The Solvent Extraction of Palladium(II) from Hydrochloric Acid with Triisobutylphosphine Sulfide

Yoshinari Baba,* Masanori Ohshima, and Katsutoshi Inoue
Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840

(Received May 22, 1986)

The equilibrium and kinetic aspects of palladium(II) extraction from hydrochloric acid with triisobutylphosphine sulfide (TIBPS) in toluene were studied, along with the aqueous solubility and interfacial adsorption equilibrium of the extractant. From the equilibrium study, palladium(II) was found to be extracted as a 1 : 1 Pd:extractant binuclear complex. The extraction rate of palladium(II) was reasonably explained by the interfacial reaction model, assuming that the elementary reactions between the extractant adsorbed at the interface and the aquatrichloro and tetrachloro complexes of palladium(II), $[PdCl_3]^-$, and $[PdCl_4]^{2-}$ in the aqueous phase are the rate-determining steps.

The solvent-extraction techniques of metals have recently become increasingly important as energy-saving and non-polluting separation and purification processes in hydrometallurgy in view of the dangers of exhausting resources and energy. While the solvent extraction of metals has so far been extensively studied with a number of commercial extractants, the majority of these have been extractants containing oxygen or nitrogen as donor atoms, such as hydroxy oximes, carboxylic acids and organophosphorus compounds. However, relatively few works have been conducted on extractants containing sulfur as the donor atom.

It is well-known that sulfur-containing extractants are highly effective and selective for palladium(II). Among the sulfur-containing extractants, dialkyl sulfides, petroleum sulfides and their oxides, and *O,O′*-dialkyl hydrogenphosphorodithioate have been extensively investigated, especially in the USSR,[1–3] though these works have not necessarily been quantitative. Actually, dialkyl sulfides are now commercially utilized for the separation of palldium(II) from platinum(IV) at the Acton precious metal refinery of INCO in the United Kingdom[4] and for the recovery of precious metals from various kinds of scrap, such as spent catalysts in Japan. However, dialkyl sulfides have a serious drawback in their slow extraction rate of palladium(II).[5]

Recently, the American Cyanamid Co. developed a new extractant for the recovery of silver(I) and palladium (II),[6] CYANEX 471, the active component of which is triisobutylphosphine sulfide. This extractant is said to have an acceptably high extraction rate of palladium (II). Following the previous investigations of the kinetics of the solvent extraction of palladium(II) from chloride media with various sulfur-containing extractants, i.e. dihexyl sulfide,[7] 1,2-bis(*t*-hexylthio)-ethane[8] and 2-(butylthio)dodecanoic acid,[9] the present authors have now conducted a quantitative investigation of the extraction kinetics of palladium(II) from hydrochloric acid with triisobutylphosphine sulfide(TIBPS) in order to elucidate its extraction mechanism. Prior to the study of the extraction kinetics, the distribution equilibrium of palladium(II), and the aqueous solubility and interfacial adsorption equilibrium of the extractant were investigated in order to obtain the fundamental information which is necessary for the analysis of the extraction kinetic data.

Experimental

Reagents. The triisobutylphosphine sulfide, abbreviated as TIBPS hereafter, used in the present study as the extractant was purified from CYANEX 471 donated by the American Cyanamid Co. by recrystallization from a water-ethanol mixture. The purity of the reagent was confirmed by elemental analysis to be as follows: Found: C, 61.3; H, 11.5%. Calcd for $C_{12}H_{27}PS$: C, 61.5; H, 11.6%. The organic phase was prepared on a gravimetric basis by diluting TIBPS with toluene of an analytical grade. The aqueous phase was prepared by dissolving palladium(II) chloride in hydrochloric acid.

Measurement of Extraction Equilibrium. As in the previous work,[7,8] it was impossible to make a precise quantitative determination of palladium(II) in the aqueous phase in the presence of a large excess concentration of the extractant because it was almost completely extracted over the whole concentration range of hydrochloric acid. Accordingly, in order to determine the mole ratio of palladium(II) to the extractant in the extracted complex under the conditions of ultimate loading, only a loading test was carried out in the presence of a large excess of the palladium(II) concentration in order to determine the mole ratio of palladium(II) extracted into the organic phase to TIBPS, in the same manner as in previous papers.[7,8]

Equal volumes (0.015 dm^3) of the organic and aqueous phases of known concentrations were vigorously shaken for 5 h in a separatory funnel using a Iwaki, V-DV-type mechanical shaker in a thermostated air bath maintained at 303 K. It had been confirmed by a preliminary experiment that the equilibrium was attained within 5 h. After the separation of the two phases, the palladium(II) concentration in the aqueous phase was determined by means of atomic absorption spectrometry using a Nippon Jarrell-Ash model AA-782 spectrophotometer. The palladium(II) concentration in the organic phase was calculated by the use of the mass balance from the aqueous palladium(II) concentrations before and after the equilibration.

