

Articles

Synergistic Extraction of Palladium(II) with Thenoyltrifluoroacetone and Tri-n-octylphosphine Oxide

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The synergistic extraction of palladium (II) was studied with 1,2-dichloroethane containing thenoyltrifluoroacetone (TTA; HA) and tri-n-octylphosphine oxide (TOPO; S). The main composition of synergistic adduct extracted into 1,2-dichloroethane phase was found to be PdA₂S₂. The equilibrium constants of the synergistic reaction were calculated. The application of this method to synthetic mixture for the separation of Pd from Pt was developed.

Introduction

The analytical application of synergism in solvent extraction system has intensively been investigated by many authors.¹⁻³ However, there are comparatively few reports on the application of synergistic extraction to platinum group metals (PGMs). The difficulties in developing this type of extraction may be due to the complex nature of the solution chemistry of the PGMs.⁴⁻⁶

During the last several years, our laboratory has been working on the synergistic extraction of PGMs with a view toward developing methods for their separation. Various mixed extractants (e.g., chloroform containing 8-hydroxyquinoline plus tri-n-octylamine) were found to extract Pd,⁷⁻⁹ Rh¹⁰ and Ir¹¹ synergistically. It is generally known that synergistic extraction lacks the selectivity for the separation of metals. However, we have found from our previous studies⁷⁻¹¹ that synergistic extraction gave not only better recovery but also selective separation of PGMs.

The synergistic effect is in general enhanced by the basicity of phosphorus containing neutral monodentate ligand. Such reagents studied included triphenyl phosphate, tributyl phosphate, triphenylphosphine oxide and trioctylphosphine oxide. For each additive the formation constants increase with increasing basicity. Tri-n-octylphosphine oxide (TOPO) and tributylphosphate (TBP) produce a marked improvement in the extraction of certain β -diketonate complexes. This was shown by Irving,^{12,13} Healy^{14,15} and other research workers.^{16,17} The effect of additives of the type of TOPO on the extraction of thenoyl-trifluoroacetones has been studied over the past few years.¹⁸⁻²⁰ However, the synergistic extraction of palladium(II) with TTA and TOPO has not been reported so far.

The present work deals with the synergistic effects that were observed in the extraction of palladium(II). The application of this method to synthetic mixture was studied for the separation of palladium(II) from platinum(IV).

Experimental

Reagents and Apparatus. The stock solutions of Pd (II) and Pt(IV) were prepared using palladium(II) chloride (Inuicho Precious Metals; Japan) and platinum(IV) chloride (Fluka; Switzerland). Thenoyltrifluoroacetone (Tokyo Kasei Kogyo; Japan) and tri-n-octylphosphine oxide (Fluka; Switzerland) were used without further purification. Thiourea (Baker; USA) was purified by recrystallization in distilled water. 1,2-Dichloroethane was purified by concentrated sulfuric acid and water. Distilled deionized water was used throughout the present work.

A flame atomic absorption spectrophotometer (Varian Techtron Model 1200) and a diode array UV-Visible spectrophotometer (HP 8452A) were used. A pH meter (Orion Research Model 605) and a reciprocal shaker (Taiyo SR-1) were also used.

Distribution of Extractant. An aliquot of an aqueous phase containing 0.1 M sodium chloride was adjusted to the desired pH with sulfuric acid or sodium hydroxide solution. An appropriate volume of 2, 4, 6, 8 mL of the aqueous phase was diluted to 10 mL with water and shaken for 2 hours with an equal volume of the organic phase containing the extractant in a 30 mL vial. After the phases were allowed to separate, the pH of the aqueous phase was measured and taken as the equilibrium value. The extractant concentration in the organic phase was determined spectrophotometrically at $\lambda = 330$ nm.

Extraction Procedure. Ten milliliters of an aqueous solution containing 2.5×10^{-4} M metal ion and 0.1 M sodium chloride, whose pH was preliminarily adjusted, was placed in a 30 mL vial. An equal volume of 1,2-dichloroethane solution containing TTA and TOPO was added. The mixture was then shaken mechanically at 150 r.p.m. for 10 hours; this was found to be sufficient to attain equilibrium. After the phases were allowed to separate, palladium remaining in the aqueous phase was determined with the atomic absorption spectrophotometer, and the pH was also measured. The metal concentration in the organic phase was calculated from the difference between the metal content in the aqueous phase before and after the extraction.

