

KINETICS OF SOLVENT EXTRACTION OF PALLADIUM WITH DIDODECYLMONOTHIOPHOSPHORIC ACID

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The extraction of palladium by didodecylmonothiophosphoric acid is carried out, using a highly stirred tank and a stirred transfer cell to clarify the extraction mechanism. Measurements of palladium-loading capacity and of interfacial adsorption equilibrium of the extractant are also conducted. The dependency of the extraction rate on the concentration of the chemical species taking part in the extraction is examined.

An interfacial reaction model in which four chloro-palladium complexes take part is proposed. The experimental results are analyzed by the model to obtain the reaction rate constants of these four complexes with the extractant. The order of magnitude of the reaction rate constants is explained qualitatively by the trans-effect.

Introduction

Recently, a solvent extraction technique as an effective and selective method of separation among the platinum-group metals has attracted practical interest from the viewpoint of energy conservation. In developing the solvent extraction process for the platinum-group metals, it is very important to elucidate the extraction mechanism. With this point as background, studies of the extraction of palladium, in particular, have extensively been conducted, but most have been limited to extraction equilibrium^{5,9,15)} or hydrometallurgical applications.^{4,6,7)}

An extractant containing sulfur as the donor atom has a high selectivity for the platinum-group metals over others. Few works on the extraction kinetics of palladium with such an extractant have been carried out so far. Al-Bazi and Freiser¹⁾ studied the extraction kinetics of palladium with dioctyl sulfide and concluded that the rate-determining step is the reaction of trichloro-palladium species with the extractant in the aqueous phase. Baba and Inoue²⁾ studied the mechanism of palladium extraction with dihexyl sulfide, concluding that the rate-determining step is the re-

action between the intermediate trichloro-palladium-extractant complex adsorbed at the interface and the extractant in the aqueous phase. They also proposed an interfacial reaction mechanism in the extraction of palladium with triisobutylphosphine sulfide.³⁾

In the studies introduced above, however, the extraction mechanism in the region of low chloride-ion concentration is not clear. In the present study, to clarify this point and the extraction mechanism further, the extraction of palladium by didodecylmonothiophosphoric acid is carried out, using a highly stirred tank and a stirred transfer cell. The extractant has a higher interfacial activity than the sulfides. Measurements of palladium-loading capacity and of interfacial adsorption equilibrium of the extractant are also conducted. The dependency of the extraction rate on the concentration of the chemical species taking part in the extraction is examined and an interfacial reaction model for the extraction is proposed to interpret the experimental results.

1. Experimental

1.1 Reagents

The extractant, didodecylmonothiophosphoric acid (hereafter abbreviated as DDTPA), was synthesized¹¹⁾ as its ammonium salt by the interaction of

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didodecyl phosphite and sulfur under ammoniacal atmosphere at 350 K. The white solid salt was filtered and recrystallized three times from dichloroethane. The product was identified by IR, NMR and elementary analysis. The result of elementary analysis was as follows. Found: C, 61.35; H, 11.60; N, 3.07%. Calcd. for $C_{24}H_{54}NO_3PS$: C, 61.63; H, 11.64; N, 3.00%.

The organic solution was prepared as follows. The ammonium salt of the extractant was first dissolved in 1000 mol/m^3 sulfuric acid aqueous solution and then this was contacted sufficiently with toluene to distribute the extractant into the toluene solution. The concentration of DDTPA in the organic solution was determined by neutralization titration with alcoholic potash solution.

The aqueous solution was prepared by dissolving perchloric acid, lithium chloride and palladium chloride into deionized water.

All organic and inorganic chemicals used were GR grade.

1.2 Measurement of molecular weight of extractant

The apparent molecular weight of DDTPA in toluene was measured by vapor-phase osmometry using benzil as a standard. It was found to be 431. Therefore, the extractant was considered to exist as the monomer in toluene because the calculated value of the molecular weight is 450.7.

1.3 Measurement of interfacial tension of extractant

The interfacial tension of DDTPA with different concentration between toluene and hydrochloric acid solutions at pH values of 0.7 and 5.0 was measured at 303 K by the pendant-drop method to examine the interfacial adsorption equilibrium of the extractant.

