

### 3 M의 염산용액에서 팔라듐(II), 백금(IV), 이리듐(IV) 및 로듐(III)의 분리를 위한 용매추출

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### Solvent Extraction for the Separation of Pd(II), Pt(IV), Ir(IV) and Rh(III) from 3 M Hydrochloric Acid Solution

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#### 요 약

LIX 63 은 6 M의 염산용액에서 백금(IV), 이리듐(IV) 및 로듐(III)에 비해 팔라듐(II)에 대한 선택성이 크다. 또한 염산용액의 농도는 이리듐과 LIX 63간에 일어나는 산화-환원반응에 큰 영향을 미친다. 따라서 상기 4개의 백금족 금속을 함유한 3 M의 염산용액에서 LIX 63에 의한 분리성을 검토하였다. 3 M의 염산용액에서 LIX 63은 오직 팔라듐만을 추출했으며, 6 M의 염산용액에 비해 추출율이 높았다. TBP를 사용하면 팔라듐 추출여액으로부터 백금만을 추출하는 것이 가능하였다. 백금 추출후 NaClO<sub>3</sub>로 추출 여액에 함유된 이리듐을 산화시킨 다음 Aliquat 336를 접촉시키면 이리듐만이 추출되었다. 각각의 용매추출단계에 대해 최적의 탈거조건을 구했다. 본 논문의 공정으로 4개의 백금족 금속을 3 M의 염산용액에서 분리하는 것이 가능하였다.

주제어 : 팔라듐, 백금, 이리듐, 로듐, 용매추출

#### Abstract

LIX 63 showed a selectivity for the extraction of Pd(II) over other PGMs, such as Pt(IV), Ir(IV) and Rh(III) from 6 M HCl solution. Moreover, HCl solution has significant effect on the oxidation-reduction reaction between Ir(IV) and LIX 63. Therefore, the applicability of employing LIX 63 for the separation of the 4 PGMs was investigated from 3 M HCl solution. From 3 M HCl solution, only Pd(II) was selectively extracted by LIX 63 and its extraction percentage was higher than from 6 M HCl solution. Extraction of the Pd(II) free raffinate with TBP led to the selective extraction of Pt(IV). After oxidation of Ir(III) with NaClO<sub>3</sub> to Ir(IV), extraction of the Pt(IV) free raffinate with Aliquat 336 selectively extracted Ir(IV). For each extraction step, optimum stripping conditions were obtained. By this process, it was possible to separate the 4 PGMs by solvent extraction from 3 M HCl solution.

**Key words** : Palladium, Platinum, Iridium, Rhodium, Solvent extraction

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## 1. Introduction

Natural resources for platinum group metals (PGMs), such as platinum (Pt), palladium (Pd), iridium (Ir) and rhodium (Rh) are limited but their demand is increasing. Therefore, it is important to recover these metals with high purity from secondary resources. After leaching of PGMs from the secondary resources by using strong hydrochloric acid solution in presence of an oxidizing agent, the PGMs are separated from the leaching solution by solvent extraction<sup>1-6</sup>, ion exchange<sup>7</sup> and precipitation<sup>8</sup>.

Especially, many works have been reported on the separation of PGMs by solvent extraction<sup>4,9-14</sup>. Most of the developed processes are complicated and complete separation from each PGM is difficult. In a previous study, Pt(IV) can be selectively extracted over Pd(II) from 6 M HCl solution using the mixture of Aliquat 336 and TBP and the mixture of thiourea and HCl solution is used for stripping<sup>15</sup>. The separation of Ir(IV) and Rh(III) from HCl solution is possible by employing the mixture of Aliquat 336 and TBP<sup>16</sup>. The mixture of thiourea and HCl could strip Ir(IV) and Rh(III) from the loaded organic. However, the co-extraction of Pd(II) or Rh(III) was so high that the separation efficiency of these metals was low.

