Comparison of the Extractabilities of Tetrachloro- and Tetrabromopalladate(II) Ions with a Thiodiglycolamide Compound

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Using *N,N,N',N'*-tetra-2-ethylhexyl-thiodiglycolamide (TEHTDGA) in *n*-dodecane as the extractant, we compared the percentages of Pd(II) extracted from HCl and HBr solutions, and analyzed the structures of the Pd(II)-extractant complexes. For comparison, similar experiments were performed with di-*n*-hexyl sulfide (DHS), a well-known sulfide-type extractant. TEHTDGA extracted Pd(II) from both HCl and HBr solutions much faster than DHS. The Pd(II)/(TEHTDGA or DHS) stoichiometry in the organic phase was 1:2. For TEHTDGA, the extractability of Pd(II) from HBr solution was inferior to that from HCl solution, whereas the opposite was true for DHS. However, FT-IR spectroscopy and EXAFS measurements indicated that the inner-sphere structure of Pd(II) in the TEHTDGA complex was almost the same as that in the DHS system: in both cases, two of the halide ions in the tetrachloro- or tetrabromopalladate(II) ion were replaced by the sulfur atoms of two extractant molecules.

Keywords Palladium, HCl, HBr, liquid-liquid extraction, thiodiglycolamide

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Introduction

The need to separate and purify platinum group metals (PGMs) from acidic chloride media often arises during mining and recycling processes because of the common use of HCl solutions with the addition of Cl₂ gas during PGM leaching.¹ Therefore, the liquid-liquid extraction of PGMs from HCl solutions has been extensively studied. In addition, PGM extraction from HNO₃ solutions has also been studied for the removal of PGMs from high-level liquid wastes generated by nuclear fuel reprocessing.² In contrast, there have been few studies of PGM extraction from acidic bromide media.³⁻⁹ The replacement of chloride ions by bromide ions in PGM complexes frequently enhances the extractability, and this phenomenon has been explained by the fact that bromo-PGM complexes are more hydrophobic than the corresponding chloro-PGM complexes.^{5,6}

Because tetrachloropalladate(II), [PdCl₄]²⁻, is substantially more extractable than other PGM ions,¹ Pd(II) can be extracted in two different modes: *via* the formation of a coordination complex or *via* the formation of an ion-pair complex. The former generally occurs in sulfide-type extractant systems, and the latter often occurs when N-donor extractants are used. Both extraction modes have also been observed for tetrabromopalladate(II), [PdBr₄]²⁻; di-*n*-octyl sulfide (DOS)

extracts Pd(II) from HBr solution *via* a coordinative complex,⁷ whereas extraction by tri-*i*-octylamine⁸ and quaternary ammonium compounds⁹ involves the formation of an ion-pair complex (anion-exchange extraction). In these systems, [PdBr₄]²⁻ ions are extracted much more readily than [PdCl₄]²⁻ ions.

We have already found that thiodiglycolamide (TDGA) compounds are promising, practical alternatives to dialkyl sulfide compounds, such as DOS, di-*n*-hexyl sulfide (DHS), which are among the most commonly used Pd(II) extractants.^{10,11} TDGA compounds show good Pd(II) extraction ability and high oxidation resistance, but the mechanisms by which they extract [PdCl₄]²⁻ and [PdBr₄]²⁻ have not yet been clarified. In this study,

Fig. 1 Structure of *N,N,N',N'*-tetra-2-ethylhexyl-thiodiglycolamide.

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we investigated the use of *N,N,N',N'*-tetra-2-ethylhexylthiodiglycolamide (TEHTDGA) in *n*-dodecane to extract Pd(II) from HCl and HBr solutions (Fig. 1), and determined the structural properties of the Pd(II) complexes extracted with TEHTDGA. For comparison, we also carried out similar analyses using DHS, a well-known sulfide-type extractant.

Experimental

Reagents

TEHTDGA (>99% purity) and DHS (>99% purity) were purchased from Chemicrea (Tokyo, Japan) and Wako Pure Chemical Industries (Osaka, Japan), respectively, and were used as supplied. Aqueous solutions of Pd(II) were prepared by dissolving PdCl₂ (Wako Pure Chemical Industries) and PdBr₂ (Tokyo Chemical Industry Co., Tokyo, Japan) in HCl and HBr solutions, respectively. All other chemicals were of reagent grade.

