Extraction Behavior of Precious Metals in Hydrochloric-acid Media Using a Novel Amine Extractant Bearing a Furan Group

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Amine extractants are effective for extracting precious metals in hydrochloric-acid media. We developed a novel secondary-amine extractant 2-ethylhexylfurfurylamine (EH-A-F). EH-A-F showed a higher Pd(II) extractability compared with many secondary-amine compounds, such as di(2-ethylhexyl)amine. Because the Pd(II) extraction from solutions of lower hydrochloric-acid concentration is small, Pd(II) and Au(III) can be extracted selectively from the trivalent metal ions Fe(III), Ga(III), and In(III). Because the extractability of hydrochloric acid using EH-A-F was lower than that of a competitive amine compound, benzyl 2-ethylhexylamine, EH-A-F was found to show a higher Pd(II) extractability because of its moderate basicity. Slope analysis for Pd(II) extraction showed that the complex stoichiometry was 2:1 for EH-A-F and Pd(II). The Pd(II) extracted by using EH-A-F was stripped quantitatively by using aqueous thiourea solution.

1. Introduction

Platinum group metals (PGMs) are used as metallic catalysts in automobiles to minimize air pollution. Natural resources of PGMs are limited, and their efficient recycle from secondary resources should be established to secure supply of these metals. Solvent extraction is a promising hydrometallurgical process for the separation and recovery of metals, including PGMs from primary and secondary resources [1-5]. As a result, many types of precious metals extractants have been developed.

Alkyl sulfides, such as dioctyl sulfide, are representative extractants for Pd(II) [6]. Additionally, amino compounds and ammonium compounds are also useful as extractants for Pd(II) from hydrochloric-acid media. Quaternary ammonium extractants can extract Pd(II) in hydrochloric-acid media [7-9]. Inoue and coworkers reported the extraction equilibrium of Pd(II) using trioctylmethylammonium chloride (TOMAC) in hydrochloric-acid media [7]. Palladium (II) was extracted by using TOMAC as a mononuclear ion pair. Tertiary amine extractants are also effective for the extraction of Pd(II) [10-14]. Kawano et al. investigated the extraction equilibrium of Pd(II) using tri-n-octylamine (TOA) in toluene. A slope analysis of the forward and back extractions for hydrochloric acid and Pd(II) showed that a complex between Pd(II) (PdCl₄²⁻) and the two ammonium chlorides of TOA was formed with the release of two chloride anions [10]. The same reaction for Pd(II) extraction into o-xylene was also reported [11]. The extraction of Pd(II) using trilaurylamine in a HNO₃–HCl system has also been studied [12]. Tertiary diamine extractants have been developed for the extraction of Pt(IV) and Pd(II) [15].

Although many reports exist on Pd(II) extraction using quaternary ammonium extractants and tertiary
amine extractants, less research has been conducted on Pd(II) extraction using secondary amino compounds. Kawano et al. reported the extraction of Pd(II) using di(2-ethylhexyl)amine (EH-A-EH) in toluene [16,17]. The extracted species formed by the reaction between the chloro-palladium complex and the ammonium chloride of EH-A-EH was determined. In general, the order of extractability of amines agrees with their basicity in the order: primary amines < secondary amines < tertiary amines < quaternary ammonium compounds [7]. It is likely that the weaker basicity results in less extractability, and therefore researchers have given less attention to secondary amino compounds.

Secondary amino compounds that bear a heteroaromatic group on the side chain show a unique extractability compared with typical secondary amines. In this study, 2-ethylhexylfurfurylamine (EH-A-F, shown in Figure 1) was prepared as a novel amine extractant for precious metal ions in hydrochloric-acid media. Furfural can be obtained from 5-hydroxymethylfurfural (HMF) by dehydration. HMF production from carbohydrate degradation has attracted attention to produce fuels and chemical building blocks from biomass resources and biorefineries [18,19]. HMF can be obtained by the dehydration of fructose. Progress in biorefinery studies, and the direct conversion of cellulosic biomass into HMF has been developed [20]. Thus, furfural is a potential building block for the development of new compounds, accompanied by progress in biorefining. The introduction of furfural at the side chain for amine extractants would influence the extractability of metal ions, by changing the basicity of the amino group and the acting furfuryl group as a chelating group. Moreover, furfural has an aldehyde group that can react easily with an amino group to form a Schiff base.