A new process for the separation of Pd(II), Pt(IV), Ir(IV) and Rh(III) from 6 M HCl solution has been reported by using solvent extraction with LIX 63<sup>17</sup>. Optimum conditions for the separation of Pd(II), Pt(IV), Ir(IV) and Rh(III) was found and pure solutions of these metals was obtained. According to this study, it was found that some of Ir(IV) was reduced to Ir(III) during the extraction with LIX 63. In general, the Ir(III)-chloro complexes cannot be extracted by amines, which makes the separation of Ir(IV) and Rh(III) complex. Moreover, it has been also reported that HCl concentration has a significant effect on the oxidation-reduction reaction between LIX 63 and Ir(IV)<sup>18</sup>. Therefore, it is necessary to verify the applicability of the developed separation process using LIX 63 to lower concentration of HCl. In this work, solvent extraction experiments were performed from 3 M HCl solution to verify this process and to investigate the optimum extraction and stripping

conditions. For this purpose, LIX 63-TBP- Aliquat 336 was sequentially contacted to the synthetic solution of 3 M HCl containing Pd(II), Pt(IV), Ir(IV) and Rh(III).

## 2. Materials and Methods

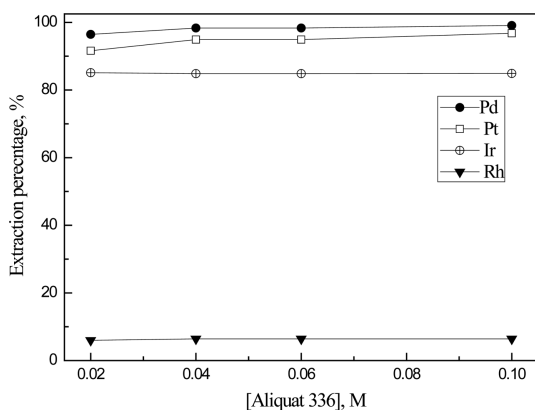
A synthetic solution containing Pd(II), Pt(IV), Ir(IV) and Rh(III) was prepared by dissolving appropriate amounts of PtCl<sub>4</sub> (99.9%), PdCl<sub>2</sub> (99.9%), H<sub>2</sub>IrCl<sub>6</sub> (99.5%) and RhCl<sub>3</sub>·xH<sub>2</sub>O (99.9%) purchased from Alfa-Aesar. The concentration of each metal and HCl in the synthetic solution was fixed at 100 ppm and 3 M, respectively. Commercial extractants, such as LIX 63 (BASF Co.), TBP (Yakuri Pure Chemical Co.) and Aliquat 336 (BASF Co.) were used without further purification. Kerosene (Samchun Pure Chem. Co.) was used as a diluent.

Solvent extraction experiments were performed by mixing equal volume (10 mL) of aqueous and organic phases for 30 min using a wrist action shaker (Burrel, model 75). After equilibrium, the two phases were separated using a separating funnel. All the experiments were performed at room temperature. Metal ion concentrations in the aqueous phase before and after extraction were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Spectro Arcos). The concentration of metal ions in the loaded organic phase was calculated by mass balance.

## 3. Results and Discussion

### 3.1. Selective extraction of Pd(II) by LIX 63

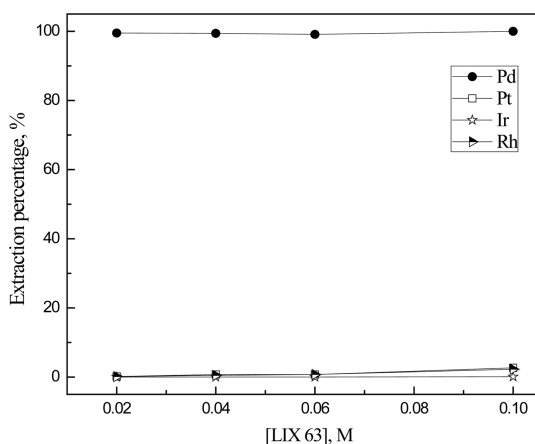
LIX 63 and Aliquat 336 can extract Pt(IV) and Pd(II) from high HCl concentration<sup>17</sup>. In order to investigate the separation of four PGMs from 3 M HCl concentration by LIX 63 and Aliquat 336, the concentration of these two extractants was varied from 0.02 to 0.1 M. In these experiments, the concentration of Pd(II), Pt(IV), Ir(IV) and Rh(III) was fixed at 100 ppm. The extraction behavior of Pt(IV), Pd(II), Ir(IV) and Rh(III) by Aliquat 336 is shown in Fig. 1. Most of Pt(IV), Pd(II) and Ir(IV) were extracted at any Aliquat 336 concentration range, while the extraction percentage of Rh(III) was negligible at the same condition. Fig. 1 indicates that it is difficult