1.4 Measurement of palladium-loading capacity of extractant

DDTPA extracted palladium completely over a wide range of experimental conditions, so that it was difficult to determine experimentally the extraction equilibrium constant. A loading test was carried out to estimate the extracted species of palladium in the organic solution. Equal volumes (5 ml) of the aqueous and the organic solutions with fixed concentrations prepared as mentioned above were placed in a test tube and shaken vigorously for about a week to attain equilibrium. After that, the organic solution was removed and palladium was stripped with 1000 mol/m^3 thiourea– 1000 mol/m^3 hydrochloric acid aqueous solution. The palladium concentration was determined by atomic absorption spectrophotometry. Palladium was confirmed beforehand to be completely extracted under the above-mentioned condition. The palladium concentration in the aqueous solution at equilibrium was also determined.

1.5 Measurement of extraction rate of palladium

A highly stirred tank of 9 cm inner diameter and 8 cm depth was mainly used to measure the extraction

Table 1. Experimental conditions for palladium extraction

Highly stirred tank	
C_{HR}	$= 1\text{--}50 \text{ mol/m}^3$
C_H	$= 200\text{--}3000 \text{ mol/m}^3$
C_{Cl}	$= 20\text{--}5000 \text{ mol/m}^3$
C_{Pd}	$= 0.5 \text{ mol/m}^3$
Stirred transfer cell	
C_{HR}	$= 5 \text{ mol/m}^3$
C_H	$= 1000 \text{ mol/m}^3$
C_{Cl}	$= 1\text{--}20 \text{ mol/m}^3$
C_{Pd}	$= 0.5 \text{ mol/m}^3$

rate of palladium. The vessel was fitted with four baffles, each 1 cm in width and 6.5 cm in length. Stirring was carried out using a turbine impeller of 4 cm diameter, having six flat blades connected with a speed controller. Equal volumes (about 180 cm^3) of the aqueous and the organic solutions were poured into the tank and immediately stirring was started. Stirring speed was maintained at 1250 r.p.m. by a stroboscope. Samples of each solution (1 cm^3) were taken out at intervals. The palladium concentration in the aqueous solution was determined by atomic absorption spectrophotometry.

A stirred transfer cell was also used under the experimental conditions where high extraction rate was observed. The stirred transfer cell used was the same as that described in a previous paper.¹⁴⁾ The aqueous solution was first poured in the lower cell and then the organic solution was carefully placed on the aqueous solution. The aqueous and the organic solutions were stirred in opposite directions at equal velocities at 150 r.p.m. by two flat-blade stirrers. The interfacial area was 15.1 cm^2 . The organic solution was sampled at intervals after stirring was started. The samples were stripped by the method mentioned above and then the palladium content was determined.

The experimental conditions are shown in **Table 1**. The extraction rates were measured at 303 K.

2. Results

2.1 Interfacial tension of extractant

The relation between the interfacial tension, γ , and the concentration of DDTPA, C_{HR} , is shown in **Fig. 1**. It is found that the extractant has an interfacial activity. In addition, it is anticipated that the anion of the extractant has a larger interfacial activity than the extractant itself from the experimental results at pH = 5.0. The relation between the interfacial tension and the amounts of DDTPA and its anion adsorbed at the interface is expressed by Gibbs' adsorption equation. Assuming a Langmuir adsorption isotherm between the amounts of DDTPA and the anion adsorbed and

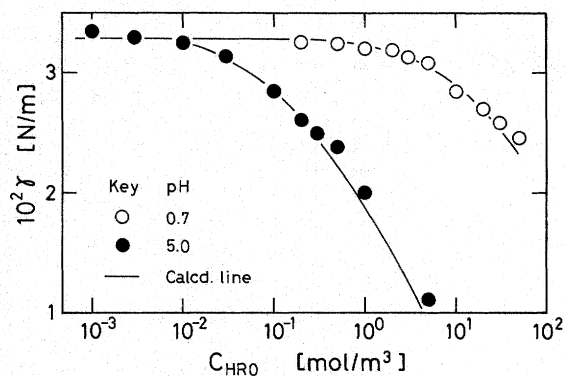


Fig. 1. Relation between interfacial tension and extractant concentration

the bulk concentration, the relation between γ and C_{HR} at temperature T is expressed as follows:

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

where K_{HR} and S_{HR} are the adsorption equilibrium constant and the interfacial area occupied by unit mole of the extractant, respectively. K_a and C_H are the dissociation constant of DDTPA at the interface and concentration of hydrogen ion, respectively, and γ_0 is the interfacial tension between toluene and the aqueous solution.