Extraction procedure

A solution of TEHTDGA or DHS at various concentrations in *n*-dodecane was pre-equilibrated with a solution of HCl or HBr at various concentrations containing no Pd(II); specifically, the mixture of organic and aqueous solutions was vertically shaken at an amplitude of 100 mm and a frequency of 200 strokes/min in a 10 mL glass tube for 30 min, and then centrifuged. A 1-mL aliquot of the pre-equilibrated organic phase and the same volume of an HCl solution containing $\sim 5 \times 10^{-4}$ M Pd(II) (10^{-3} to 10^{-2} M for the loading capacity test) were similarly shaken for various durations, and then centrifuged. All of the operations were carried out at room temperature ($23 \pm 2^\circ\text{C}$). Extraction of the acids was evaluated on the basis of the difference between the H⁺ concentrations in the initial aqueous phase and the equilibrated aqueous phases, as measured by titration with NaOH. The concentrations of metal ions in the aqueous phase were measured by means of ICP-AES (Horiba ULTIMA2). The extraction percentages (*E*%) were determined by means of the following equation: $E\% = \{([\text{Pd(II)}] \text{ in the initial aqueous phase}) - ([\text{Pd(II)}] \text{ in the equilibrated aqueous phase})\} / ([\text{Pd(II)}] \text{ in the initial aqueous phase})$. The *E*% values for Pd(II) were measured in triplicate. The error in the *E*% values was estimated to be <5%.

FT-IR spectroscopy

Five types of organic samples were prepared for FT-IR spectroscopy: (i) 0.50 M TEHTDGA in *n*-dodecane, (ii) 0.50 M TEHTDGA in *n*-dodecane pre-equilibrated with 1.0 M HCl, (iii) 0.50 M TEHTDGA in *n*-dodecane pre-equilibrated with 1.0 M HBr, (iv) a Pd(II) complex sample obtained by using solution (ii) to extract a solution of 0.30 M PdCl₂ in 1.0 M HCl, and (v) a Pd(II) complex sample obtained by using solution (iii) to extract a solution of 0.30 M PdBr₂ in 1.0 M HBr. Samples (ii) – (v) were prepared by means of the extraction procedure described above, with a shaking time of 120 min. The concentration of Pd(II) in samples (iv) and (v) was 0.25 M. Each of the five organic samples was placed in a diamond compression cell (Systems Engineering). FT-IR spectra were collected with a PerkinElmer Spectrum 100 instrument.

EXAFS measurements

The following four samples were prepared for EXAFS measurements: 0.10 M Pd(II) in 1.0 M HCl (designated CL-Aq), 0.10 M Pd(II) in 1.0 M HBr (BR-Aq), a 0.10 M Pd(II) sample obtained by extraction of a solution of 0.10 M PdCl₂ in

Fig. 2 Relationship between the Pd(II) concentrations in equilibrated organic and aqueous phases. [TEHTDGA] = 0.010 M, [HCl, HBr] = 1.0 M, shaking time = 90 min.

1.0 M HCl with 0.50 M TEHTDGA in *n*-dodecane (CL-Ex), and a 0.10 M Pd(II) sample obtained by extraction of 0.10 M PdBr₂ in 1.0 M HBr with 0.50 M TEHTDGA in *n*-dodecane (BR-Ex). The CL-Ex and BR-Ex samples were prepared by means of the extraction procedure described above. Samples with DHS were prepared in a similar manner.

The EXAFS measurements were performed on BL11XU at SPring-8 by a method similar to that described previously.¹² As model compounds for the FEFF calculations, we used the reported crystal structures of [PdCl₄]²⁻,¹³ [PdBr₄]²⁻,¹⁴ and a dichloro-bis(*p*-*t*-butylphenylbutyl sulfide) Pd(II) complex.¹⁵ For the complex between the sulfide-containing ligand and palladium bromide, we used a hypothetical structure in which two Br⁻ ions in the [PdBr₄]²⁻ complex were replaced by two sulfur atoms. Multiple scattering paths were ignored because their contribution was not significant in the studied systems.

Results and Discussion

Effect of the shaking time on the extraction percentage

Analysis of the effect of the shaking time on the percentage of Pd(II) extracted from 1.0 M HCl or HBr with 0.010 M TEHTDGA revealed that approximately 100% of the Pd(II) was extracted from both HCl and HBr solutions in <5 min. In contrast, when 0.010 M DHS was used, ~20 and ~90 min were required to achieve nearly 100% Pd(II) extraction from HBr and HCl, respectively (Fig. S1, Supporting Information). It has already been reported that Pd(II) extraction in the TDGA-HCl system is faster than that in the DHS-HCl system.^{10,11} In this study, we found that Pd(II) in a HBr solution was also extracted rapidly with TDGA.

