Article

Extraction of Palladium(II) from Hydrochloric Acid Solutions by Solvent Extraction with Mixtures Containing Either Cyanex 301 or LIX 63

Hoai Thanh Truong [1], Man Seung Lee [1,*] and Seong Ho Son [2]

[1] Department of Advanced Materials Science & Engineering, Institute of Rare Metal,
   Mokpo National University, Jeollanamdo 534-729, Korea; truonghoaithanhcm@gmail.com
[2] Korea Institute of Industrial Technology, Incheon Technology Service Centre, 7-47, Songdo-Dong,
   Incheon 406-840, Korea; shson@kitech.re.kr
* Correspondence: mslee@mokpo.ac.kr; Tel.: +82-614-502-492

Abstract: Cyanex 301 and 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63) can selectively extract Pd(II) over Pt(IV) from concentrated 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 mixtures of Cyanex 301, the highest synergistic enhancement coefficient was achieved by mixing Cyanex 301 and trioctylphosphine oxide (TOPO). However, it was very difficult to strip the Pd(II) from the loaded mixture phase. Among the mixtures 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 phase 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 industries [1,2]. Because the consumption of Pd increases each year, the recovery of this metal from either ores or secondary resources is essential. Several methods are used in the separation of Pd(II) from the leaching solutions of HCl or HNO_3, 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) because of its high selectivity and the purity of metals thus obtained [9].

Various extractants, such as 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63), 2-hydroxy-5-nonylacetophenone oxime (LIX 84I), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC 88A), trioctyamine (TOA), bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), tricaprylamine (alamine 336), tributyl phosphate (TBP), and trioctylphosphine oxide (TOPO) have been employed to separate Pd(II) from hydrochloric acid solutions in the presence of other metals. Although Pd(II) can be extracted by Cyanex 301, the stripping is very difficult owing to the strong interaction between Pd(II) and Cyanex 301 [6,11]. A 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 a 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 a low extraction percentage are drawbacks in the extraction of Pd(II) by TBP and TOPO. To solve these problems, many attempts have been made by using mixture systems. Lee and Chung [8] reported that a mixture of TOPO and thenoyltrifluoroacetone (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 the HCl concentration was higher than 7 mol/L. Although Pd(II) was completely extracted by Cyanex 301 in the HCl concentration range from 0.5 to 9 mol/L, it was challenging to strip the Pd(II) in the loaded Cyanex 301 phase [11]. Various extractant mixtures have been employed to separate PGMs, but only a few papers have reported the synergistic extraction of Pd(II). In solvent extraction with extractant mixtures, the synergistic enhancement coefficient (R) is defined as $R = D_{A+B}/(D_A + D_B)$, where D_A and D_B represent the distribution ratio of Pd(II) by the single A or B, and D_{A+B} represents the distribution ratio of Pd(II) by the mixture of A and B. $R > 1$ indicates the occurrence of synergism, while $R < 1$ shows antagonism. In order to study the effect of mixing extractants on the extraction of Pd(II), experiments were performed. For this purpose, several cationic (Cyanex 272/PC 88A/D2EHPA), anionic (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 phase was obtained.

2. Experimental

2.1. Reagents and Chemicals

The commercial extractant TOPO was supplied by Sigma-Aldrich (St. Louis, MO, USA). Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) and Cyanex 301 were purchased from Cytec Inc. (Thorold, ON, Canada). LIX 63 and Alamine 336 were supplied by BASF Co. (Ludwigshafen, Germany). D2EHPA, and PC 88A and TBP were products of Daihachi Chemical Industry Co. (Osaka, Japan) and Yakuri Pure Chemicals Co. (Uji, Japan), respectively. All the extractants were used as received without any further purification, and the chemical structure of the extractants is shown in Table 1. Kerosene (Daejung Co., Siheung, Korea) was employed as a diluent for the present work.

A stock solution of palladium was prepared by dissolving the necessary amount of PdCl$_2$ (99.9%; Sigma-Aldrich, St. Louis, MO, USA). The desired acidity of the synthetic solution was controlled by adding pure HCl solution (35%; Daejung Co., Siheung, Korean). Ascorbic acid (99.5%; Samchun Pure Chemical Co., Pyeongtaek, Korea), and KI (99.5%; Daejung Co., Siheung, Korea) were employed to prepare the solutions for the measurement of the Pd(II) concentration in the aqueous phase. All other reagents used were of analysis grade.

