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# Extraction of Palladium(II) from Hydrochloric Acid Solutions by Solvent Extraction with Cationic Mixtures

Hoai Thanh Truong <sup>1</sup>, Man Seung Lee <sup>1,\*</sup> and Seong Ho Son <sup>2</sup>

<sup>1</sup> Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Jeollanamdo 534-729, Korea; truonghoaithanhcm@gmail.com

<sup>2</sup> Korea Institute of Industrial Technology, Incheon Technology Service Centre, 7-47, Songdo-dong, Incheon 406-840, Republic of Korea ; shson@kitech.re.kr

\* Correspondence: mslee@mokpo.ac.kr (M.S. Lee); Tel.: +82 61 450 2492

**Abstract:** Cyanex 301 and LIX 63 can selectively extract Pd(II) over Pt(IV) from strong hydrochloric acid solutions. Therefore, solvent extraction experiments have been performed by extractant mixtures containing either Cyanex 301 or LIX 63 and the extraction behavior of Pd(II) was compared. Among the mixture of Cyanex 301, the highest synergistic enhancement coefficient was achieved by mixing Cyanex 301 and TOPO. However, it was very difficult to strip the Pd(II) from the loaded mixture. Among the mixture of LIX 63, the mixture of LIX 63 and Alamine 336/TOPO enhanced the extraction of Pd(II). Although the synergistic coefficient by Cyanex 301 + TOPO was higher than that by LIX 63 + Alamine 336, the Pd(II) in the loaded mixture of LIX 63 and Alamine 336 was easily stripped by thiourea.

**Keywords:** palladium; hydrochloric acid; Cyanex 301; LIX 63; synergism

## 1. Introduction

Palladium (Pd) is widely employed in the manufacture of advanced materials for automobile, chemical, and electronic industry [1,2]. Since the consumption of Pd increases each year, the recovery of this metal from either ores or secondary resources is important. Several methods are used in the separation of Pd(II) from the leaching solutions of HCl or HNO<sub>3</sub>, such as precipitation [3], ion exchange [2,4], and solvent extraction [5-12]. Among these methods, solvent extraction is suitable for the separation of platinum group metals (PGMs) due to its high selectivity and the purity of metals thus obtained [9].

Various extractants, such as LIX 63, LIX 84I, PC 88A, Cyanex 301, Alamine 336, TOA, TBP, and TOPO have been employed to separate Pd(II) from hydrochloric acid solutions in presence of other metals. Although Pd(II) can be extracted by Cyanex 301 but the stripping is very difficult owing to the strong interaction between Pd(II) and Cyanex 301 [6,11]. Low acid concentration is favorable for the extraction of Pd(II) with LIX 84I and PC 88A [13,14]. Most amines can extract Pd(II) with high extraction efficiency but the co-extraction of Pt(IV) is high and thus the separation factor is generally low [10,15]. Third phase formation and low extraction percentage are drawbacks in the extraction of Pd(II) by TBP and TOPO. In order to solve these problems, many attempts have been tried by using mixture systems. Lee and Chung [8] reported that a mixture of TOPO and TTA could enhance the extraction of Pd(II). The use of either TOPO or Aliquat 336 with LIX 63 improves the extraction of Pd(II) [16].

In our work on the extraction of Pd(II) from hydrochloric acid solution, it was found that LIX 63 and Cyanex 301 could extract Pd(II) from HCl solution [11,17]. However, the extraction percentage of Pd(II) with LIX 63 was decreased rapidly when HCl concentration was higher than 7 M. Although Pd(II) was completely extracted by Cyanex 301 in the HCl concentration range from 0.5 to 9 M, it was very difficult to strip the Pd(II) in the loaded Cyanex 301 [11]. Although various extractant mixtures have been employed to separate PGMs, only a few papers have reported the synergistic extraction of

Pd(II). In this work, the solvent extraction of Pd(II) by some new extractant mixtures was investigated. For this purpose, several cationic (Cyanex 272/PC 88A/D2EHPA), amine (Alamine 336), and neutral (TBP and TOPO) extractants were mixed with either Cyanex 301 or LIX 63. The extraction behavior of Pd(II) among these mixtures was compared. Moreover, the stripping of the Pd(II) from the loaded mixture was obtained.

