EXTRACTION KINETICS OF PALLADIUM WITH DIOCTYLMONOTHIOPHOSPHORIC ACID

KAZUO KONDO, JITSUO OISHI AND FUMIYUKI NAKASHIO

Department of Organic Synthesis, Kyushu University, Fukuoka 812

Introduction

In a previous paper,[1] it was reported that the extraction of palladium with didodecylmonothiophosphoric acid (abbreviated as DDTPA) is interpreted by an interfacial reaction model between four chloro-palladium complex ions and the extractant adsorbed at the interface, and that reactivities of the complex ions to the extractant are different from one another. The authors also reported previously[2] that the extraction rate is enhanced by addition of thiocyanate ion to the aqueous solution. This result was explained by the trans-effect of thiocyanate ion substituted.

In the present study, the extraction of palladium with dioctylmonothiophosphoric acid (DOTPA) is carried out to confirm further the validity of the interfacial reaction model presented previously.

1. Experimental

The extractant, DOTPA, was synthesized as follows. First, dioctyl phosphite was made by an ester exchange reaction[3] between diethyl phosphite and octanol. Then DOTPA was synthesized as its ammonium salt by the reaction of the dioctyl phosphite and sulfur under an ammoniacal atmosphere, following the previous paper.[1] The product was identified by IR, NMR and elementary analysis.

The aqueous and organic solutions (toluene diluent) were prepared in the manner described in the previous paper.[1] All organic and inorganic chemicals used were GR grade.

Prior to measurement of the extraction rate, the interfacial tension of DOTPA was measured at 303 K by the pendant-drop method. The palladium-loading capacity of DOTPA was also measured. The extraction rate of palladium was measured using the same stirred transfer cell as described previously.[1]

2. Results and Discussion

2.1 Interfacial tension of extractant

The relation between the interfacial tension, γ, and the concentration of DOTPA, C_{HR}, is shown in **Fig. 1**. It is found that the extractant has an interfacial activity. Assuming a Langmuir adsorption isotherm between the amounts of DOTPA adsorbed and the bulk concentration, the following relation between γ and C_{HR} is derived from a Gibbs adsorption equation expressing the relation between γ and the amounts of DOTPA adsorbed at the interface.

$$\gamma = \gamma_0 - (RT/S_{HR})\ln(1 + K_{HR}C_{HR}) \tag{1}$$

where K_{HR} and S_{HR} are respectively the adsorption equilibrium constant and the interfacial area occupied by unit mole of DOTPA. γ_0 is the interfacial tension between toluene and the acidic aqueous solution.

The values of K_{HR} and S_{HR} were obtained from the experimental results and Eq. (1), and the results are shown in **Table 1**. The solid curve in Fig. 1 was calculated by Eq. (1), using the constants obtained.

2.2 Extraction rate of palladium

From experiments of palladium-loading capacity of DOTPA, it was found that a complex of palladium 1: DOTPA 2 is formed under the experimental conditions. This is identical to the result for DDTPA.[1]

The relation between the initial extraction rate of palladium, J_0, and the DOTPA concentration is
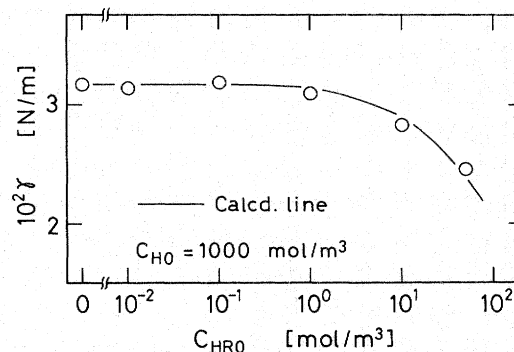

