SOLVENT EXTRACTION OF PALLADIUM WITH DIHEXYL SULFIDE

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The mechanism of palladium extraction from aqueous ammonium chloride solutions with dihexyl sulfide in toluene was investigated at 303 K from the viewpoints of extraction equilibrium and kinetics. The result of a loading test suggests that palladium is extracted as a 1 : 2 metal–reagent complex. The concentration dependencies of the reactant species were examined using a stirred transfer cell with a constant interfacial area to investigate the extraction rate mechanism. The observed extraction rate was reasonably explained in terms of a simple reaction scheme involving complex formation between the intermediate complex adsorbed at the interface and a free extractant molecule dissolved in the aqueous phase as the rate-determining step.

Introduction

Palladium is one of the very important rare metals indispensable for high-technology industries as a raw material of catalysts, electronic materials and so on. From the practical viewpoint of refining and recovering palladium from anode slime by-products of copper, nickel and zinc in the metallurgical industries or from spent catalysts and scraps of electronic materials, palladium is extracted from chloride media rather than from nitrate, sulfate, cyanide or thiocyanide media.

National Institute for Metallurgy of South Africa (NIM)[5)] developed a separation process for the refining of palladium using solvent extraction techniques which have potential economic advantages over conventional selective precipitation processes on a commercial scale. Dihexyl sulfide was used as a selective extractant to palladium over platinum. A similar process was developed by International Nickel Ltd. (INCO) and has been successfully operated at their Acton precious metal refinery in West London,[2)] where dioctyl sulfide has been used instead of dihexyl sulfide.

Although Soviet investigators[8,11-13)] have conducted extensive studies on the extraction of various metals including palladium with various dialkyl sulfides and petroleum sulfides, the majority of their studies have been limited to those on extraction equilibria or their hydrometallurgical applications and no work has been done on the extraction kinetics with these extractants. Since palladium extraction needs a long time to attain equilibrium, it is necessary to obtain exact and detailed information not only on the extraction equilibrium but also on the extraction kinetics for the process and reactor design of solvent extraction of palladium.

In the previous study,[1)] the mechanism of palladium extraction from chloride media with 1,2-bis(*tert*-hexylthio)ethane with two sulfur atoms as donating atoms was investigated in terms of extraction equilibrium and kinetics.

In the present study, solvent extraction of palladium by a dialkyl sulfide with one sulfur atom as a donor atom was investigated, and the extraction behavior was compared with that by 1,2-bis(*tert*-hexylthio)ethane.

1. Experimental

1.1 Reagents

As the extractant, SFI-6, which was kindly supplied by Daihachi Chemical Industry Co., Ltd., Japan, was used without further purification. This commercial extractant contains dihexyl sulfide, abbreviated as DHS hereafter, with a purity above 98%. Toluene was used as a diluent. All inorganic reagents and toluene were of Wako's analytically pure reagent grade. Organic solutions were prepared on a gravimetric basis by diluting DHS with toluene to a required concentration. Aqueous solutions were prepared by dissolving palladium chloride into ammonium chloride solutions containing a small amount of hydrochloric acid (0.01 mol/dm^3).

1.2 Distribution equilibrium

As in the case of the previous work,[1)] it was impossible to carry out quantitative analysis of palladium in the aqueous phase under the conditions of excess concentration of the extractant over palladium because it was almost completely extracted over the

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whole concentration range of chloride ion. Accordingly, only a loading test was carried out at 303 K to examine the mole ratio of palladium extracted into the organic phase to DHS, in the same manner as in the previous work.[1)]

Equal volumes of organic and aqueous phases of known concentrations were vigorously shaken for 3 days in a separatory funnel using a mechanical shaker (Iwaki, type V-DV) in a thermostated air bath maintained at 303 K. Palladium concentration in the aqueous phase was determined by atomic absorption spectrochemical analysis using a Nippon Jarrell-Ash model AA-782 spectrophotometer. Its concentration in the organic phase was calculated by mass balance using the aqueous metal concentrations before and after equilibration.

