Effect of HNO₃ Concentration on the Pd(II) Extraction Properties using a Thiodiglycolamide Compound

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Dependence of the Pd(II) complexes extracted with N,N'-dimethyl-N,N'-ditolyl-thiodiglycolamide (MTTDGA) in chloroform on HNO₃ concentrations in the aqueous phase was investigated by liquid-liquid extraction experiments and Fourier-transform infrared spectroscopy (FT-IR) measurements. The extraction behavior of Pd(II) clearly differed between 0.5 M and 8 M HNO₃ concentrations. It took ~8 h and <5 min to attain the extraction equilibrium at 0.5 M and 8 M HNO₃, respectively. The apparent stoichiometry of MTTDGA:Pd(II) in the extracted complexes obtained from the loading test was 1:1 at 0.5 M HNO₃ and 2:1 at 8 M HNO₃. FT-IR spectroscopy results suggested that the amide oxygen atom(s) coordinated to Pd(II) in both the 1:1 and 2:1 MTTDGA:Pd(II) complexes, but the coordination mode of the MTTDGA molecule(s) differed.

1. Introduction

In recent years, extraction of platinum group metals (PGMs) from hydrochloric acid has been studied extensively, mainly for the purpose of recycling PGMs from industrial wastes [1]. Similarly, extraction of PGM from nitric acid solutions has been attracting attention in the field of nuclear waste management. High-level liquid waste (HLLW) from the Plutonium Uranium Redox Extraction (PUREX) process contains significant amounts of PGMs dissolved in high concentrations of nitric acid [2]. Removal of PGMs to some extent from HLLW prior to its vitrification can lead to more stable operation of the glass melter, higher quality of the final product (vitrificate), and eventually to safer final disposal of radioactive waste [3]. For this purpose, extractants that separate PGMs from concentrated nitric acid solutions with high efficiency are required. PGMs generated as byproducts of nuclear fission are potentially an alternative resource because of their extensive use by various industries [4, 5].

Because Pd(II) is a soft acid, extractants containing S-donor atoms tend to have high selectivity for palladium over other hard-acid ions [6]. To date, many studies of Pd(II) separation from highly acidic solutions have been conducted using quaternary amines [7], oximes [8], calixarenes [9], malonamides [10], and sulfur-containing extractants [11-14]. Among the sulfur-containing extractants, thiodiglycolamide (TDGA) extractants have exhibited both good selectivity and rapid extraction of Pd(II), and they are very durable in strongly acidic environments [15-19]. Some studies have used Fourier-transform infrared
spectroscopy (FT-IR), extended X-ray absorption fine structure, and computational methods to investigate the extraction properties of TDGA-HNO₃ systems and have shown that TDGA molecules probably act as multidentate ligands through both the thioetheric sulfur atom and the carbonyl oxygen atom [20, 21]. However, there have been no reports of the effects of acid concentrations on the coordination mode of TDGA.

In the present work, changes in the extraction properties of Pd(II) with a new TDGA extractant, N,N'-dimethyl-N,N'-ditolyl-thiodiglycolamide (MTTDGA), were investigated by means of batch extraction experiments and FT-IR spectroscopy.

2. Experimental

2.1 Reagents

All chemicals used in this work were purchased from Wako Pure Chemical Industries, Ltd. as analytical-grade reagents and used without further purification.