EH-A-F was prepared from 2-ethylhexylamine and furfural by the formation of a Schiff base followed by reduction. The effect of the furfuryl group in EH-A-F on the extraction of Pd(II) has been discussed by comparing the extractability using different amine extractants. A secondary amino compound that bears an HMF group (EH-A-HMF) was prepared as a reference because HMF is considered to be a platform compound in biomass conversion. The extraction selectivity for metal ions using EH-A-F in hydrochloric-acid media was also studied. As a typical extraction system, the extraction reaction for Pd(II) using EH-A-F in hydrochloric acid was confirmed by a slope analysis of Pd(II) extraction, and by considering the extraction of hydrochloric acid. Conditions for the stripping of Pd(II) extracted with EH-A-F were also studied.

Figure 1. Extractant molecular structures and abbreviations.
2. Experimental

2.1 Reagents

Analytical-grade Au(III), Pd(II), Pt(IV), Fe(III), Ga(III), and In(III) chlorides (Wako Pure Chemical Ind. Ltd., Japan) were used to prepare test solutions of the metal ions. Figure 1 shows the molecular structures of the amine extractants used in this study. Analytical-grade di(2-ethylhexyl)amine (EH-A-EH) for the extraction tests was provided by Tokyo Kasei Co., Ltd. (Tokyo, Japan). EH-A-F, 2-(2-ethylhexylmethylamino)-5-hydroxymethylfuran (EH-A-HMF), benzyl 2-ethylhexylamine (B-A-EH), 2-(2-ethylhexylaminomethyl) phenol (EH-A-P), and 2-butoxyethyl-2-ethylhexyl amine (BO-A-EH) were synthesized as shown in Section 2.2. All other reagents and solvents were of analytical grade and were used as received.

2.2 Synthesis of amine extractants

2.2.1 2-Ethylhexylfurfurylamine (EH-A-F)

The synthesis scheme for 2-ethylhexylfurfurylamine (EH-A-F) is shown in Figure 2. EH-A-F was prepared by the formation of a Schiff base using 2-ethylhexylamine and furfural (2-furancarboxaldehyde), followed by the reduction of the Schiff base, as follows. 2-Ethylhexylamine (8.4 g, 65 mmol) was dissolved in 100 cm³ methanol. To the solution, a methanol solution that contained 9.4 g (98 mmol) furfural was added dropwise, and the mixture was stirred for 2 h at 50°C. After cooling, 2.5 g (65 mmol) of sodium tetrahydroborate was added slowly to the mixture, and the mixture was stirred again for 24 h at 50°C. After methanol evaporation in vacuo, a chloroform solution of the residue was washed with an aqueous solution of sodium hydroxide and distilled water. After drying with anhydrous sodium sulfate, the solution was dried in vacuo. To the residue was added 200 cm³ hexane and a small quantity of 4 M HCl in 1,4-dioxane to obtain the ammonium salt of the product. The formation of the ammonium salt results in the phase separation of the hexane solution, and the lower liquid phase that contained the product was collected. The solution was diluted using distilled water and an aqueous solution of sodium hydroxide was added to deprotonate the product. From the aqueous solution, the product was extracted three times by using chloroform. After drying with anhydrous sodium sulfate, the chloroform solution was dried in vacuo. The final EH-A-F product was obtained as a light-yellow liquid. The resulting EH-A-F product has the following properties: ¹H-NMR (400 MHz, CDCl₃, 25°C) 0.90 (6H, m, CCH₃), 1.35 (9H, m, C-CH₂-C and (C₄H₉)(C₂H₅)-CH-CH₂), 2.50 (2H, d, CH-CH₂-NH), 3.75 (2H, s, NH-CH₂-C), 6.15 (1H, m, OC-CH-CH), 6.29 (1H, m, OCH-CH-CH), 7.33 (1H, m, O-CH-CH).

