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Short Communication

Electronic absorption spectra of palladium(II) in concentrated nitric acid solutions

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Abstract

Palladium complexation in concentrated nitric acid solutions was studied by UV/Vis absorption spectrophotometry. The ionic strength of the solutions was fixed to $I = 1, 3,$ or $5 \text{ mol dm}^{-3} \text{ (M)}$ by mixing of HNO_3 and HClO_4 . The major palladium species were found to be Pd^{2+} , PdNO_3^+ , and $\text{Pd}(\text{NO}_3)_2$. The formation constant of PdNO_3^+ was determined to be $\beta_1 = 1.32$ ($I = 1 \text{ M}$), 1.49 ($I = 3 \text{ M}$), or 1.47 ($I = 5 \text{ M}$), while that of $\text{Pd}(\text{NO}_3)_2$ to be $\beta_2 = 0.45$ ($I = 3 \text{ M}$) or 0.14 ($I = 5 \text{ M}$).

Keywords

Palladium · Nitric acid · Absorption spectrophotometry · Ionic strength · Formation constant

Introduction

Molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), and palladium (Pd) are known as the noble metal fission product (NMFP) elements in reprocessing of spent nuclear fuels. In the vitrification process, since the solubility of NMFPs to glass materials is very low, their existence sometimes leads to an inhomogeneity of the vitrified waste. Separating NMFPs from the high radioactive liquid waste (HAW) in advance may be preferable to avoid degrading the vitrified waste. Solvent extraction is a promised technique to separate NMFPs from HAW, but the complicated chemical behavior of these elements in nitric acid solutions is problematic. The reliable complexation data of NM nitrates in HNO₃ are essential.

There are only a few literatures [1-4] that report the formation constants of Pd nitrates. These are widely dispersed, *e.g.*, the formation constant of PdNO₃⁺ (β_1) reported is ranged from 1.2 [1] to 14 [3]. The β values have been determined by solvent extraction technique [3] and absorption spectrophotometry [1,4]. The higher β values, that is, β_3 for Pd(NO₃)₃⁻ and β_4 for Pd(NO₃)₄²⁻, were determined in solvent extractions [3], while the latter analysis was applied for only β_1 and β_2 , Pd(NO₃)₂ [1,4]. The solvent extraction technique has a difficulty to keep the constant ionic strength due to the extraction of acid and/or solutes of buffer solutions. The activity coefficient of extracted species in organic phase is also difficult to know. The absorption spectrophotometry is free from these difficulties.

Palladium complexes generally have the square-planar structure via the hybrid orbital dsp^2 . This means that Pd²⁺ has four coordination sites. An XAFS (x-ray absorption fine structure) study [5] suggests that 1-2 NO₃⁻ ions coordinate to Pd²⁺ at ~3

mol dm⁻³ (M) HNO₃, which is a typical acidity of the aqueous reprocessing of spent nuclear fuels. The formation constants β_1 and β_2 are therefore most important. In the present study, β_1 and β_2 were determined for ionic strength 1, 3, and 5 M by UV/Vis absorption spectrophotometry.

Experimental

Because of the formation of Pd oxide and hydroxide [6], preparing nitric acid solutions of Pd(II) from Pd(OH)₂ or hydrated Pd(NO₃)₂ was not applied in the present study. The most reliable preparation method is dissolving Pd metal by boiling HNO₃ [1]. 1.6 mg of Pd metal with 0.1 μ m grain size (Nilaco Co., 99.5% purity) was dissolved in boiling 190 mL of 13.3 M HNO₃. After the complete dissolution, the solution was continuously heated for 6 hours to destroy an unidentified source of NO₂, and then the solution was cooled down. The solution was filtered by a Nuclepore track-etched polycarbonate membrane with 0.015 μ m pore size. The concentration of Pd(II) was determined by ICP-QMS (Yokogawa, HP-4500) and [HNO₃] by neutralization titration with NaOH. This solution of 0.088 M Pd in 13.3 M HNO₃ was used as the starting material.