Measurement of Aqueous Solubility of the Extractant. The distribution of TIBPS between the organic and aqueous phases was measured spectrophotometrically at 303 K in a method similar to that described in a previous paper.[8] A

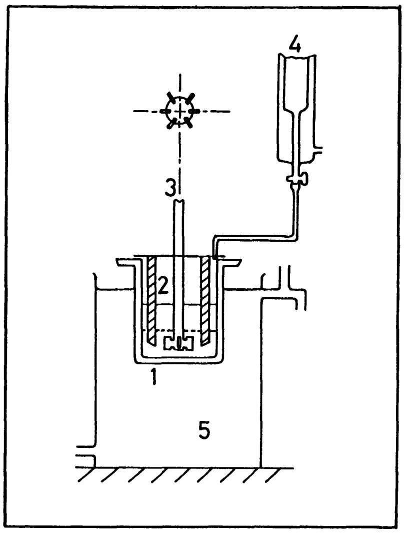

Fig. 1. Experimental apparatus.
1: Stirred glass cell, 2: baffle, 3: impeller, 4: reservoir with jacket, 5: thermostat.

toluene solution of TIBPS of a known concentration and 1 mol dm^{-3} of hydrochloric acid were shaken vigorously for 24 h with a volume ratio of the aqueous phase to the organic phase of 10 : 1 using an Iwaki mechanical shaker, V-VD-type. After phase separation, a sample of the aqueous phase (0.19 dm^3) was transferred to a separatory funnel. In order to completely convert any TIBPS dissolved in the aqueous phase to its palladium(II) complexes, 5×10^{-2} dm^3 of a 2×10^{-3} mol dm^{-3} aqueous palladium(II) chloride solution containing 0.01 mol dm^{-3} of hydrochloric acid and 1×10^{-2} dm^3 of toluene were added to the aqueous sample, and the mixture was shaken for 24 h using a mechanical shaker. The absorbance of the palladium(II) complex in toluene was measured at 329 nm against a toluene blank using a Shimadzu UV 140 spectrophotometer.

Measurement of Interfacial Adsorption Equilibrium. The interfacial tension between the organic solution and 1 mol dm^{-3} of aqueous hydrochloric acid was measured at 303 K by means of the drop-weight method in order to elucidate the interfacial adsorption equilibrium of TIBPS.

Measurement of Extraction Kinetics. The apparatus used in this study was a batch-type stirred glass cell, as is shown in Fig. 1. It is the same as that used in the previous kinetic studies of the palladium(II) extraction with 1,2-bis(*t*-hexylthio)ethane[8] or 2-(butylthio)dodecanoic acid.[9]

Equal volumes (0.3 dm^3) of hydrochloric acid containing palladium(II) and toluene solutions of TIBPS of known concentrations were carefully introduced into the cell so as not to disturb the interface. After that, stirring was initiated at a constant stirring speed and 10-cm^3 portions samples were taken out at definite time intervals. After the phase separation, the palladium(II) concentration in the aqueous phase was determined using the atomic-absorption spectrophotometer. The initial palladium(II) concentration was 1×10^{-3} mol dm^{-3} in all kinetic runs. The concentrations of the extractant and hydrochloric acid varied over the range from 8×10^{-3} to 1.6×10^{-1} mol dm^{-3} and from 1×10^{-1} to 4.7 mol dm^{-3} respectively.

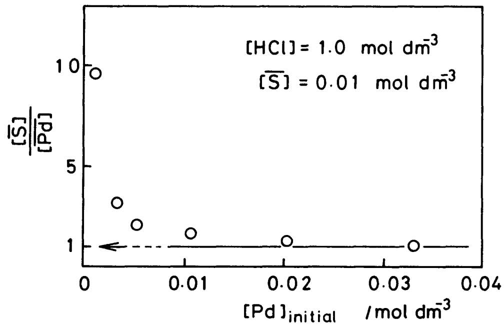

Fig. 2. Experimental results of the loading test.

