



Selective extraction of Pt(IV) over Fe(III) from HCl with an amide-containing tertiary amine compound



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ABSTRACT

The separation properties of Pt(IV) over Fe(III) in HCl solutions using *N*-2-ethylhexyl-bis(*N*-di-2-ethylhexyl-ethylamide)amine (EHBAA) were investigated and then compared with those using the conventional extractant tri-*n*-octylamine (TOA). Also, the structural analyses of Pt(IV) in both of the aqueous (HCl solution) and organic (EHBAA in *n*-dodecane–2-ethylhexanol solution) phases were performed with EXAFS spectroscopy. The extractability of Pt(IV) was much higher with EHBAA than with TOA in the studied HCl concentration range (0.2–8 M HCl); additionally, EHBAA selectively extracted Pt(IV) over Fe(III) under the condition of [EHBAA] ≤ 0.1 M and [HCl] ≤ 1 M. The Pt(IV) loading capacity of 0.1 M EHBAA was about 9.2 g/L (about 0.05 M). Most of the Pt(IV) extracted with 0.1 M EHBAA from 1 M HCl was stripped with 0.1 M NaOH; the co-extracted Fe(III) was selectively scrubbed with distilled water. The structural studies indicated that the Pt(IV) extracted with EHBAA from 1 M HCl formed an ion-pair complex, [PtCl₆]²⁻·(EHBAA·H)₂.

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1. Introduction

In recent years, platinum has been widely used as an industrial catalyst in the motor vehicle industries (especially, for diesel vehicles and fuel cells), as well as in the silicone and petroleum industries [1–5]. The demand for platinum will probably increase as the prevalence of fuel cell vehicles increases in the future [6]. Therefore, it is indispensable to improve the platinum separation and purification technologies. That requires efficient separation of platinum from highly concentrated iron because iron is one of the main impurities found in platinum recycling processes [4,7,8]. In acidic chloride media, which are commonly used in hydrometallurgical processes involving platinum group metals (PGMs) [9], both Pt(IV) and Fe(III) exist predominantly as their respective chlorometallate anion [10,11]. Accordingly, the selective recovery of Pt(IV) over Fe(III) is quite difficult.

Well-known commercial amines (Alamine304-1, Alamine308, Alamine336, and Aliquat336), tri-isobutylphosphine sulphide (Cyanex 471X), tri-*n*-butylphosphate, and tri-

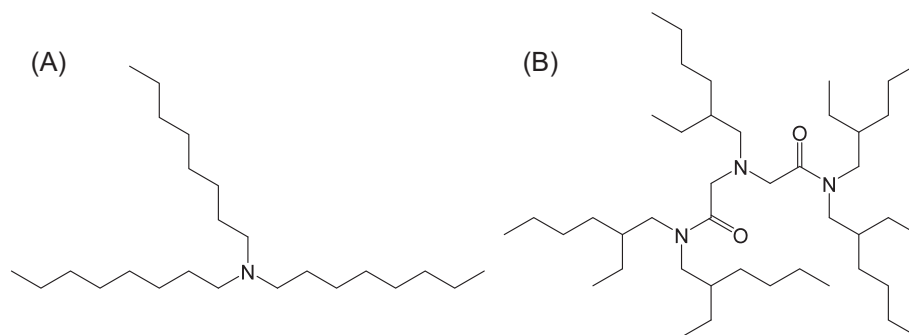
octylphosphineoxide extract both Pt(IV) and Fe(III) simultaneously [4,12,13]. Reddy et al. reported that the selective scrubbing of Fe(III) is achieved with dilute HCl after co-extraction of Pt(IV) and Fe(III) using Alamine336 [14]. Similarly, Pt(IV) in dilute HCl solutions can be separated from Fe(III) using tri-*n*-octylamine (TOA) (Fig. 1) [15], *N*-*n*-octylaniline [16], and *N,N*-di(2-ethylhexyl)amino methylquinoline [17]. In highly concentrated HCl solution, Cyanex 923 [18] or *N,N*-dimethyl-*N,N*-diphenyltetradecylmalonamide [19] can extract Pt over Fe by the addition of ascorbic acid or tin(II) chloride, respectively. However, there appears to be no effective extractant that can separate Pt(IV) from highly concentrated Fe(III) in HCl solutions.

We have recently reported on amide-containing tertiary amines (ACTAs), which exhibit high extraction efficiency for chloro-Rh(III) anions [20,21]. Additional studies, in which we have checked solubility of extractants in practical diluents, formation of a third phase, and selectivity for PGMs from base metals, indicated that *N*-2-ethylhexyl-bis(*N*-di-2-ethylhexyl-ethylamide)amine (EHBAA) (Fig. 1) is the most suitable among ACTA compounds for practical use [22,23].

In this study, we investigated the selectivity of EHBAA and TOA for Pt(IV) over Fe(III) from HCl solutions. Furthermore, we discussed the extraction mechanism in the EHBAA–Pt(IV) system

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by slope analyses of the distribution of HCl and Pt(IV) between the organic and aqueous phases and structural analyses of Pt(IV) in 1 M HCl solution and the extracted complex with EXAFS spectroscopy.

2.1. Reagents

The stock solutions of metal ions were prepared by dissolving the metal chlorides ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Wako Pure Chemical Industries, Tokyo; $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Soekawa Chemical Co., Tokyo) and/or the iron(III) sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, Wako Pure Chemical Industries, Tokyo) into HCl solution. EHBAA (purity: 96%) was gratefully provided by Chemicrea Inc., Tokyo. TOA was purchased from Tokyo Chemical Industry Co. (Tokyo). These extractants were used without further purification. All the other chemicals used in this study were of reagent grade.