The starting material was diluted by HNO₃ and HClO₄ to prepare sample solutions with various [NO₃⁻] at ionic strength $I = 1, 3, \text{ and } 5$ M. The sample was transferred in a quartz cell with 10 mm light path length. A Pd free reference solution with the same acid condition was also prepared. In order to decrease uncertainty of volumetric treatment, all sample solutions were prepared gravimetrically. Volumetric concentration was calculated from weight and density of solution. The absorption spectrum was measured by using an UV/Vis/NIR spectrophotometer (JASCO, V-7200)

at room temperature. The absorbance was measured in the wavelength range of 350-600 nm at 1 nm intervals.

Results and discussion

The electronic absorption spectra obtained are shown in Fig. 1. The absorption band of $d-d$ transitions is clearly seen at 400 nm. The energy levels of the $d-d$ transition have been investigated in detail for Pd(II) halides [7]. In a pioneering spectroscopic study on Pd(II) in acid solutions, addition of HNO₃ in a Pd(II)/HClO₄ solution has been tested [8]. The absorbance of the $d-d$ transition band was found to increase with [HNO₃], in which the absorption maximum shifted to longer wavelength. The same absorption characteristics are found in our results. The shift of the absorption maximum suggests the complexation of Pd(II) nitrate, Pd(NO₃)⁺. The spectrum shape changed at high acidity region, *e.g.*, at 5 M HNO₃ shown in Fig. 1c. This may be due to a higher complexation of Pd(II) nitrate as Pd(NO₃)₂. In the present paper, Pd²⁺, Pd(NO₃)⁺, and Pd(NO₃)₂ were considered as major species under our experimental conditions. For Pd(NO₃)_{*n*}^{2-*n*} (*n* = 0, 1, or 2), the complexation reaction and its formation constant (apparent) are,



$$\beta_n = \frac{[\text{Pd}(\text{NO}_3)_n^{2-n}]}{[\text{Pd}^{2+}][\text{NO}_3^-]^n} \quad (2)$$

The absorbance at a wavelength λ , $A(\lambda)$, observed is the product of $\varepsilon(\lambda)$ shown in Fig. 1

and total concentration of Pd(II) in solutions,

$$\begin{aligned} A(\lambda) &= \varepsilon(\lambda)[\text{Pd(II)}] \\ &= \sum_{n=0}^2 \varepsilon_n(\lambda)[\text{Pd(NO}_3)_n]^{2-n} \end{aligned} \quad (3)$$

where $\varepsilon_n(\lambda)$ means the molar absorptivity of $\text{Pd(NO}_3)_n$ at λ . From Eqs. (2) and (3), $\varepsilon(\lambda)$ obtained in the present study is shown as,

$$\varepsilon(\lambda) = \frac{\varepsilon_0(\lambda) + \varepsilon_1(\lambda)\beta_1[\text{NO}_3^-] + \varepsilon_2(\lambda)\beta_2[\text{NO}_3^-]^2}{1 + \beta_1[\text{NO}_3^-] + \beta_2[\text{NO}_3^-]^2} \quad (4)$$

Dependence of $\varepsilon(\lambda)$ on $[\text{HNO}_3]$ for $\lambda = 400, 450,$ and 500 nm at $I = 3$ M is shown in Fig. 2 as an example. $[\text{HNO}_3]$ is approximated to be $[\text{NO}_3^-]$ in this study. At each wavelength, $\varepsilon(\lambda)$ vs $[\text{HNO}_3]$ shows a function expressed as Eq. 4. Since spectra shown in Fig. 1 were measured in wavelength range from 350 to 600 nm at 1 nm intervals, 251 curves for different 251 wavelengths like Fig. 2 can be obtained for $I = 1, 3$, or 5 M. This means that 251 sets of $\varepsilon_0(\lambda)$, $\varepsilon_1(\lambda)$, $\varepsilon_2(\lambda)$, β_1 , and β_2 are obtained, in which β_1 and β_2 are constants. This multiple analysis was performed by employing a computational program, HypSpec [9]. The calculation results are shown in Table 1. The literature data are shown together.