1.3 Interfacial pressure

Interfacial pressure between the toluene solution of DHS and the aqueous ammonium chloride solution after equilibration was measured by the drop-weight method at 303 K to examine the interfacial adsorption equilibrium of DHS.

1.4 Kinetics

The stirred transfer cell used in this experiment was the same as that used by Yoshizuka *et al.*[18)] The partition plate and the flat-blade impeller which contact the aqueous phase were made of Teflon, and another impeller contacting the organic phase was made of stainless steel. The glass cell was placed in a thermostated bath maintained at 303 K.

An aqueous phase of 0.136 dm^3 was introduced to the glass cell from a burette fitted with a jacket maintained at 303 K. An equal volume of organic phase was then carefully introduced in such a manner as not to disturb the interface. Then the stirring of both phases was initiated in opposite directions at a constant speed. A small amount (1×10^{-3} dm^3) of the organic phase was taken at time intervals. After stripping with 2 mol/dm^3 ammonia, the palladium content in the organic phase was determined by atomic absorption spectrochemical analysis.

2. Experimental Results

2.1 Distribution equilibrium

Figure 1 shows the results of the loading test, which indicates that the mole ratio of DHS to palladium extracted in the organic phase asymptotically approaches 2. The stoichiometric relation of this extraction reaction is considered to be expressed as follows.

$$PdCl_2 + 2\bar{S} \rightleftharpoons \overline{PdCl_2S_2} \qquad (1)$$

where $\bar{S}$ denotes the extractant in toluene.

2.2 Interfacial adsorption equilibrium

Figure 2 shows the relation between interfacial pressure and the concentration of DHS. The experimental result shows that DHS is interfacially active

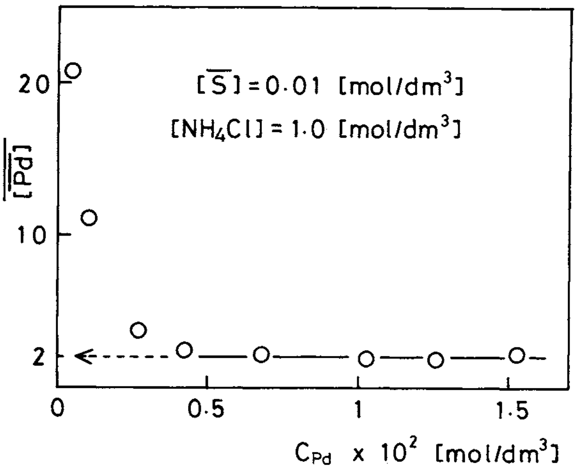

Fig. 1. Experimental results of loading test.

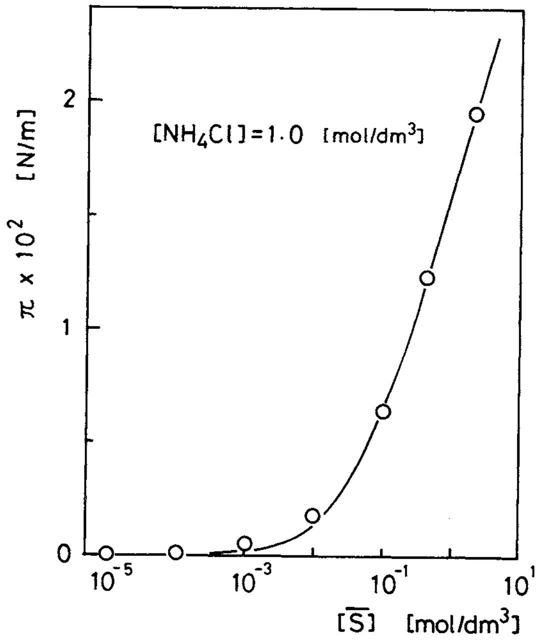

Fig. 2. Relation between interfacial pressure and $[\bar{S}]$.