Estimated Pd(II)/TEHTDGA stoichiometry

We estimated the Pd(II)/TEHTDGA stoichiometry of the complex extracted into the organic phase by measuring the Pd(II) loading capacity. Figure 2 shows the relationship between the equilibrated Pd(II) concentrations in the organic and aqueous phases for extraction conditions of 0.010 M TEHTDGA and 1.0 M HCl or HBr. The profile for extraction from HCl was the same as that for extraction from HBr. The Pd(II) concentration at saturation was approximately 0.005 M, indicating that a 1:2 Pd(II)/TEHTDGA complex predominated in both systems. The same stoichiometry was observed in the DHS system (Fig. S2, Supporting Information).

Fig. 3 Relationship between the Pd(II) extraction percentage ($E\%$) and the HCl and HBr concentrations. [TEHTDGA] = 0.0010 M, shaking time = 90 min.

Effects of the HCl and HBr concentrations on the extraction percentage

We began by investigating the extraction of HCl and HBr with 0.50 M TEHTDGA or DHS at acid concentrations ranging from 0.50 to 6.0 M. We found that extraction of the acids into the organic phase was negligible under the condition of ≤ 0.50 M TEHTDGA or DHS.

When we plotted the $E\%$ values for the extraction of Pd(II) with 0.0010 M TEHTDGA or DHS as a function of the HCl and HBr concentrations (Fig. 3), we found that $E\%$ decreased with increasing the HCl and HBr concentrations in both extractant systems. In the case of Pd(II) extraction *via* the formation of an ion-pair complex (anion-exchange extraction), a competitive reaction of a metal anion and counter ions can decrease $E\%$. However, neither TEHTDGA nor DHS extracted HCl or HBr (that is, no protonation reaction occurred). Considering that the anionic complexes (*i.e.*, $[\text{PdCl}_4]^{2-}$ and $[\text{PdBr}_4]^{2-}$) predominated under our extraction conditions (as will be mentioned later), the decrease in $E\%$ with increasing acid concentration was probably caused by the replacement of two of the Cl^- or Br^- ions with two extractant molecules:

Interestingly, in the TEHTDGA system, the $E\%$ values for HCl were higher than those for HBr; this contrasts with the results in the DHS system and the previously reported DOS system.⁷ To explore the reason for the difference between these results, we analyzed the structures of the Pd(II) complexes in the organic phase.

Properties of the amide oxygen atom

To clarify the role of the amide oxygen atoms in the TEHTDGA molecule, we compared the frequencies of the carbonyl stretching vibration at around 1645 cm^{-1} in the FT-IR spectra of organic solutions of TEHTDGA before and after equilibration with 1.0 M HCl or HBr solution in the absence and presence of Pd(II) (Fig. 4). The spectra of the equilibrated solutions showed almost the same shape and position as the spectrum of the free TEHTDGA solution. This result is consistent with our observation that neither HCl nor HBr was extracted into the TEHTDGA solution. In contrast, the spectra of the solutions containing extracted Pd(II) complexes showed a small new peak at lower wavenumber (approx. 1570 cm^{-1}).

Fig. 4 Carbonyl stretching frequencies in the FT-IR spectra of TEHTDGA: (i) free, (ii) equilibrated with HCl, (iii) equilibrated with HBr, (iv) in complex with Pd(II) extracted from HCl, and (v) in complex with Pd(II) extracted from HBr. [TEHTDGA] = 0.50 M, [HCl, HBr] = 1.0 M, [Pd(II)] in organic phase (iv and v) = 0.25 M.

Such a difference in wavenumber (approx. 75 cm^{-1}) has been observed for an extractant molecule containing a free amide and the same molecule containing an amide bound to a lanthanide ion.¹⁶ However, the intensity of the new peak that we observed was too weak to be attributed to Pd(II) extraction; that is, the intensity of the 1645 cm^{-1} peak was approximately 80 times that of the 1570 cm^{-1} peak, whereas the Pd(II) concentration in the organic phase was half of the TEHTDGA concentration.