Back extraction of palladium(II) was studied as follows. Ten milliliters of Pd solution that was transferred into the

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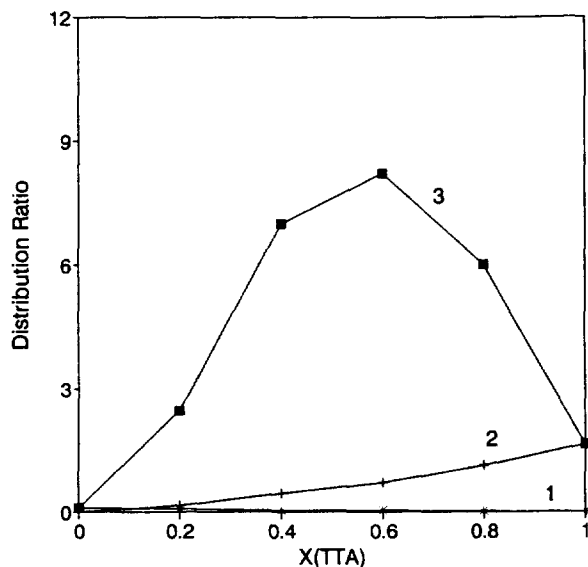


Figure 1. Synergistic diagram for the Pd(II) extraction with TTA plus TOPO mixed ligand system. Total ligand concentration ($[TTA]_{org} + [TOPO]_{org}$) = 0.01 M, pH 3, organic phase: 1,2-dichloroethane, 1. TOPO alone, 2. TTA alone, 3. TTA+TOPO mixed ligand system.

1,2-dichloroethane phase and equal volume of aqueous hydrochloric acid solution containing thiourea were shaken mechanically for 30 min. After the phase separation, the concentration of back extracted Pd was determined by the atomic absorption spectrophotometer.

Results and Discussion

Synergistic Effect. In order to confirm the synergistic effect of the TTA plus TOPO system, the synergistic diagram of Pd(II) was prepared as follows; While the total concentration of extractant ($[TTA]_{org} + [TOPO]_{org}$) in 1,2-dichloroethane phase was maintained at 1.0×10^{-2} M, the ratio of TTA and TOPO concentration was varied, and the distribution ratio was plotted versus the mole fraction of TTA ($X(TTA)$) as shown in Figure 1. This figure indicates that the present system of the mixed extractant shows better efficiency in the extraction of Pd as compared to either of the extractants alone.

Distribution of Extractant. The acid dissociation constant (K_{HA}) and the partition coefficient (P_{HA}) of thenoyltrifluoroacetone were determined by a liquid-liquid distribution method as follows. The total concentration of TTA in aqueous phase can be written as ($[HA] + [A^-]$). The distribution ratio of TTA (HA) between the organic and aqueous phase, D_{HA} , can be written as

$$D_{HA} = \frac{[HA]_{org}}{([HA] + [A^-])} = \frac{P_{HA}}{1 + K_{HA}/[H^+]} \quad (1)$$

where P_{HA} and K_{HA} are defined as $[HA]_{org}/[HA]$ and $[H^+][A^-]/[HA]$, respectively.

When the pH is low enough, D_{HA} is equal to P_{HA} , while $\log D_{HA}$ corresponds to $\log P_{HA} + pK_{HA} - pH$ for high pH. In Figure 2, the relationship between $\log D_{HA}$ and pH for the

