Mechanism of Palladium(II) Adsorption from Nitric Acid Solutions by a Styrene–Divinylbenzene Copolymer Functionalized with N,N,N-Trimethylglycine

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The ability of AMP03, a styrene–divinylbenzene copolymer functionalized with N,N,N-trimethylglycine moieties, to adsorb Pd(II) from HNO3 solutions was investigated to elucidate the affinity of N,N,N-trimethylglycine for Pd(II). AMP03 effectively adsorbed Pd(II) from 0.10–0.50 M solutions in HNO3, and the adsorption ability decreased with increasing HNO3 concentration owing to competitive adsorption of the acid. In contrast, the presence of added NO3− increased the Pd(II) adsorption ability of the copolymer. On the basis of slope analysis of data for Pd(II) and HNO3 at adsorption equilibrium, the Pd(II)/NO3−/ligand stoichiometry of the adsorbed Pd(II) species was determined to be 1 : 2 : 1. Structural studies performed by means of Fourier transform infrared spectroscopy and extended X-ray absorption fine structure spectroscopy revealed that the N,N,N-trimethylglycine moieties on AMP03 and NO3− coordinated to Pd(II) via their oxygen atoms. The adsorption selectivity of AMP03 for Pd(II), Ni(II), Cu(II), and Fe(III) was compared with the selectivities of commercially available carboxylic acid and iminodiacetic acid resins. AMP03 selectively adsorbed Pd(II) over Ni(II), Cu(II), and Fe(III) compared with that of the other resins. Our results suggest that AMP03 can be used for selective recovery of Pd(II) from HNO3 solution.

1. Introduction

Separation and purification of platinum group metals from mined ores are generally accomplished by leaching with highly concentrated acidic solutions [1], and the recovery of Pd(II) from these solutions by means of adsorbents has been extensively studied [2–7]. However, there are few reports on adsorbents for efficient, selective removal of Pd(II) from HNO3 solutions. Iminodiacetic acid resins (e.g., IRC748, Figure 1) strongly adsorb Pd(II) as well as base metals [6, 8–11]. In addition, carboxylic acid resins (e.g., IRC76, Figure 1) selectively adsorb Pd(II) [12], but their adsorption ability decreases markedly with increasing acid concentration [6,13].
Recently, we found that AMP03 (Figure 1), a styrene–divinylbenzene copolymer with
$N,N,N$-trimethylglycine (betaine) moieties, efficiently adsorbs Pd(II) from HNO$_3$ solution [14]. The
adsorption equilibrium was attained within 5 min, and that thiourea was effective as the eluent for Pd(II).
We compared the Pd(II) adsorption behavior of AMP03 with that of polystyrene functionalized with
$N,N,N$-trimethylammoniumpropanesulfonate ($\text{–CH}_2\text{N}^+(\text{CH}_3)_2\text{(CH}_2)_3\text{SO}_3^–$) moieties. Our results revealed
that the carboxylate groups of AMP03 efficiently adsorb Pd(II), but the nature of the interactions between
Pd(II) and the betaine moieties were not explored.

In the present study, we investigated the mechanism of Pd(II) adsorption by AMP03 by means of
adsorption experiments, Fourier transform infrared (FT-IR) spectroscopy, and extended X-ray absorption
fine structure (EXAFS) spectroscopy. In addition, the selectivities of AMP03 for adsorption of Pd(II),
Ni(II), Cu(II), and Fe(III) were determined and compared with those of IRC76 and IRC748, which also
have carboxylate groups.

2. Experimental

2.1 General

AMP03 was obtained from Mitsubishi Chemical Co., and IRC76 and IRC748 were purchased from
Organo Corporation. Nitric acid solutions containing 1000 ppm of Pd(II), Ni(II), Cu(II), or Fe(III)
(analytical-grade, Wako Pure Chemical Industries and Kanto Chemical Co.) were used to prepare initial
solutions for the adsorption experiments. Reagent-grade Pd(NO$_3$)$_2\cdot n$H$_2$O, HNO$_3$, and
tetramethylammonium nitrate were purchased from Wako Pure Chemical Industries and Kanto Chemical
Co. and were used without further purification. All experiments were performed at room temperature.

