

MECHANISM AND KINETICS OF PALLADIUM EXTRACTION WITH β -HYDROXYOXIME

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Extraction rates of palladium(II) with 2-hydroxy-5-nonyl acetophenone oxime were measured by use of a Lewis-type cell to elucidate the extraction mechanism. It was found that the rate of complex formation both at the interface and in the aqueous phase was determined by the 1:1 complex formation between trihalo complex of palladium, $\text{PdX}_3(\text{H}_2\text{O})^-$ and the neutral species of β -hydroxyoxime, HR. The extraction rate of the bromo complex of palladium was faster than that of the chloro complex. The rate constants for the complex formation obtained from the extraction rate were compatible with those obtained in an 80 wt% ethanol-water mixture.

Introduction

Many kinetic models have been proposed to explain the extraction rate for several extraction sys-

tems.^{6,15,16)} Since these models involve several parameters, they can be made to fit the kinetic data by adjusting the parameter values.^{15,16)} It is necessary for elucidating the kinetics and mechanism to discuss how rational the model parameters are.

We have proposed a general model to explain the

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kinetics of metal ion extraction with a chelating agent.⁴⁾ The parameters involved in this model are the rate constant of metal complex formation and the physicochemical terms. The latter terms are the partition constant and the adsorption constant of the chelating agent, the mass transfer coefficients, and the specific interfacial area of the experimental apparatus used. These values can be determined from the results of individual experiments.

The rate constant for metal-complex formation in the aqueous phase is difficult to determine, because the chelating agent has poor solubility. The rate constant is frequently treated as an adjusting parameter to interpret the extraction rate. The resultant value must be checked for rationality.

We have elucidated the kinetic mechanism of copper extraction with the help of experimental results for the effects of the alkyl chain length of β -hydroxyoxime^{5,12)} and of diluent⁵⁾ on the rate of copper extraction. These results can be quantitatively interpreted by the proposed model. The parameter values were ascertained to be rational. The role of α -hydroxyoxime, which is used as a catalyst for the copper extraction with β -hydroxyoxime, was also interpreted by this model.⁵⁾

There are three loci for complex formation: the interface between the organic and aqueous phases, the aqueous stagnant film and the aqueous bulk phase. The individual contribution of these reaction fields to the extraction rate⁴⁾ can be estimated from the model. The interface itself is important when the partition constant of the chelating agent to the organic phase and the rate constant for complex formation are large.

This work aims at elucidation of the mechanism and kinetics of palladium extraction with β -hydroxyoxime on the basis of the proposed model. The complex formation of a platinum-group metal is much different from that of a transition metal.⁹⁾ Since the complex formation of a platinum-group metal is very slow, an intensive-mixing vessel has frequently been used for studying the extraction kinetics and mechanisms.^{7,8,10)} Lack of knowledge of the interfacial area of the liquid droplets in the vessel prevents grasping the kinetic nature of the metal extraction. We used a Lewis-type cell with a constant interfacial area. The rate constants for the complex formation were measured in the homogeneous phase of 80wt% ethanol and water mixture, because the β -hydroxyoxime and metal complex could not be dissolved in water.

1. Experimental

1.1 Preparation of organic and aqueous phases

2-hydroxy-5-nonyl acetophenone oxime (HNAPO or HR) was purified from commercial SME529 by a method described elsewhere.¹¹⁾ The diluents, benzene

and *n*-heptane of analytical grade, were used without further purification. The concentration of HNAPO in the organic phase was determined spectroscopically with the help of an extinction coefficient of 3800 dm³mol⁻¹cm⁻¹ at 315 nm.

Both palladium (II) solutions in the presence of chloride and bromide ions were prepared by dissolving palladium chloride and palladium nitrate in deionized water, respectively. The pH was adjusted to be in the range 0.0–2.0 with perchloric acid, and ionic strength was adjusted to 0.2 mol/dm³ with sodium perchlorate except in the low-pH case. The total concentrations of halide ions were adjusted by addition of sodium chloride or sodium bromide. All inorganic chemicals used were of analytical grade.

The concentration of palladium in the aqueous phase was determined by a spectrophotometer at 500 nm. The complex of palladium in the organic phase was also measured by the spectrophotometer at 380 nm.

1.2 Experimental procedure

The extraction rates were measured by means of the modified Lewis cell described in the previous paper.⁵⁾ The time courses of the concentration of palladium complex in the organic phase were measured by spectrophotometry.

The rate of palladium-HNAPO complex formation was measured by means of a stopped-flow spectrophotometer in an 80wt% ethanol-water mixture, because both HNAPO and its palladium complex do not dissolve in the aqueous phase.

All experiments were carried out at 298 K.