and is adsorbed at the interface. Based on Langmuir's monolayer adsorption model, adsorption of DHS is expressed as follows:

$$\bar{S} \rightleftharpoons S_{ad}\,; \quad K_{ad} \qquad (2)$$

Interfacial pressure is correlated with the concentration of DHS in the organic phase based on Gibbs' adsorption isotherm as expressed by Eq. (3).[9)]

$$\pi = \gamma_0 - \gamma = (\mathscr{R}T/S_s)\ln(1 + K_{ad}[\bar{S}]) \qquad (3)$$

where γ_0 is the interfacial tention between toluene and the aqueous phase. S_s is the interfacial area occupied by unit mole of DHS. The values of K_{ad} and S_s were evaluated from the experimental results shown in Fig. 2 on the basis of Eq. (3) by the nonlinear least squares method as follows: $K_{ad} = 3.4 \times 10^1$ dm^3/mol, $S_s = 5.5 \times 10^5$ m^2/mol.

The solid line in Fig. 2 is the calculated result based on Eq. (3) using these values. This calculated curve is in good agreement with the experimental results.

2.3 Kinetics

The initial extraction rate was calculated from the slope of the linear relation between the palladium concentration in the organic phase and contact time. First of all, the effect of stirring speed on the initial extraction rate was studied in order to examine the diffusional contribution to the extraction rate in the high concentration range of DHS as shown in **Fig. 3**. It is obvious that the initial extraction rate becomes independent of stirring speed in the range greater than 150 rpm, which suggests that the diffusional contribution can be ignored in this range. Hence, subsequent experiments were carried out at a constant stirring speed of 150 rpm.

Figure 4 shows the effect of initial palladium concentration in the aqueous phase on the initial extraction rate from 1 mol/dm^3 aqueous ammonium chloride solution. The plots in Fig 4 lie on a straight line of slope 1 in this concentration range. It can be concluded that the initial extraction rate is first-order with respect to palladium at this chloride ion concentration.

Figure 5 shows the effect of initial palladium concentration in the extraction from 0.2 mol/dm^3 aqueous ammonium chloride solution. Although the initial extraction rate increases with increasing palladium concentration in its low concentration range in the same manner as shown in Fig. 4, it tends toward a constant value in its high concentration range.

Figure 6 shows the effect of the concentration of DHS on the initial extraction rate from 1 mol/dm^3 aqueous ammonium chloride solution. As is evident from Fig. 6, the plots lie on a straight line of slope 2 in the low-concentration range of DHS, and on that of slope 1 in the high-concentration range. Therefore, it may be concluded that the initial extraction rate varies from second-order to first-order with respect to DHS as its concentration increases.

The effect of chloride ion concentration on the initial extraction rate is shown in **Fig. 7** for both concentration ranges of DHS. The plotted points lie on straight lines of slope 2 and on those of slope -1 in the low- and high-concentration regions of chloride ion, respectively, while the initial extraction rate appears to be constant in the intermediate concentration range.

3. Extraction Mechanism of Palladium

From the experimental results mentioned in the preceding section, the extraction mechanism for this system was inferred on the basis of the interfacial reaction scheme proposed for the extraction kinetics of nickel with a hydroxyoxime extractant in the

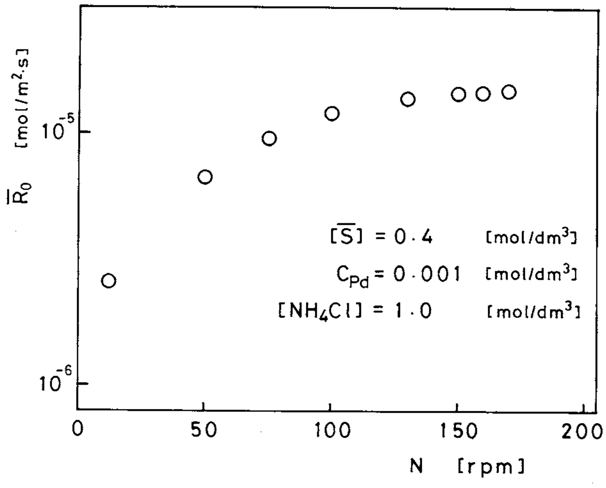

Fig. 3. Effect of stirring speed on initial extraction rate.