2.2 Adsorption of Pd(II), Cu(II), Ni(II), and Fe(III) from HNO$_3$ solutions

Nitric acid solutions (3.0 mL) containing 0.93 mM Pd(II), 1.7 mM Ni(II), 1.6 mM Cu(II), or 1.8 mM
Fe(III) were mixed with AMP03, IRC76, or IRC748 (0.100 g) in 10 mL plastic tubes. The mixtures were
shaken on a high-speed mixer (CM-1000, Tokyo Rikakikai Co.) at 1800 rpm for 60 min. After
centrifugation of the mixtures, the metal concentrations in the aqueous supernatants were determined by
means of inductively coupled plasma atomic emission spectroscopy (Ultima2, Horiba). Distribution
coefficients ($K_d$, mL/g) and adsorption ratios (AR, %) were calculated by means of the following equations:

$$K_d = \frac{\left([M]_{\text{initial}}-[M]_{\text{aq}}\right)}{[M]_{\text{aq}}} \times \frac{V}{m}$$

and

$$\text{(1)}$$
\[ \text{AR} = \frac{[\text{M}]_{\text{init}} - [\text{M}]_{\text{aq}}}{[\text{M}]_{\text{init}}} \times 100 \quad (2) \]

where \([\text{M}]_{\text{init}}\) and \([\text{M}]_{\text{aq}}\) are the initial and equilibrium metal concentrations, respectively, in the aqueous phases; \(V\) is the volume of the aqueous phase; and \(m\) is the weight of dry AMP03.

The \(H^+\) concentrations in the aqueous solutions were determined with an automatic potentiometric titrator (AUT501, DKK-TOA Corp.). Since AMP03 adsorbed \(H^+\) together with \(NO_3^-\) \([14]\), the concentration of adsorbed \(HNO_3\) per unit of AMP03 dry weight (\([HL \cdot NO_3]\)resin, mmol/g) was calculated as follows:

\[ [HL \cdot NO_3]_{\text{resin}} = ([H^+]_{\text{init}} - [H^+]_{\text{aq}}) \times \frac{V}{m} \quad (3) \]

where \([H^+]_{\text{init}}\) and \([H^+]_{\text{aq}}\) are the initial and equilibrium \(H^+\) concentrations, respectively, in the aqueous solutions, and \(L\) represents the betaine groups in the AMP03.

### 2.3 Adsorption of Pd(II) by AMP03 from HNO3 solutions containing added tetramethylammonium nitrate

AMP03 was mixed with HNO3 solutions (3.0 mL) containing 0.94 mM Pd(II) and 0.10–0.40 M tetramethylammonium nitrate, which was used to adjust \([H^+]_{\text{init}}\) at a constant \([NO_3^-]_{\text{init}}\) value (0.50 M). After the mixtures were shaken for 60 min and centrifuged, the Pd concentrations in the aqueous supernatants were determined by means of inductively coupled plasma atomic emission spectroscopy.

### 2.4 FT-IR and EXAFS measurements

Samples of AMP03 containing adsorbed Pd(II) at 0.27 and 0.75 mmol/g were powdered, and the FT-IR spectra of the powders were measured by means of an attenuated total reflection method with a Perkin Elmer Spectrum 100 instrument. Data were collected at 600–4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\); data collection was repeated 15 times, and the data sets were then merged.

EXAFS measurements of powdered samples were performed at BL11XU of SPring-8. Specifically, powdered AMP03 containing 0.75 mmol/g Pd(II) was pelletized, and 0.5 and 7.0 M HNO3 solutions containing 25 mM and 0.1 M Pd(II), respectively, were prepared. The EXAFS spectra of the pellet and the solutions were measured and analyzed as described elsewhere \([15]\).

### 3. Results and Discussion

#### 3.1 Correlation between Pd(II) adsorption ability and HNO3 concentration

The extents to which Pd(II) and HNO3 were adsorbed by AMP03 were compared by plotting the Pd(II) \(K_d\) value and the adsorbed HNO3 concentration (\([HL \cdot NO_3]\)resin) against the equilibrium HNO3 concentration (\([HNO_3]_{\text{aq}}\)) (Figure 2). The largest \(K_d\) value was observed at \([HNO_3]_{\text{aq}} = 0.26\) M. In a previous paper \([14]\), we attributed the decrease in \(K_d\) at higher \([HNO_3]_{\text{aq}}\) values to the inhibition of Pd(II) adsorption by HNO3 adsorption. Interestingly, in this study, we found that the \(K_d\) value at the lowest \([HNO_3]_{\text{aq}}\) (0.069 M) was slightly lower than the peak \(K_d\) value. The fact that the proportions of Pd\(^{2+}\) and Pd\(NO_3^+\) were 92% and 8%, respectively, at \([HNO_3]_{\text{aq}} = 0.069\) M and were 75% and 25%, respectively, at \([HNO_3]_{\text{aq}} = 0.26\) M (as estimated from the stability constant of the mononitrate complex) \([16]\) suggests that...
AMP03 interacted preferentially with PdNO₃⁺.