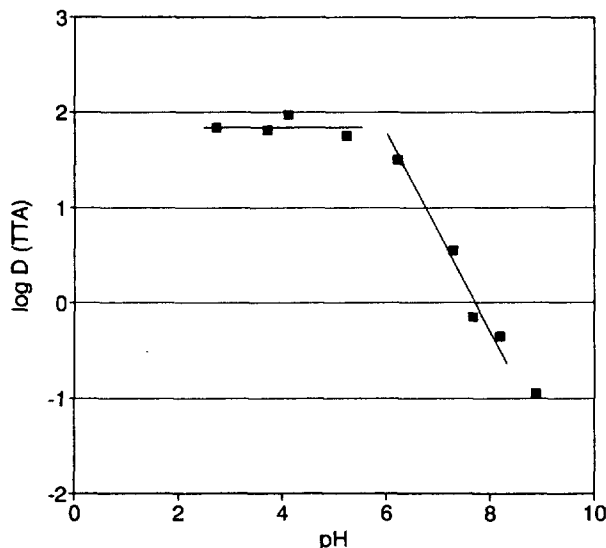


Figure 2. Distribution of thenoyltrifluoroacetone (TTA). $[NaCl] = 0.1$ M, $[HA]_{total} = 5 \times 10^{-2}$ M.

1,2-dichloroethane-water system is shown. Analysing the plots on the basis of Eq. (1) gives the values of $\log P_{HA}$ and pK_{HA} as 1.80 and 6.03, respectively. The pK_{HA} value is close to the reported value, 6.23²¹, within experimental error. If the amount of TTA chelated with a Pd(II) can be neglected compared with that of free TTA, the total concentration of TTA can be written as Eq. (2).

$$[HA]_{total} = [HA]_{org} + [HA] + [A^-] = [HA]_{org}(1 + 1/P_{HA} + K_{HA}/P_{HA}[H^+]) \quad (2)$$

Eq. (2) can be written as

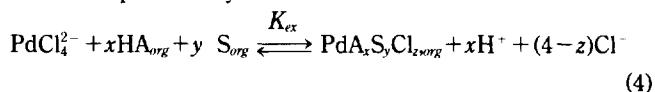
$$[HA]_{total} = [HA]_{org}(1 + 0.016 + 1.48 \times 10^{-8} [H^+]) \quad (3)$$

Eq. (3) enables us to calculate $[TTA]_{org}$ in 0.1 M NaCl solution.

In the case of TOPO, however, the P_S and K_{SH} of TOPO could not be determined because of its extremely low solubility in the aqueous solution.

Composition of the Extracted Species. The method of slope analysis was used in this work to determine the composition of ternary complexes, Pd(II)-TTA-TOPO, as well as the equilibrium constants of the synergistic extraction.

By assuming that the main species extracted with TTA (HA) plus TOPO (S) is $PdA_xS_yCl_z$, the extraction reaction can be expressed by



where the subscript "org" denotes the organic phase. The extraction constant of the above synergistic system is defined by Eq. (5).

$$K_{ex} = \frac{[PdA_xS_yCl_z]_{org} [H^+]^x [Cl^-]^{4-z}}{[PdCl_4^{2-}] [HA]_{org}^x [S]_{org}^y} \quad (5)$$

If the main species remaining in the aqueous phase is $PdCl_4^{2-}$, the distribution ratio can be written as,

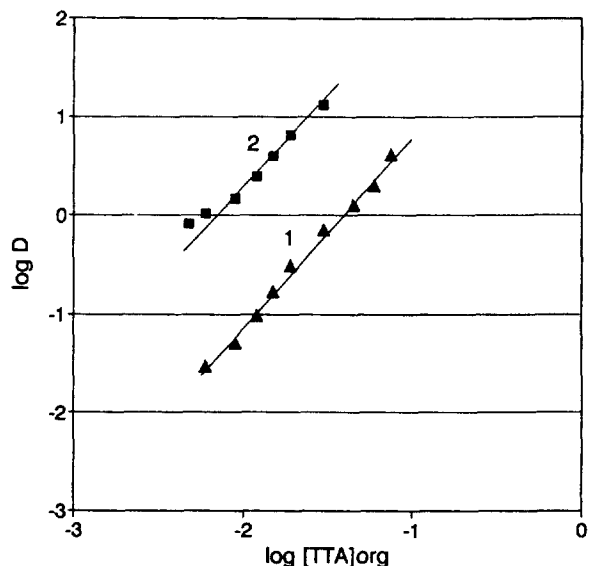


Figure 3. Plots of $\log D$ against TTA (HA) concentration. pH 2.9, $[\text{NaCl}] = 0.1 \text{ M}$, 1. $[\text{TOPO}]_{\text{org}} = 0.00 \text{ M}$, 2. $[\text{TOPO}]_{\text{org}} = 0.02 \text{ M}$.