The values of K_{HR} , S_{HR} and K_a were obtained from the experimental results and Eq. (1) by nonlinear regression using a modified Marquardt method. The results are shown in Table 2. The solid curve in Fig. 1 was calculated by Eq. (1), using the constants obtained.

2.2 Palladium-loading capacity of extractant

Figure 2 shows the relation between the ratio of the initial concentration of DDTPA to the concentration of palladium extracted into the organic solution and the initial concentration of palladium in the aqueous solution. It is found that a complex of palladium 1: DDTPA 2 is formed under the experimental conditions.

The effect of chloride-ion concentration on the loading ratio is shown in Fig. 3. At a chloride-ion concentration less than about 500 mol/m³, the loading ratio decreases from 2 to about 1. It is anticipated that a polymerized palladium complex is extracted in the organic solution.

The loading ratio was not affected by the concentration of hydrogen ion and the ratio was still 2 over a wide range of concentration.

2.3 Extraction rate of palladium

A typical experimental result in the highly stirred tank is shown in Fig. 4 as the concentration change of palladium in the aqueous solution with the extraction time. The extraction rates are found to decrease as the chloride-ion concentration increases.

As anticipated from Fig. 4, the extraction rate may

Table 2. Values of constants for palladium extraction

K_{HR}	$= 1.0 \times 10^{-1} \text{ m}^3/\text{mol}$
S_{HR}	$= 4.0 \times 10^5 \text{ m}^2/\text{mol}$
K_a	$= 9.4 \times 10^{-1} \text{ mol/m}^3$
k_1	$= 1.5 \times 10^{-3} \text{ m}^3/(\text{mol} \cdot \text{s})$
k_2	$= 2.0 \times 10^{-2} \text{ m}^3/(\text{mol} \cdot \text{s})$
k_3	$= 8.7 \times 10^{-1} \text{ m}^3/(\text{mol} \cdot \text{s})$
k_4	$= 3.8 \text{ m}^3/(\text{mol} \cdot \text{s})$

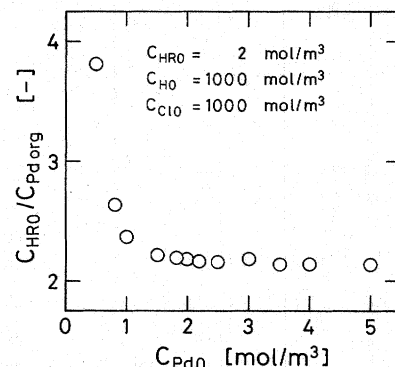


Fig. 2. Effect of palladium concentration on loading capacity

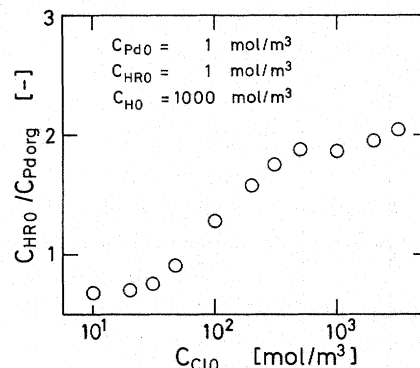


Fig. 3. Effect of chloride-ion concentration on loading capacity

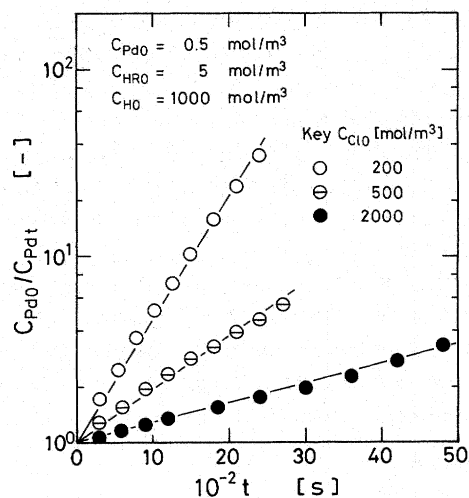


Fig. 4. Change of palladium concentration with time

be expressed by a pseudo-first order process with respect to the palladium concentration, C_{Pd} , as follows:

