·s ⁻¹]
J_F	= flux of iron	[mol·m ⁻² ·s ⁻¹]
K	= equilibrium constant	[in mol, dm³ unit]
K_{ov}	= overall mass transfer coefficient	[m·s ⁻¹]
K_{41}	= equilibrium constant for reaction Eq. (2)	[mol⁴·dm ⁻¹²]
K'_{41}	= equilibrium constant for reaction Eq. (17)	[mol³·dm ⁻⁹]
k	= interfacial reaction coefficient defined by Eq. (22)	[m⁴·mol ⁻¹ ·s ⁻¹]
$\bar{k}, \bar{k}$	= reaction rate constants defined by Eq. (18)	[m·s ⁻¹]
k_a	= rate constant of adsorption	[m·s ⁻¹]
k_d	= rate constant of desorption	[mol·m ⁻² ·s ⁻¹]
k_b	= Boltzmann constant	[N·m·K ⁻¹]
k_o	= mass transfer coefficient in organic phase	[m·s ⁻¹]
k_r	= rate coefficient permeating through inter-	

	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_3NHC
THF	= $\text{R}_3\text{NHCFeCl}_3$
—	= organic phase

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

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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

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