## 2. Experimental

### 2.1. Reagents and chemicals

The commercial extractants, Cyanex 272 and Cyanex 301 were purchased from Cytec Inc. LIX 63 and Alamine 336 were supplied by BASF Co. D2EHPA, PC 88A, and TBP were products of Daihachi Chem. and Yakuri Pure Chemical Co., respectively. All the extractants were used as received without any further purification. Kerosene (Daejung Co.) was employed as a diluent for the present work.

Stock solution of palladium was prepared by dissolving the necessary amount of PdCl<sub>2</sub> (Sigma-Aldrich, 99.9%). The desired acidity of the synthetic solution was controlled by adding pure HCl solution (Daejung Co., 35%). Ascorbic acid (Samchun Pure Chem. Co., 99.5%) and KI (Daejung Co., 99.5%) were employed to prepare the solutions for the measurement of Pd(II) concentration in the aqueous phase. All other reagents used were of analysis grade.

### 2.2. Solvent extraction procedure

The general extraction and stripping experiments were carried out by shaking equal volume (10 mL) of the aqueous and organic phases for 30 min in a 100 mL screwed cap bottle using a wrist action shaker (Burrell model 75, USA). After separation, the two phases were separated using a separating funnel. All the extraction experiments were done at ambient temperature. The concentration of Pd(II) in the aqueous phase before and after the extraction was determined in the form of iodine complexes by using ultraviolet spectrophotometer (UV-1800, Shimadzu, Japan) [18]. Metal concentration in the organic phase was calculated by mass balance. The synergistic enhancement coefficient (R) is defined as follows

$$R = \frac{D_{A+B}}{D_A + D_B} \quad (1)$$

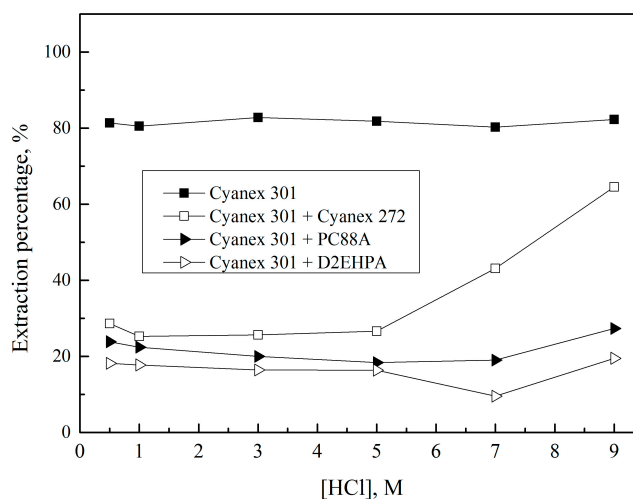
where  $D_A$  and  $D_B$  represent the distribution coefficient of Pd(II) by single A and B and  $D_{A+B}$  represents the distribution coefficient of Pd(II) by the mixture of A and B.