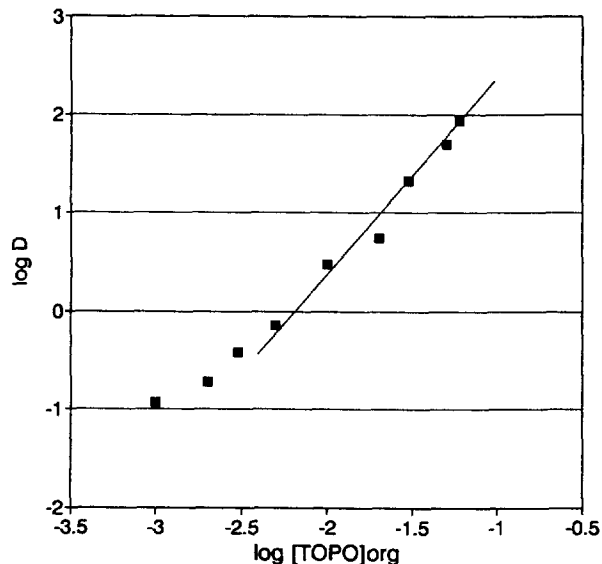


Figure 5. Plots of $\log D$ against TOPO (S) concentration. pH 2.9, $[\text{NaCl}] = 0.1 \text{ M}$, $[\text{TTA}]_{\text{org}} = 9.0 \times 10^{-3} \text{ M}$.

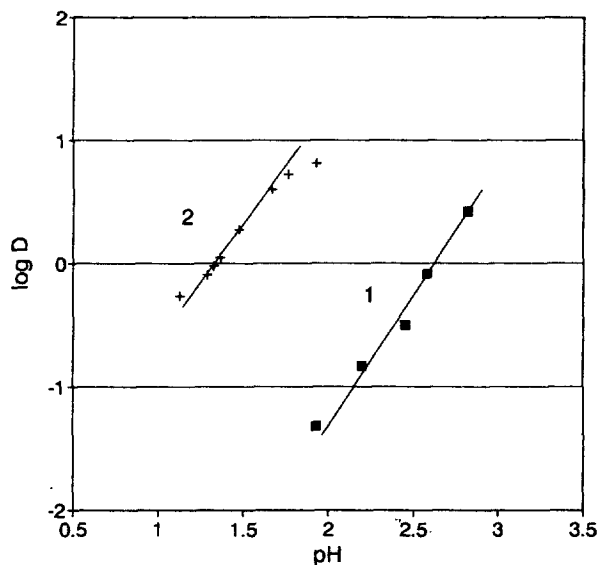


Figure 4. Plots of $\log D$ against pH. $[\text{NaCl}] = 0.1 \text{ M}$, 1. $[\text{TTA}]_{\text{org}} = 7.5 \times 10^{-2} \text{ M}$, 2. $[\text{TTA}]_{\text{org}} = 1.5 \times 10^{-2} \text{ M}$, $[\text{TOPO}]_{\text{org}} = 3.0 \times 10^{-2} \text{ M}$.

$$D = \frac{[\text{PdA}_x\text{S}_y\text{Cl}_z]_{\text{org}}}{[\text{PdCl}_2^{2-}]} \quad (6)$$

From Eq. (5) and (6), we obtain Eq. (7) and (8).

$$D = \frac{K_{ex} [\text{HA}]^x_{\text{org}} [\text{S}]^y_{\text{org}}}{[\text{H}^+]^x [\text{Cl}^-]^{4-z}} \quad (7)$$

$$\log D = \log K_{ex} + x \log [\text{HA}]_{\text{org}} + y \log [\text{S}]_{\text{org}} + x\text{pH} - (4-z) \log [\text{Cl}^-] \quad (8)$$