Inner-sphere structure of Pd(II)

To investigate the local structures of Pd(II) ions in the organic and aqueous phases, we obtained the Pd K-edge k^3 -weighted EXAFS spectra and their corresponding Fourier transforms for CL-Aq, CL-Ex, BR-Aq, and BR-Ex (Fig. 5). The curve fits results are tabulated in Table 1. Because the FT-IR results indicated that the amide oxygen atom hardly coordinated to the Pd(II), the Pd-O correlation was not included in the EXAFS analyses. Speciation studies of HCl solutions containing Pd(II)^{12,17} have shown that $[\text{PdCl}_4]^{2-}$ predominates at HCl concentrations of $\geq 1\text{ M}$; therefore, the number of Pd-Cl correlations (N) was held constant at 4, and the amplitude reduction factor (S_0^2) was refined for CL-Aq. The obtained Pd-Cl bond length (r) was similar to that in the crystal structure of $[\text{PdCl}_4]^{2-}$.¹³ The EXAFS oscillation of CL-Aq was mirrored by that of CL-Ex. First, we used the Pd-Cl and Pd-S correlations for CL-Ex to carry out curve fits: N , r , and the Debye-Waller factor squared (σ^2) of Pd-Cl were fixed at the same values as for CL-Aq. However, the difference between the obtained r values for the Pd-Cl ($2.31\text{ \AA}$) and Pd-S ($2.31\text{ \AA}$) bonds of CL-Ex was smaller than the EXAFS resolution,¹⁸ $\Delta r = \pi/2k_{\text{max}} = 0.12\text{ \AA}$. Therefore, we performed curve fits with one correlation, Pd-Cl/S, and obtained $2.32\text{ \AA}$ for its bond length. These results mean that the Pd-Cl bond length was similar to the Pd-S length.

Unlike in the HCl system, in the HBr system, the EXAFS oscillation for BR-Aq differed distinctly from that for BR-Ex. The structural parameter for BR-Aq was in good agreement with that for the square-planar single crystal complex, $[\text{PdBr}_4]^{2-}$.¹⁴ For BR-Ex, the curve fits were carried out with the parameters for the Pd-Br correlation obtained for BR-Aq. The N value for

Fig. 5 (A) Pd K-edge k^3 -weighted EXAFS spectra and (B) corresponding Fourier transforms. Dotted lines, theoretical fits; solid lines, experimental data. Sample designations: CL-Aq, Pd(II) in HCl; BR-Aq, Pd(II) in HBr; CL-Ex, Pd(II) extracted from HCl with TEHTDGA; and BR-Ex, Pd(II) extracted with from HBr with TEHTDGA. [TEHTDGA] = 0.50 M, [HCl, HBr] = 1.0 M, [Pd(II)] = 0.10 M for all samples.

Table 1 Structural information obtained from curve fits of EXAFS^a

		S_0^2	N	$r/\text{\AA}$	$\sigma^2/\text{\AA}^2$	$\Delta E/\text{eV}$	R-factor
CL-Aq	Pd-Cl	0.95 (6)	4 ^b	2.31 (1)	0.0032 (4)	5.3	5.9
CL-Ex	Pd-Cl/S	0.95 ^b	4.1 (3)	2.32 (1)	0.0031 (4)	5.6	5.0
BR-Aq	Pd-Br	0.95 ^b	4.3 (4)	2.45 (1)	0.0038 (5)	5.2	6.3
BR-Ex	Pd-S	0.95 ^b	2.3 (4)	2.33 (1)	0.0034 (8)	7.5	5.0
	Pd-Br		2 ^b	2.45 ^b	0.0038 ^b		
[PdCl ₄] ²⁻ c	Pd-Cl		4	2.295 ^d			
[PdCl ₂ (SR) ₂] ^e	Pd-Cl		2	2.295 ^d			
	Pd-S		2	2.325 ^d			
[PdBr ₄] ²⁻ f	Pd-Br		4	2.444 ^d			

a. The R-factor is given by $\{\sum[k^3\chi(k)_{\text{obs}} - k^3\chi(k)_{\text{calc}}]/\sum[k^3\chi(k)_{\text{obs}}]\} \times 100$, estimated errors are given in parentheses, the k -range for Fourier transformation was 3.1–16.1 $\text{\AA}^{-1}$, and the curve-fitting R -range was 1–3 $\text{\AA}$.

b. Fixed parameter.

c. Ref. 11.

d. Average bond distance.

e. Ref. 13 (R = *p*-*t*-butylphenylbutyl).

f. Ref. 12.