2. Results and Discussion

2.1 Effects of concentrations of reagents on the initial extraction rate

When HNAPO dissolved in *n*-heptane was contacted with an aqueous solution of palladium, the absorbance of the *n*-heptane phase changed with time *t* as shown in Fig. 1. The absorbances at 380 nm increased with time, while those at 310 nm decreased. The absorbance at 380 nm is assigned to the 1:2 complex of Pd and HNAPO and the extinction coefficient was obtained as 5830 dm³/(mol·cm). The extraction rate of Pd (II) can be evaluated from the change in absorbance at 380 nm.

Figure 2 shows the effects of total concentration of chloride ion on the initial extraction rate (open circles), which has a maximum value at [Cl]_T = 20 mmol dm⁻³. The fractions of chloro-complexes of palladium to the total concentration of palladium can be calculated from the reaction schemes in the aqueous phase^{1–3)}:



$$\beta_i = [\text{PdCl}_{i+1}] / ([\text{PdCl}_i][\text{Cl}^-]) \quad (1b)$$

$$\beta_0 = 10^{4.7}, \quad \beta_1 = 10^{3.0}, \quad \beta_2 = 10^{2.6}, \quad \beta_3 = 10^{1.3}$$

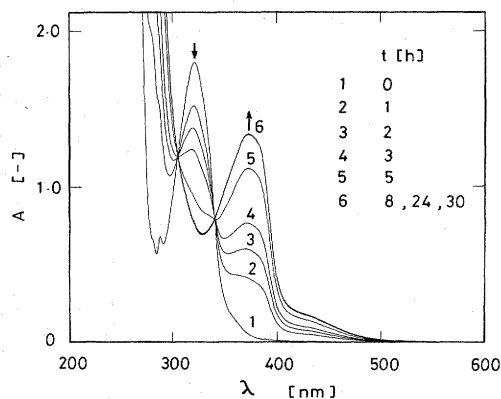


Fig. 1. Change of absorbance in *n*-heptane with time
aqueous phase: $[Pd]_t = 3.0 \text{ mmol dm}^{-3}$, $I = 0.2 \text{ mol dm}^{-3}$
 $[Cl^-]_t = 20 \text{ mmol dm}^{-3}$, $pH = 2.0$
organic phase: $[HR]_0 = 0.45 \text{ mmol dm}^{-3}$

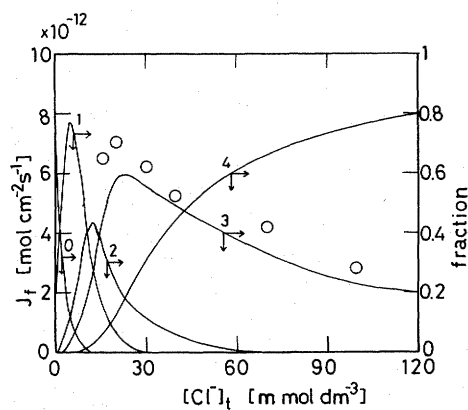


Fig. 2. Relationships between initial extraction rate (open circles) and total concentration of chloride ion. Solid lines show the fraction of chloro complex of palladium to total palladium. 0: Pd^{2+} ; 1: $PdCl^+$; 2: $PdCl_2$; 3: $PdCl_3^-$; 4: $PdCl_4^{2-}$
aqueous phase: $[Pd]_t = 5.0 \text{ mmol dm}^{-3}$; $I = 0.2 \text{ mol dm}^{-3}$
 $pH = 2.0$
organic phase: $[HR]_0 = 3.7 \text{ mmol dm}^{-3}$ in *n*-heptane

$$[Cl^-]_t = \sum_{i=0}^4 i[PdCl_i] + [Cl^-] \quad (2)$$

$$[Pd]_t = \sum_{i=0}^4 [PdCl_i] \quad (3)$$

The solid lines in Fig. 2 show the calculated fractions of chloro-complexes of palladium with the total palladium concentration, 5 mmol dm^{-3} . The fraction of $PdCl_3(H_2O)^-$ reaches a maximum value at $[Cl^-]_t = 20 \text{ mmol dm}^{-3}$, and decreases with increase in $[Cl^-]_t$. This pattern is similar to the change in extraction rate with $[Cl^-]_t$. It is deduced from this result that the extracted species is $PdCl_3(H_2O)^-$. $PdCl_3(H_2O)^-$ is labile due to the trans effect, i.e., the water molecule is easily released.