It has been suggested that the Pd nitrates are markedly dissociated at low nitrate concentrations [8]. This means the small formation constants of the Pd nitrates. The β values obtained by absorption spectrophotometry showed similar values. The magnitude of the PdNO_3^+ formation constant is $\log \beta_1 < 0.18$, which is much smaller

than that of Pd halides, *e.g.*, $\log \beta_1^\circ$ for PdCl^+ at ionic strength $I = 0$ M is reported to be 5.08 [10]. The β_1 values determined by absorption spectrophotometry listed in Table 1 are shown in Fig. 3 as a function of ionic strength in molality unit (mol/kg). From the specific ion interaction theory (SIT) (see a review [11]), the following formula is given for Eq. 1 with $n = 1$,

$$\log \beta_1 + 4D = \log \beta_1^\circ - \Delta\varepsilon I \quad (5)$$

where $\Delta\varepsilon$ is the ionic strength dependence of ion interaction coefficient and D the Debye-Hückel term,

$$D = \frac{0.5091\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (6)$$

The constants 0.5091 and 1.5 were found to minimize $\Delta\varepsilon$ at $I = 0.5\text{-}3.5$ mol/kg. A straight line shown in Fig. 3 was fitted for two our data and that of [1] at $I \leq 3.5$ mol/kg considering experimental uncertainties. Though it is a rough SIT correction, $\log \beta_1^\circ = 0.84$ and $\Delta\varepsilon = 0.01$ kg/mol were determined. Pd(II) has a large hydrolysis constant [12], from which $\sim 0.5\%$ of Pd(II) is estimated to form $\text{Pd}(\text{OH})^+$ even in high acidic region of $[\text{H}^+] = 1$ M. Because of the strong hydrolysis and weak association with NO_3^- , the SIT correction for Pd nitrates must be performed in a lack of data at low acidity.

As shown in Fig. 3, β_1 at high acidity ~ 5 M HNO_3 was not ruled by the SIT correction of cation-anion interactions. This may be due to the cation-cation, anion-anion, or higher interactions taken place in concentrated electrolytes. The β_2 value

was determined only at high acidity. Though our data at 5 M agreed with the literature data [4], it is out of the SIT correction region.

In order to clarify the separation performance of Pd from HAW solutions, solvent extraction behavior of Pd from HNO₃ solutions with various extractants has been studied [2,3,13,14]. Since the complex formation constant of Pd-extractant is evaluated from distribution ratios of Pd and β values of Pd nitrates, accurate β values covering wide [HNO₃] region are required. Our data covering 1-5 M HNO₃ region are hence useful for this purpose.

Conclusions

The formation constant of PdNO₃⁺ in HNO₃-HClO₄ mixtures was determined to be $\beta_1 = 1.32$ ($I = 1$ M), 1.49 ($I = 3$ M), or 1.47 ($I = 5$ M), while that of Pd(NO₃)₂ to be $\beta_2 = 0.45$ ($I = 3$ M) or 0.14 ($I = 5$ M). The β values agreed with the literature values determined by absorption spectrophotometry. The obtained data covering 1-5 M HNO₃ region are useful for the aqueous reprocessing process of spent nuclear fuels.

Acknowledgment

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Table 1 Stability constants of palladium nitrates.

Method	I [M]	β_1	β_2	Reference
Absorption spectrophotometry	2.0-2.1	1.2 ± 0.4	–	[1]
Spectrophotometry ^a	0.95-3.04 ^a	3.28	2.13	[2]
Solvent extraction	0.25-2.0	14	2	[3]
Absorption spectrophotometry	5.18	1.47 ± 0.08	0.173 ± 0.015	[4]
Absorption spectrophotometry	1.0	1.32 ± 0.02^b	–	This study
Absorption spectrophotometry	3.0	1.49 ± 0.04^b	0.45 ± 0.06^b	This study
Absorption spectrophotometry	5.0	1.47 ± 0.03^b	0.14 ± 0.06^b	This study

^a Experimental details were not reported in [2]. The β values were used in a solvent extraction (PUREX) study at 0.95-3.04 M HNO₃.

^b Errors are 1σ in analysis of HypSpec [9].

