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The Solvent Extraction of Palladium(II) from Aqueous Chloride Media with 7-Tridecanone Oxime

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The extraction behavior of palladium(II) from the aqueous ammonium chloride solutions with the title extractant in toluene was investigated in terms of the equilibrium and the kinetics, while the aqueous solubility and the interfacial adsorption equilibrium of the extractant were estimated. The extraction rate of the 1:2 palladium(II)–extractant complex was explained by the interfacial reaction model, in which the rate-determining steps were assumed to be the elementary reactions between the aquatrichloro- and tetrachloropalladate(II) in the aqueous phase and the extractant molecule adsorbed at the interface.

Great attention has been paid to developing solvent extraction or chelating ion exchange techniques in order to replace the conventional precipitation techniques for the recovery and purification of precious metals on commercial scale. Various extracting agents and chelating resins with high loading capacities and excellent selectivities to precious metals have become commercially available as novel techniques have been developed. The precious metals are extracted or adsorbed from aqueous chloride media rather than from nitrate, sulfate, cyanide, or thiocyanide media in the currently applied techniques.

Recently we have investigated the solvent extraction of palladium(II) from aqueous chloride media with various extracting agents, such as sulfur-containing extractants[1–4] and a hydroxy oxime.[5] In these works, the kinetics of the solvent extraction has been found to be significantly affected by the interfacial activities of the extracting agents as well as by their aqueous solubilities. In the extraction with dihexyl sulfide (DHS), triisobutylphosphine sulfide (TIBPS), and 2′-hydroxy-5′-nonylacetophenone oxime, all of which have low aqueous solubilities and high interfacial activities, the rate-determining complex formation reaction takes place at the interface between the aqueous and organic phases, while it takes place in the aqueous phase in the extraction with 1,2-bis(*tert*-hexylthio)ethane (*t*-BHTE), which has a very low interfacial activity and a relatively high aqueous solubility. The kinetic data of the former extraction systems were reasonably interpreted in terms of the heterogeneous interfacial reaction model, while those of the latter extraction system were interpreted in terms of the classical homogeneous heterophase reaction model of complex formation.

Holland et al.[6,7] investigated extensively the solvent extraction of metals with various kinds of dialkyl ketone oximes with relatively short alkyl chains, either symmetric or unsymmetric, and found that the so-called soft metals, such as palladium(II), silver(I), mercury(II), and gold(III), are effectively extracted into chloroform. However, their studies aimed at the analytical use of these oximes as extractants and were rather qualitative; the extraction mechanisms have remained unclarified.

This paper will report in detail on the extraction behavior of palladium(II) from aqueous chloride media with 7-tridecanone oxime, one of the symmetric dialkyl ketone oximes. The extraction equilibrium and kinetics, including the interfacial adsorption equilibrium of the extractant, were investigated quantitatively; the aqueous solubility of the extractant was also determined.

Experimental

Reagents. The 7-tridecanone oxime, abbreviated as 7-TDO and denoted by HR hereafter, was synthesized from 7-tridecanone in ethanol and an aqueous mixture of hydroxylamine hydrochloride and sodium acetate by a conventional method according to the following reaction:

$$(C_6H_{13})_2CO + NH_2OH\cdot HCl + CH_3COONa \longrightarrow (C_6H_{13})_2C{=}NOH + CH_3COOH + NaCl + H_2O$$

After washing with water and phase separation, the product was purified by means of vacuum distillation (bp 109—110 °C/0.1 mmHg (1 mmHg=133.322 Pa)). The purified viscous, pale yellow liquid product was identified by means of IR and NMR spectroscopies; the purity was confirmed by means of elemental analysis. Found: C, 73.11; H, 12.76; N, 6.63%. Calcd for $C_{13}H_{27}NO$: C, 73.18; H, 12.75; N, 6.56%. The organic phase was prepared on a gravimetric basis by diluting the purified reagent with toluene of an analytical grade. The aqueous phase was prepared by dissolving palladium(II) chloride in aqueous ammonium chloride solutions containing a small amount of hydrochloric acid (about 0.01 mol dm^{-3}).