Figure 3 shows the effects of the concentrations of HR, $PdCl_3(H_2O)^-$ and proton on the initial rates of palladium extraction with HNAPO in *n*-heptane. The initial extraction rate is proportional to the concentration of $PdCl_3(H_2O)^-$ as shown in Fig. 3(b), while the rate is almost independent of the concentrations of HNAPO and proton. Similar behavior was observed

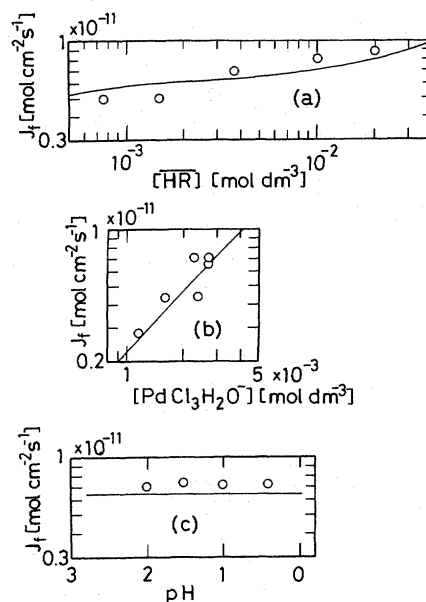


Fig. 3. Effects of concentration of reagents on initial extraction rate. Solid lines show calculated values (see in text).

(a) Dependence of rate on HNAPO concentration in *n*-heptane.

aqueous phase: $[Pd]_t = 5 \text{ mmol dm}^{-3}$, $pH = 2.0$,
 $[Cl^-]_t = 20 \text{ mmol dm}^{-3}$

(b) Dependence of rate on concentration of tri-chloro-complex of palladium.

organic phase: $[HR] = 3.6 \text{ mmol dm}^{-3}$ in *n*-heptane
aqueous phase: $[Pd]_t = 5 \text{ mmol dm}^{-3}$,
 $[Cl^-]_t = 15\text{--}100 \text{ mmol dm}^{-3}$,
 $pH = 2.0$

(c) Dependence on pH in the aqueous phase

organic phase: $[HR] = 3.6 \text{ mmol dm}^{-3}$ in *n*-heptane
aqueous phase: $[Pd]_t = 5 \text{ mmol dm}^{-3}$,
 $[Cl^-]_t = 30 \text{ mmol dm}^{-3}$

in the extractions of both chloro-complex and bromo-complex of palladium with HNAPO in benzene diluent.

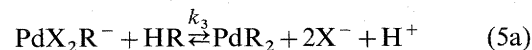
2.2 Reaction mechanism

1) Reaction rate in 80wt% ethanol-water mixture

We postulate the reaction schemes:



$$K_1 = [PdX_2R^-][X^-][H^+]/([PdX_3(H_2O)^-][HR]) \quad (4b)$$



$$K_2 = [PdR_2][X^-]^2[H^+]/([PdX_2R^-][HR]) \quad (5b)$$

where $X^- = Cl^-$ or Br^- .

We apply the stationary state for PdX_2R^- and assume $K_1 \ll K_2$. In this case, the rate of PdR_2 formation can be expressed by:

$$\begin{aligned} d[PdR_2]/dt &= k_{II}([HR][PdX_3(H_2O)^-] \\ &\quad - [PdR_2][H^+]^2[X^-]^3/(K_1K_2[HR])) \end{aligned} \quad (6a)$$

$$k_{II} = k_1/(1 + k_1[H^+][X^-]/(k_3K_1[HR])) \quad (6b)$$

When both palladium and HNAPO solutions in 80wt% ethanol-water mixture solvent were mixed, the absorbance at wave length 380 nm, which is assigned to 1:2 complex of Pd and HNAPO, increased exponentially:

$$d[\text{PdR}_2]/dt = k_{\text{obs}}([\text{PdR}_2]_{\infty} - [\text{PdR}_2]) \quad (7)$$

If we neglected the terms of higher order than second order of the concentration of PdR_2 , k_{obs} can be expressed with the initial concentrations of reactants, by Eq. (6a) as (Appendix (1))

$$k_{\text{obs}} = k_{\text{II}}(2[\text{PdX}_3(\text{H}_2\text{O})^-]_0 + [\text{HR}]_0 + \alpha/(K_1 K_2)) \quad (8a)$$

$$\alpha = [\text{X}^-]_0^3[\text{H}^+]^2/[\text{HR}]_0 \quad (8b)$$

The concentration of $\text{PdX}_3(\text{H}_2\text{O})^-$ was estimated by using the stability constants in the aqueous phase, because there are no data for these values in the 80 wt% ethanol-water mixture. The concentration of $\text{PdBr}_3(\text{H}_2\text{O})^-$ was evaluated by the following relation¹⁴⁾:

$$[\text{PdBr}_3(\text{H}_2\text{O})^-] = [\text{Pd}]_t / (1 + \beta[\text{Br}^-]_t) \quad (9)$$

$$\beta = 158 \text{ dm}^3 \text{ mol}^{-1}$$

where the stability constant in the aqueous phase is used.