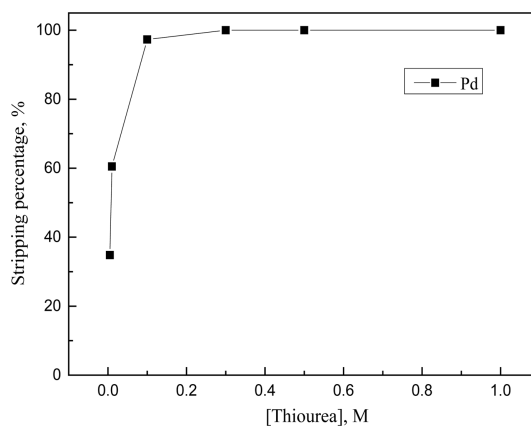
**Fig. 1.** Effect of Aliquat 336 concentration on the extraction of Pd(II), Pt(IV), Ir(IV) and Rh(III). Aqueous: Pd = Pt = Ir = Rh = 100 ppm, [HCl] = 3 M; [Aliquat 336] = 0.003-0.1 M.

to separate the PGMs by employing Aliquat 336 from 3 M HCl solution.

Fig. 2 shows LIX 63 can selectively extract Pd(II) over Pt(IV), Ir(IV) and Rh(III). Most Pd(II) was extracted at any LIX 63 concentration range, while the extraction percentage of Pt(IV), Ir(IV) and Rh(III) was negligible. In the HCl solution, Pd(II), Pt(IV), Ir(IV) and Rh(III) exist as anionic species, such as  $\text{PtCl}_6^{2-}$ ,  $\text{PdCl}_4^{2-}$ ,  $\text{IrCl}_6^{2-}$  and  $\text{RhCl}_6^{3-}$ <sup>19,20</sup>. Selective extraction of Pd(II) over other three PGMs is ascribed to the ease of ligand donation

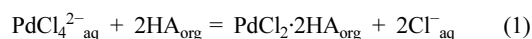


**Fig. 2.** Effect of LIX 63 concentration on the extraction of Pd(II), Pt(IV), Ir(IV) and Rh(III). Aqueous: Pd = Pt = Ir = Rh = 100 ppm, [HCl] = 3 M; [LIX 63] = 0.02-0.1 M.



**Fig. 3.** Effect of thiourea concentration on the stripping of Pd(II) from the loaded 0.02 M LIX 63. [Pd(II)]<sub>org</sub> = 99.5 ppm; [Thiourea] = 0.005-1 M.

of  $\text{PdCl}_4^{2-}$  compared to other anionic species<sup>17</sup>. Compared to the reported results in previous study<sup>17</sup>, the extraction percentage of Pd(II) from 3 M HCl was higher than that from 6 M HCl at the same LIX 63 concentration. This agrees well with the extraction reaction of Pd(II) by LIX 63 reported in a previous study<sup>17</sup> (see Eq. (1)).

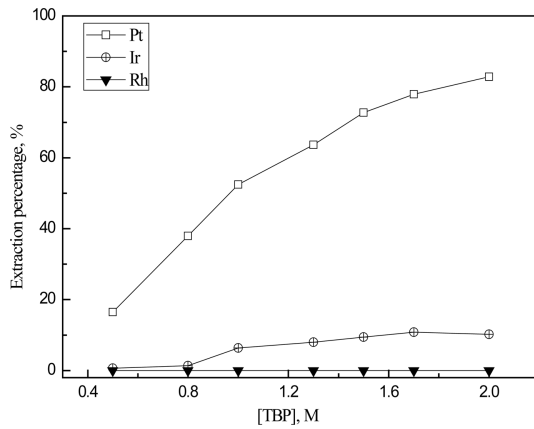


where HA represents LIX 63 and the subscripts aq and org denote the aqueous and organic phase, respectively.

For stripping experiments, the loaded LIX 63 was prepared by extracting the synthetic solution of 3 M HCl with 0.02 M LIX 63. The concentration of Pd(II) in the loaded LIX 63 was 100 ppm, while no other metals were co-extracted in this condition. Thiourea was chosen as a stripping agent and its concentration was varied from 0.05 to 1 M. Fig. 3 shows the variation in stripping percentage of Pd(II) with thiourea concentration. The stripping percentage of Pd(II) increased from 35 to 99% as thiourea concentration increased from 0.005 to 0.3 M and then was constant with the further increase of thiourea concentration. From this data, 0.3 M thiourea was chosen as an optimum condition to strip Pd(II) from the loaded LIX 63.