Determination of the Stoichiometry of the Extracted Species. Under an excess concentration of 7-TDO over the palladium(II) concentration in the aqueous phase, the palladium(II) was almost completely extracted over the whole concentration region of chloride ions in the present experiment (0.01—6 mol dm^{-3}). The remaining amount of palladium(II) was too small for a precise quantitative analysis to be made. Therefore, only a loading test was carried out to determine the molar ratio of palladium(II) extracted into the organic phase to 7-TDO by varying the concentration ratio of 7-TDO in the organic phase to that of palladium(II) in the aqueous phase under the conditions of a large excess of the palladium(II) concentrations, as in the extraction with DHS, TIBPS, and *t*-BHTE.[1,3,4)]

Equal volumes (0.02 dm^3) of two phases of known concentrations were vigorously shaken for 2 h in a separatory funnel using an 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 2 h. After the separation of the two phases, the palladium(II) concentration in the aqueous phase was determined by means of atomic absorption spectroscopy using a Nippon Jarrell-Ash model AA 782 spectrophotometer. The palladium(II) concentration in the organic phase was calculated from the mass balance of the aqueous palladium(II) concentrations before and after the equilibration.

Measurement of Aqueous Solubility of the Extractant. The distribution of 7-TDO between the organic and aqueous phases was measured spectrophotometrically at 303 K by a method similar to that described in previous papers.[1,4)]

A toluene solution of 7-TDO of a known concentration and a 0.1 mol dm^{-3} aqueous ammonium choride solution with a volume ratio of the aqueous phase to the organic phase of 10:1 were shaken vigorously for 24 h using the mechanical shaker. After phase-separation, a portion of the aqueous phase (0.19 dm^3) was transferred into a separatory funnel. In order to convert completely any 7-TDO dissolved in the aqueous phase to its palladium(II) complex, 5×10^{-2} dm^3 of a 2 mmol dm^{-3} aqueous palladium(II) chloride solution containing 10 mmol dm^{-3} of hydrochloric acid and 1×10^{-2} dm^3 of toluene were added to the separatory funnel, after which the mixture was shaken for 24 h using a mechanical shaker. The absorbance of the palladium(II) complex in toluene was measured at 284 nm against a toluene blank using a Shimadzu UV 140 spectrophotometer.

Measurement of Interfacial Adsorption Equilibrium. The interfacial tension between the organic solution and the 0.1 mol dm^{-3} aqueous ammonium chloride solution was measured at 303 K by means of the pendant-drop method in order to examine the interfacial adsorption equilibrium of 7-TDO.

Measurement of Extraction Rate. The extraction rate of palladium(II) was measured using a batch-type glass stirred cell with an inner diameter of 0.1 m and a depth of 0.15 m; it was fitted with four baffles made of poly(tetrafluoroethylene), each of which was 0.01 m wide and 0.15 m long. It was the same as that used for the measurement of the extraction rate of palladium(II) with *t*-BHTE and TIBPS in the previous works.[1,4)]

Stirring was carried out at a constant stirring speed of 1500 min^{-1} using a turbine impeller with six flat blades connected to a speed controller. Equal volumes (0.3 dm^3) of the organic and aqueous phases were introduced into the cell placed in a water bath maintained at 303 K. After the initiation of stirring, small amount of samples were taken out at definite time intervals in order to measure the variation in the palladium(II) concentration in the aqueous phase with time; the concentration was determined by means of atomic absorption spectrophotometry.

The initial palladium(II) concentration was 0.5 mmol dm^{-3} in all kinetic runs, while the concentrations of the extractant and chloride ion were varied over the ranges of 2—150 mmol dm^{-3} and 5×10^{-3}—5 mol dm^{-3} respectively.

Results

Selectivity of 7-TDO to Various Metals. Figure 1 shows the results of the solvent extraction of various metals from hydrochloric acid solutions with 7-TDO. Palladium(II) is completely extracted over the whole concentration region of hydrochloric acid, while relatively small amounts of mercury(II) and platinum(IV) are extracted, especially in the low-concentration region of hydrochloric acid. The base metals, such as copper(II), zinc(II), nickel(II), cobalt(II), and aluminum(III), are not practically extracted, not even in the high-concentration region of hydrochloric acid, though considerable amounts of copper(II) and nickel(II) were extracted in such high-concentration regions as above 0.1 and 2 mol dm^{-3} respectively in the extraction with 2-ethylhexanal oxime in a previous work[8)]. Palladium(II) extracted by 7-TDO can be