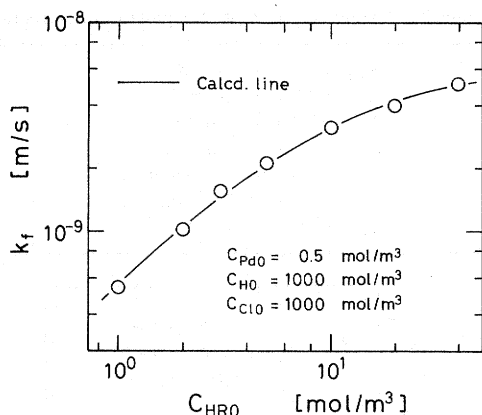


Fig. 5. Relation between extraction rate constant and extractant concentration

$$\ln(C_{Pd0}/C_{PdI}) = A \cdot k_f \cdot t = k'_f \cdot t \quad (2)$$

where k'_f is the apparent extraction rate constant and A is the specific interfacial area. Subscripts 0 and t indicate initial state and elapsed time, respectively. The value of k'_f is evaluated from the slope of the straight line in Fig. 4. Then k'_f is converted to k_f by considering the increase in A accompanied by the decrease in γ , as follows.¹³⁾

$$A = A_0(\gamma_0/\gamma)^{0.75} \quad (3)$$

where A_0 is the interfacial area when using no extractant and was estimated as follows. First, A was estimated by comparing the extraction rate in the highly stirred tank with that in the stirred transfer cell whose interfacial area is known, under the same experimental condition. Then A_0 was obtained from Eq. (3) using the value of A . The value of A_0 at 1250 r.p.m. was $1.66 \times 10^5 \text{ m}^{-1}$.

The effect of DDTPA concentration on k_f is shown in Fig. 5. The concentration dependency of DDTPA on k_f is first-order in the low concentration range of DDTPA, but in the high concentration range it approaches zero because the adsorption of DDTPA at the interface attains the saturated state.

The effect of the concentration of hydrogen ion on k_f is shown in Fig. 6. The concentration of hydrogen ion scarcely affects the extraction rate constant under the experimental conditions.

The effect of the concentration of chloride ion, C_{Cl} , on k_f is shown in Fig. 7. The concentration dependency of chloride ion on k_f is inversely first-order in the low concentration range of chloride ion, but approaches zero in the high concentration range.

3. Discussion

It is well known that palladium ion forms the stable complexes with chloride ion in aqueous solution, as follows.

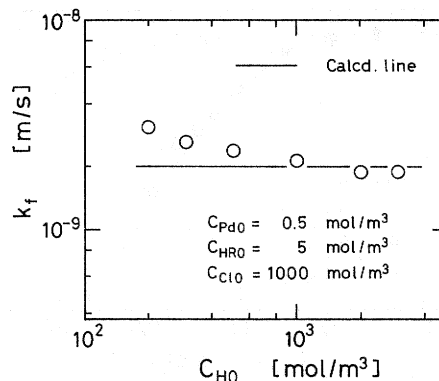
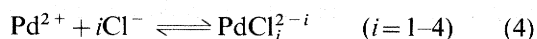