### 3.2. Selective extraction of Pt(IV) by TBP

After separation of Pd(II), the Pd(II) free raffinate

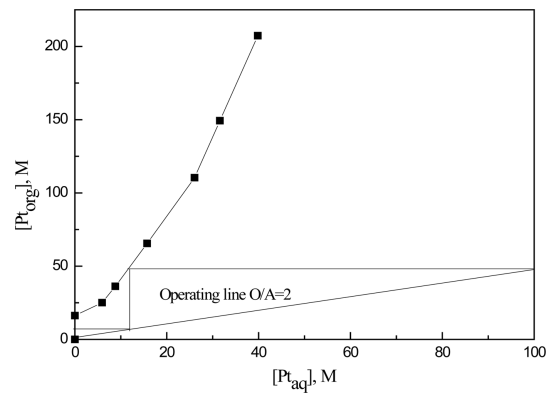


**Fig. 4.** Effect of TBP concentration on the extraction of Pt(IV), iridium and Rh(III). Raffinate: Pt = Ir = Rh = 100 = ppm, [HCl] = 3 M; [TBP] = 0.5-2 M.

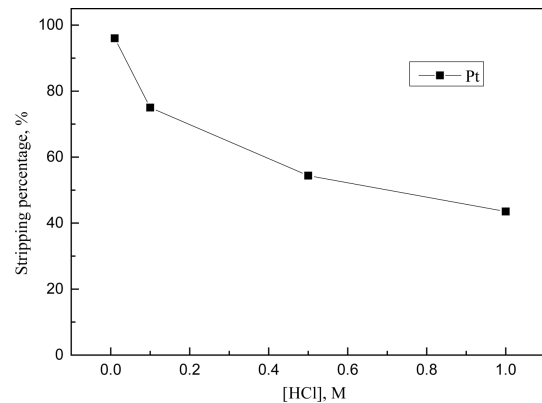
contained 100 ppm of Pt(IV), iridium and Rh(III) at 3 M HCl. The raffinate was contacted to TBP (0.5-2 M) to investigate the extraction behaviour of these metals. The extraction percentage of Pt(IV) increased steadily from 18 to 80% as TBP concentration increased from 0.5 to 2 M, while the co-extraction of iridium and Rh(III) was negligible (see Fig. 4). The negligible extraction of Rh(III) by TBP in our condition can be ascribed to the formation of  $\text{RhCl}_5(\text{H}_2\text{O})_2^{2-}$  which cannot be extracted by TBP<sup>16</sup>. It has been reported that during extraction with LIX 63, Ir(IV) can be reduced to Ir(III) and this reduced Ir(III) cannot be extracted by TBP<sup>17</sup>.

In order to find the theoretical number of stages for complete extraction of Pt(IV) from Pd(II) free raffinate containing 100 ppm of Pt(IV), Ir(III) and Rh(III) at 3 M HCl, extraction isotherms for Pt(IV) was obtained by contacting the raffinate with 2 M TBP at different O/A ratios from 1:5 to 5:1. McCabe-Thiele diagram indicates that two theoretical extraction stages are needed to extract most of Pt(IV) at an O/A ratio of 2:1 using 2 M TBP (see Fig. 5). The batch simulation experiments for two stages counter-current extraction were performed with 2 M TBP at an O/A ratio of 2:1. From the batch simulation experiments, it was found that 99.9% of Pt(IV) was extracted from the Pd(II) free raffinate.

Previous work indicates that the Pt(IV) in the loaded TBP can be stripped by using weak HCl solution<sup>17</sup>. In



**Fig. 5.** Extraction isotherm of Pt(IV) by 2 M TBP. Raffinate, Pt = Ir = Rh = 100 ppm; [HCl] = 3 M.

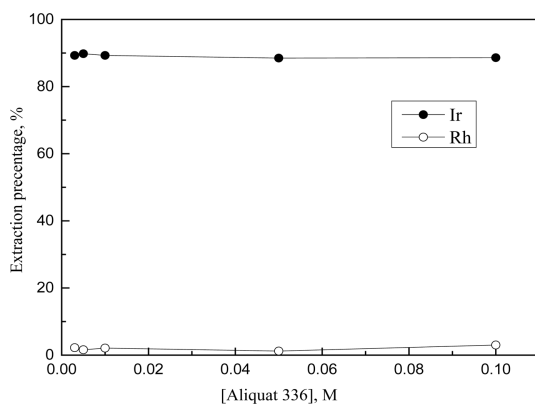


**Fig. 6.** Effect of HCl concentration on the stripping of Pt(IV) from the loaded 2 M TBP.  $[\text{Pt}(\text{IV})]_{\text{org}} = 84$  ppm; [HCl] = 0.01-1 M.

order to verify this, HCl concentration was varied from 0.01 to 1 M to strip Pt(IV) from the loaded TBP where the concentration of Pt(IV) was 84 ppm. Fig. 6 shows that the stripping percentage of Pt(IV) from the loaded TBP decreased from 96 to 43.5% as HCl concentration increased from 0.01 to 1 M.