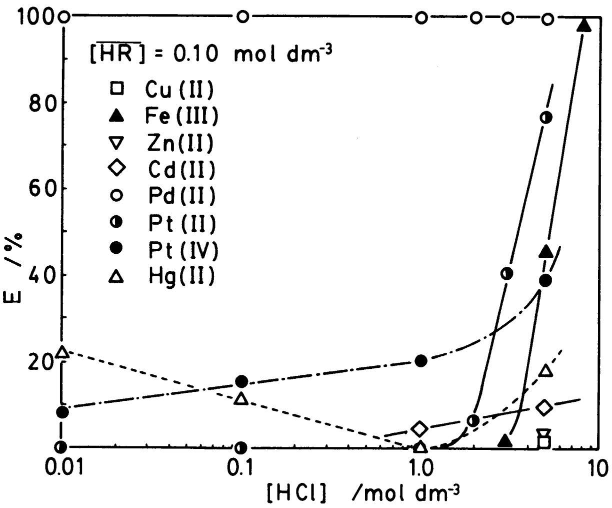

Fig. 1. Percentage extraction of various metals from hydrochloric acid with 0.1 mol dm^{-3} 7-tridecanone oxime in toluene. Initial metal concentration=100 ppm for Pd(II) and Pt(II and IV) or 0.01 mol dm^{-3} for other metals.

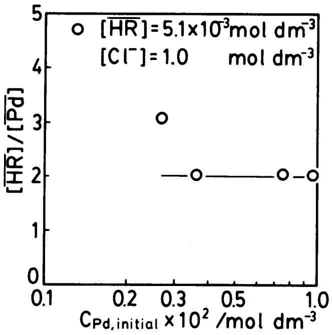

Fig. 2. Experimental results of the loading test.

easily and completely stripped by aqueous thiourea or ammonium thiocyanate solutions; however, only a partial stripping can be accomplished by aqueous ammonia and sodium or ammonium thiosulfate solutions. Thus, 7-TDO is an excellent extracting reagent, suitable for the separation of palladium(II) from platinum(II and IV) and base metals in the low-concentration region of hydrochloric acid in particular.

Stoichiometry of the Extracted Species. Figure 2 shows the result of the loading test. The mole ratio of 7-TDO to palladium(II) in the organic phase asymptotically approaches 2 with an increase in the aqueous palladium(II) concentration. This suggests that palladium(II) is extracted as a 1:2 metal:reagent complex into the organic phase.

Taking account of the results of the previous work,[8] the stoichiometry is expressed in manner similar to that used for copper(II) with 2-ethylhexanal oxime:

$$\mathrm{PdCl}_i^{(i-2)-} + \overline{2\mathrm{HR}} \rightleftharpoons \overline{\mathrm{PdCl_2 \cdot 2HR}} + (i-2)\mathrm{Cl}^- \qquad (1)$$

where the overline denotes the species existing in the organic phase.

Aqueous Solubility of 7-TDO. Assuming that free 7-TDO is monomeric, the distribution of 7-TDO between the organic and aqueous phases is expressed as follows:

$$\overline{\mathrm{HR}} \rightleftharpoons \mathrm{HR} \qquad (2)$$

$$K_\mathrm{D} = [\mathrm{HR}]/[\overline{\mathrm{HR}}] \qquad (3)$$

where K_D is the partition coefficient of 7-TDO. From Eq. 3, we obtain:

$$\log[\mathrm{HR}] = \log[\overline{\mathrm{HR}}] + \log K_\mathrm{D} \qquad (4)$$

The partition coefficient is so small that the concentration of 7-TDO in the organic phase, $[\overline{\mathrm{HR}}]$, is nearly equal to its initial concentration, C_B0.

As may be expected from Eq. 4, the plot of the logarithm of the concentration of 7-TDO in the aqueous phase against that in the organic phase gives a linear relationship, as is shown in Fig. 3. From the intercept of the straight line with the ordinate in Fig. 3, the partition coefficient was evaluated as K_D= 7.0×10^{-6} according to Eq. 4. This value is very close to that of TIBPS (=5.4×10^{-6}).[4]

This result supports the idea that 7-TDO is monomeric in toluene, as has been confirmed by the measurement of the molecular weight by means of vapor-phase osmometry.

Interfacial Tension. Figure 4 shows the plot of the interfacial tension, γ, between an organic solution containing 7-TDO and a 0.1 mol dm^{-3} aqueous ammonium chloride solution against the concentration of 7-TDO in the organic phase. The interfacial tension decreases with an increase in the concentration of 7-TDO in its high-concentration region, which indicates that 7-TDO is interfacially active.