2.2.2 2-(2-Ethylhexylmethylamino)-5-hydroxymethylfuran (EH-A-HMF)

EH-A-HMF was prepared by the formation of a Schiff base using 2-ethylhexylamine and 5-(hydroxymethyl)furfural (HMF), followed by reduction of the Schiff base, in a similar manner as that for the
EH-A-F. The resulting EH-A-HMF product had the following properties: \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25°C) 0.85 (6H, m, C\(_{\text{CH}_3}\)), 1.23–1.32 (8H, m, C-CH\(_2\)-C), 1.42 (1H, m, (C\(_4\)H\(_9\))(C\(_2\)H\(_5\))-CH-CH\(_2\)), 2.47 (2H, d, CH-CH\(_2\)-NH), 3.70 (2H, s, NH-CH\(_2\)-C), 4.48 (2H, s, C-CH\(_2\)-OH), 6.10 (1H, s, OC(CH\(_2\)OH)-CH-CH), 6.14 (1H, s, OC(CH\(_2\)OH)-CH).

### 2.2.3 Benzyl 2-ethylhexylamine (B-A-EH)

B-A-EH was prepared by the formation of a Schiff base using 2-ethylhexylamine and benzylaldehyde, followed by a reduction of the Schiff base, in a similar manner to that used for the EH-A-F. The resulting B-A-EH product had the following properties: \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25°C) 0.82–0.90 (6H, m, CH\(_2\)CH\(_3\)), 1.24–1.43 (9H, m, C-CH\(_2\)-C, (C\(_4\)H\(_9\))(C\(_2\)H\(_5\))-CH-CH\(_2\)), 2.50 (2H, d, CH-CH\(_2\)-NH), 3.75 (2H, s, NH-CH\(_2\)-C), 7.21–7.30 (5H, m, Ar-H).

### 2.2.4 2-(2-Ethylhexylaminomethyl) phenol (EH-A-P)

EH-A-P was prepared by the formation of a Schiff base using 2-ethylhexylamine and salicylaldehyde (o-hydroxybenzaldehyde), followed by reduction of the Schiff base, in a similar manner as that used for the EH-A-F. The resulting EH-A-P product had the following properties: \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25°C) 0.87–0.91 (6H, m, C-CH\(_2\)-C, (C\(_4\)H\(_9\))(C\(_2\)H\(_5\))-CH-CH\(_2\)), 2.57 (2H, d, CH-CH\(_2\)-NH), 3.93 (2H, s, NH-CH\(_2\)-C), 6.73 (1H, t, Ar-H), 6.83 (1H, d, Ar-H), 6.96 (1H, d, Ar-H), 7.12 (1H, t, Ar-H).

### 2.2.5 2-Butoxyethyl-2-ethylhexyl amine (BO-A-EH)

The synthesis scheme for 2-butoxyethyl-2-ethylhexyl amine (BO-A-EH) is shown in Figure 3. 2-Ethylhexylamine (8.07 g, 40.0 mmol) was dissolved in 150 cm\(^3\) DMF. To the solution, a DMF solution that contained 8.20 g (60.0 mmol) of butyl 2-chloroethyl ether was added dropwise, and the mixture was stirred for 48 h at 60°C. After cooling, the solvent was removed in vacuo. A chloroform solution of the residue was washed with an aqueous solution of sodium hydroxide, and distilled water. After drying with anhydrous magnesium sulfate, the solution was dried in vacuo. The product was purified by liquid chromatography using a silica-gel column. The resulting BO-A-EH product had the following properties: \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25°C) 0.85–0.94 (9H, m, C\(_{\text{CH}_3}\)), 1.24–1.42 (10H, m, C-CH\(_2\)-C), 1.52–1.59 (1H, m, (C\(_4\)H\(_9\))(C\(_2\)H\(_5\))-CH-CH\(_2\)), 1.69 (1H, s(br), OCH\(_2\)-CH\(_2\)-C\(_3\)H\(_7\)), 2.50 (2H, d, CH-CH\(_2\)-NH), 2.76 (2H, t, CH\(_2\)-CH\(_2\)-NH), 3.44 (2H, t, O-CH\(_2\)-C\(_3\)H\(_7\)), 3.51 (2H, t, O-CH\(_2\)-CH\(_2\)-NH).