### 3.3. Selective extraction of Ir(IV) by Aliquat 336

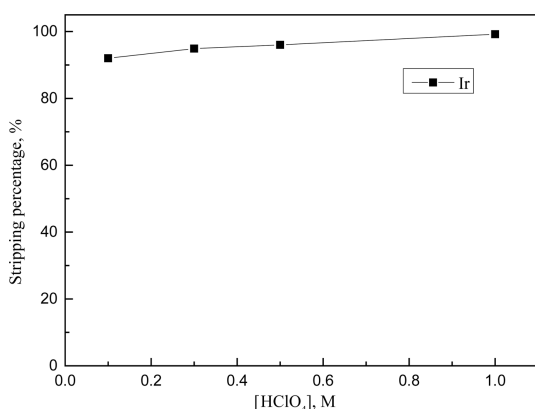
Since some of Ir(IV) is reduced to Ir(III) during the extraction with LIX 63, it was difficult to extract the remaining iridium and Rh(III) after the extraction by LIX 63 and TBP<sup>17</sup>. Therefore, oxidation of Ir(III) to Ir(IV) is necessary to separate iridium and Rh(III). For this purpose,  $8 \times 10^{-4}$  M  $\text{NaClO}_3$  was added as an oxidiz-



**Fig. 7.** Effect of Aliquat 336 concentration on the extraction of Ir(IV) and Rh(III). Raffinate: Ir = 91 ppm; Rh = 100 = ppm, [HCl] = 3 M; Oxidizing agent =  $8 \times 10^{-4}$  M NaClO<sub>3</sub>; [Aliquat 336] = 0.003-0.1 M.

ing agent to the Pd(II) and Pt(IV) free raffinate containing Ir(III) and Rh(III). Aliquat 336 (0.003 to 0.1 M) was contacted to the Pd(II) and Pt(IV) raffinate. Fig. 7 shows that most of the Ir(IV) was extracted at any Aliquat 336 concentration, while the extraction percentage of Rh(III) was negligible. According to the obtained results, 0.01 M Aliquat 336 was chosen for the separation of Ir(IV) and Rh(III) from the raffinate at 3 M HCl.

At the optimum extraction condition for the separation of Ir(IV) from Rh(III), the concentration of Ir(IV) in the loaded 0.01 M Aliquat 336 was 82 ppm Ir(IV). HClO<sub>4</sub> solution was employed as a stripping reagent



**Fig. 8.** Effect of HClO<sub>4</sub> concentration on the stripping of Ir(IV) from the loaded 0.01M Aliquat 336. [Ir(IV)]<sub>org</sub> = 82 ppm; [HClO<sub>4</sub>] = 0.1-1 M.

and its concentration was varied from 0.1 to 1 M. Fig. 8 shows that the stripping percentage of Ir(IV) increased from 92 to 99.2% as HClO<sub>4</sub> concentration increased from 0.1 to 1 M.

#### 4. Conclusions

The possibility of complete separation of 4 PGMs (Pd(II), Pt(IV), Ir(IV) and Rh(III)) was investigated from 3 M HCl solution by solvent extraction. First, only Pd(II) was extracted from the synthetic solution by LIX 63 and thiourea could strip this Pd(II) from the loaded LIX 63. Second, employment of TBP resulted in selective extraction of Pt(IV) from the Pd(II) free raffinate. The Pt(IV) in loaded TBP was completely stripped by weak HCl solution. After adding NaClO<sub>3</sub> to the raffinate after Pt(IV) extraction as an oxidizing agent, Ir(IV) was selectively extracted by Aliquat 336 and the Ir(IV) in the loaded Aliquat 336 was completely stripped by HClO<sub>4</sub> solution. Our data indicates that sequential extraction with LIX 63-TBP-Aliquat 336 can separate the 4 PGMs from both 3 M and 6 M HCl solution.

#### Acknowledgements

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