Figures 4(a) and (b) show the relationship between k_{obs}/α and $(2[\text{PdX}_3(\text{H}_2\text{O})^-]_0 + [\text{HR}]_0)/\alpha$ in the presence of chloride and bromide ions respectively. In both cases, the observed data can be correlated with straight lines through the origin. This result shows that the reverse reaction process can be neglected ($1/K_1 K_2 \sim 0$) and that k_{II} is constant irrespective of $[\text{H}^+][\text{X}^-]/[\text{HR}]$. Then k_{II} is equal to k_1 , i.e., the reaction is determined by the 1:1 complex formation step between HR and $\text{PdX}_3(\text{H}_2\text{O})^-$. The values of k_1 were obtained as $1.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{PdCl}_3(\text{H}_2\text{O})^-$ and $250 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{PdBr}_3(\text{H}_2\text{O})^-$. The rate constants between $\text{PdX}_3(\text{H}_2\text{O})^-$ and phenanthroline in the aqueous phase were reported as $71 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{PdCl}_3(\text{H}_2\text{O})^-$ and $210 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{PdBr}_3(\text{H}_2\text{O})^-$ ¹³⁾. This is consistent with the present result in that the rate constant for bromo complex is greater than that for chloro complex, though the k_1 value for HNAPO in chloride solution is much lower than that for phenanthroline.

2) Extraction mechanism and rate The initial rate of metal ion extraction with a chelating agent can be described in terms of the equivalent circuit for HR flow¹³⁾:

$$J_f = R_o^{-1}(R_a^{-1} + R_s^{-1})/(R_a^{-1} + R_s^{-1} + R_o^{-1})P_{\text{HR}}^{-1} \times ([\text{HR}]_i - [\text{PdR}_2]_i[\text{X}^-]_i^3[\text{H}^+]_i^2 / K_{\text{ex}}[\text{HR}]_i[\text{PdX}_3(\text{H}_2\text{O})^-]_i) \quad (10a)$$

where

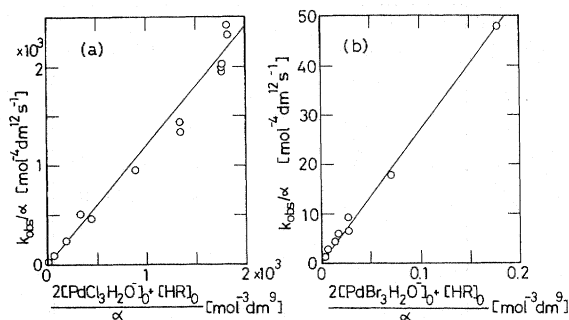


Fig. 4. Relationship of Eq. (8)

- (a) Relationship in chloride solution
 $[\text{Cl}^-]_t = 15\text{--}100 \text{ mmol dm}^{-3}$, $[\text{Pd}]_t = 1\text{--}15 \text{ mmol dm}^{-3}$
 $[\text{HR}] = 0.03\text{--}0.17 \text{ mmol dm}^{-3}$, pH = 0–2.0
- (b) Relationship in bromide solution
 $[\text{Br}^-]_t = 50\text{--}150 \text{ mmol dm}^{-3}$,
 $[\text{Pd}]_t = 0.5\text{--}5 \text{ mmol dm}^{-3}$
 $[\text{HR}] = 0.1\text{--}0.5 \text{ mmol dm}^{-3}$, pH = 0.7–2.0

Table 1. Parameters used for calculation of extraction rate

	Heptane	Benzene
$\Gamma^\infty [\text{mol cm}^{-2}]$	4.0×10^{-10}	4.1×10^{-10}
$\bar{K}_{\text{HR}} [\text{cm}^3 \text{ mol}^{-1}]$	2.0×10^7	2.0×10^6
$P_{\text{HR}} [—]$	3.8×10^3	3.5×10^4

$$k_w = 4.0 \times 10^{-4} \text{ cm s}^{-1}, (V/S) = 2.75 \text{ cm}$$

$$R_o^{-1} = k_o P_{\text{PdR}_2} \tilde{K} \quad (10b)$$

$$R_a^{-1} = R_f^{-1} + R_b^{-1} \quad (10c)$$

$$R_b = \bar{R}_f + \tilde{R}_f + R_b \quad (10d)$$

$$R_f = (1 + \tilde{K}^{-1}) \coth(\zeta_b)/(k_w \zeta_b) \quad (10e)$$

$$\bar{R}_f + \tilde{R}_f = (1 + \tilde{K}^{-1}) \sinh(2\zeta_b)/(2k_w \zeta_b) \quad (10f)$$