## 3. Results and Discussion

### 3.1. Extraction of Pd(II) with mixture of Cyanex 301 and various extractants

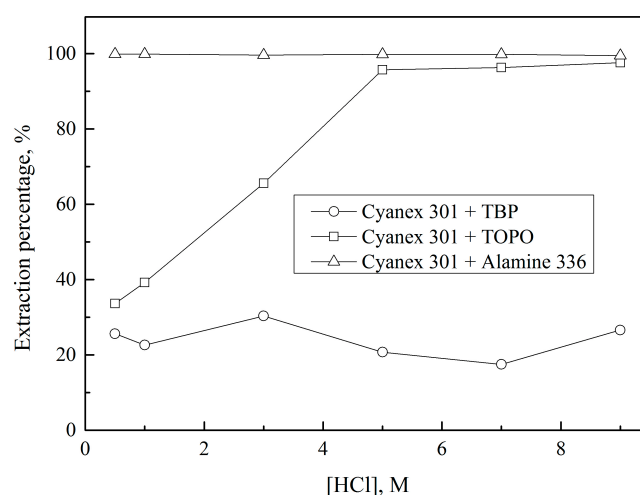
In previous works, we have investigated the extraction of Pd(II) with some single extractants [11]. In that study, Cyanex 301 and LIX 63 were found to selectively extract Pd(II) over Pt(IV) with high efficiency. In order to compare the extraction behavior of Pd(II) between single Cyanex 301 and its mixture with cationic (D2EHPA, PC 88A, and Cyanex 272), neutral (TBP and TOPO), anionic (Alamine 336) extractants, solvent extraction experiments were performed. In these experiment, the concentration of Pd(II) was fixed at 100 mg/L and the concentration of HCl was varied from 0.5 to 9 M. The concentration of Cyanex 301 was fixed at 0.01 M and that of D2EHPA/PC 88A/Cyanex 272/TBP was 0.1 M. In the case of Alamine 336 and TOPO, the concentration was 0.02 and 0.01 M respectively. Figure 1 shows the effect of HCl concentration on the extraction of Pd(II) by single Cyanex 301 as well as its mixture with cationic extractants (Cyanex 272, PC 88A, and D2EHPA). Pd(II) was completely extracted by single Cyanex 301 irrespective of HCl concentration. The extraction percentage of Pd(II) by single Cyanex 301 was higher than that by the mixtures. According to the hard-soft acid base concept, Pd(II) is regarded as a soft acid. Cyanex 301 is a soft base and thus the interaction between Pd(II) and Cyanex 301 should be strong, which can explain the complete

extraction of Pd(II) in the HCl concentration range from 0.5 to 9 M. While the other organophosphorus extractants (D2EHPA, PC 88A, Cyanex 272) contain oxygen and is regarded as a hard base. Therefore, the interaction between Pd(II) and organophosphorus extractants is not so strong that the extraction percentage of Pd(II) by the mixture was lower than that by single Cyanex 301.



**Figure 1.** Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5-9 M. Organic: 0.01 M Cyanex 301, 0.01 M Cyanex 301 + 0.1 M Cyanex 272/PC 88A/ D2EHPA. O/A = 1. Diluent: kerosene.

Figure 2 shows the effect of HCl concentration on the extraction of Pd(II) by the mixture of Cyanex 301 and TBP, TOPO and Alamine 336. Pd(II) was completely extracted by the mixture of Cyanex 301 and Alamine 336. Most of Pd exists as  $\text{PdCl}_4^{2-}$  when HCl concentration is higher than 0.1 M [12] and this Pd(II) can be extracted even by single Alamine 336. Therefore, complete extraction of Pd(II) was obtained by this mixture of Cyanex 301 and Alamine 336.



**Figure 2.** Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5-9 M. Organic: 0.01 M Cyanex 301 + 0.1 M TBP, 0.01 M Cyanex 301 + 0.02 M Alamine 336, 0.01 M Cyanex 301 + 0.01 M TOPO. O/A = 1. Diluent: kerosene.

When Cyanex 301 was mixed with TOPO, the extraction percentage of Pd(II) increased rapidly from 34 to 97% as HCl concentration increased from 0.5 to 5 M and then was kept as a constant with the further increase of HCl concentration up to 9 M. The extraction percentage of Pd(II) by the mixture

of Cyanex 301 and TBP was around 25%. Grigorieva *et al.* [19] and Batchu *et al.* [20] reported that the strength of the interaction between Cyanex 301 and electron-donor additives decreased in the following order TOA > TOPO > TBP, which is in good agreement with our data.