Results

Distribution Equilibrium of Palladium(II). Figure 2 shows the results of the loading test. The mole ratio of TIBPS to palladium(II) in the organic phase asymptotically approaches unity with an increase in the palladium(II) concentration in the aqueous phase. This result indicates that palladium(II) is present as a metal : reagent 1 : 1 complex in the organic phase. Taking account of the coordination number of palladium(II)(=4), the stoichiometry of this extraction reaction may be expressed as follows:

$$2[\mathrm{PdCl}_i]^{(i-2)-} + 2\bar{\mathrm{S}} \rightleftharpoons [\overline{(\mathrm{PdCl}_2)_2\mathrm{S}_2}] + 2(i-2)\mathrm{Cl}^- \quad (1)$$

where S is TIBPS and where bars denote the organic phase.

Aqueous Solubility of TIBPS. The distribution of TIBPS between the organic and aqueous solutions is expressed as follows:

$$\bar{\mathrm{S}} \rightleftharpoons \mathrm{S} \quad ;K_\mathrm{D}, \quad (2)$$

where K_D is the partition coefficient of TIBPS and is expressed as follows:

$$K_\mathrm{D} = [\mathrm{S}]/[\bar{\mathrm{S}}]. \quad (3)$$

The logarithm of Eq. 3 gives:

$$\log[\mathrm{S}] = \log[\bar{\mathrm{S}}] + \log K_\mathrm{D}. \quad (4)$$

The partition coefficient is so small that the concentration of TIBPS in the organic phase, $[\bar{\mathrm{S}}]$, is nearly equal to its initial concentration, $C_{\mathrm{B}0}$.

The concentration of TIBPS in the aqueous phase was plotted against that in the organic phase, as is shown in Fig. 3. The points plotted in this figure appear to lie on a straight line with a slope of 1, as is to be expected from Eq. 4. From the intercept of the straight line with the ordinate, the partition coefficient, K_D, was evaluated as 5.4×10^{-6} for 1 mol dm^{-3} of hydrochloric acid.

Interfacial Tension. Figure 4 shows the plot of the interfacial tension, γ, between the organic solution containing TIBPS and 1 mol dm^{-3} of aqueous hydrochloric acid against the concentration of TIBPS. The results shown in Fig. 4 suggest that TIBPS is interfacially active and is adsorbed at the interface between

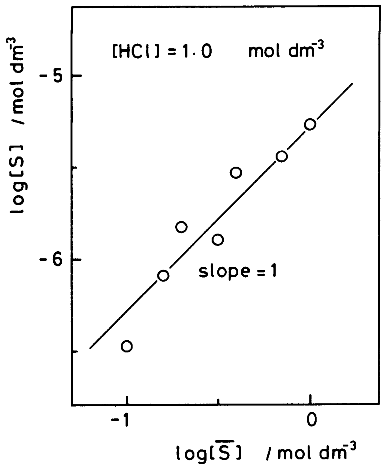

Fig. 3. Aqueous solubility of TIBPS to 1 mol dm^{-3} hydrochloric acid.

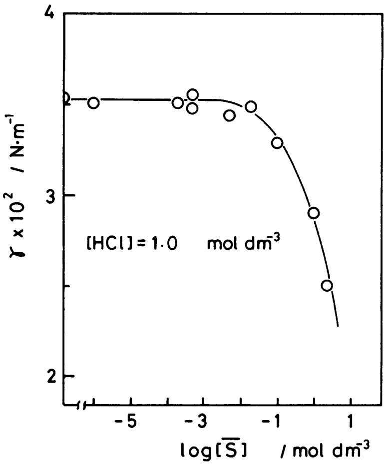

Fig. 4. Relation between interfacial tension, γ, and log [$\overline{S}$].

the two phases. The adsorption equilibrium of TIBPS is expressed as follows:

$$\overline{\mathrm{S}} \rightleftharpoons \mathrm{S}_{\mathrm{ad}} \quad ; K_{\mathrm{ad}} \tag{5}$$

where K_{ad} is the adsorption equilibrium constant defined by Eq. 6 and where the subscript "ad" denotes the adsorbed species at the interface:

$$K_{\mathrm{ad}} = \frac{\theta_s}{[\overline{\mathrm{S}}](1-\theta_s)} \tag{6}$$

Here, θ_s denotes the fractional coverage of the interface by TIBPS.