$$R_b = (S/V) \coth(\zeta_b) \sinh(2\zeta_b)/(2k_1') \quad (10g)$$

$$R_s^{-1} = k_1'(\delta P_{\text{HR}} + \Gamma^\infty \bar{K}_{\text{HR}} P_{\text{HR}}/(1 + \bar{K}_{\text{HR}}[\text{HR}])) \quad (10h)$$

$$\zeta_b = (2k_1' D(1 + \tilde{K}^{-1}))^{0.5}/k_w \quad (10i)$$

$$k_1' = k_1[\text{PdX}_3(\text{H}_2\text{O})^-] \quad (10j)$$

$$\tilde{K} = 2K_1 K_2 [\text{PdX}_3(\text{H}_2\text{O})^-][\text{HR}]/([\text{H}^+]^2[\text{X}^-]^3) \quad (10k)$$

The R_s and R_f values are the resistances due to the reactions in the interfacial zone and in the aqueous stagnant film respectively. The $(\bar{R}_f + \tilde{R}_f)$ value is the resistance for the ligand-group through the aqueous stagnant film, and R_b corresponds to the resistance of the reaction in the aqueous bulk phase.

The values of these resistances can be evaluated with the help of parameter values such as the physicochemical properties of HNAPO, reaction rate constant and mass transfer coefficient. These values are summarized in Table 1. The \tilde{K} value is very large due to the low value of $[\text{X}^-]$, and the ζ_b value is less than unity. Thus, Eq. (10a) is simplified as (Appendix (2))

$$J_f = k_1 [\text{PdX}_3(\text{H}_2\text{O})^-] [\overline{\text{HR}}] \Gamma^\infty \bar{K}_{\text{HR}} / (1 + \bar{K}_{\text{HR}} [\overline{\text{HR}}]) + ([\overline{\text{HR}}]/P_{\text{HR}}) \{1/k_w + S/(Vk_1 [\text{PdX}_3(\text{H}_2\text{O})^-])\}^{-1} \quad (11)$$

The first term on the right-hand side of Eq. (11) corresponds to the contribution of the interfacial reaction to the overall rate. The second term is the reaction rate concerning the HR diffusion in the aqueous stagnant film and the reaction process of complex formation in the aqueous bulk phase.

The solid lines in Fig. 3 show the values calculated by Eq. (11) based on the parameters summarized in Table 1. The rate constant for 1 : 1 complex formation was assumed as $k_1 = 5.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is the same order of magnitude as that obtained in the 80wt% ethanol-water mixture.

Figure 5 shows the effects of HNAPO concentrations in both *n*-heptane and benzene diluents on the initial rate of palladium extraction in the presence of chloride ion. The solid lines are calculated from Eq. (11). The extraction rate obtained in *n*-heptane at $[\overline{\text{HR}}]$ lower than $10^{-6} \text{ mol dm}^{-3}$ agrees with the value calculated from the first term of Eq. (11), i.e., the term due to the interfacial reaction, which is shown by the broken curve in the same figure. The contribution of the second term in Eq. (11) cannot be neglected in higher ranges of $[\overline{\text{HR}}]$. In benzene diluent, the contribution of interfacial reaction dominates the overall rate until $[\overline{\text{HR}}]$ becomes large. This trend arises from the much lower partition of HNAPO in the aqueous phase for benzene diluent than that in *n*-heptane diluent. Eq. (11) fits observed data in benzene diluent with $k_1 = 4.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The discrepancy between the rate constants in the two diluents may arise from uncertainties of the physicochemical properties.⁵⁾

Figure 6 shows the effect of $\text{PdX}_3(\text{H}_2\text{O})^-$ concentration on the initial extraction rate in the presence of chloride and bromide ions. The solid curves are calculated from Eq. (11). The rate constant obtained for bromo complex, $40 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, is ten times that for chloro complex. The increase in the rate constant qualitatively agrees with the trend observed in the homogeneous phase.

3) Discussion of the extraction rate observed using intensive-mixing apparatus The mechanism and rate of palladium extraction with β -hydroxyoximes were studied by using an intensive-mixing apparatus. Ma *et al.*¹⁰⁾ and Inoue *et al.*⁸⁾, respectively, used chelating agents, unpurified LIX65N (active species, 2-hydroxy-5-nonylbenzophenone oxime, HNBPO) dissolved in chloroform and HNAPO in the commercial diluent MSB210. They measured the change of Pd concentration in the aqueous phase under the conditions in which the rate was independent of stirring speed, i.e.,