Figure 3 and Figure 4 show that the logarithm of the distribution ratio of Pd(II) plotted against the logarithm of TTA concentration and pH, respectively. The slope of the straight

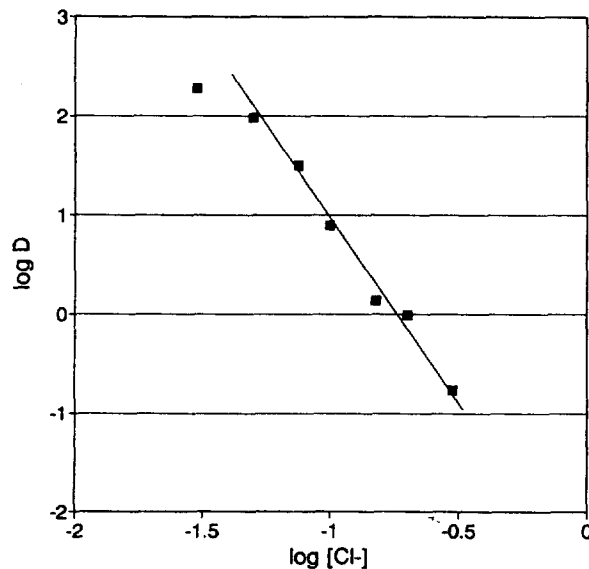


Figure 6. Plots of $\log D$ against chloride ion concentration. total ionic strength 0.2 with $[\text{NaCl}, \text{Na}_2\text{SO}_4]$, pH 2.9, $[\text{TTA}]_{\text{org}} = 1.5 \times 10^{-2} \text{ M}$, $[\text{TOPO}]_{\text{org}} = 3.0 \times 10^{-2} \text{ M}$.

line obtained is about 2, which suggests that two TTA molecules are complexed to each Pd(II) ion in both of the systems using the mixed ligand and TTA alone.

Figure 5 is the plot of $\log D$ against the logarithm of TOPO concentration while TTA concentration was kept constant. The slope value of two suggests that two TOPO molecules are complexed to Pd(II)-thenoyltrifluoroacetate. At TOPO concentration below $ca. 5 \times 10^{-3} \text{ M}$, deviation from a straight line was observed. The deviation in this region may be ascribable to the existence of other complexes, such as PdA_2 or PdA_2S .

The effect of chloride ion concentration was shown in Figure 6. The ionic strength was kept at 0.2 with NaCl and

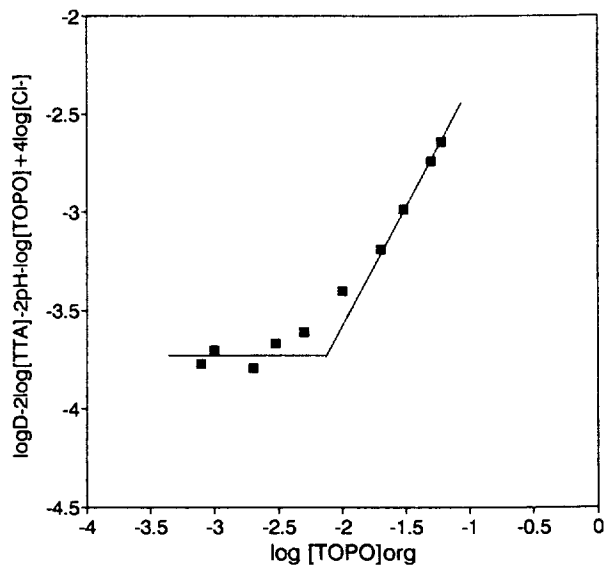
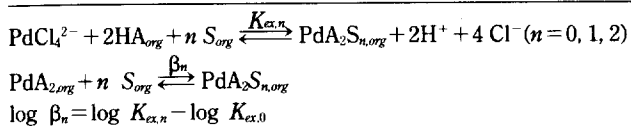


Figure 7. Effect of TOPO concentration on the extraction of Pd(II) pH 3.2, [NaCl]=0.1 M, [TTA]_{org}=9.0×10⁻³ M.