Figure captions

Fig. 1 Electronic absorption spectra of Pd(II) in HNO₃-HClO₄ mixtures. Ionic strength was set to be 1, 3, or 5 M. **a** $I = 1$ M. **b** $I = 3$ M. **c** $I = 5$ M

Fig. 2 Molar absorptivities of Pd(II) at 400, 450, and 500 nm wavelength. The solutions were the mixtures of HNO₃-HClO₄ with ionic strength $I = 3$ M

Fig. 3 $\log \beta_1 + 4D$ vs I

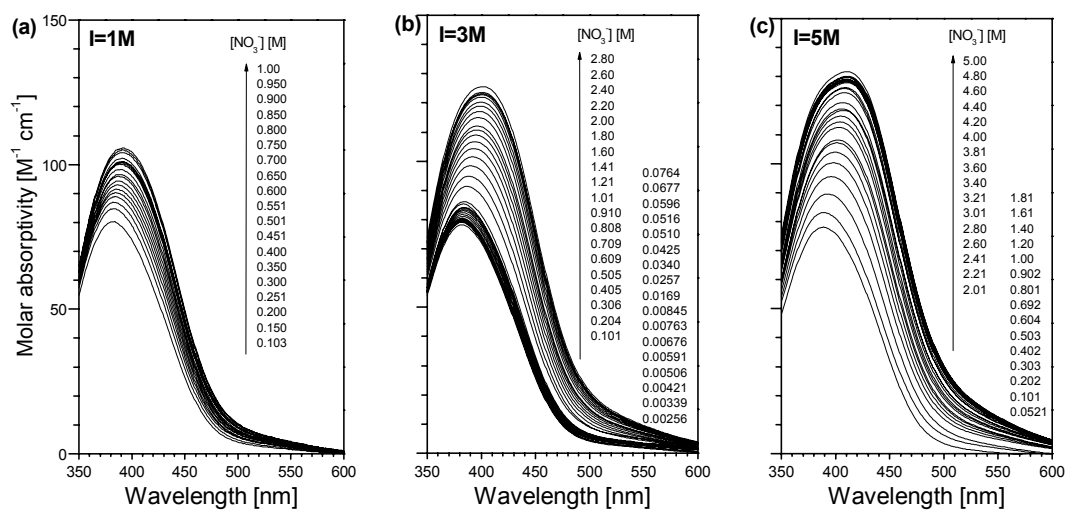


Figure 1 (Fujii et al.)

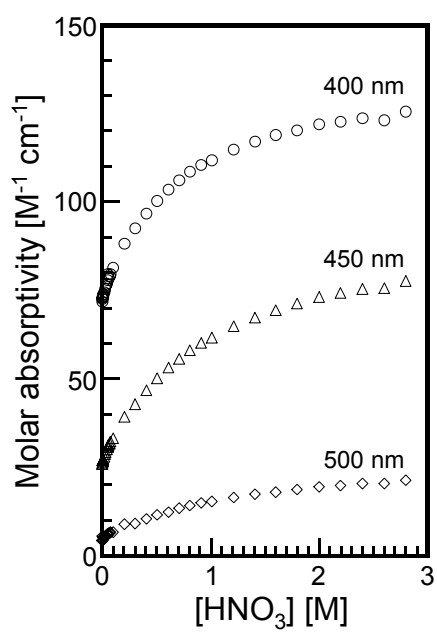


Figure 2 (Fujii et al.)

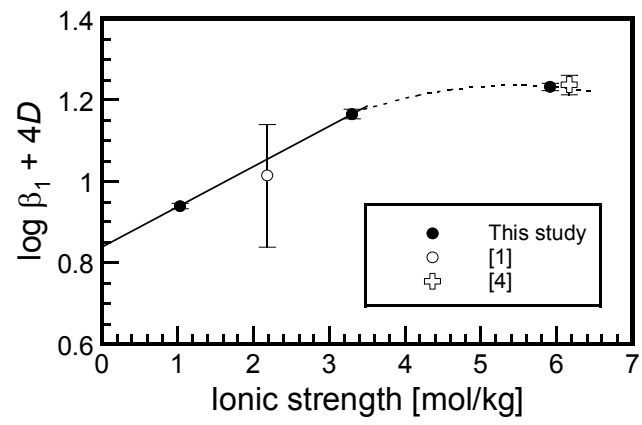


Figure 3 (Fujii et al.)