The combination of Gibb's adsorption isotherm and Langmuir's monolayer adsorption model gives the following relation[10] between the interfacial tension, γ, and the TIBPS concentration, [$\overline{\mathrm{S}}$]:

$$\gamma = \gamma_0 - (RT/S_s)\ln(1+K_{\mathrm{ad}}[\overline{\mathrm{S}}]) \tag{7}$$

where γ_0 denotes the interfacial tension between the pure diluent and 1 mol dm^{-3} of aqueous hydrochloric acid, and where S_s denotes the interfacial area occupied by a unit mole of TIBPS. From the experimental results shown in Fig. 4, the values of K_{ad} and S_s were evaluated by the nonlinear least-squares method based on Eq. 7 to be as follows: K_{ad}=4.4 dm^{3}mol^{-1}, S_s=6.3×10^5 m^2 mol^{-1}.

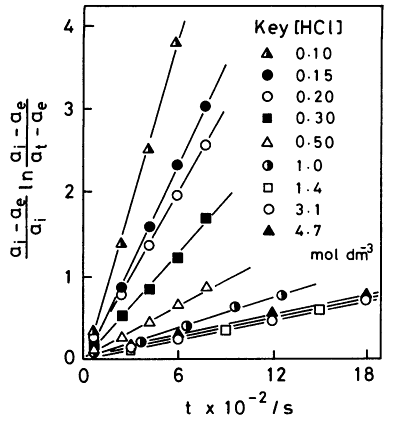

Fig. 5 A typical plot of the experimental results based on the pseudo-first-order rate expression (C_{B0} =0.01 mol dm^{-3}).

The solid curve in Fig. 4 is the curve calculated from Eq. 7 using the above values. The calculated curve is in good agreement with the experimental results.

Extraction Kinetics. If it is assumed that the forward and reverse reactions are pseudo-first-order with respect to palladium(II) in the aqueous and organic phases respectively, the relation between the palladium(II) concentration(a) in the aqueous phase and the contact time(t) is expressed as follows[11]:

$$\frac{a_i-a_e}{a_i}\ln\frac{a_i-a_e}{a_t-a_e} = k_f t, \tag{8}$$

where k_f represents the observed reaction-rate constant for the forward reaction and where the quantities with the subscripts "t", "i", and "e" denote the concentrations after time t, at t=0, and at equilibrium respectively.

Figure 5 shows a typical experimental result plotted on the basis of Eq. 8. The plots in this figure give straight lines passing through the point of origin, as is to be expected from Eq. 8. This result suggests that the forward reaction rate of palladium(II) extraction is first-order with respect to palladium(II) in the aqueous phase. The apparent reaction-rate constants were obtained from the slopes of these straight lines. Since the apparent reaction-rate constant was found in the preliminary experiment to be independent of the stirring speed over the range greater than 1300 rpm, subsequent experiments were carried out at a constant stirring speed of 1500 rpm.

Figure 6 shows the effect of the chloride-ion concentration on the observed reaction rate constant. As is evident from Fig. 6, the plotted points lie on a straight line, with a slope of −1, in the low-concentration region of chloride ions and tend to approach a con-

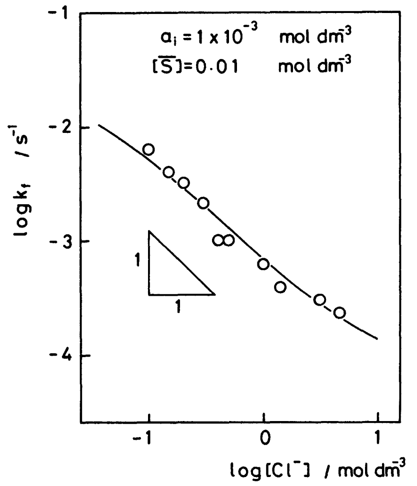

Fig. 6. Effect of chloride ion concentration on the observed extraction rate constant.