Fig. 6. Relation between extraction rate constant and hydrogen-ion concentration

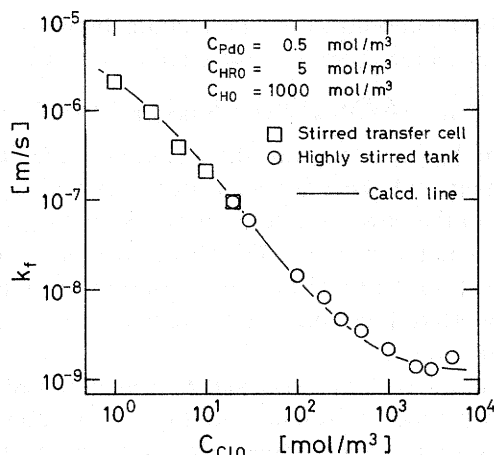


Fig. 7. Relation between extraction rate constant and chloride-ion concentration

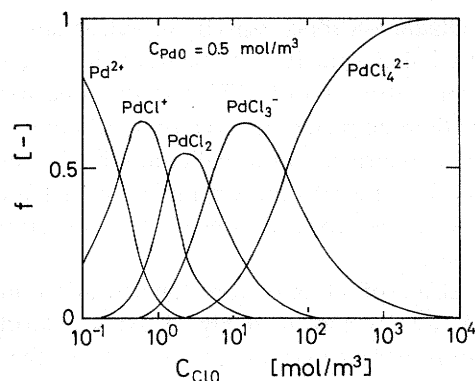


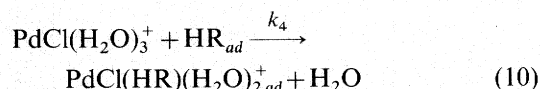
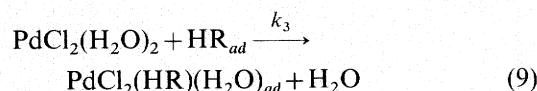
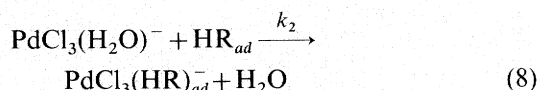
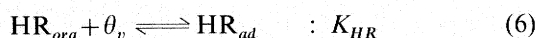
Fig. 8. Distribution of chloro-palladium species in aqueous solution

$$\beta_i = [\text{PdCl}_i^{2-i}]/([\text{Pd}^{2+}][\text{Cl}^-]^i) \quad (5)$$

where β_i is the stability constant of the complex. Using the values of β_i ($\beta_1 = 10^{4.47}$, $\beta_2 = 10^{7.76}$, $\beta_3 = 10^{10.17}$ and $\beta_4 = 10^{11.54}$)⁸⁾, the distribution percentage of the complexes was calculated as shown in Fig. 8. The four chloro-palladium complexes must be taken into consideration when analyzing the extraction rates of palladium.

Considering that the extractant, DDTPA, exists as

the monomer in toluene and has interfacial activity as mentioned above, the following interfacial reaction model for the extraction of palladium with DDTA is proposed.



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. (7) to (10), respectively. Assuming that Eqs. (7) to (10) are the rate-determining steps, the reaction rate can be expressed as Eq. (11).

$$r = (k_1[\text{PdCl}_4^{2-}] + k_2[\text{PdCl}_3(\text{H}_2\text{O})^-] + k_3[\text{PdCl}_2(\text{H}_2\text{O})_2] + k_4[\text{PdCl}(\text{H}_2\text{O})_3^+])C_{HRad} \quad (11)$$

Using the stability constants, β_i , of the chloro-palladium complexes, Eq. (11) is rewritten as follows.

$$r = \frac{k_1\beta_4[\text{Cl}^-]^4 + k_2\beta_3[\text{Cl}^-]^3 + k_3\beta_2[\text{Cl}^-]^2 + k_4\beta_1[\text{Cl}^-]}{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i} \times C_{HRad}C_{Pd} \quad (12)$$

In the equation above, the concentrations of palladium, DDTA and chloro-palladium complexes close to the interface are assumed to be equal to those in the bulk phase because the reaction rate is considered to be much lower than the diffusion rates. Assuming that the adsorptions of chloro-palladium complexes are ignored at the early stage of extraction, Eq. (13) is derived from a Langmuir adsorption isotherm.

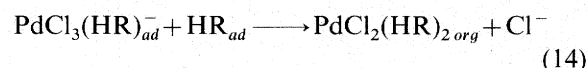
$$r = \frac{k_1\beta_4[\text{Cl}^-]^4 + k_2\beta_3[\text{Cl}^-]^3 + k_3\beta_2[\text{Cl}^-]^2 + k_4\beta_1[\text{Cl}^-]}{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i} \times \frac{K_{HR}}{S_{HR}} \frac{C_{HR}C_{Pd}}{1 + K_{HR}C_{HR}} \quad (13)$$

By analyzing the results of extraction rate measurements using Eqs. (2) and (13), the values of the constants listed in Table 2 were obtained. The solid

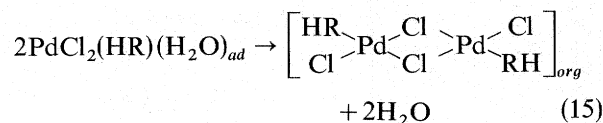
lines in Figs. 5, 6 and 7 are the calculated results by using the constants. The calculated results are found to agree approximately with the experimental ones. In Fig. 6, the experimental results in the low hydrogen-ion concentration range deviate slightly from the calculated ones. This is not due to the increase in interfacial area accompanied by the decrease in interfacial tension caused by the lowering of the hydrogen-ion concentration, because $C_H \gg K_a$ under the experimental condition. Further study is necessary with respect to this point.