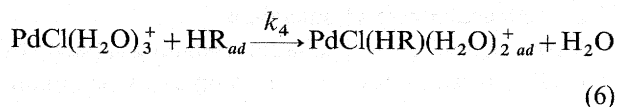**Fig. 1.** Relation between interfacial tension and extractant concentration
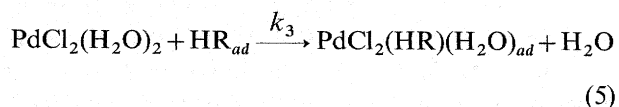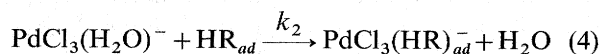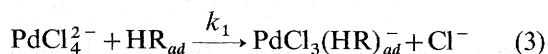
Table 1. Values of constants for palladium extraction

	DOTPA	DDTPA[1]
K_{HR} [m³/mol]	5.0×10^{-2}	1.0×10^{-1}
S_{HR} [m²/mol]	4.0×10^{5}	4.0×10^{5}
k_1 [m³/(mol·s)]	1.3×10^{-2}	1.5×10^{-3}
k_2 [m³/(mol·s)]	2.5×10^{-1}	2.0×10^{-2}
k_3 [m³/(mol·s)]	5.0	8.7×10^{-1}
k_4 [m³/(mol·s)]	1.0×10^{1}	3.8

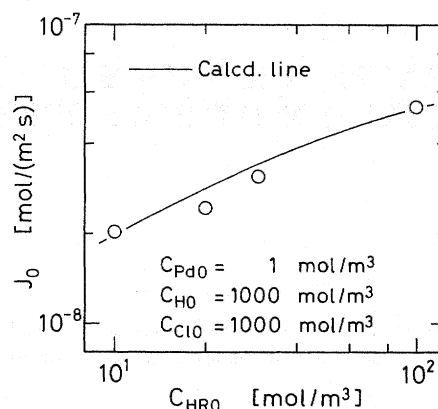**Fig. 2.** Relation between initial extraction rate of palladium and extractant concentration
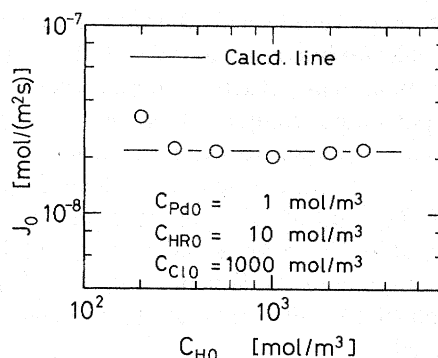

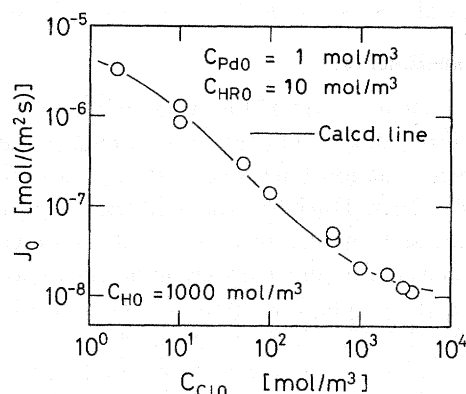**Fig. 3.** Relation between initial extraction rate of palladium and hydrogen-ion concentration

Fig. 4. Relation between initial extraction rate of palladium and chloride-ion concentration

shown in **Fig. 2**. The relation between J_0 and the concentration of hydrogen ion (adjusted using perchloric acid), C_H, is shown in **Fig. 3**. It is found that the hydrogen-ion concentration scarcely affects the extraction rate under the experimental conditions. **Figure 4** shows the relation between J_0 and the concentration of chloride ion, C_{Cl}. The concentration dependency of chloride ion on J_0 is found to be inversely first-order in the low range of C_{Cl}, but approaches zero-order in the high-concentration range.