### 2.3. Liquid–liquid extraction tests

Liquid–liquid extraction tests were conducted batchwise with a typical procedure as follows. An aqueous solution was prepared by dissolving metal ions Au(III), Pd(II), Pt(IV), Fe(III), Ga(III), or In(III) to form 0.1 mM solutions in hydrochloric acid. The initial concentration of hydrochloric acid was adjusted from 0.1 to 8.0 M. An organic solution was prepared by dissolving an amine extractant (EH-A-F, EH-A-HMF, B-A-EH, EH-A-P, BO-A-EH, or EH-A-EH, 5 mM) in chloroform. Equal volumes (10 cm\(^3\)) of the aqueous and organic solutions were mixed in a stoppered Erlenmeyer flask and shaken (120 rpm) in a thermostated water bath at 30°C. After shaking for 48 h to attain equilibrium, the phases were separated.

The equilibrium concentration of hydrochloric acid in the aqueous solution was determined by acid-
base titration by using an automatic potentiometric titrator (Kyoto Electronics Manufacturing AT-700). The initial and equilibrium concentrations of metal ions in the aqueous phases were determined by using a polarized Zeeman atomic absorption spectrometer (HITACHI Z-2310). The extraction percentage and distribution ratio \(D\) of the metal were calculated according to Eqs. (1) and (2), respectively:

\[
\text{Extraction} [\%] = \frac{[M]_{\text{org, eq}}}{[M]_{\text{aq, init}}} \times 100 = \frac{[M]_{\text{aq, eq}} - [M]_{\text{aq, init}}}{[M]_{\text{aq, init}}} \times 100
\]  

(1)

\[
D = \frac{[M]_{\text{org, eq}}}{[M]_{\text{aq, eq}}} = \frac{[M]_{\text{aq, eq}} - [M]_{\text{aq, eq}}}{[M]_{\text{aq, eq}}}
\]  

(2)

where \([M]_{\text{aq, init}}\) represents the initial concentration of metal ions in the aqueous phase, and \([M]_{\text{aq, eq}}\) and \([M]_{\text{org, eq}}\) are the total concentrations of metal ions in the aqueous and organic phases, respectively, at equilibrium.

The reaction for the extraction of Pd(II) using EH-A-F was investigated by slope analysis. Before the slope analysis for Pd(II) extraction, the reactions for the extraction of hydrochloric acid using EH-A-F and B-A-EH were studied by extraction isotherms. The concentration of hydrochloric acid in the organic phase was calculated from the balance. The effect of the equilibrium concentration of hydrochloric acid on the distribution ratio \(D\) of Pd(II) was investigated using 5.0 mM EH-A-F. The effect of the equilibrium concentration of hydrogen ions (0.5–1.0 M) on the distribution ratio \(D\) at a constant chloride-ion concentration (1.0 M) was also investigated, using an aqueous Pd(II) solution prepared by mixing hydrochloric acid and lithium chloride (LiCl). Additionally, the effect of the equilibrium concentration of the chloride ion (0.5–1.0 M) on the distribution ratio \(D\) at a constant hydrogen-ion concentration (0.50 M) was investigated.

2.4 Back Extraction of Pd(II)

The forward extraction of 0.1 mM Pd(II) using EH-A-F from 0.1 M hydrochloric acid was performed from the aqueous to the organic phase (100 cm\(^3\)/100 cm\(^3\)) in a similar manner as described above. The organic phase that contained Pd(II) was divided into 10-cm\(^3\) portions, and each portion was contacted with a 10-cm\(^3\) fresh aqueous solution that contained a mineral acid, namely, hydrochloric acid, sulfuric acid, or nitric acid ([H\(^+\)]\(_{ini}\) = 0.01–5.0 M), and thiourea (0, 0.1 or 0.1 M). Both phases were mixed and shaken at 30°C for 48 h. The stripping solution was separated from the organic phase and the back-extraction percentage \((B.E.\ [\%])\) was calculated according to Eq. (3):

\[
B.E. [\%] = \frac{[\text{Pd(II)}]_{\text{aq, eq}}}{[\text{Pd(II)}]_{\text{org, ini}}} \times 100
\]

(3)

where \([\text{Pd(II)}]_{\text{org, ini}}\) represents the initial concentration of Pd(II) in the organic phase and \([\text{Pd(II)}]_{\text{aq, eq}}\) is the total concentration of the metal ion in the aqueous phase after equilibrium.