The adsorption equilibrium of 7-TDO at the interface is described as follows:

$$\overline{\mathrm{HR}} \rightleftharpoons \mathrm{HR_{ad}} \qquad ;K_\mathrm{ad} \qquad (5)$$

where the subscript "ad" denotes the adsorbed species at the interface. The relationship between the interfacial tension, γ, and the concentration of 7-TDO in the organic phase, $[\overline{\mathrm{HR}}]$, is given in Eq. 6, which has been obtained by combining the Gibbs adsorption isotherm with Langmuir's monolayer adsorption model applied to the above-mentioned adsorption equilibrium similarly as to the adsorption equilibrium of TIBPS:[4]

$$\gamma = \gamma_0 - (RT/S_\mathrm{HR})\ln(1 + K_\mathrm{ad}[\overline{\mathrm{HR}}]) \qquad (6)$$

where γ_0 denotes the interfacial tension between the pure diluent and the 0.1 mol dm^{-3} aqueous ammonium chloride solution and where S_HR denotes the interfacial area occupied by a unit mole of 7-TDO. From the results shown in Fig. 4, the values of K_ad and S_HR were evaluated by the nonlinear, least-squares

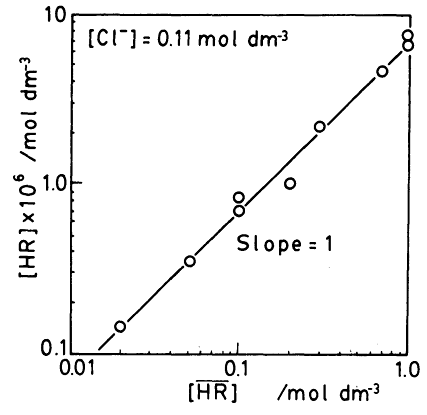

Fig. 3. Aqueous solubility of 7-TDO to aqueous ammonium chloride solution.

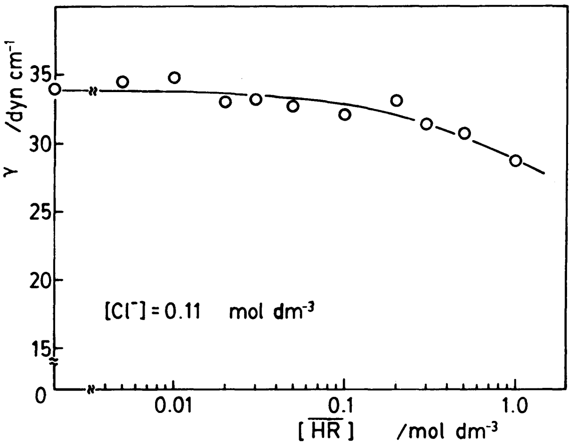

Fig. 4. Relation between interfacial tension and 7-TDO concentration in the organic phase.

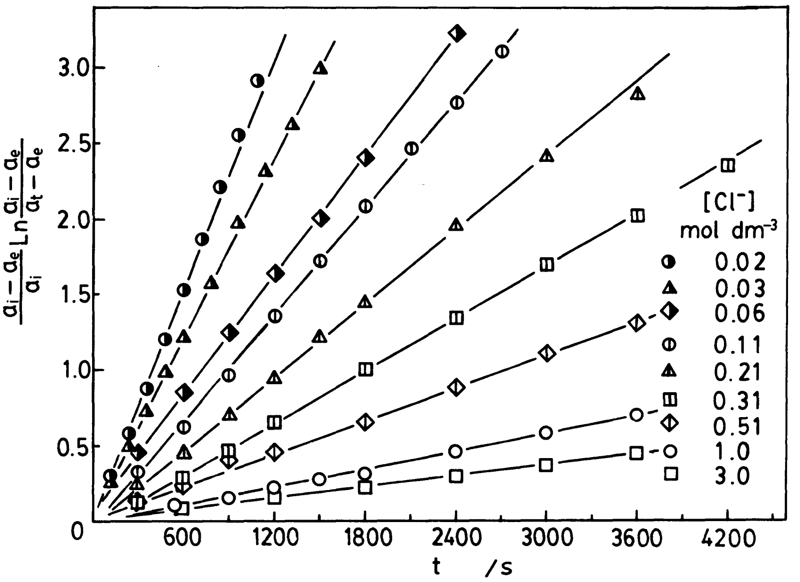

Fig. 5. A typical plot of the experimental results of extraction rate based on the pseudo-first-order rate expression ([$\overline{\text{HR}}$]=0.01 mol dm^{-3}).