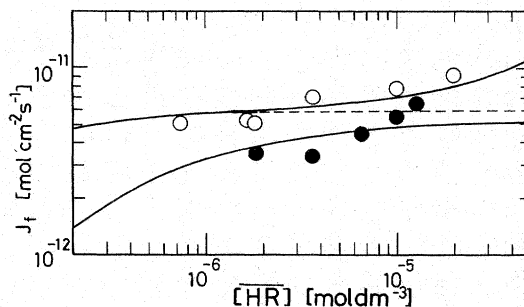


Fig. 5. Solvent effect on initial extraction rate of palladium (○) *n*-heptane; (●) benzene $[\text{Pd}]_i = 5 \text{ mmol dm}^{-3}$, $[\text{Cl}^-]_i = 20 \text{ mmol dm}^{-3}$, pH = 2.0

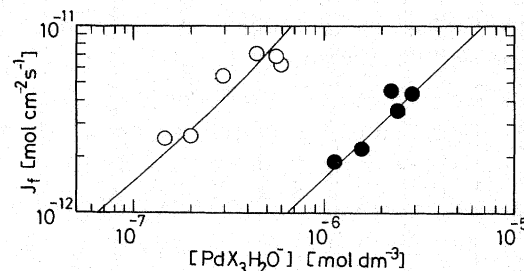


Fig. 6. Medium effect on initial extraction rate (○) Bromide ion; (●) Chloride ion organic phase: $[\overline{\text{HR}}] = 3.6 \text{ mmol dm}^{-3}$ in benzene aqueous phase: $[\text{Pd}]_i = 1.0\text{--}5.0 \text{ mmol dm}^{-3}$, pH = 2.0 $[\text{Cl}^-]_i = 20\text{--}100 \text{ mmol dm}^{-3}$ $[\text{Br}^-]_i = 50\text{--}150 \text{ mmol dm}^{-3}$

in the plateau region. The observed data can be correlated by:

$$-d[\text{Pd}]_i/dt = k_f [\text{Pd}]_i \quad (12)$$

The apparent rate constants k_f were proportional to $[\overline{\text{HR}}]/[\text{Cl}^-]$ for LIX65N and $[\overline{\text{HR}}]/([\text{Cl}^-][\text{H}^+])$ for HNAPO. The difference in dependency may be due to the difference in experimental conditions. In particular, the proton concentration in the work of Inoue *et al.* was much higher than in that of Ma *et al.*

Though the plateau region does not always suggest the presence of a chemical reaction-controlled process, we accept this assertion. In this case, the apparent rate constant is expressed with the help of Eqs. (6) and (11):

(Appendix (3))

$$([\overline{\text{HR}}]/k_f)(1 + \beta_3 [\text{Cl}^-]) = A(1 + B[\text{Cl}^-][\text{H}^+]/[\overline{\text{HR}}]) \quad (13a)$$

$$A^{-1} = ak_1 \{ \Gamma^\infty \bar{K}_{\text{HR}} (1 + \bar{K}_{\text{HR}} [\overline{\text{HR}}])^{-1} + (aP_{\text{HR}})^{-1} \} \quad (13b)$$

$$B = k_1 P_{\text{HR}} / k_3 K_1 \quad (13c)$$

where a is the specific interfacial area per unit organic volume.

The data reported by Ma *et al.* and Inoue *et al.* were rearranged according to Eq. (13) in **Fig. 7**. From this relationship, the values of A and B respectively are evaluated as $55 \text{ mol} \cdot \text{s} \cdot \text{dm}^{-3}$ and 0.4 for

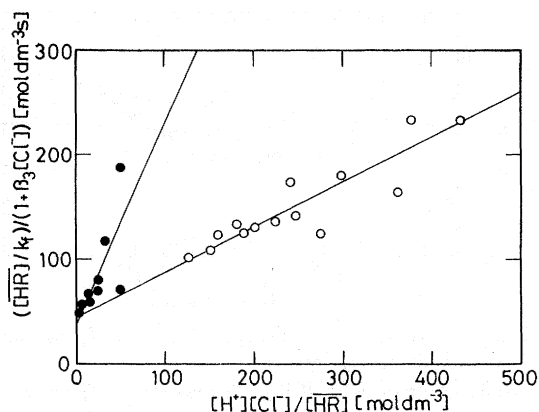


Fig. 7. Relationship of Eq. (13) by use of the Inoue *et al.* data (○), and Ma *et al.* data (●)

Experimental conditions:

	Inoue <i>et al.</i> data	Ma <i>et al.</i> data
$[Cl^-]_i$	1.6–3	0.05–1.0
$[H^+]$	0.85–2.5	0.1–1.0
$[HR]$	0.0064–0.116	0.005–0.03
	(HNAPO in MSB210)	(LIX65N in chloroform)

HNAPO, and $40 \text{ mol} \cdot \text{s} \cdot \text{dm}^{-3}$ and 1.9 for LIX65N. Since the values of a , Γ^∞ and \bar{K}_{HR} are not known to be available, they were estimated as follows:

a is equal to $6/d$ (d is the diameter of droplets
ca. 10^{-2} cm),

Γ^∞ is $10^{-10} \text{ mol cm}^{-2}$

and \bar{K}_{HR} is ca. 10^7 – $10^6 \text{ cm}^3 \text{ mol}^{-1}$ (see Table 1).