### 3.2 Effects of the H⁺ and NO₃⁻ concentrations on Pd(II) adsorption

The effects of H⁺ and NO₃⁻ concentrations on the Pd(II) \( K_d \) value were evaluated by means of adsorption experiments at various [H⁺]\(_{\text{init}}\) values and a constant [NO₃⁻]\(_{\text{init}}\) (Figure 3). These experiments revealed that Pd(II) \( K_d \) decreased with increasing [H⁺]\(_{\text{init}}\), indicating that the adsorption reactions of H⁺ and Pd(II) were competitive. We also found that NO₃⁻ affected Pd adsorption, as indicated by the finding that the \( K_d \) values at [NO₃⁻]\(_{\text{init}}\) = 0.50 M (Figure 3) were substantially larger than those at [HNO₃]\(_{\text{aq}}\) = 0.069 – 0.46 M (Figure 2). Increasing the amount of [NO₃⁻] facilitated the formation of PdNO₃⁺ from Pd²⁺. This result confirms that AMP03 preferentially adsorbed PdNO₃⁺.

### 3.3 Mechanism of Pd(II) adsorption by AMP03

We used our experimental results to draw some inferences about the mechanism of Pd(II) adsorption by AMP03. AMP03 interacts mainly with PdNO₃⁺. The adsorbed Pd(II) species can be expected to have two nitrate ions because of its electroneutrality. The Pd(II) adsorption reaction can therefore be expressed by the following equations:

\[
PdNO₃⁺_{\text{aq}} + NO₃⁻_{\text{aq}} + nL_{\text{resin}} \rightleftharpoons [PdNO₃Lₙ]_{\text{resin}}(NO₃⁻)_{\text{resin}} \quad (4)
\]

\[
K_1 = \frac{[PdNO₃Lₙ]_{\text{resin}}(NO₃⁻)_{\text{resin}}}{[PdNO₃⁺]_{\text{aq}}[NO₃⁻]_{\text{aq}}L_{\text{resin}}^n} \quad (5)
\]

where [PdNO₃⁺]\(_{\text{aq}}\) is the equilibrium PdNO₃⁺ concentration in the aqueous solution, [NO₃⁻]\(_{\text{aq}}\) is the equilibrium NO₃⁻ concentration in the aqueous solution, [L]\(_{\text{resin}}\) is the concentration of free betaine groups in AMP03, and \( n \) is the number of betaine groups per adsorbed Pd(II) species. Since Pd(II) and HNO₃ adsorption reactions are competitive, the following equations are considered in connection with Eqs. (4) and (5):
Combination of Eqs. (4) and (6) and Eqs. (5) and (7) gives

\[
PdNO_3^+ + nHL \cdot NO_3^{-} \rightleftharpoons [PdNO_3L_n](NO_3)_{resin} + nH^+ + (n-1)NO_3^{-}
\]  

(8)

\[
K_d = \frac{[Pd(NO_3)_nL_resin][NO_3^{-}]_aq}{[Pd(NO_3)_n]^n_aq[HL \cdot NO_3^{-}]_aq}
\]  

(9)

In our HNO3 solutions, Pd^{2+} and PdNO^{3+} were the predominant species. The Pd(II) \(K_d\) value can be expressed as follows:

\[
K_d = \frac{[Pd(II)]_{resin}}{[Pd(II)]_{aq}} = \frac{[PdNO_3^+L_aq][NO_3^{-}]_aq}{(Pd^{2+})_{aq}[PdNO_3^{-}]_{aq}}
\]  

(10)

where \([Pd^{2+}]_{aq}\) is the equilibrium Pd^{2+} concentration in the aqueous solution. Pd^{2+} in HNO3 solution exists in equilibrium with PdNO^{3+}:

\[
Pd^{2+} + NO_3^{-} \rightleftharpoons PdNO_3^+
\]  

(11)

\[
K_{pd} = \frac{[PdNO_3^+]_{aq}}{[Pd^{2+}]_{aq}[NO_3^{-}]_{aq}}
\]  

(12)

Insertion of Eqs. (9) and (12) into Eq. (10) results in the following equation:

\[
K_d = \frac{K_{pd}[HL \cdot NO_3^{-}]_aq}{[H^+]_aq^{2n-1}}
\]  

(13)

Since AMP03 adsorbed H^+ together with NO_3^{-}, and therefore \([NO_3^{-}]_{aq}\) was comparable to \([H^+]_{aq}\) in the adsorption experiments, eq. (13) can be simplified to

\[
K_d = \frac{K_{pd}[HL \cdot NO_3^{-}]_aq}{[H^+]_aq^{2n-1}}
\]  

(14)

which in logarithmic form gives

\[
\log \left( \frac{K_d}{[H^+]_{aq}} \right) = \log K_{pd} + n \log \frac{[HL \cdot NO_3^{-}]_aq}{[H^+]_aq^{2}}
\]  

(15)

