Rapid Separation of Palladium(II) from Platinum(IV) in Hydrochloric Acid Solution with Thiodiglycolamide

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Solvent extraction of some platinum group metals (Pd(II), Pt(IV), Rh(III)) and base metals (Fe(III), Cu(II), Zn(II)) in hydrochloric acid solution with *N*,*N*′-dimethyl-*N*,*N*′-di-*n*-octyl-thiodiglycolamide (MOTDA) was investigated. The extraction percentage of Pd(II) with MOTDA was nearly 100%, while MOTDA hardly extracted any of the other metal ions. It is noteworthy that the extraction of Pd(II) was extremely fast compared with the conventional extraction reagent, di-*n*-hexyl sulfide.

Since platinum group metals (PGMs) are extensively used for catalysts, electronic devices, and so on,[1] the recovery of PGMs from their wastes has received much attention. Therefore, the separation of PGMs is one of the most important studies concerning solvent extraction. Among the PGM separations, the Pd(II)/Pt(IV) mutual separation has been extensively investigated due to its difficulty based on their chemically similar properties. The large difference in the extraction rate between Pd(II) and Pt(IV) from aqueous chloride solutions, which is attributable to the extremely inert properties of Pt(IV) compared with Pd(II), is usually applied to their separation.[2] However, the extraction rate of Pd(II) is also much lower than that of base metals, so that a long contact time is required. Such a slow extraction of Pd(II) from aqueous chloride media has been one of the toughest problems for a long time.

Many studies on the extractions of PGMs using various extraction reagents have been reported.[3] Almost all of them have not found acceptance in industry for solvent extraction in spite of their high extractability of PGMs, since they use organic halides and aromatic compounds as diluents, which are not preferable for industrial applications because of their toxicity. Additionally, their synthetic procedures are mostly complicated. In commercial processes, di-*n*-alkyl sulfide compounds have been widely used.[4] They show a high selectivity for the Pd(II) extraction and good stripping properties; however, the extraction of Pd(II) is very slow.

Tridentate diamide compounds have been extensively studied as useful extraction reagents for trivalent lanthanides and actinides.[5] We are considering their application for the extraction of PGMs by introducing a sulfur atom into them, since sulfur-containing extraction reagents can extract metals which belong to soft acids like Pd based on the HSAB theory. In this study, we used *N*,*N*′-dimethyl-*N*,*N*′-di-*n*-octyl-thiodiglycolamide (MOTDA) (Figure 1) as the separation reagent for Pd(II), which is soluble in many organic solvents and simply synthesized. We carried out extractions of Pd(II), Pt(IV), Rh(III) for the PGMs and Fe(III), Zn(II), Cu(II) for the base metals in HCl solutions with MOTDA and compared the extraction rate of Pd(II) by MOTDA with that using the conventional reagent, di-*n*-hexyl sulfide (DHS).

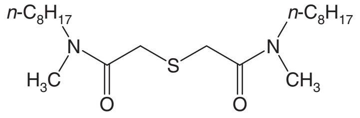

Figure 1. Structure of MOTDA.

MOTDA was synthesized using a two-step procedure.[6] DHS purchased from Wako Pure Chemical Industries, Ltd., was used without further purification. All the other chemicals used in this study were of reagent grade. The extraction of metal ions was carried out batchwise at $23 \pm 1\,^{\circ}\mathrm{C}$. The mixed solvent (80 vol % *n*-dodecane and 20 vol % 2-ethylhexanol) was used as a diluent in order to prevent the third phase formation at the higher HCl and/or metal concentrations. The organic solution was pre-equilibrated with the same volume of HCl solution in the absence of metal ions. After that, 1 mL of the pre-equilibrated organic phase and the same volume of the HCl solution containing 10^{-4} M metal ions (Pd(II), Pt(IV), Rh(III), Fe(III), Zn(II), and Cu(II)) were poured into a 10-mL glass tube, vertically shaken at the amplitude of 100 mm and a frequency of 200 spm, and then centrifuged. The Pd(II) loading capacity was determined by the saturated concentration of Pd(II) in the organic phase (0.1 M MOTDA) in a single extraction for 10 min from a 3.0 M HCl solution, which was evaluated by increasing the initial Pd(II) concentration from 0.01 to 0.1 M. The back-extraction of Pd(II) from 0.05 M MOTDA after the extraction from a 3.0 M HCl solution was done by a 1.0 M thiourea in 1.0 M HCl solution whose volume was ten times greater than that of the organic solution. The metal concentrations in the aqueous phase were measured by ICP-AES (Seiko SPS4000). The concentrations in the organic phase were calculated by the mass balance of the metals before and after the extraction.