Table 1 shows the enhancement coefficients of Pd(II) by the mixture of Cyanex 301 and several extractants. The enhancement coefficients by most of the mixtures employed in this work were negligible. However, the synergistic effect of the mixture of Cyanex 301 and TOPO became pronounced as HCl concentration increased from 5 to 9 M and the highest enhancement coefficient of 6.4 was obtained at 9 M HCl.

**Table 1.** Synergistic enhancement coefficient (R) of Pd(II) with mixture of Cyanex 301 and various extractants.

[HCl], M	R <sub>Cyanex 272</sub>	R <sub>PC 88A</sub>	R <sub>D2EHPA</sub>	R <sub>TBP</sub>	R <sub>TOPO</sub>	R <sub>Alamine 336</sub>
0.5	0.1	0.1	0.0	0.1	0.1	1.0
1.0	0.1	0.1	0.1	0.1	0.2	1.2
3.0	0.1	0.1	0.0	0.1	0.4	0.3
5.0	0.1	0.1	0.0	0.1	4.4	0.7
7.0	0.2	0.1	0.0	0.1	6.0	0.6
9.0	0.4	0.1	0.1	0.1	6.4	0.2

Where:  $R_A = R_{A + \text{Cyanex301}}$

Figure 2 shows that the extraction of Pd(II) by the mixture of Cyanex 301 and TOPO rose rapidly with the increase of HCl concentration. Therefore, low acid concentration would be favorable for the stripping of Pd(II) from this mixture. Base on of HSAB concept, some hard-soft ligands such as  $\text{SCN}^-$ ,  $\text{CS}_2^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{RCOO}^-$  were chosen for stripping experiments. In the recovery of the PGMs, the concentration of acid is often controlled to 6 M in presence of oxidizing agents [1,5]. The synthetic solution containing 100 mg/L Pd(II) was prepared and HCl concentration was adjusted to 5 M HCl for stripping experiments. These solutions were contacted with mixture of Cyanex 301 and TOPO. After the extraction by the mixture of 0.01 M Cyanex 301 and 0.01 M TOPO, the concentration of Pd(II) in the loaded organic was 97 mg/L Pd(II) and this loaded organic was employed for stripping experiments. Table 2 shows the stripping percentage of Pd(II) by several agents. The stripping percentage was negligible by the stripping agents employed in this work, which could be ascribed to the strong interaction between Pd(II) and sulfur in Cyanex 301 [6,11].

**Table 2.** Stripping of Pd(II) in loaded mixture of Cyanex 301 and TOPO using various reagents.

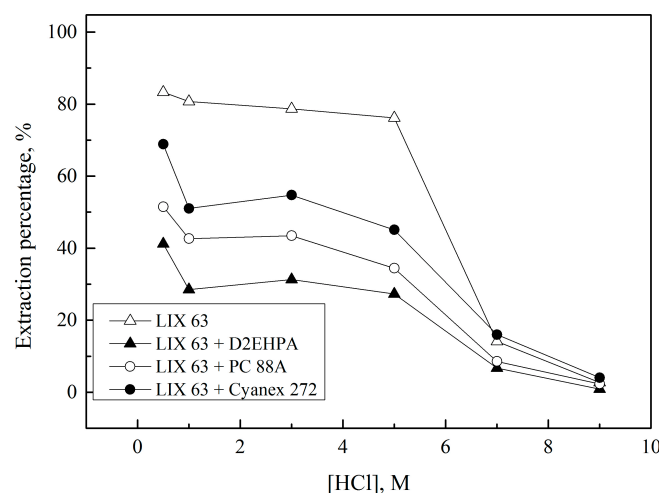
Stripping reagent	Pd(II) stripping, %
0.5 M HCl	0.5
5.0 M HCl	1.0
0.5 M NaSCN	0.5
0.1 M $\text{Na}_2\text{S}_2\text{O}_3$	0.5
0.5 M $(\text{NH}_4)_2\text{CS}$	2.0
0.5 M $\text{Na}_2\text{CO}_3$	0.5
0.5 M Oxalic acid	0.5
0.5 M $(\text{NH}_2)_2\text{CS}$ + 5.0 M HCl	1.0

Loaded organic: Pd-97.0 mg/L; O/A = 1.