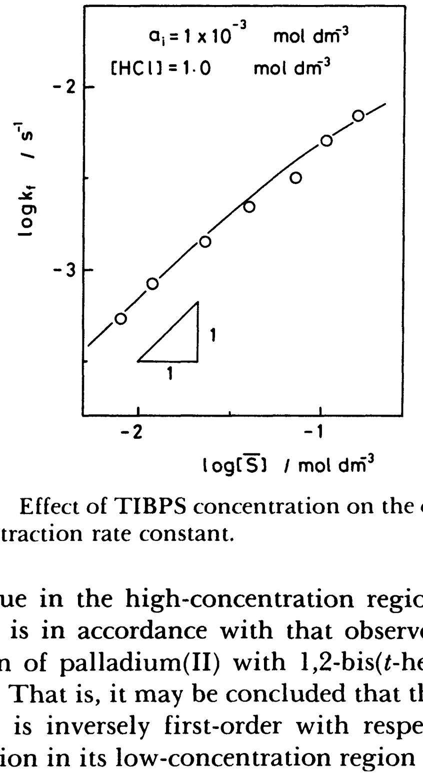

Fig. 7. Effect of TIBPS concentration on the observed extraction rate constant.

stant value in the high-concentration region. This tendency is in accordance with that observed in the extraction of palladium(II) with 1,2-bis(*t*-hexylthio)ethane.[8] That is, it may be concluded that the extraction rate is inversely first-order with respect to the chloride ion in its low-concentration region and zeroth-order in its high-concentration region.

Similarly, the effect of the TIBPS concentration on the observed reaction rate constant is shown in Fig. 7. In this figure, the plots appear to lie on a straight line, with a slope of about 0.75. This result suggests that the extraction-reaction mechanism of this system can not be interpreted in terms of the classical homogeneous heterophase reaction mechanism.[12] Therefore, we in the following section will analyse the experimental results of the extraction kinetics based on the heterogeneous interfacial reaction model.

Discussion

The following results obtained in the present experiment suggest that a certain elementary process taking place at the interface plays an important role in the extraction mechanism: (1) The aqueous solubility of TIBPS is too low to assume that homogeneous reactions take place to any considerable extent in the aqueous phase; (2) TIBPS is adsorbed at the interface, and (3) the reaction order with respect to the extractant is less than unity. The great majority of palladium(II) exists as the tetrachloro complex, $[PdCl_4]^{2-}$, and a small amount of the aquatrichloro complex, $[PdCl_3(H_2O)]^-$, coexists in the aqueous phase over the range of chloride-ion concentrations studied. Of these, Rund,[13] in his paper on the reaction rates of palladium(II) with 1,10-phenanthroline and 2,2′-bipyridyl, reported that the latter is much more labile than the former. Taking account of these facts, the following reaction scheme was proposed to explain the extraction kinetics of palladium(II) with TIBPS:

$$[PdCl_3(H_2O)]^- + S_{ad} \xrightarrow{k_1} [PdCl_3S]^-_{ad} + H_2O \qquad (9)$$

$$[PdCl_4]^{2-} + S_{ad} \xrightarrow{k_2} [PdCl_3S]^-_{ad} + Cl^- \qquad (10)$$

$$[PdCl_3S]^-_{ad} + S \rightleftharpoons \overline{[PdCl_2S_2]} + Cl^- \qquad (11)$$

$$2\overline{[PdCl_2S_2]} \rightleftharpoons \overline{[(PdCl_2)_2S_2]} + 2\overline{S} \qquad (12)$$

The elementary steps described by Eqs. 9 and 10 form the parallel reaction; of these steps, the former is much more rapid than the latter, as has been mentioned earlier. From the fact that the reaction order with respect to TIBPS is less than unity, the interfacial steps expressed by Eqs. 9 and 10 may be considered to be the rate-determining steps. Assuming that the parallel reactions of $[PdCl_3(H_2O)]^-$ and $[PdCl_4]^{2-}$ with TIBPS adsorbed at the interface are the rate-determining steps, the rate expression can be described as follows:

$$-\frac{da_t}{dt} = (k_1[[PdCl_3(H_2O)]^-] + k_2[[PdCl_4]^{2-}])\theta_s \qquad (13)$$

where k_1 and k_2 are the forward reaction rate constants of Eqs. 9 and 10 respectively.