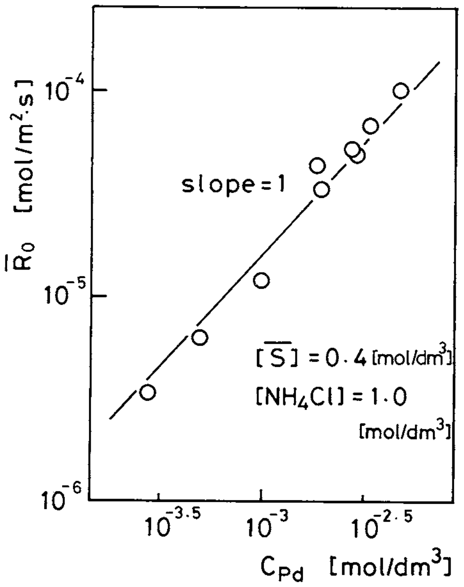

Fig. 4. Effect of palladium concentration on initial extraction rate.

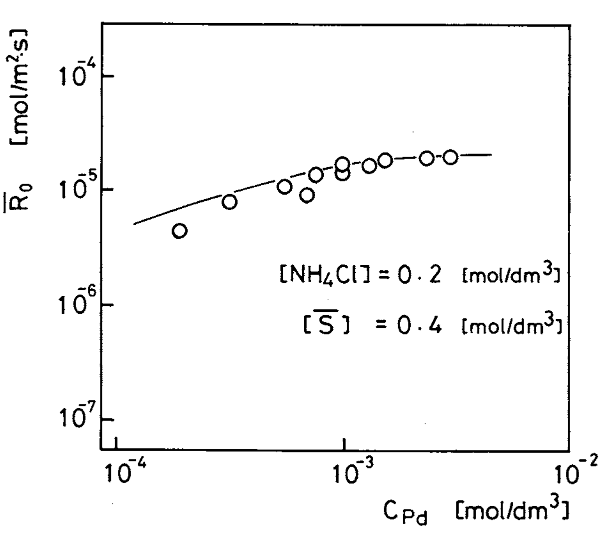

Fig. 5. Effect of palladium concentration on initial extraction rate.

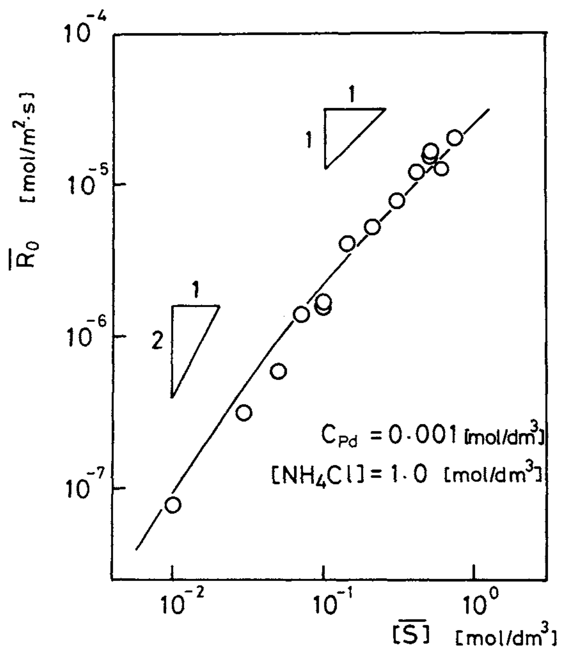

Fig. 6. Effect of DHS concentration on initial extraction rate.