3. Results and Discussion

3.1 Extractability of different amine extractants for Pd(II)

EH-A-F was prepared as a novel extractant for precious metals in hydrochloric-acid media. The
extractability of Pd(II) using a series of secondary-amine extractants that bear different side chains was compared to study the effect of the furfuryl group in EH-A-F on the extraction. As shown in Figure 4, Pd(II) is extracted using secondary-amine extractants at a lower hydrochloric-acid concentration. The extraction decreases with an increase in hydrochloric-acid concentration. Pd(II) was extracted quantitatively using EH-A-F from 0.1–0.3 M HCl. At 0.3 M HCl, EH-A-F and BO-A-EH showed a higher extractability for Pd(II) compared with other secondary-amine extractants. Because EH-A-F and BO-A-EH have an oxygen atom at the peripheral amino group, the oxygen atom may influence the Pd(II) extractability. The presence of oxygen changes the basicity of the amino group, and oxygen may act as a coordination atom. The extractability of EH-A-F and BO-A-EH is higher than that of an aliphatic secondary-amine extractant EH-A-EH. Because the extractability using aromatic amine extractants B-A-EH and EH-A-P is smaller than that using EH-A-F, the aromatic functionality at the side chain is not the only requirement for a high Pd(II) extractability. Although the extractability of EH-A-HMF is small, it bears a furfuryl group. The hydrophobicity of EH-A-HMF should be smaller than that of EH-A-F because of the presence of a hydroxyl group. Therefore, the extractant hydrophobicity can be an important factor for the extraction of Pd(II). From the results, EH-A-F and BO-A-EH were more effective extractants compared with other secondary-amine extractants. Pd(II) extraction using EH-A-F is smaller than that by using a quaternary-ammonium extractant, trioctylmethylammonium chloride (TOMAC) [7].

3.2 Extractability of different amine extractants for Pd(II)

The extraction behavior of various metal ions using EH-A-F in hydrochloric-acid media was studied (Figure 5). The extraction of Au(III) decreases with an increase in hydrochloric-acid concentration, probably because of the competitive extraction of chloride anions (Cl\textsuperscript{-}). The dependence on hydrochloric-acid concentration is different from that using the tertiary-amine extractant Hostarex A327 [21]. Because the separation between Au(III) and Pd(II) appears to be difficult, Au(III) should be extracted using other extractants, such as dibutyl carbitol [22,23] before the extraction of Pd(II) by using EH-A-F. The extraction

![Figure 4](image-url)  
**Figure 4.** Extraction profiles for Pd(II) using different amine extractants as a function of hydrochloric-acid concentration. [extractant] = 5.0 mM, [Pd(II)]\textsubscript{ini} = 0.1 mM.

![Figure 5](image-url)  
**Figure 5.** Extraction profiles for metal ions using EH-A-F as a function of hydrochloric-acid concentration. [EF-A-F] = 5.0 mM, [metal ion]\textsubscript{ini} = 0.1 mM.
of Pt(IV) is approximately 30\%–50\% in 0.1–8.0 M HCl and is almost independent of hydrochloric-acid concentration. Because the extraction of trivalent metal ions Fe(III), Ga(III), and In(III) in the lower hydrochloric-acid concentration solution is very small, Pd(II) can be extracted selectively from many metal ions using EH-A-F. Fe(III) and Ga(III) was extracted partially at higher HCl concentrations ([HCl] = 7.7–7.8 M). Because Fe(III) and Ga(III) are present as anionic chloride complexes at higher HCl concentrations [24], they must be extracted by the formation of an ion-pair with the cationic amine extractant EH-A-F.