3.2. Extraction of Pd(II) with mixture of LIX 63 and various extractants

In order to compare the extraction behavior of Pd(II) by the mixtures between Cyanex 301 and LIX 63, similar experiments were done by using single LIX 63 and its mixture with other extractants. The concentration of LIX 63 was fixed at 0.01 M and that of Cyanex 272/PC 88A/D2EHPA/TBP was 0.1 M, whereas that of TOPO/Alamine 336 was 0.01 M. Figure 3 shows the extraction of Pd(II) by

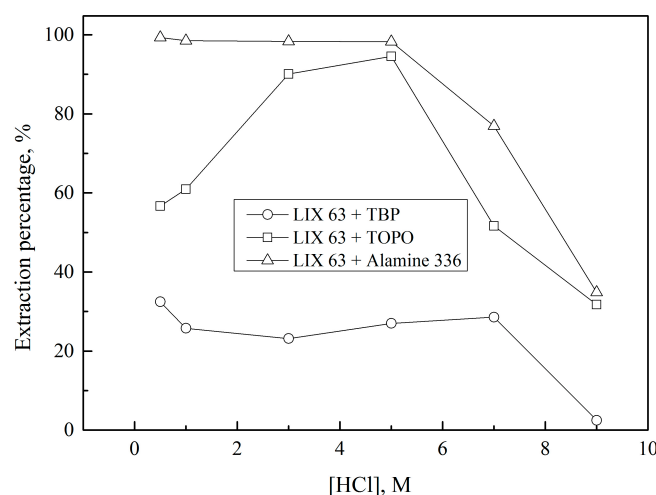
single LIX 63 and its mixtures at several HCl concentrations. As HCl concentration increased from 0.5 to 9 M, the extraction percentage of Pd(II) by single LIX 63 decreased from 83 to 9%.



**Figure 3.** Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5-9 M. Organic: 0.01 M LIX 63, 0.01 M LIX 63 + 0.1 Cyanex 272/PC 88A/D2EHPA. O/A = 1. Diluent: kerosene.

Similar to LIX 63, the extraction of Pd(II) by its mixture with D2EHPA, PC 88A and Cyanex 272 fell down rapidly with the increase of HCl concentration. The extraction percentage of Pd(II) by the mixtures was much lower than that by single LIX 63. The extraction order of Pd(II) was LIX 63 + Cyanex 272 > LIX 63 + PC 88A > LIX 63 + D2EHPA. The reason for the difference in the extraction performance of three mixtures might be related to their structures [21].

In the case of the mixture of LIX 63 and TOPO, the extraction of Pd(II) increased from 58 to 90% as HCl concentration increased from 0.5 to 5 and then declined rapidly with the further increase of HCl concentration to 9 M (see Figure 4).



**Figure 4.** Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5-9 M. Organic: 0.01 M LIX 63 + 0.1 M TBP, 0.01 M LIX 63 + 0.01 M Alamine 336/TOPO. O/A = 1. Diluent: kerosene.

The extraction of Pd(II) by the mixture of LIX 63 and TBP was approximately 25% in the HCl concentration range from 0.5 to 7 M and reduced to zero at 9 M HCl. The difference in the extraction behavior of Pd(II) between TOPO and TBP may be ascribed to the high lipophilicity and polarity of TOPO [22]. The mixture of LIX 63 and Alamine 336 extracted completely Pd(II) in the HCl concentration range from 0.5 to 5 M and the extraction percentage decreased sharply with the further increase of HCl concentration up to 9 M. Liu *et al.* indicated that the interaction between LIX 63 and Alamine 336 in the organic phase could affect the ability to extract the metals [23].

The synergistic coefficient during extraction of Pd(II) with mixtures of LIX 63 and above extractants is shown in Table 3.