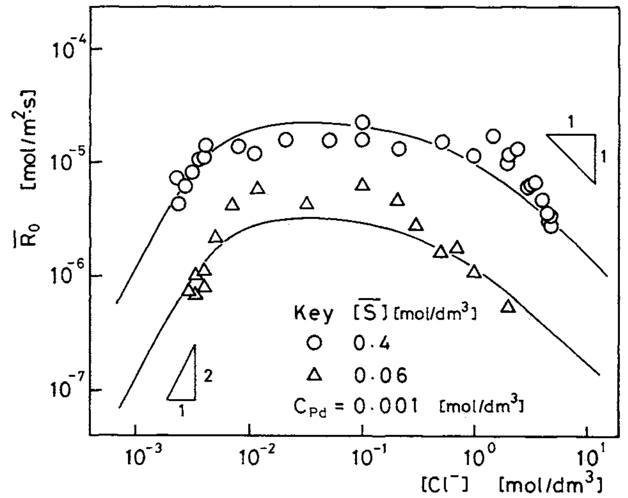

Fig. 7. Effect of chloride ion concentration on initial extraction rate.

previous paper[10)] as follows.

First, the extractant in the organic phase is physically partitioned to the aqueous phase and is adsorbed at the interface. The extractant adsorbed at the interface undergoes the complex-formation reaction with an aquatrichloro complex of palladium, $Pd(H_2O)Cl_3^-$, which is much more labile than other chloro complexes,[15)] to form an intermediate complex of the 1 : 1 metal–reagent, $PdCl_3S^-$, at the interface. The intermediate complex, $PdCl_3S^-$, is likely to be strongly oriented at the interface by the partially chlorinated palladium ion pointing toward the aqueous phase. Subsequently, the extractant molecules in the aqueous phase attack the intermediate complex at the interface to form the final complex.

$$\bar{S} \rightleftharpoons S \ ; \ K_D \tag{4}$$

$$\bar{S} \rightleftharpoons S_{ad} \ ; \ K_{ad} \tag{5}$$

$$Pd(H_2O)Cl_3^- + S_{ad} \rightleftharpoons PdCl_3S_{ad}^- + H_2O \ ; \ K_1 \tag{6}$$

$$PdCl_3S_{ad}^- + S \xrightarrow{k_2} \overline{PdCl_2S_2} + Cl^- \tag{7}$$

From the fact that the reaction order with respect to DHS is greater than unity in its low-concentration region, the interfacial reaction step described by Eq. (7) is considered to be the rate-determining step and, consequently, the reaction rate is expressed as

$$\bar{R}_0 = k_2\theta_{PdS}[S] = k_2K_D[\bar{S}]\theta_{PdS} \tag{8}$$

where k_2 is the reaction rate constant of Eq. (7), and θ_{PdS} is the fraction of interfacial area occupied by the intermediate complex.

From the equilibrium relations of the elementary steps of Eqs. (5) and (6), θ_{PdS} is expressed on the basis of Langmuir's monolayer adsorption model as follows.

$$\theta_{PdS} = \frac{K_{ad}K_1[Pd(H_2O)Cl_3^-][\bar{S}]}{1 + K_{ad}[\bar{S}] + K_{ad}K_1[Pd(H_2O)Cl_3^-][\bar{S}]} \tag{9}$$

Combination of Eqs. (8) and (9) gives the following rate expression for the initial extraction rate.

$$\bar{R}_0 = \frac{k_2K_DK_{ad}K_1[Pd(H_2O)Cl_3^-][\bar{S}]^2}{1 + K_{ad}[\bar{S}] + K_{ad}K_1[Pd(H_2O)Cl_3^-][\bar{S}]} \tag{10}$$

In Eq. (10), the concentration of aquatrichloro complex, $[Pd(H_2O)Cl_3^-]$, is expressed by Eq. (11) using the stability constant of the i-th chlorocomplex of palladium, β_i, defined by Eqs. (12) and (13).

$$[Pd(H_2O)Cl_3^-] = \frac{\beta_3[Cl^-]^3}{1 + \sum_{i=1}^{4} \beta_i[Cl^-]^i} C_{Pd} \tag{11}$$

$$Pd^{2+} + iCl^- \rightleftharpoons PdCl_i^{(i-2)-} \ ; \ \beta_i \tag{12}$$

$$\beta_i = \frac{[PdCl_i^{(i-2)-}]}{[Pd^{2+}][Cl^-]^i} \tag{13}$$

Therefore, the initial extraction rate, $\bar{R}_0$, is finally expressed by Eq. (14) from Eqs. (10) and (11).