The P_{HR} values are 4×10^4 for HNBPO in chloroform and 4×10^3 for HNAPO in MSB230. The second term in Eq. (13b) can be neglected compared to the first term, suggesting that the complex formation mainly proceeds at the interface due to the large specific interfacial area. Thus, the rate constant k_1 can be estimated as 0.3 – $30 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Considering the uncertainty of the parameter values used, the estimated rate constants for complex formation are of reasonable order of magnitude. Notice that the rate of the 1:2 complex formation determines the extraction rate in the high $[Cl^-][H^+]/[HR]$ ranges.

Conclusion

(1) The extraction rate of palladium with HNAPO is determined by the rate of 1:1 complex formation between $\text{PdX}_3(\text{H}_2\text{O})^-$ and HR at low concentration of halide ion.

(2) The complex formation proceeds both in the aqueous bulk phase and at the aqueous-organic interface. The contribution of the interfacial reaction to the extraction rate can be interpreted by the help of a model in which the parameters can be evaluated by the use of physicochemical properties of the chelating agent.

(3) The extraction rate of bromo complex of

palladium is faster than that of chloro complex. The enhancement arises from an increase in the rate constant.

Appendix

(1) Derivation of Eq. (8)

It is assumed that the concentration of PdX_2R^- is very much lower than that of PdR_2 . The concentration of PdR_2 is very much lower than the initial concentrations of HR, $\text{PdX}_3(\text{H}_2\text{O})^-$, H^+ and X^- under these experimental conditions. Then the mass balance equations are expressed as

$$[\text{HR}]_0 = [\text{HR}] + 2[\text{PdR}_2] \quad (\text{A-1})$$

$$[\text{PdX}_3(\text{H}_2\text{O})^-]_0 = [\text{PdX}_3(\text{H}_2\text{O})^-] + [\text{PdR}_2] \quad (\text{A-2})$$

$$[\text{H}^+]_0 = [\text{H}^+] - 2[\text{PdR}_2] \quad (\text{A-3})$$

$$[\text{X}^-]_0 = [\text{X}^-] - 3[\text{PdR}_2] \quad (\text{A-4})$$

Inserting these mass balance equations into Eq. (6a) and neglecting the terms of more than second order of the concentration of PdR_2 , the following equation is derived.

$$-d[\text{PdR}_2]/dt = k_{II}\{[\text{HR}]_0[\text{PdX}_3(\text{H}_2\text{O})^-]_0 - \{2[\text{PdX}_3(\text{H}_2\text{O})^-]_0 + [\text{HR}]_0 + [\text{X}^-]_0^3[\text{H}^+]_0^2/(K_1K_2[\text{HR}]_0)\}[\text{PdR}_2]\} \quad (\text{A-5})$$

Here, the k_{II} value is assumed to be constant. Eq. (8) is obtained by the comparing Eq. (7) and Eq. (A-5).

(2) Derivation of Eq. (11)

Since the values of ζ_b and \bar{K}^{-1} for this system are less than unity, Eqs. (10) can be simplified as

$$J_f = (R_a^{-1} + R_s^{-1})([\text{HR}]_i/P_{HR}) \quad (\text{A-6})$$

$$R_a^{-1} = R_b^{-1} = 1/\{1/k_w + S/(Vk'_1)\} \quad (\text{A-7})$$

$$R_s^{-1} = k'_1\Gamma^\infty\bar{K}_{HR}P_{HR}/(1 + \bar{K}_{HR}[\text{HR}]) \quad (\text{A-8})$$

Then the extraction rate J_f can be expressed by Eq. (11).