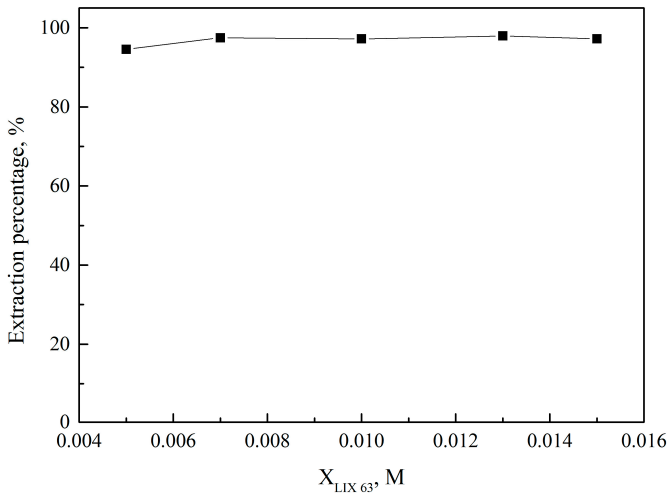
**Table 3.** Synergistic enhancement coefficient (R) of Pd(II) with mixture of LIX 63 and various extractants.

[HCl], M	R <sub>Cyanex 272</sub>	R <sub>PC 88A</sub>	R <sub>D2EHPA</sub>	R <sub>TBP</sub>	R <sub>TOPO</sub>	R <sub>Alamine 336</sub>
0.5	0.4	0.2	0.1	0.1	0.3	2.3
1.0	0.3	0.2	0.1	0.1	0.4	1.2
3.0	0.2	0.2	0.1	0.1	2.2	3.9
5.0	0.4	0.2	0.1	0.1	4.4	8.5
7.0	1.4	0.7	0.5	3.0	5.7	2.6
9.0	5.3	3.0	1.1	3.2	9.6	2.0

Where:  $R_A = R_A + \text{LIX 63}$

From the Table 3, the enhancement coefficient in mixture of LIX 63 and organophosphorous extractants was less than 1. Therefore, addition of Cyanex 272/PC 88A/D2EHPA into LIX 63 system would reduce synergism during the extraction of Pd(II). On the contrary, LIX 63 mixed with TOPO/Alamine 336 enhanced extraction. Although the highest synergistic enhancement coefficient of 9.6 was observed at 9 M with mixing TOPO, the HCl concentration was very high. Among tested mixtures, mixture of LIX 63 and Alamine 336 was suitable for extraction of Pd(II). Thus, this mixture was selected for further experiments.

In order to find an optimum composition of the mixture of LIX 63 and Alamine 336, solvent extraction experiments were performed by varying the concentration of each extractant from 0.005 to 0.015 M, while keeping the total concentration of the mixture to 0.02 M. The concentration of HCl in the synthetic Pd(II) solution was fixed at 5 M. Figure 5 shows the extraction of Pd(II) by the mixture of LIX 63 and Alamine 336. In the experimental ranges tested in this work, Pd(II) was almost completely extracted by the mixture of LIX 63 and Alamine 336.



**Figure 5.** The effect of LIX 63 and Alamine 336 concentration on extraction of Pd(II). Aqueous: Pd = 100 mg/L, [HCl] = 5 M. Organic: [LIX 63] + [Alamine 336] = 0.02 M. O/A = 1. Diluent: kerosene.