3.3 Determination of complex species

The Pd(II) extraction reaction using EH-A-F was investigated by slope analysis. Before the study of the Pd(II) extraction system, the extraction of hydrochloric acid using EH-A-F was studied.

Figure 6 shows the extraction profile or isotherms of hydrochloric acid using EF-A-F and B-A-EH at varying equilibrium concentrations of hydrochloric acid. The vertical axis [HCl]_{org.eq.}/[extractant]_{org.ini.} is the molar ratio between the equilibrium concentration of hydrochloric acid in the organic phase and the initial concentration of extractant in the organic phase. As shown in Figure 6, the extraction of hydrochloric acid increases with an increase in hydrochloric-acid concentration. For EH-A-F and B-A-EH, the extraction of hydrochloric acid plateaus at a ratio of 1, which suggests that one amine extractant molecule extracts one hydrochloric acid molecule. Additionally, plateaus of hydrochloric-acid extraction suggest that the amine extractants rarely leak into the aqueous phase. Because B-A-EH extracts hydrochloric acid at a lower concentration than EH-A-F, B-A-EH should have a higher extractability for hydrochloric acid. The extraction reaction of hydrochloric acid with EF-A-F and B-A-EH can be represented by Eq. (4):

\[
\text{RN} + \text{HCl} \rightleftharpoons \text{RN} \cdot \text{HCl} \quad (4)
\]

The bar denotes the species in the organic phase, and [HCl]_{org.eq.}/[extractant]_{org.ini.} is theoretical curves. [extractant] = 5.0 mM, [HCl]_{ini} = 0.1–5.0 M.

RN denotes EF-A-F and B-A-EH. The extraction equilibrium constant \(K_{\text{HCl}}\) is given by Eq. (5):

\[
K_{\text{HCl}} = \frac{[\text{RN} \cdot \text{HCl}]}{[\text{RN}][\text{HCl}]} \quad (5)
\]

Based on a mass balance of the extractant, the initial extractant concentration \([\text{RN}]_{\text{ini}}\) can be expressed by Eq. (6):

\[
[\text{RN}]_{\text{org.}} = [\text{RN}] + [\text{RN} \cdot \text{HCl}] \quad (6)
\]

From Eqs. (5) and (6), Eqs. (7) and (8) are obtained:
\[
\frac{[\text{RN}]}{[\text{RN} - \text{HCl}]} = \frac{[\text{RN} \cdot \text{HCl}]}{K_{\text{HCl}}[\text{HCl}]} + [\text{RN} \cdot \text{HCl}] = \frac{[\text{RN} \cdot \text{HCl}](1 + K_{\text{HCl}}[\text{HCl}])}{K_{\text{HCl}}[\text{HCl}]} \quad (7)
\]

\[
\frac{[\text{RN}]}{[\text{RN} - \text{HCl}]} = \frac{K_{\text{HCl}}[\text{HCl}]}{1 + K_{\text{HCl}}[\text{HCl}]} \quad (8)
\]

Because hydrochloric acid can be present only as \(\text{RN} \cdot \text{H}^+ \cdot \text{Cl}^-\) in the organic phase, the vertical axis in Figure 6 is the left side in Eq. (8). Equation (9) is obtained from Eq. (8):

\[
\frac{[\text{RN}]}{[\text{RN} - \text{HCl}]} = \frac{1}{K_{\text{HCl}}[\text{HCl}]} + 1 \quad (9)
\]

From the slope of the relationship between the reciprocal value of \([\text{HCl}]_{\text{org.eq.}}/\text{[extractant]}_{\text{org.ini}}\) and that of \([\text{HCl}],\) the extraction equilibrium constants \(K_{\text{HCl}}\) were evaluated as 10.4 [M\(^{-1}\)] for EH-A-F and 163 [M\(^{-1}\)] for B-A-EH, respectively. B-A-EH has a higher extractability for hydrochloric acid than EH-A-F probably because of its higher basicity. Because the extraction of Pd(II) is affected by hydrochloric acid, B-A-EH showed a lower Pd(II) extractability than EH-A-F. Consequently, EH-A-F should show a good extractability for Pd(II) because of its moderate basicity.