method based on Eq. 6: K_{ad}=6.3 dm^3 mol^{-1}, S_{HR}=9.6×10^5 m^2 mol^{-1}. These values are very close to those of TIBPS (K_{ad}=4.4 dm^{3}mol^{-1}, S_S=6.3×10^5 m^2 mol^{-1})[4]. The curve in Fig. 4 is calculated from Eq. 6 using these values. The calculated curve is in good agreement with the experimental results.

Extraction Kinetics. The variation in the palladium(II) concentration in the aqueous phase with time was rearranged and plotted according to Eq. 7 on the assumption that the forward and reverse reactions are pseudo-first-order with respect to the palladium(II) concentration in the aqueous and organic phases respectively:

$$\frac{a_i - a_e}{a_i} \ln \frac{a_i - a_e}{a_t - a_e} = k_f t \qquad (7)$$

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 concentration after time t, at t=0, and at equilibrium respectively.

Figure 5 shows a typical set of the experimental results plotted according to Eq. 7. The plots in this figure give straight lines, as is to be expected from Eq. 7, suggesting that the forward reaction rate of palladium(II) extraction is first-order with respect to the palladium(II) concentration 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 min^{-1}, subsequent experiments were carried out at a constant stirring speed of 1500 min^{-1}, as will be discussed earlier.

Figure 6 shows the effect of the chloride-ion concentration on the observed reaction-rate constant. The plots in this figure appear to approach a constant value with decrease or increase of the chloride-ion concentration in its low- and high-concentration regions respectively. Figure 7 shows the effect of the

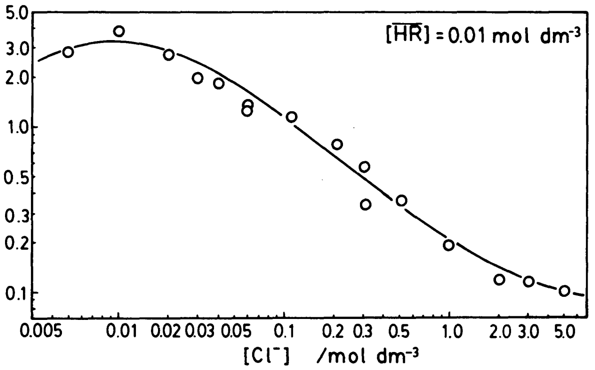

Fig. 6. Effect of chloride ion concentration on the observed extraction rate constant.

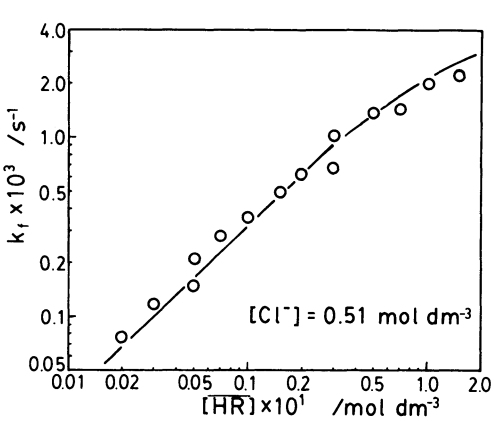

Fig. 7. Effect of 7-TDO concentration on the observed extraction rate constant.

7-TDO concentration on the observed reaction rate constant. The plots in this figure lie on a straight line with a slope of 1 and tend to approach a constant value in the high-concentration region.

These tendencies of the concentration dependencies of the reactant species on the extraction rate of palladium(II) are partly similar to those observed in the extraction with TIBPS.4) Therefore, the experimental results of the extraction kinetics were analyzed on the basis of the heterogeneous interfacial reaction model applied to the analysis of the extraction kinetics by TIBPS4), as will be described in the following section.

Discussion

The following results obtained in the present work suggest that a certain elementary process taking place at the interface plays an important role in the reaction mechanism of the present extraction system: (1) The aqueous solubility of 7-TDO is too low to assume that homogeneous reactions take place to any considerable extent in the aqueous phase; (2) 7-TDO has interfacial activity, and (3) the reaction order with respect to the extractant is less than unity in its high-concentration region.