(3) Derivation of Eq. (13)

It is assumed that the resistance of mass transfer can be neglected. Then the flux can be written by the use of Eq. (11) as

$$\begin{aligned} -d[\text{Pd}]_i/dt &= aJ_f \\ &= ak_{II}[\text{PdX}_3(\text{H}_2\text{O})^-][\text{HR}] \\ &\quad (\Gamma^\infty\bar{K}_{HR}(1 + \bar{K}_{HR}[\text{HR}])^{-1} + (aP_{HR})^{-1}) \end{aligned} \quad (\text{A-9})$$

Since $[Cl^-]$ is quite large, $[\text{PdX}_3(\text{H}_2\text{O})^-]$ can be approximately expressed as

$$[\text{PdX}_3(\text{H}_2\text{O})^-] = [\text{Pd}]_i/(1 + \beta_3[Cl^-]) \quad (\text{A-10})$$

Since the value of $[H^+][Cl^-]/[HR]$ is very large due to high $[Cl^-]$, the apparent rate constant can be expressed by Eq. (6b). Then Eq. (A-9) can be written as

$$\begin{aligned} -d[\text{Pd}]_i/dt &= ak_{II}[\text{Pd}]_i(1 + \beta_3[Cl^-])^{-1}[\text{HR}] \\ &\quad (\Gamma^\infty\bar{K}_{HR}(1 + \bar{K}_{HR}[\text{HR}])^{-1} + (aP_{HR})^{-1}) \end{aligned} \quad (\text{A-11})$$

Eq. (13) can be derived from Eqs. (6b), (12) and (A-11).

Nomenclature

A	= parameter defined in Eq. (13a)	$[\text{mol dm}^{-3} \text{ s}]$
a	= specific interfacial area per unit organic volume	$[\text{cm}^{-1}]$
B	= parameter defined in Eq. (13a)	$[\text{dm}^3 \text{ mol}^{-1}]$
D	= diffusion coefficient	$[\text{cm}^2 \text{ s}^{-1}]$
d	= diameter of droplet	$[\text{cm}]$
J_f	= extraction rate of palladium	$[\text{mol cm}^{-2} \text{ s}^{-1}]$
\bar{K}	= overall equilibrium constant defined in Eq. (10j)	$[-]$
K_{ex}	= overall equilibrium constant of extraction	

K_1	= of palladium = equilibrium constant for PdR formation from HR and $\text{PdX}_3(\text{H}_2\text{O})^-$	$[\text{mol}^3 \text{dm}^{-9}]$ $[\text{mol dm}^{-3}]$
K_2	= equilibrium constant for PdR_2 formation from PdX_2R and HR	$[\text{mol}^2 \text{dm}^{-6}]$
\bar{K}_{HR}	= adsorption equilibrium constant of HR between organic phase and interfacial zone	$[\text{cm}^3 \text{mol}^{-1}]$
k_1	= forward reaction rate constant for PdX_2R formation from $\text{PdX}_3(\text{H}_2\text{O})^-$ and HR	$[\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}]$
k_3	= forward reaction rate constant for PdR_2 formation from PdX_2R and HR	$[\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}]$
k_f	= apparent overall rate coefficient	$[\text{s}^{-1}]$
k_{obs}	= observed rate constant for pseudo-first order reaction	$[\text{s}^{-1}]$
k_o	= mass transfer coefficient in organic stagnant film	$[\text{cm s}^{-1}]$
k_w	= mass transfer coefficient in aqueous stagnant film	$[\text{cm s}^{-1}]$
P_{HR}	= distribution constant of HR	[—]
P_{PdR_2}	= distribution constant of PdR_2	[—]
R_a	= resistance for extraction rate in aqueous phase	$[\text{s cm}^{-1}]$
R_B	= resistance for extraction rate for aqueous phase reaction	$[\text{s cm}^{-1}]$
R_b	= resistance for extraction rate in aqueous bulk phase	$[\text{s cm}^{-1}]$
R_f	= resistance for extraction rate in aqueous stagnant film	$[\text{s cm}^{-1}]$
\bar{R}_f	= resistance for mass transfer coefficient from interface to aqueous bulk phase	$[\text{s cm}^{-1}]$
\tilde{R}_f	= resistance for mass transfer coefficient from aqueous bulk phase to interface	$[\text{s cm}^{-1}]$
R_o	= resistance for extraction rate in organic stagnant film	$[\text{s cm}^{-1}]$
R_s	= resistance in interfacial zone	$[\text{s cm}^{-1}]$
S	= interfacial area	$[\text{cm}^2]$
t	= time	$[\text{s}]$
V	= volume of aqueous bulk phase	$[\text{cm}^3]$
X	= halide ion	
α	= parameter defined by Eq. (8b)	$[\text{mol}^4 \text{dm}^{-12}]$
β_i	= stability constant	$[\text{dm}^3 \text{mol}^{-1}]$
Γ^∞	= saturated interfacial excess quantity	$[\text{mol cm}^{-2}]$

δ	= thickness of interfacial zone	$[\text{cm}]$
ζ_b	= parameter defined by Eq. (10i)	[—]

<Subscript>

o	= initial value
t	= total value
i	= value at interface
HR	= chelating agent
PdR_2	= Pd-complex in organic phase

<Superscript>

—	= species in organic phase
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