In case the preceding elementary step expressed by Eq. 5 is in equilibrium, θ_s is expressed by Eq. 14 from Eq. 6:

$$\theta_s = \frac{K_{ad}[\overline{S}]}{1+K_{ad}[\overline{S}]} \qquad (14)$$

The substitution of Eq. 14 into Eq. 13 gives the following rate expression.

$$-\frac{da_t}{dt} = \frac{K_{ad}[\overline{S}]}{1+K_{ad}[\overline{S}]}(k_1[[PdCl_3(H_2O)]^-] + k_2[[PdCl_4]^{2-}]) \qquad (15)$$

It is well known that palladium(II) gives rise to chloro complexes in hydrochloric acid as follows:

$$Pd^{2+} + iCl^- \rightleftharpoons [PdCl_i]^{(i-2)-} \qquad ;\beta_i \qquad (16)$$

$$\beta_i = \frac{[[PdCl_i]^{(i-2)-}]}{[Pd^{2+}][Cl^-]^i} \qquad (17)$$

where β_i indicates the stability constants of the ith chloro complex of palladium(II).

The concentrations of the aquatrichloro complex, $[PdCl_3(H_2O)]^-$, and the tetrachloro complex, $[PdCl_4]^{2-}$, in Eq. 15 are expressed by Eqs. 18 and 19, using the equilibrium relations of the chloro complexes in the aqueous phase mentioned above:

$$[[PdCl_3(H_2O)]^-] = \beta_3[Cl^-]^3 a_t/\alpha \tag{18}$$

$$[[PdCl_4]^{2-}] = \beta_4[Cl^-]^4 a_t/\alpha, \tag{19}$$

where α is defined by the following equation:

$$\alpha = 1 + \sum_{i=1}^{4} \beta_i[Cl^-]^i \tag{20}$$

As has been mentioned earlier, over the chloride-ion-concentration range studied, α may be approximated as follows:

$$\alpha \simeq \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4 \tag{21}$$

Consequently, Eq. 15 is ultimately expressed by Eq. 22:

$$-\frac{da_t}{dt} = \frac{K_{ad}[\bar{S}]}{1+K_{ad}[\bar{S}]}\left(\frac{k_1\beta_3+k_2\beta_4[Cl^-]}{\beta_3+\beta_4[Cl^-]}\right)a_t \tag{22}$$

The effects on the extraction rate of varying the concentrations of each reactant species, shown in Figs. 6 and 7, can be qualitatively interpreted by means of Eq. 22, derived from the proposed interfacial reaction scheme.

The optimum values of k_1 and k_2 in Eq. 22 were evaluated by the nonlinear least-squares method from the data shown in Fig. 6, using the K_{ad} value evaluated earlier and the stability constants of the palladium(II) chloro complexes reported in the literature[14] ($\beta_3 = 2.00 \times 10^{10}$, $\beta_4 = 7.94 \times 10^{11}$) as follows: $k_1 = 6.1 \times 10^{-1}$ s^{-1}, $k_2 = 1.7 \times 10^{-3}$ s^{-1}. The solid lines shown in Figs. 6 and 7 were obtained by inserting these values into Eq. 22. The calculated lines are in fairly good agreement with the experimental results.

Conclusion

The kinetic study of the solvent extraction of palladium(II) from hydrochloric acid with triisobutylphosphine sulfide (TIBPS=S) in toluene was conducted using a stirred cell, along with studies of the aqueous solubility or the equilibrium distribution of the extractant between the organic and aqueous phases, its adsorption equilibrium at the interface, and the distribution equilibrium of palladium(II).

The experimental results on the distribution equilibrium of palladium(II) showed that palladium(II) is extracted as a Pd : extractant 2 : 2 complex, $[(PdCl_2)_2S_2]$.

From the experimental results of the equilibrium distribution and the interfacial adsorption equilibrium of the extractant, it was elucidated that TIBPS has a very low aqueous solubility and a fairly high interfacial activity, suggesting the importance of the interfacial reaction in the extraction of palladium(II) with TIBPS.

The experimental results of the extraction kinetics were quantitatively explained by the interfacial reaction model on the assumption that the ligand substitutions between the extractant adsorbed at the interface and the aquatrichloro and tetrachloro complexes of palladium(II) in the aqueous phase are the rate-determining steps. That is, the extraction rate was found to be satisfactorily expressed by the rate equation described by Eq. 22, derived from the interfacial reaction model presented above.

The authors are deeply indebted to American Cyanamid Co. for supply of the sample of CYANEX 471.

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