Figure 2 shows the extraction percentages of Pd(II) and Pt(IV) from the 3.0 M HCl solution using MOTDA and DHS as a function of the contact time. In both systems, Pt(IV) is hardly extracted during this extraction time. The extraction rate of Pd(II) with DHS is very low as already reported, and thus it takes about 240 min to reach the extraction equilibrium. In contrast, the extraction percentage of Pd(II) with MOTDA reaches almost 100% in the very short contact time of less than 2 min. The extraction systems having such a rapid extraction of Pd(II) from aqueous chloride solutions with a good mutual separation of Pd(II)/Pt(IV) have been limited. Each extraction of Pd(II) from chloride media with 3,3-diethylthietane,[7] *N*-*n*-octylamine,[8] nonylthiourea,[9] and dialkyl sulphoxides[10] is also fast, however, their extraction systems use toxic organic diluents (toluene, chloroform, and xylene) and/or the selectivity for Pd(II) over Pt(IV)

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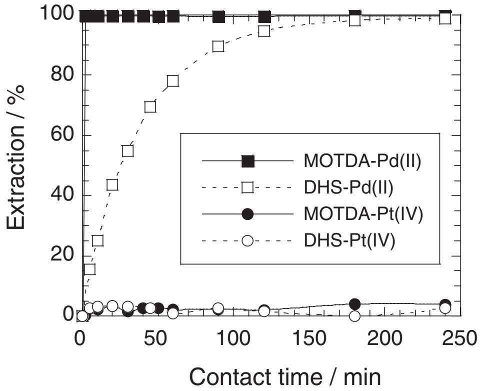

Figure 2. Extraction percentages of Pd(II) and Pt(IV) with MOTDA and DHS as a function of the contact time. Organic phase: 0.05 M MOTDA or DHS; Aqueous phase: 3.0 M HCl.

is decreased with an increase in the contact time.

The plots of the extraction percentages of Pd(II), Pt(IV), Rh(III), Fe(III), Cu(II), and Zn(II) with 0.05 M MOTDA vs the HCl concentration are shown in Figure 3. Pd(II) is well extracted in the HCl concentration range from 0.2 to 3.0 M. On the other hand, the extractions of the other metals are poor. This indicates that MOTDA efficiently extracts Pd(II) over a wide HCl concentration range without extracting the other metal ions. These extraction patterns, which are obtained at the 90 min contact time, are the same as those obtained at 2 min.

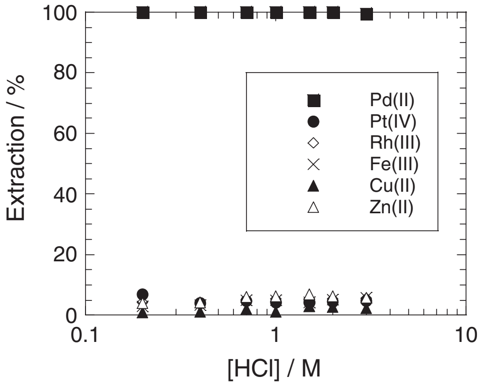

Figure 3. Extraction percentages of precious and base metal ions with MOTDA as a function of the HCl concentration. Organic phase: 0.05 M MOTDA. Extraction time: 90 min.

An evaluation of the Pd(II) loading capacity of 0.1 M MOTDA revealed that, when the initial Pd(II) concentration in the aqueous phase increases, the Pd(II) concentration in the organic phase is first enhanced and then saturated at around 0.06 M. This suggests that two moles of MOTDA are required in order to extract one mole of Pd(II).

The back-extraction of the Pd(II) using a 1.0 M thiourea in 1.0 M HCl solution showed that over 94% of the 0.06 M Pd(II) was transferred to the aqueous phase within a contact time of 10 min.

In summary, the new extraction reagent, MOTDA, is promising for practical use because of its good separation properties for Pd(II) (i.e., high selectivity, quantitative, and rapid extraction, and easy stripping).

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6 Thiodiglycolic acid was converted to thiodiglycolic chloride by refluxing a solution of thiodiglycolic acid dissolved in thionyl chloride with a small amount of *N*,*N*-dimethylformamide for 3 hours at 50 °C. After removing the thionyl chloride, the crude thiodiglycolic chloride remained as a dark brown oil. The crude extract was dropwise added to a mixed solution of triethylamine and *N*-methyloctylamine in chloroform at 10 °C. The resulting solution was then refluxed with stirring for 3 h at 60 °C. After cooling to room temperature, the organic solution was successively washed with water, 1 M HCl and a 5% aq. sodium carbonate solution. The organic phase was next dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was purified by column chromatography (elution with 3:2 *n*-hexane:ethylacetate). The yield of the product based on the thiodiglycolic acid was 48%. Its purity was over 98% on the basis of ^{1}H NMR and gas chromatography.

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