Table 1. Equilibrium constants of the extraction reaction

log $K_{ex,0}$	-7.22	(± 0.18)
log $K_{ex,1}$	-3.61	(± 0.16)
log $K_{ex,2}$	-1.22	(± 0.05)
log β_1	3.61	(± 0.24)
log β_2	6.01	(± 0.19)



Na₂SO₄. The ratio of chloride ion concentration was varied. The slope of about -4 suggests that this synergistic extraction reaction is adversely affected by increase in chloride ion concentration. The slope of -4 (*i.e.*, $z=0$) also indicates that all of the four chloride ions were replaced by the reaction with TTA and TOPO during the extraction. Consequently, the assumption in Eq. (4) that the initial form of palladium in the aqueous phase was PdCl₄²⁻, is justified. The results obtained above show that the coefficient of the logarithm of concentration x , y and $-(4-z)$ in Eq. (8) are 2, 2 and -4, respectively. From these slope analyses, the extracted species into the 1,2-dichloroethane phase appears to have the composition, Pd : TTA : TOPO = 1 : 2 : 2.

Determination of the Equilibrium Constants. The metal complexes that are extracted into the organic phase can be either PdA₂S or PdA₂S₂ in accordance with the magnitude of the TOPO (S) concentration.

If the main species extracted into the organic phase are PdA₂S and PdA₂S₂, the distribution ratio is expressed as,

$$D = \frac{[\text{HA}]_{org}^2 \sum_n K_{ex,n} [\text{S}]_{org}^n}{[\text{H}^+]^2 [\text{Cl}^-]^4} \quad (n=1, 2) \quad (9)$$

$$\log D = 2 \log [\text{HA}]_{org} + \log (K_{ex,1} + K_{ex,2} [\text{S}]_{org}) + \log [\text{S}]_{org} + 2\text{pH} - 4 \log [\text{Cl}^-] \quad (10)$$

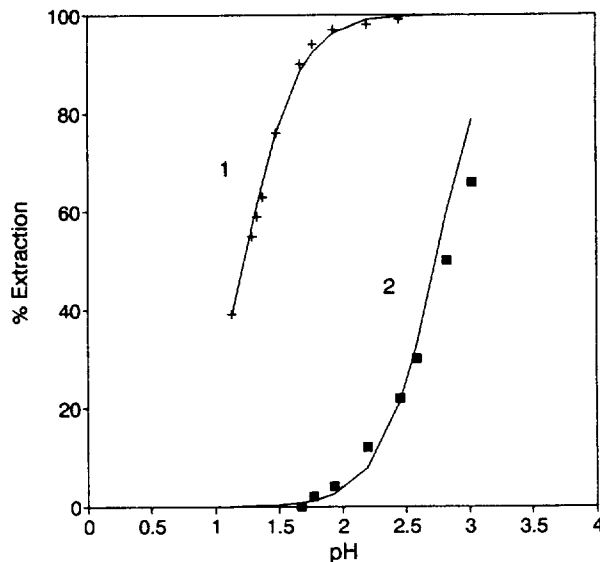


Figure 8. Shifting the optimum pH range. [NaCl]=0.1 M, 1. [TTA]_{org}=7.5×10⁻² M, [TOPO]_{org}=3.0×10⁻² M, 2. [TTA]_{org}=7.5×10⁻² M.

Eq. (10) can be rewritten as

$$\log D - 2 \log [\text{HA}]_{org} - 2\text{pH} - \log [\text{S}]_{org} + 4 \log [\text{Cl}^-] = \log K_{ex,1} + \log (1 + K_{ex,2} [\text{S}]_{org}/K_{ex,1}) \quad (11)$$

Plotting the left side of Eq. (11) against the logarithm of TOPO concentration, two regions of straight line are shown in Figure 7. In the case of low concentration of TOPO ($K_{ex,2} [\text{S}]_{org}/K_{ex,1} \ll 1$), a horizontal line is obtained and the intercept on the y-axis of this line is $\log K_{ex,1}$. In the case of high concentration of TOPO ($1 \ll K_{ex,2} [\text{S}]_{org}/K_{ex,1}$), a straight line with a slope of 1 is obtained and the y intercept of this line at $\log [\text{S}]_{org}=0$ is $\log K_{ex,2}$.