All the results mentioned above are very similar to those for DDTPA.[1] So the same interfacial reaction model as proposed previously[1] is considered here.

$$HR_{org} + \theta_v \rightleftharpoons HR_{ad} \quad : K_{HR} \quad (2)$$

$$PdCl_4^{2-} + HR_{ad} \xrightarrow{k_1} PdCl_3(HR)_{ad}^- + Cl^- \quad (3)$$

$$PdCl_3(H_2O)^- + HR_{ad} \xrightarrow{k_2} PdCl_3(HR)_{ad}^- + H_2O \quad (4)$$

$$PdCl_2(H_2O)_2 + HR_{ad} \xrightarrow{k_3} PdCl_2(HR)(H_2O)_{ad} + H_2O \quad (5)$$

$$PdCl(H_2O)_3^+ + HR_{ad} \xrightarrow{k_4} PdCl(HR)(H_2O)_{2\,ad}^+ + H_2O \quad (6)$$
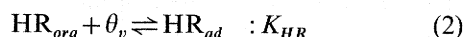
where subscripts *org* and *ad* denote organic phase and adsorption state respectively. θ_v is the fraction of active vacant site at the interface. k_1 to k_4 are the reaction rate constants corresponding to Eqs. (3) to (6) respectively. Assuming that Eqs. (3) to (6) are the rate-determining steps and that adsorption of the chloro-palladium complexes can be ignored at the early stage of extraction, the reaction rate can be expressed as follows.[1]

$$r = \frac{k_1\beta_4[Cl^-]^4 + k_2\beta_3[Cl^-]^3 + k_3\beta_2[Cl^-]^2 + k_4\beta_1[Cl^-]}{1 + \sum_{i=1}^{4} \beta_i[Cl^-]^i}$$

$$\times \frac{K_{HR}}{S_{HR}} \frac{C_{HR}C_{Pd}}{1 + K_{HR}C_{HR}} \quad (7)$$

where β_i ($i = 1-4$) is the stability constant of the

chloro-palladium complex as mentioned previously.[1]

By analyzing the results of extraction rate measurements using Eq. (7), the values of the reaction rate constants listed in Table 1 were obtained. The solid lines in Figs. 2, 3 and 4 are the calculated results by using the constants. The calculated results are found to agree with the experimental ones.

The reaction rate constants for DDTPA[1] are also shown in Table 1. It is clear that the reaction rate constants for DOTPA are larger than those for

366

DDTPA. One reason for this result is considered to be the higher solubility of DOTPA in water than that of DDTPA. In other words, the apparently large rate constants of DOTPA were obtained because of a small contribution of the reaction in the aqueous solution. It is concluded that DOTPA is a better extractant than DDTPA in respect of the rate of palladium extraction. Further study of extracting palladium efficiently by using sulfur-containing extractant is now in progress.

Conclusion

Using a stirred transfer cell, the extraction rate of palladium with dioctylmonothiophosphoric acid was measured, along with measurements of the interfacial tension and the palladium-loading capacity of the extractant. The experimental results were analyzed by an interfacial reaction model proposed to obtain the reaction rate constants of four chloro-palladium complexes with the extractant.

Nomenclature

C	= concentration	[mol/m³]
J_o	= initial extraction rate of palladium	[mol/(m²·s)]
K_{HR}	= adsorption equilibrium constant of extractant	[m³/mol]
k_i	= reaction rate constant ($i=1-4$)	[m³/(mol·s)]
R	= gas constant	[N·m/(mol·K)]
r	= reaction rate	[mol/(m²·s)]
S_{HR}	= interfacial area occupied by unit mole of extractant	[m²/mol]
T	= absolute temperature	[K]
β_i	= stability constant of chloro-palladium complex ($i=1-4$)	[(m³/mol)^i]
γ	= interfacial tension	[N/m]
γ_o	= interfacial tension between toluene and water	[N/m]
θ_v	= fraction of active vacant site at interface	[—]
[ ]	= concentration	[mol/m³]

⟨Subscripts⟩

ad	= adsorption state
Cl	= chloride ion
H	= hydrogen ion
HR	= extractant
org	= organic phase
Pd	= palladium
0	= initial value

Literature Cited

1) Kondo, K., H. Nishio and F. Nakashio: *J. Chem. Eng. Japan*, **22**, 269 (1989).
2) Kondo, K., H. Nishio and F. Nakashio: *J. Chem. Eng. Japan*, **23**, 236 (1990).
3) Malowan, J. E.: "Inorganic Syntheses," Vol. 4, p. 61, McGraw-Hill Book Co., Inc., New York (1953).