2.2 N,N'-dimethyl-N,N'-ditolyl-thiodiglycolamide (MTTDGA)

Thiodiglycolic acid (5.00 g, 31.64 mmol) was dissolved in a solution of thionyl chloride (7.66 mL, 101.23 mmol) and stirred for 30 min. After the thiodiglycolic acid was completely dissolved, N,N-dimethylformamide (0.30 mL, 3.16 mmol) was added dropwise to the mixture, and hydrochloric acid gas was emitted. The reaction mixture was stirred for 3 h at 50°C. After 3 h, the color of the solution changed from yellow-green to red, an indication that thiodiglycol chloride had condensed. Triethylamine (11.28 mL, 79.00 mmol) and N-methyl-p-toluidine (8.23 mL, 63.27 mmol) were added successively to a solution of chloroform. The reaction mixture was stirred for 30 min at room temperature. The thiodiglycolyl chloride was added dropwise to the mixture of triethylamine and N-methyl-p-toluidine at 10°C. The resulting solution was then refluxed with stirring for 4 h at 60°C followed by washing with water, 1 M HCl, and a 5% aq. sodium carbonate solution. After drying and evaporation of the solvent, the crude product was purified by column chromatography on silica gel and eluted with chloroform/ethyl acetate (v/v, 2:1) to give orange crystals, which were further purified by recrystallization from methanol. The recrystallization yielded 3.92 g of white crystals, a yield of 35%. The purity of the obtained extractant exceeded 99% on the basis of ¹H NMR and elemental analysis: ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, J=8 Hz, 1H), 7.13 (d, J=8 Hz, 1H), 3.24 (s, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 140.96, 137.86, 130.35, 127.08, 37.55, 33.83, 21.03; elemental analysis found for C₂₀H₂₄N₂O₂S (in wt. %): C, 67.47%; H, 6.93%; N, 7.82%; O, 9.02%; S, 9.09%. Calculated: C, 67.39%; H, 6.79%; N, 7.86%; O, 8.98%; S, 8.99%.

![Figure 1. Synthesis scheme of N,N'-dimethyl-N,N'-ditolyl-thiodiglycolamide (MTTDGA).](image)

2.3 Solvent extraction

A stock solution of Pd(II) was prepared by dissolving Pd(NO₃)₂ salt in 13.2 M HNO₃. The mixture was stirred for 4 h before filtering any undissolved Pd(NO₃)₂. The resulting solution was kept at room
temperature for at least 3 days before the extraction experiments. The concentration of Pd(II) in the resulting solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Shimadzu, ICPE 9800). Chloroform was used as the diluent for the organic phase. The extractant dissolved in chloroform was pre-equilibrated with an equal volume of an aqueous HNO₃ solution of a concentration equivalent to the studied case in the absence of the metal ions. Five milliliters of the pre-equilibrated organic phase containing MTTDGA and the same volume of the aqueous solution containing Pd(II) ions were horizontally shaken in a 13-mL glass vial at a frequency of 180 rpm and then centrifuged. All extraction experiments were carried out at room temperature. The concentrations of the metal ions in the aqueous phase were measured by ICP-AES (Shimadzu, ICPE 9800) and inductively coupled plasma mass spectrometry (Shimadzu, ICPMS-2030). The concentrations of metal ions in the organic phase were calculated on the basis of the mass balance of metal ions before and after extraction. The distribution ratio, \( D_{Pd} \), was determined as the ratio of metal concentration in the organic phase to that in the aqueous phase. All of the experiments were duplicated, and the values were averaged.

2.4 FT-IR measurements

Five samples for FT-IR measurements were prepared by dissolving MTTDGA in CHCl₃, pre-equilibrating 10 mM MTTDGA with 0.5 M and 8 M HNO₃ solutions, and then contacting 10 mM MTTDGA dissolved in CHCl₃ with 20 mM Pd(II) in 0.5 M HNO₃ and with 10 mM Pd(II) in 8 M HNO₃. After the extraction, centrifugation, and phase separation, the aqueous phase was subjected to ICP-AES analysis (Shimadzu, ICPE 9800) to determine the amount of Pd(II) loaded in the organic phase based on mass balance equations. The organic phase was analyzed by FT-IR (PerkinElmer Spectrum 100) in transmission mode using a diamond cell for liquid samples. The data for each sample were collected 16 times.

3. Results and Discussion

3.1 Effect of HNO₃ concentration on extraction of Pd(II)

Figure 2 shows the effect of HNO₃ concentration on \( D_{Pd} \), which increased with increasing HNO₃ concentration to a maximum at around 6 M HNO₃.