By using Eq. (15) and slope analysis of the data shown in Figure 2 and a \(K_{pd}\) value of 1.32 [16]), we were able to determine \(n\). The plot in Figure 4 shows a linear relationship with a slope of 1.17 ± 0.08. Therefore, we propose the following adsorption reaction:

\[
PdNO_3^+ + HL \cdot NO_3^{-} \rightleftharpoons [PdNO_3L](NO_3)_{resin} + H^+
\]  

(16)
3.4 Structural analysis of Pd(II) adsorption by AMP03 by means of FT-IR spectroscopy and EXAFS spectroscopy

FT-IR spectroscopy indicated that structural changes in the betaine groups of AMP03 occurred upon adsorption of HNO3 (Figure 5). Specifically, changes were observed in the broad peak at 1618 cm⁻¹ in the spectrum of free AMP03 (peak 1), which was assigned to overlapping bands for stretching vibrations of –C=C– in the styrene–divinylbenzene moieties and of C=O in the carboxylate groups [17,18]. Upon adsorption of HNO3, this peak separated into three peaks, at 1613, 1629, and 1732 cm⁻¹ (peaks 2–4, respectively). Peaks 3 and 4 correspond to carbonyl and carboxyl groups, respectively, and the wavenumbers of the two peaks are consistent with those of the peaks in the FT-IR spectrum of betaine (νC=O at 1629 cm⁻¹) and its nitrate salt (νCOOH at 1737 cm⁻¹) [18,19]. The absorption band at 1366 cm⁻¹ (peak 5) was attributed to the stretching vibration of noncoordinated NO₃⁻ [19]. These results indicate that HL·NO₃, where L is a betaine group of AMP03, formed upon adsorption of HNO3 by AMP03.

The FT-IR spectra obtained upon adsorption of Pd(II) and HNO3 also showed the three peaks for νC=C (peak 2), νC=O (peak 6), and νCOOH (peak 4). The stretching vibration for the carbonyl groups shifted from 1629 cm⁻¹ to a higher wavenumber. When the Pd(II) content in the AMP03 was increased, the transmittance of the νC=O band (peak 6) decreased and that of the νCOOH band (peak 4) increased. These spectral changes suggest that the carboxylate groups of AMP03 released protons upon coordination with Pd(II). Additionally, a band at 1265 cm⁻¹ (peak 7) appeared upon adsorption of Pd(II), implying the presence of NO₃⁻ coordinated to Pd(II) in AMP03 [20,21].

The Pd K-edge $k^3$-weighted EXAFS data and the corresponding Fourier transforms for 0.50 and 7.0 M HNO₃ solutions of Pd(II) and AMP03-adsorbed Pd(II) were obtained (Figure 6). All the spectra were
similar. The large peak in the Fourier transformed spectra of the three systems can be assigned to four oxygen atoms in the Pd(II) coordination sphere [22], indicating that the betaine moieties coordinated to Pd(II) via their oxygen atoms. Notably, a small peak at $R = 2.3$ Å was present in the spectra measured for Pd(II) in AMP03 and 7.0 M HNO$_3$ solution but not in the spectrum measured in the 0.50 M HNO$_3$ solution. According to a previous report [23], the small peak results from multiple scatterings related to N and distal O atoms in the NO$_3^-$ coordinating to Pd(II) in a unidentate manner. Since the Fourier-transformed spectra of Pd(II) in AMP03 and 7.0 M HNO$_3$ solution were similar to each other, we concluded that the adsorbed Pd(II) species was coordinated to NO$_3^-$. This conclusion is consistent with our FT-IR analysis results and supports our contention that AMP03 preferentially adsorbed PdNO$_3^+$ from the 0.50 M HNO$_3$ solution.

### 3.5 Selectivity of AMP03 for Pd(II) adsorption

The selectivity of AMP03 for Pd(II) was evaluated by means of adsorption experiments involving HNO$_3$ solutions containing Pd(II), Ni(II), Cu(II), and Fe(III) (Figure 7). These experiments showed that AMP03 selectively adsorbed Pd(II) although Fe(III) was slightly adsorbed at [HNO$_3$] = 0.10 M. IRC76 also adsorbed Pd(II) selectively over the other metals, except for Fe(III) at [HNO$_3$] = 0.10 M, in which case the AR value decreased markedly with increasing [HNO$_3$]. Considering that acetate ($pK_a = 4.76$ [24]) is more basic than $N,N,N$-trimethylglycine ($pK_a = 1.84$ [24]), protonation of the $-COO^-$ groups in IRC76 may have inhibited Pd(II) adsorption. IRC748 strongly adsorbed Pd(II) but it also adsorbed the base metals. These experiments indicate that the Pd(II) selectivity of AMP03 was superior to the selectivities of the tested commercial adsorbents.
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