The results of the extraction constants obtained are listed in Table 1, where β_n shows the adduct formation constant for PdA₂S_n. $K_{ex,0}$ was calculated from Eq. (8) in the absence of TOPO (S).

Shifting the Optimum Extraction pH Range. It has been reported that by adding a neutral base to a chelate extraction system, the extraction curve can be shifted to the acidic region.²² This phenomenon is also observed in the present system. In Figure 8, pH_{1/2}, the value of the pH corresponding to the extraction of 50% extraction, was shifted to a lower pH region of about 1.5 pH unit. It will be very useful for practical analysis (for example, separation of Pd from other elements by adding a neutral base to the extraction system, Pd can be extracted in the acidic region). An alkaline medium is generally favorable for the formation of the metal chelate. However, metal ions tend to form stable hydroxo complexes in an alkaline medium and thus interfere with chelate formation. Accordingly, an acidic medium is preferable to avoid such interference.

The solid curves given in Figure 8 were obtained by calculations using Eq. (8), which agree well with the experimental results. However, the extraction curves for the simple chelate extraction system (line 2) estimated from Eq. (8) deviate

Table 2. Distribution coefficients of Pd and Pt

Extractant	distribution coefficient (D)	
	Pd	Pt
TTA alone	0.72	0.14
TOPO alone	0.56	0.21
TTA+TOPO	210	0.24

[TTA] = 6×10^{-3} M. [TOPO] = 6×10^{-2} M.

from those obtained by experiments, especially at higher pH region, probably because of hydrolysis of palladium(II).

Separation of Pd(II) from Pt(IV). It was thought desirable to evaluate the applicability of the present system of extraction for the separation of Pd from Pt.

The hydrochloric acid solution containing the synthetic mixture of Pd(II) and Pt(IV) was extracted with 1,2-dichloroethane containing TTA plus TOPO. The distribution coefficients of two elements were obtained as shown in Table 2. The results indicate that the present synergistic system can provide an extraction method that enables the separation of Pd from Pt. As explained below, by applying the present method, one can separate Pd from Pt with much better efficiency, almost more than 100-fold, than is possible with a TTA alone.

The separation ratio (SR) is defined as $D(\text{Pd})/D(\text{Pt})$, where $D(\text{Pd})$ and $D(\text{Pt})$ are the distribution coefficients of each metal between the two phases. SR(TTA+TOPO) is 900, whereas SR(TTA) is about 5. and SR(TOPO) is about 3.

Thiourea has been used effectively for the back extraction of PGMs.²³ In the present system, trace amounts of Pd (ca. 2.5×10^{-4} M) in 1,2-dichloroethane phase could be quantitatively back-extracted into the aqueous phase by shaking with 0.5 M HCl containing 0.5 M thiourea within 30 min. After back extraction with 0.5 M hydrochloric acid solution containing 0.5 M thiourea, the separation ratio becomes much larger, e.g., $D(\text{Pd})_{\text{back}}$ and $D(\text{Pt})_{\text{back}}$ is 100 and ca. 0.1, respectively. The separation ratio of back extraction is ca. 1000. Therefore, the total separation procedure (synergistic extraction followed by back extraction) has the separation ratio of ca. 9×10^5 .

Conclusion

An extraction method was developed for the Pd(II) with 1,2-dichloroethane containing thenoyltrifluoroacetone and trin-octylphosphine oxide. In this system of mixed ligand, synergistic enhancement was observed.

The composition of extracted species was determined by slope analysis, which shows that the extracted species has the composition Pd : TTA : TOPO = 1 : 2 : 2.

The equilibrium constants found for the present system are comparatively smaller than those of other extraction sys-

tems. This may be attributable to difficulty in the replacement of chloride ion with TTA or TOPO.

The proposed method followed by back extraction using thiourea can be applicable to real sample as a method of preconcentration of palladium(II).

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