Consequently, in a manner similar to that employed in the analysis of the extraction kinetics with TIBPS,4) palladium(II) is considered to be extracted by 7-TDO from aqueous chloride media according to the following reaction scheme:

$$[\mathrm{PdCl_3(H_2O)}]^- + \mathrm{HR_{ad}} \xrightarrow{k_1} [\mathrm{PdCl_3\cdot HR}]^-_{\mathrm{ad}} + \mathrm{H_2O} \tag{8}$$

$$[\mathrm{PdCl_4}]^{2-} + \mathrm{HR_{ad}} \xrightarrow{k_2} [\mathrm{PdCl_3\cdot HR}]^-_{\mathrm{ad}} + \mathrm{Cl^-} \tag{9}$$

$$[\mathrm{PdCl_3\cdot HR}]^-_{\mathrm{ad}} + \mathrm{HR} \rightleftharpoons [\overline{\mathrm{PdCl_2\cdot 2HR}}] + \mathrm{Cl^-} \tag{10}$$

Assuming that the parallel elementary reactions to form the intermediate complex at the interface, $[\mathrm{PdCl_3\cdot HR}]^-_{\mathrm{ad}}$, as described by Eqs. 8 and 9, are rate-determining, and taking account of the fact that the aquatrichloro complex, $[\mathrm{PdCl_3(H_2O)}]^-$, and the tetrachloro complex, $[\mathrm{PdCl_4}]^{2-}$, are predominant under the present experimental conditions, the rate of the present extraction reaction can be approximately described as follows:

$$-\frac{\mathrm{d}a_t}{\mathrm{d}t} = \frac{K_{\mathrm{ad}}[\overline{\mathrm{HR}}]}{1 + K_{\mathrm{ad}}[\overline{\mathrm{HR}}]} \left(\frac{k_1\beta_3 + k_2\beta_4[\mathrm{Cl^-}]}{\beta_3 + \beta_4[\mathrm{Cl^-}]} \right) a_t \tag{11}$$

where β_3 and β_4 denote the stability constants of aquatrichloro- and tetrachloropalladate(II). The effects of varying the concentrations of each reactant species on the extraction rates shown in Figs. 6 and 7 can be qualitatively interpreted by Eq. 11, derived from the proposed interfacial reaction scheme.

The optimum values of the rate constants, k_1 and k_2, of the rate-determining steps described by Eqs. 8 and 9 were calculated by the nonlinear, least-squares method from the data in Figs. 6 and 7, using the value of K_{ad} obtained in the preceding section and the stability constants of the palladium(II) chloro complexes in the literature10) ($\beta_3=2.00\times10^{10}$, $\beta_4=7.94\times10^{11}$): $k_1=9.7\times10^{-2}\,\mathrm{s^{-1}}$, $k_1=1.3\times10^{-3}\,\mathrm{s^{-1}}$. The magnitudes of the orders of these values are very close to those observed in the extraction with TIBPS from hydrochloric acid ($k_1=6.1\times10^{-1}\,\mathrm{s^{-1}}$, $k_2=1.7\times10^{-3}\,\mathrm{s^{-1}}$). The solid lines shown in Figs. 6 and 7 are the curves calculated from Eq. 11 using these values. These lines are in fairly good agreement with the experimental results.

Conclusion

The partition coefficient of 7-TDO to the aqueous solution and its adsorption equilibrium parameters, the interfacial area occupied by a unit mole of the extractant, and the interfacial adsorption equiibrium constant are very close to those of triisobutylphosphine sulfide (TIBPS) as reported in a previous work.4) Palladium(II) is extracted as a mononuclear complex by the use of 7-TDO, while it is extracted as a binuclear complex when TIBPS is used.

The experimental results of the extraction kinetics were quantitatively explained by the interfacial reaction model proposed for the kinetics of extraction with TIBPS, in which the ligand substitution between the extractant molecule adsorbed at the interface and aquatrichloro- and tetrachloropalladate(II) in the aqueous phase are rate-determining. The extraction rate was satisfactorily expressed by Eq. 11, which was derived from the interfacial reaction model presented above. The values of the reaction-rate constants in Eq. 11 were found to be close to those observed in the extraction with TIBPS.

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