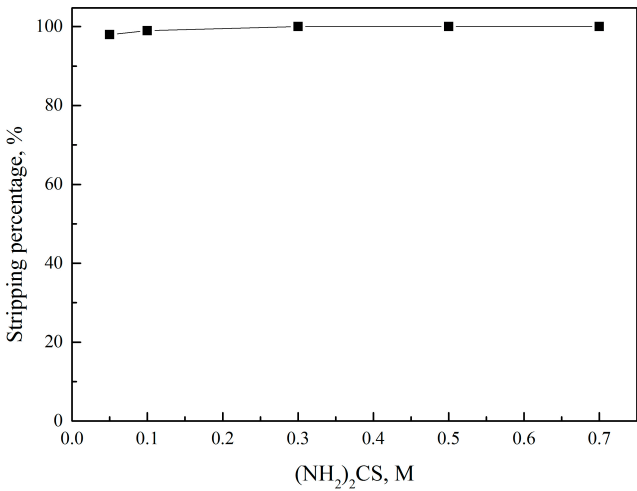
The stripping behavior of Pd(II) from the loaded mixture of LIX 63 and Alamine 336 was investigated. For this purpose, the loaded organic was prepared by extraction with a mixture of 0.01 M LIX 63 and 0.01 M Alamine 336. The concentration of Pd in the loaded mixture was 97 mg/L. In general, thiocyanate and thiosulfate ions are soft ligands and are usually employed as the stripping agents of Pd(II) [4,7]. Further, Pd(II) could be quantitatively stripped by acidic aqueous solutions containing thiourea [17]. Therefore, several agents, such as, HCl, NaSCN, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, (NH<sub>2</sub>)<sub>2</sub>CS, and (NH<sub>2</sub>)<sub>2</sub>CS + HCl, were used in the stripping experiments. Table 4 shows the stripping percentage of Pd(II) by the reagents. The Pd(II) in the loaded organic was completely stripped by (NH<sub>2</sub>)<sub>2</sub>CS. Moreover, the addition of HCl to (NH<sub>2</sub>)<sub>2</sub>CS had negative effect on the stripping of Pd(II). Except (NH<sub>2</sub>)<sub>2</sub>CS, the stripping percentage of Pd(II) by HCl, NaSCN and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was very low. Therefore, (NH<sub>2</sub>)<sub>2</sub>CS was selected for the stripping of Pd(II) from the loaded mixture of LIX 63 and Alamine 336.

**Table 4.** Stripping of Pd(II) in loaded mixture of LIX 63 and Alamine 336 using various reagents

Stripping reagent	Pd(II) stripping, %
0.5 M HCl	0.0
5.0 M HCl	2.0
0.5 M NaSCN	3.0
0.1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.9
0.5 M (NH <sub>4</sub> ) <sub>2</sub> CS	100.0
0.5 M (NH <sub>2</sub> ) <sub>2</sub> CS + 5.0 M HCl	27.0

Loaded organic: Pd-97.0 mg/L; O/A = 1.

Since (NH<sub>2</sub>)<sub>2</sub>CS could strip Pd(II) in loaded organic, the effect of (NH<sub>2</sub>)<sub>2</sub>CS concentration was investigated. As is shown in Figure 6, Pd(II) was completely stripped by (NH<sub>2</sub>)<sub>2</sub>CS in the concentration range from 0.05 to 0.7 M.



**Figure 6.** Effect of thiourea concentration on stripping of Pd(II).

#### 4. Conclusions

The extraction of Pd(II) with mixtures of Cyanex 301/LIX 63 and several extractants was investigated in the HCl concentration range from 0.5 to 9 M. In the case of the mixture with Cyanex 301, only its mixture with TOPO showed synergistic effect on the extraction of Pd(II) when HCl concentration was higher than 7 M. However, it was very difficult to strip Pd(II) from the loaded mixture of Cyanex 301 and TOPO. While the mixture of LIX 63 and Alamine 336 showed synergistic effect in the whole HCl concentration range, the mixture of LIX 63 and TOPO was favorable for the

extraction only when HCl concentration was higher than 3 M. Compared to the mixture of Cyanex 301 and TOPO, Pd(II) was completely stripped from the mixture of LIX 63 and Alamine 336 by using thiourea as a stripping agent.

**Acknowledgments:** This work was supported by the Global Excellent Technology Innovation of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No.20165010100810).

**Author Contributions:** Man Seung Lee designed the research, helped to analyze data. Hoai Thanh Truong performed experiments and wrote the paper. Seong Ho Sohn participated in the discussion on the results.

**Conflicts of Interest:** The authors declare no conflict of interest.

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