After the rate-determining steps, Eqs. (7) to (10), the following reactions are thought to take place considering the experimental results of the palladium-loading capacity of DDTA.

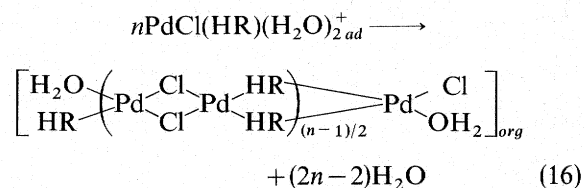
In the range of high concentration of chloride ion, the reaction shown by Eq. (14) is considered to take place following Eq. (7) or (8).



In the range of low concentration of chloride ion,⁵⁾ the reaction shown by Eq. (15) is considered to take place following Eq. (9).



In the range of extremely low concentration of chloride ion, the reaction shown by Eq. (16) is considered to take place following Eq. (10).



A polynuclear complex formed according to Eq. (16) is considered to be scarcely soluble in aqueous solution. Under the experimental condition of very low concentration range of chloride ion, a small amount of brown solid was precipitated at the interface. The precipitate may be considered to be, for example, such a polynuclear complex.

As is found from Table 2, the magnitude of the reaction rate constants is in the order $k_1 < k_2 < k_3 < k_4$. This is considered to be due to the trans-effect¹²⁾ of chloride ion substituted. That is, the bond between the central metal ion and the ligand at trans position against the ligand with the highest polarizability among the four ligands coordinated to the metal ion is weakened more than that between the ligand at cis position and the metal ion. So the ligand at trans position against the ligand with the highest polarizability can be most substituted. In addition,

the trans-effect becomes large as the polarizability and the softness of ligand increase.

In regard to the complex, $\text{PdCl}_2(\text{H}_2\text{O})_2$, the chloride ion tends to take cis conformation^{8,10)} because chloride ion is a softer ligand than oxygen in the water molecule, so the trans effect is also shown.

Conclusion

Using a highly stirred tank and a stirred transfer cell, the extraction rate of palladium with didodecylmonothiophosphoric acid was measured, along with measurements of the interfacial tension and the palladium-loading capacity of the extractant. An interfacial reaction model in which four chloropalladium complexes take part was proposed. The experimental results were analyzed by the interfacial reaction model to obtain the reaction rate constants of the four chloro-palladium complexes with the extractant. The order of magnitude of the reaction rate constants was explained qualitatively by the trans-effect.

Nomenclature

A	= specific interfacial area	$[\text{m}^{-1}]$
A_0	= specific interfacial area using no extractant	$[\text{m}^{-1}]$
C	= concentration	$[\text{mol}/\text{m}^3]$
f	= fraction of chloro-palladium complex in aqueous solution	$[-]$
K_a	= dissociation constant of extractant at interface	$[\text{mol}/\text{m}^3]$
K_{HR}	= adsorption equilibrium constant of extractant	$[\text{m}^3/\text{mol}]$
k_f	= extraction rate constant	$[\text{m}/\text{s}]$
k_f'	= apparent extraction rate constant	$[\text{s}^{-1}]$
k_i	= reaction rate constant ($i=1-4$)	$[\text{m}^3/(\text{mol}\cdot\text{s})]$
R	= gas constant	$[\text{N}\cdot\text{m}/(\text{mol}\cdot\text{K})]$
r	= reaction rate	$[\text{mol}/(\text{m}^2\cdot\text{s})]$
S_{HR}	= interfacial area occupied by unit mole of extractant	$[\text{m}^2/\text{mol}]$
T	= absolute temperature	$[\text{K}]$
t	= extraction time	$[\text{s}]$
β_i	= stability constant of chloro-palladium complex ($i=1-4$)	$[(\text{m}^3/\text{mol})^i]$

γ	= interfacial tension	$[\text{N}/\text{m}]$
γ_0	= interfacial tension between toluene and water	$[\text{N}/\text{m}]$
θ_r	= fraction of active vacant site at interface	$[-]$
$[]$	= concentration	$[\text{mol}/\text{m}^3]$

<Subscripts>

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

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