The effect of contact time on the extraction percentage of Pd(II) was evaluated using two aqueous solutions: 0.5 M and 8 M HNO₃. The percent extraction of Pd(II) was very different in the 0.5 M and 8 M HNO₃ systems (Figure 3). In the 0.5 M HNO₃ system, about 8 h were required to attain extraction equilibrium. In contrast, the percent extraction reached equilibrium within 5 min in the 8 M HNO₃ system. This difference in the extraction rate between the two different HNO₃ concentrations is noteworthy. In general, a change in the mechanism of PGM extraction
affects the extraction rate. For example, the extraction occurs more rapidly via anion exchange compared to the coordination mechanism. In the case of the TDGA–Pd(II)–HCl system, the Pd(II) extraction is fast, although the coordination reaction is dominant; this behavior seems to be due to the involvement of the amide groups [22]. Hence, our results indicated that the coordination of the amide oxygen atoms would depend on the HNO₃ concentration in the aqueous phase.

3.2 Loading experiments

Loading tests were performed to evaluate metal-ligand ratios in the organic phase. The ratio of the concentration of MTTDGA, [MTTDGA], to that of the Pd(II) extracted in the organic phase, [Pd]_{org}, was plotted against the initial concentration of Pd(II) in the aqueous phase, [Pd]_{aq,ini} (Figure 4). For the 0.5 M HNO₃ system, the fact that the maximum loaded concentration of Pd(II) in the organic phase was nearly equal to [MTTDGA] suggested that a 1:1 MTTDGA:Pd(II) complex was predominantly formed. In contrast, the minimum value of [MTTDGA]/[Pd] at 8 M HNO₃ was about 2. This result indicated that two MTTDGA molecules were involved in the Pd(II) complex. The extraction reaction can be expressed as follows:

\[ \text{Pd}^{2+} + x \text{H}^{+} + (x + 2)\text{NO}_3^- + n\text{MTTDGA} \Rightarrow \text{Pd(NO}_3)_2x\text{H}_x(\text{MTTDGA})_{n(o)} \] (1)

where \( n = 1 \) or 2, \( x \geq 0 \), (o) refers to the organic phase, and (aq) refers to the aqueous phase.

Taking into account the difference in extraction rates noted in section 3.1 (0.5 M << 8 M), it seems likely that the coordination modes of the MTTDGA molecule differed significantly between the 1:1 and 1:2 complexes.

3.3 Structural analyses of complexes

FT-IR measurements were used to analyze the coordination properties of the amide oxygen atoms. Figure 5 shows the FT-IR spectra of free MTTDGA, MTTDGA equilibrated with 0.5 or 8 M HNO₃, and
MTTDGA fully-loaded with Pd(II). For free MTTDGA (Figure 5(a)), the carbonyl stretching frequency, \( \nu_{C=O} \), appeared at \( \sim 1645 \text{ cm}^{-1} \), which corresponds to uncoordinated C=O. In addition, a small peak was observed at \( \sim 1603 \text{ cm}^{-1} \), which corresponds to the tolyl group [23]. In Figures 5(b) and 5(c), which are spectra of MTTDGA equilibrated with 0.5 M and 8 M HNO₃, respectively, there were no significant changes in the peak shape of \( \nu_{C=O} \) at \( \sim 1645 \text{ cm}^{-1} \); however, the peak intensity at \( \sim 1603 \text{ cm}^{-1} \) increased slightly. Because the tolyl group could not have been affected by the HNO₃ extraction, this result may have stemmed from a shift of the \( \nu_{C=O} \) to a lower wave number, which suggests that the amide oxygen atoms were protonated to a small extent. The Pd(II) complex extracted from 0.5 M HNO₃ (Figure 5(d)) was a 1:1 MTTDGA:Pd(II) complex, and an intense peak appeared at a lower wavenumber of \( \sim 1585 \text{ cm}^{-1} \). This large shift indicated that the amide oxygen atom was bonded to Pd(II) [24]. Likewise, a large shift of \( \nu_{C=O} \) to a lower wavenumber (\( \sim 1575 \text{ cm}^{-1} \)) was apparent in the spectrum of Figure 5(e) for the 2:1 MTTDGA:Pd(II) complex extracted from 8 M HNO₃. The different peak shapes and positions in Figures 5(d) and 5(e) mean that the coordination modes of the amide oxygen atoms differed in the 1:1 complex and 2:1 complex. In Figure 5(d), the peak related to the uncoordinated C=O was very weak compared with that of the C=O coordinated to Pd(II), indicating that both of the amide oxygen atoms were involved in complexes with Pd(II). However, in Figure 5(e), the intensity of the peak associated with the uncoordinated C=O was similar to that of the Pd(II) complex with a free amide oxygen. Considering the fact that there are only a few free MTTDGA molecules in the organic phase, it is likely that only one of the amide oxygen atoms was coordinated in the 2:1 complex.