Pd-S was approximately 2, which was consistent with the above-mentioned stoichiometry, that is, 1:2 Pd(II)/TEHTDGA.

Similar EXAFS analyses were carried out for the Pd(II) complexes extracted with DHS (Fig. S3 and Table S1, Supporting Information). The obtained N and r values were as follows: (1) DHS-HCl system: $N = 4.1$, $r = 2.31 \text{ \AA}$ for Pd-Cl/S, and (2) DHS-HBr system: $N = 2.1$, $r = 2.33 \text{ \AA}$ for Pd-S, and $N = 2$ (fixed), $r = 2.45 \text{ \AA}$ (fixed) for Pd-Br. In comparison to the TEHTDGA complexes, the Pd-S bond length in the Pd(II) complexes extracted from HCl or those from HBr was nearly the same.

In all of the systems, the inner-sphere structure of Pd(II) was similar, comprising two sulfur atoms and two halogen atoms.

This similarity is consistent with the small difference in the $E\%$ with between TEHTDGA and DHS. In contrast, the extraction efficiency decreased in the order TEHTDGA-HCl $\geq$ DHS-HBr $>$ DHS-HCl $>$ TEHTDGA-HBr. Remarkably, the order of the extraction efficiencies from HCl and HBr in the TEHTDGA system was the opposite of the order in the DHS system. According to HSAB theory,¹⁹ disubstituted sulfides (R_2S) and Pd(II) ion are a soft base and a soft acid, respectively, whereas, Cl^- and Br^- are a hard base and a border base, respectively, suggesting that the affinity of the ligands for the Pd(II) decreases in the order $R_2S > \text{Br}^- > \text{Cl}^-$. This order means that the $[\text{PdBr}_4]^{2-}$ complex is more stable than the $[\text{PdCl}_4]^{2-}$ complex. In contrast, the $[\text{PdBr}_4]^{2-}$ complex is more hydrophobic than the $[\text{PdCl}_4]^{2-}$ complex. This can be beneficial for metal extraction, as mentioned in the introduction; hence, the extraction efficiency in the DHS system is probably related to the hydrophobicity of the Pd(II) complex, rather than to the substitution property of the sulfur donor atoms with the halogen atoms. The order of the extraction efficiency for the TEHTDGA system was opposite to that for the DHS system, despite the fact that the considerations discussed above for the DHS system are also applicable to the TEHTDGA system. Therefore, some other factors must be responsible for the order of the extraction efficiencies in the TEHTDGA system. Because the inner-sphere structures of Pd(II) in the two systems were nearly identical, the outer-sphere structures of Pd(II) must be considered. The amide groups of TEHTDGA were not involved in the inner-sphere coordination, suggesting that they can interact repulsively with the halogen atom in the outer-sphere of Pd(II). It can be assumed that this repulsive interaction is more significant for Br^- than for Cl^- (owing to the larger size of the former), and this difference could explain the lower extraction efficiency of Pd(II) from HBr. Elucidation of the outer-sphere interaction will require additional research, by methods such as single-crystal structural analyses.

Conclusions

TEHTDGA extracted approximately 100% of Pd(II) from HCl and HBr solutions, much faster than DHS. Measurements of the Pd(II) loading capacity indicated that the predominant complex in the organic phase was 1:2 Pd(II)/(TEHTDGA or DHS) in both the HCl system and the HBr system. In the TEHTDGA system, the percentage of Pd(II) extracted from HBr was lower than that extracted from HCl, whereas the opposite order was observed for the DHS system. A structural study indicated that two sulfur atoms directly coordinated to the Pd(II) atom in all of the complexes, $[\text{PdX}_2\text{E}_2]$ (where X = Cl or Br and E = TEHTDGA or DHS); that is, the inner-sphere structures of the DHS and TEHTDGA complexes extracted from HCl or HBr were nearly identical. These results suggest that the bulky substituents (including the amide groups) of TEHTDGA affect the extraction behavior of Pd(II).

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Supporting Information

The effects of the shaking time, Pd loading capacity in the DHS system, and Pd K-edge EXAFS spectra and corresponding FTs of the DHS-Pd complexes are shown in Figs. S1–S3, respectively. The EXAFS structural parameters are given in Table S1. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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