$$\bar{R}_0 = \frac{k_2K_DK_{ad}K_1f_3([Cl^-])C_{Pd}[\bar{S}]^2}{1 + K_{ad}[\bar{S}] + K_{ad}K_1f_3([Cl^-])C_{Pd}[\bar{S}]} \tag{14}$$

where

$$f_3([Cl^-]) = \frac{\beta_3[Cl^-]^3}{1 + \sum_{i=1}^{4} \beta_i[Cl^-]^i} \tag{15}$$

Under the present experimental conditions, Eq. (15) is approximated by Eq. (16).

$$f_3([\mathrm{Cl}^-]) \simeq \frac{\beta_3[\mathrm{Cl}^-]^2}{\sum_{i=1}^{4} \beta_i[\mathrm{Cl}^-]^{i-1}} \tag{16}$$

The proposed rate expression, Eq. (14), can be approximated by Eq. (17) if the extractant concentration, $[\bar{\mathrm{S}}]$, is low enough and by Eq. (18) if it is high enough.

$$\bar{R}_0 \simeq k_2 K_D K_{ad} K_1 f_3([\mathrm{Cl}^-]) C_{\mathrm{Pd}} [\bar{\mathrm{S}}]^2 \quad \text{for low } [\bar{\mathrm{S}}] \tag{17}$$

$$\bar{R}_0 \simeq \frac{k_2 K_D K_1 f_3([\mathrm{Cl}^-]) C_{\mathrm{Pd}} [\bar{\mathrm{S}}]}{1 + K_1 f_3([\mathrm{Cl}^-]) C_{\mathrm{Pd}}} \quad \text{for high } [\bar{\mathrm{S}}] \tag{18}$$

Equation (17) suggests that the initial extraction rate is first-order with respect to palladium in the aqueous phase and second-order with respect to the extractant in its low-concentration range, while Eq. (18) suggests that it is first-order with respect to the extractant in its high-concentration range. Equation (18) is further approximated by Eq. (19) if $f_3([\mathrm{Cl}^-])C_{\mathrm{Pd}}$ is low enough and by Eq. (20) if it is high enough.

$$\bar{R}_0 \simeq k_2 K_D K_1 f_3([\mathrm{Cl}^-]) C_{\mathrm{Pd}} [\bar{\mathrm{S}}] \tag{19}$$

$$\bar{R}_0 \simeq k_2 K_D [\bar{\mathrm{S}}] \tag{20}$$

Equations (16) and (19) suggest that the initial extraction rate is second-order and inversely first-order with respect to chloride ion in its low- and high-concentration regions, respectively, while if $f_3([\mathrm{Cl}^-])C_{\mathrm{Pd}}$ is high enough it is expected to be dependent on neither the chloride ion concentration nor the aqueous palladium concentration from Eq. (20). These tendencies expected from Eqs. (17)–(20) can qualitatively interpret the experimental results shown in Figs. 4–7.

The parameters in Eq. (14), β_i/β_3 $(i=1, 2, 4)$, K_1 and k_2K_D were evaluated by the nonlinear least squares method[17] from the data shown in Fig. 7, using K_{ad} evaluated earlier.* The ratios of the stability constants, β_i/β_3 $(i=1, 2, 4)$, evaluated in this manner are listed in **Table 1** along with the values reported in the literature[3-4,6-7,14,16] for comparison. β_2/β_3 and β_4/β_3 are nearly of the same order as those reported by other investigators while β_1/β_3 is much higher. Further examination is considered necessary in this respect. The values of K_1 and k_2K_D were evaluated as follows: $K_1 = 1.1 \times 10^4$ dm^3/mol and $k_2K_D = 6.8 \times 10^{-8}$ m/s.

The solid lines in Figs. 5, 6 and 7 are the calculated results from Eq. (14) using these values. The calculated results are in fairly good agreement with the experimental results. However, at high concentrations of DHS the experimental results in the high-concentration range of chloride ion deviate upward from the calculated curve as shown in Fig. 7. Although it is considered that these deviations are attributable to a decrease in activity of water by the salting-out effect, further detailed study is necessary in this respect.