Because HSAB (hard and soft acids and bases) theory [6] indicates that the sulfur atom has a high affinity for Pd(II), the sulfide of MTTDGA was probably bonded to Pd(II). Hence, in the 2:1 MTTDGA:Pd(II) complex obtained from 8 M HNO₃, the MTTDGA molecule was...
probably coordinated to Pd(II) in a bidentate mode via an amide oxygen atom and a sulfur atom; i.e., the first coordination sphere of Pd(II) consisted of two amide oxygen atoms and two sulfur atoms (Figure 6). This hypothesis is in agreement with the conclusions reached by other research groups that TDGA acts as a bidentate ligand that is coordinated with Pd(II) directly through sulfur and one amide oxygen atom of each TDGA molecule [16]. Ruhela et al. [21] came to the same conclusion after further investigating the Pd(II) complexes formed with \textit{N,N,N',N'-}tetra-(2-ethylhexyl) thioglycolamide using extended X-ray absorption fine structure analysis and computational methods. In the 1:1 MTTDGA:Pd(II) complex obtained from 0.5 M HNO\textsubscript{3}, the sulfur atom could likewise bind to Pd(II). Unlike the 2:1 complex, the FT-IR results indicated that both of the amide oxygen atoms interacted with Pd(II) or some similar species (e.g., H\textsuperscript{+}). The implication is that one MTTDGA molecule could have coordinated to Pd(II) via two amide oxygen atoms and one sulfur atom in a tridentate mode or via one amide oxygen atom and one sulfur atom in a bidentate mode in which another amide oxygen atom was protonated or interacted with another species. Further structural analyses of the Pd(II) complexes extracted with MTTDGA are needed to unequivocally explain the relationship between the extraction rate and extraction complexes.

4. Conclusion

Newly synthesized MTTDGA quantitatively extracted Pd(II) at HNO\textsubscript{3} concentrations of 0.5–8 M. The \(D_{Pd}\) value was a maximum at around 6 M HNO\textsubscript{3}. The extraction equilibrium was achieved in a much shorter time at 8 M HNO\textsubscript{3} (<5 min) than at 0.5 M HNO\textsubscript{3} (around 8 h). The results of the loading test suggested that the dominant complexes were the 1:1 and 2:1 MTTDGA:Pd(II) complexes at 0.5 M and 8 M HNO\textsubscript{3}, respectively. FT-IR spectra analyses showed that the coordination mode of MTTDGA in these MTTDGA:Pd(II) complexes differed, although the amide oxygen atom(s) coordinated to Pd(II) in both complexes. In the 2:1 complex, two MTTDGA molecules could bind to Pd(II) in a bidentate mode (O and S), whereas for the 1:1 complex, all the donor atoms (2O and S) of the MTTDGA molecule could be involved in the coordination to Pd(II) and/or other species, including H\textsuperscript{+}.

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