2.2. Solvent extraction

EHBAA or TOA diluted with an 80/20 (v/v) *n*-dodecane/2-ethylhexanol mixture and then added to the same volume of a metal-free HCl solution. This mixture was vertically shaken for 30 min in a 10 ml glass tube at an amplitude of 100 mm and a frequency of 200 S/min and then centrifuged. The H^+ concentration in the organic phase was determined by measuring the difference in H^+ concentration between the initial and equilibrated aqueous phases by titration with 0.01 M NaOH using an automatic potentiometric titrator (Kyoto Electronics AT-610, Kyoto). One milliliter of the HCl-equilibrated organic phase and the same volume of HCl solution containing only platinum ions (Pt(IV), 0.1–20 g/L) or mixed metal ions (Pt(IV), 0.1 g/L, and Fe(III), 0.1–50 g/L) were similarly shaken for 60 min and then centrifuged. The extraction of Pt(IV) and Fe(III) reached equilibrium within 10 min under these conditions. A portion of the organic phase and the same volume of an aqueous solution (0.1 M NaOH or distilled water) were shaken for 60 min to strip the metal ions in the organic phase into the aqueous solution. The Pt(IV) loading capacity was determined by measuring the saturated concentration of Pt(IV) in the organic phase (0.1 M EHBAA) after extraction from 1 M HCl. The concentrations of metal ions in the aqueous phase were measured by ICP-AES (Horiba ULTIMA2, Tokyo). The concentrations in the organic phase were calculated from the mass balance of the metal ions before and after extraction. The organic phase/aqueous phase (O/A) volume ratio was 1 for all of the experiments. All the extractions were carried out at room temperature ($23 \pm 2^\circ\text{C}$). The extraction percentage ($E\%$) and distribution ratio (D) were calculated with the equations given below, where $[M]_{init,aq}$, $[M]_{eq,org}$, and $[M]_{eq,aq}$ denote the metal concentration in the initial aqueous phase, the

equilibrated organic phase after extraction and the equilibrated aqueous phase after extraction, respectively.

$$E\% = ([M]_{eq,org}/[M]_{init,aq}) \times 100$$

$$= \{([M]_{init,aa} - [M]_{eq,aa})/[M]_{init,aa}\} \times 100 \quad (1)$$

$$D = [\text{M}]_{\text{eq.org}} / [\text{M}]_{\text{eq.aq}} = ([\text{M}]_{\text{init.aq}} - [\text{M}]_{\text{eq.aq}}) / [\text{M}]_{\text{eq.aq}} \quad (2)$$

2.3. EXAFS measurements and data analyses

As sample solutions, an aqueous Pt(IV) solution (0.1 M Pt(IV) in 1 M HCl) and the Pt(IV) complex extracted with EHBAA were prepared. The latter was obtained by solvent extraction under the condition of 0.5 M EHBAA in an 80/20 (v/v) *n*-dodecane/2-ethylhexanol mixture – 0.1 M Pt(IV) in 1 M HCl, in which Pt(IV) was quantitatively extracted.

The EXAFS measurements were carried out at the BL11XU beamline of SPring-8. The operating energy and the ring current were 8 GeV and ~ 99 mA. The synchrotron radiation was monochromatized using Si(111) crystal monochromators. The Pt-L_{III} edge X-ray absorption spectra were collected in transmission mode using two ion chambers (both filled with N₂) at room temperature (~ 25 °C). Energy calibration was performed using a Pt metal foil (11,563 eV).

The experimental data were analyzed with the software package WinXAS, Ver. 3.1 [24]. The EXAFS oscillation $\chi(k)$ was weighted by k^3 and windowed using a Gaussian window function. The program FEFF8 [25] was used for the calculation of theoretical phases and amplitudes. In the FEFF calculation, by reference to the crystal structure of octahedral hexachloroplatinate $[\text{PtCl}_6]^{2-}$ [26], a regular octahedral PtCl_6 structure, in which all the Pt-Cl lengths are the same (2.32 Å), was used. As a result, the following two paths were significant under the condition of $R \leq 5$ Å and the number of legs (nleg) ≤ 4 : (1) the number of the correlation, $N = 6$, $\text{Pt} \rightarrow \text{Cl} \rightarrow \text{Pt}$, nleg = 2, the bond distance, $R = 2.32$ Å; (2) $N = 6$, $\text{Pt} \rightarrow \text{Cl} \rightarrow \text{Pt} \rightarrow \text{Cl}' \rightarrow \text{Pt}$, nleg = 4, $R = 4.64$ Å. Regarding (2), Cl' is located diagonally to Cl (i.e., $N = 1$ $\text{Cl}' \times 6$ $\text{Cl} = 6$). The coordination geometry of Pt(IV) in an aqueous solution is known to be octahedral [10]. For the curve fits for Pt(IV) in 1 M HCl, N was held constant at 6 and the amplitude reduction factor, S_0^2 , was refined. The obtained S_0^2 value (0.89) was fixed during the fit for the Pt(IV) complex extracted with EHBA. The Debye-Waller factor squared, σ^2 (Å²), the shift in threshold energy, ΔE_0 (eV), and R (Å) were allowed to vary in the fit. Error values were determined by the F-test (95% confidence) [27]. The fitting quality was checked using the R-factor: $\{\sum |k^3\gamma(k)_{\text{obs}} - k^3\gamma(k)_{\text{calc}}| / \sum |k^3\gamma(k)_{\text{obs}}|\} \times 100$.

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