Table 1. Ratios of stability constants of palladium(II) chloro-complexes

β_1/β_3	β_2/β_3	β_4/β_3	Literature
7.94×10^{-8}	3.16×10^{-3}	100.0	3)
6.31×10^{-6}	7.24×10^{-3}	21.9	4)
1.86×10^{-6}	3.63×10^{-3}	19.9	6)
2.51×10^{-6}	2.51×10^{-3}	39.8	7)
7.24×10^{-6}	4.47×10^{-3}	12.6	14)
1.86×10^{-6}	5.75×10^{-3}	24.0	16)
2.22×10^{-4}	2.18×10^{-3}	15.6	This work

In comparison with the extraction mechanism with 1,2-bis(*tert*-hexylthio)ethane(*t*-BHTE) investigated in the previous work,[1] there are some large differences in the concentration dependencies of the reactant species, chloride ion and the extractant, on the initial extraction rate. The extraction mechanism for DHS is more complicated than for *t*-BHTE, which is considered to be attributable to the fact that the former, with one sulfur atom as a donating atom, undergoes two-step consecutive reactions to form the final complex while the latter, with two sulfur atoms, undergoes a single reaction. On the other hand, the reaction order with respect to chloride ion for *t*-BHTE changes from inverse first order to 0-th order with increasing chloride ion concentration while that for DHS remains inverse first-order over its high concentration range (1–5 mol/dm^3). This is due to the fact that DHS undergoes complexation only with the aquatrichloro complex, $\mathrm{Pd(H_2O)Cl_3^-}$, while *t*-BHTE undergoes parallel complexations, not only with the aquatrichloro complex but also with tetrachloro complex, $\mathrm{PdCl_4^{2-}}$.

Conclusion

From the experimental results of extraction equilibrium, it was clarified that palladium (II) is extracted as a 1 : 2 Pd–extractant complex, $\mathrm{PdCl_2S_2}$, according to the stoichiometric relation described by Eq. (1).

The concentration dependencies of the reactant species on the initial extraction rate were explained in terms of the interfacial reaction mechanism which involves the complex-formation reaction of the intermediate complex adsorbed at the interface with an extractant molecule dissolved in the aqueous phase as the rate-determining step. The rate expression described by Eq. (14) was derived from this extraction mechanism and the kinetic parameters were evaluated

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* No values of β_i/β_3 reported in the literature could provide simulation curves in good agreement with the kinetic data, especially in the low-concentration range of chloride ion.

as $K_{ad} = 3.4 \times 10^1$ dm^3/mol, $K_1 = 1.1 \times 10^4$ dm^3/mol and $k_2 K_D = 6.8 \times 10^{-8}$ m/s; the ratios of the stability constants of the chloro complex of palladium, β_1/β_3, β_2/β_3 and β_4/β_3, were also evaluated as listed in Table 1.

Nomenclature

C_{Pd} = total palladium concentration at time t [mol/dm^3]

K_{ad} = equilibrium constant of the elementary step described by Eq. (5) [dm^3/mol]

K_D = partition coefficient of DHS to aqueous phase [—]

K_1 = equilibrium constant of the elementary step described by Eq. (6) [dm^3/mol]

k_2 = forward reaction rate constant of the elementary reaction described by Eq. (7) [m/s]

$\mathcal{R}$ = gas constant [N·m/(mol·K)]

$\bar{R}_0$ = initial extraction rate of palladium [mol/(m^2·s)]

S_s = interfacial area occupied by unit mole of DHS [m^2/mol]

T = temperature [K]

β_i = stability constant of i-th chloro-complex of palladium [(mol/dm^3)$^{-i}$]

γ = interfacial tension [N/m]

γ_0 = interfacial tension of diluent [N/m]

θ_{PdS} = fraction of interfacial area occupied by the intermediate complex, $PdCl_3S^-$ [—]

π = interfacial pressure [N/m]

⟨Superscript⟩

— = organic phase

⟨Subscript⟩

ad = adsorbed

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