The results in Figure 4 show the effect of equilibrium hydrochloric-acid concentration on the distribution ratio of Pd(II) with EH-A-F (Figure 7). The slope of the relationship between \(\log D\) versus the logarithm of the equilibrium hydrochloric-acid concentration is \(-4\). Therefore, the presence of hydrogen and/or chloride ions interferes with the extraction of Pd(II).

Because hydrogen and chloride ions are involved in the extraction reaction of Pd(II) using EH-A-F, the effect of the hydrogen ion at a constant chloride-ion concentration and that of the chloride ion at a constant hydrogen-ion concentration was studied by adding lithium chloride. Figure 8 shows the effect of
hydrogen ions on the extraction of Pd(II) at a constant chloride-ion concentration ([Cl\(^{-}\)] = 1.0 M). The slope of the relationship between \( \log D \) versus the logarithm of the equilibrium hydrogen ion concentration is \(-1\). The result suggests that one hydrogen ion is released by the extraction of Pd(II). Figure 9 shows the effect of the chloride ion on the extraction of Pd(II) at a constant hydrogen-ion concentration ([H\(^{+}\)] = 0.5 M). The slope of the relationship between \( \log D \) versus the logarithm of the equilibrium chloride-ion concentration is \(-3\). The result suggests that three chloride anions are released on the extraction of Pd(II).

Figure 10 shows the effect of the EH-A-F concentration on the distribution ratio of Pd(II). The slope of the relationship between \( \log D \) versus the logarithm of the equilibrium concentration of EH-A-F is 2, which indicates that two EH-A-F molecules take part in the extraction of Pd(II). The stoichiometry agrees with that of the complex between EH-A-EH and Pd(II) reported in a previous paper [14]. Pd(II) is present as a divalent anion PdCl\(_4^{2-}\) on the basis of stability constants [24]. From the results of the slope analysis, the extraction reaction for Pd(II) using protonated EH-A-F can be expressed as shown in Eqs. (4) and (10):

\[
2\text{RN} \cdot \text{HCl} + \text{PdCl}_4^{2-} \rightleftharpoons \text{RN(RNH)} \cdot \text{PdCl}_3 + \text{H}^+ + 3\text{Cl}^{-}
\]  

The extraction equilibrium constant for Pd(II) \( K_{\text{Pd(II)}} \) is given by Eq. (11):

\[
K_{\text{Pd(II)}} = \frac{[\text{RN(RNH)} \cdot \text{PdCl}_3][\text{H}^+][\text{Cl}^{-}]^3}{[\text{RN} \cdot \text{HCl}]^2[\text{PdCl}_4^{2-}]} \tag{11}
\]

and the distribution ratio of Pd(II) between the organic and aqueous phases is defined as:

\[
D = \frac{[\text{Pd(II)}]_{\text{org,eq}}}{[\text{Pd(II)}]_{\text{aq,eq}}} = \frac{[\text{RN(RNH)} \cdot \text{PdCl}_3]}{[\text{PdCl}_4^{2-}]} \tag{12}
\]

Figure 9. Effect of chloride ion on the extraction of Pd(II) at a constant hydrogen-ion concentration. [EH-A-F] = 5.0 mM, [H\(^{+}\)]\(_{\text{ini}}\) = 0.5 M, [Cl\(^{-}\)]\(_{\text{ini}}\) = 0.5–1.0 M (by adding LiCl), [Pd(II)]\(_{\text{ini}}\) = 0.1 mM.

Figure 10. Effect of the concentration of EH-A-F on the distribution ratio of Pd(II). [EH-A-F] = 1.0–10.0 mM, [HCl]\(_{\text{ini}}\) = 0.6 M, [Pd(II)]\(_{\text{ini}}\) = 0.1 mM.
Based on a mass balance of the extractant, the initial concentration of extractant $[\text{RN}]_{\text{ini}}$ can be expressed by Eq. (13):

$$[\text{RN}]_{\text{ini}} = [\text{RN}] + [\text{RN} \cdot \text{HCl}] + [\text{RN} \cdot \text{RN} \cdot \text{HCl}^+]$$  

(13)

Because the initial concentration of extractant $[\text{RN}]_{\text{ini}}$ is in excess of that of Pd(II), Eq. (13) can be approximated by Eq. (14):

$$[\text{RN}]_{\text{ini}} \approx [\text{RN}] + [\text{RN} \cdot \text{HCl}]$$  

(14)

Eq. (15) is obtained from Eq. (8):

$$[\text{RN} \cdot \text{HCl}] = \frac{K_{\text{HCl}[\text{HCl}] [\text{RN}]_{\text{ini}}}}{1 + K_{\text{HCl}[\text{HCl}]}}$$  

(15)

By combining Eqs. (11), (12) and (15), Eq. (16) in its logarithmic form can be obtained:

$$\log D = \log K_{\text{Pd(II)}} + 2 \log K_{\text{HCl}} + \log[H^+] + 2 \log[\text{RN}]_{\text{ini}} - \log[\text{Cl}^-] - 2 \log(1 + K_{\text{HCl}[\text{HCl}]})$$  

(16)

The experimental log$D$ data for the extraction of Pd(II) using EH-A-F based on the results in Figures 8, 9, and 10 are plotted in Figure 11. The extraction equilibrium constants ($K_{\text{Pd(II)}}$) of Pd(II) were evaluated from the intercept of the straight line with the ordinate of Figure 11 as $1.66 \times 10^4$ [M$^2$]. Because the theoretical curves that use calculated values agree with the experimental data in Figures 8, 9, and 10, the extraction equilibrium of Pd(II) using EH-A-F agrees with Eqs. (4) and (10).

![Figure 11. Logarithmic distribution ratio of Pd(II) using EH-A-F as a function of the concentrations of the hydrogen ion, chloride ion, and EH-A-F. The solid line is the theoretical line.](image-url)
3.4. Back extraction of Pd(II)

Table 1 summarizes the back-extraction percentage of Pd(II) extracted using EH-A-F and various back-extraction agents. Pd(II) was not stripped from the organic phase by using distilled water, 0.1 M HCl, or 1.0 M HCl. Pd(II) was not extracted by using EH-A-F at 3.0–8.0 M HCl, however, back extraction by using 3.0 M HCl was small. Neither nitric acid (1.0 M) nor sulfuric acid (0.05 M) was effective for stripping Pd(II). Thiourea is known to be an effective stripping agent for Pd(II) [25,26]. The addition of thiourea was useful for stripping Pd(II) extracted using EF-A-F. Back extraction using 0.1 M thiourea was relatively high (94.8 %). The mechanism of stripping for Pd(II) from a tertiary amine extractant Alamine 330 by thiourea ((NH₂)₂CS) is regarded as the coordination of the stripping agents to palladium, as shown in the following reaction (Eq. (17)) [26]:

\[
(RNH)_2 \cdot PdCl_4 + 2(NH_2)_2CS \rightleftharpoons 2RN \cdot HCl + PdCl_2((NH_2)_2CS)_2
\] (17)

Similarly, thiourea would coordinate with Pd(II) in EH-A-F system by exchange with a chloride ion.

4. Conclusion

The novel secondary-amine extractant 2-ethylhexylfurfurylamine (EH-A-F) showed a higher Pd(II) extractability in hydrochloric-acid media than many of the secondary-amine extractants. Pd(II) was extracted selectively using EH-A-F from many base metals, such as Fe(III), although precious metals Au(III) and Pt(IV) were also extracted. Pd(II) extraction using amine extractants from hydrochloric-acid media competes with that of hydrochloric acid. EH-A-F had a moderate basicity, which favors Pd(II) extraction compared with hydrochloric acid. The extraction reaction for Pd(II) by using EH-A-F was confirmed by the slope analysis results. Pd(II) was stripped quantitatively from the organic phase by using aqueous thiourea solution. In future, furfural will be a cheaper building block in the biorefinery progress. Therefore, chemicals that bear furfural are a potential new series of extractants for metal ions.

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