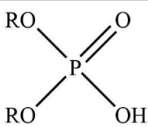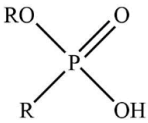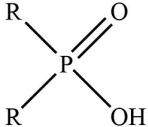**Table 1.** Chemical structure of extractants used in the study.

Extractant	Structure	R or R' Group
D2EHPA	RO—P(=O)(OR)(OH)	R = C$_8$H$_{17}$–
PC 88A	RO—P(=O)(R)(OH)	R = C$_8$H$_{17}$–
Cyanex 272	R—P(=O)(R)(OH)	R = C$_7$H$_{15}$–

Table 1. *Cont.*

| Extractant	Structure	R or R' Group
Cyanex 301		$R = C_7H_{15}-$
LIX 63		$R = H$ $R' = C_7H_{15}-$
TBP		$R = C_4H_9-$
TOPO		$R = C_8H_{17}-$
Alamine 336		$R = C_8H_{17}-$ or $C_{10}H_{21}-$

2.2. Solvent Extraction Procedure

The general extraction and stripping experiments were carried out by shaking an 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, Pittsburgh, PA, USA). After separation, the two phases were separated using a separating funnel. All the extraction experiments were performed 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 an ultraviolet spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) [18]. The metal concentration in the organic phase was calculated by mass balance. The distribution ratio (*D*) was determined by the concentration ratio of the metal present in the organic phase to that in the aqueous phase at equilibrium. The extraction percentage of Pd(II) was calculated from the *D* values by $E\% = D \times 100/(D + 1)$. The errors correlated with the extraction and stripping percentage of metals were within $\pm 5\%$.

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. 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), and anionic (Alamine 336) extractants, solvent extraction experiments were performed. In these experiments, the concentration of Pd(II) was fixed at 100 mg/L, and the concentration of HCl was varied from 0.5 to 9 mol/L. 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 entirely 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 (HSAB) 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 mol/L, while the other organophosphorus extractants (D2EHPA, PC 88A, Cyanex 272) contain oxygen and are regarded as hard bases. Therefore, the interaction between Pd(II) and organophosphorus extractants was not so strong that the extraction percentage of Pd(II) by the mixture was lower than that by single Cyanex 301.
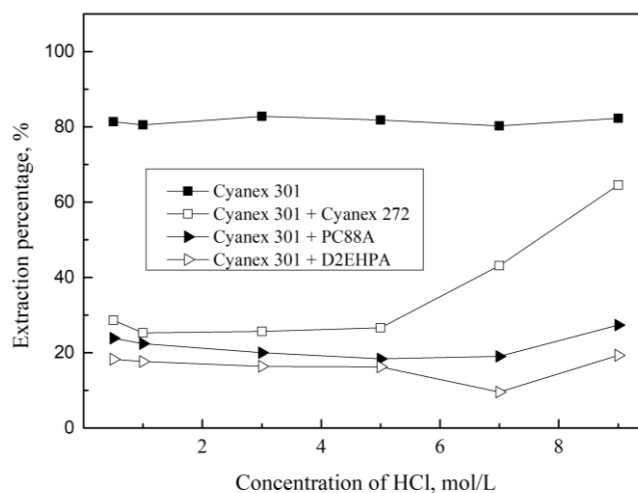
Figure 1. Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5–9 mol/L. Organic: 0.01 mol/L Cyanex 301, 0.01 mol/L Cyanex 301 + 0.1 mol/L Cyanex 272/PC 88A/D2EHPA. Organic per aqueous phase ratio (O/A) = 1. Diluent: kerosene.

Table 2 illustrates the difference in the distribution ratio of Pd(II) with Cyanex 301 and its mixture with organophosphorus extractants. As can be seen in Table 2, the *D* value of single Cyanex 301 was much higher and less varied than that by its mixtures at the same conditions. The addition of D2EHPA, PC 88A, and Cyanex 272 did not enhance the extraction percentage of Pd(II) compared to single Cyanex 301.

Table 2. Distribution ratio of Pd(II) with single Cyanex 301, Cyanex 301 + Cyanex 272, Cyanex 301 + PC 88A, and Cyanex 301 + D2EHPA.

[HCl], M	$D_{Cyanex\ 301}$	$D_{Cyanex\ 301+Cyanex\ 272}$	$D_{Cyanex\ 301+PC\ 88A}$	$D_{Cyanex\ 301+D2EHPA}$
0.5	4.6	0.4	0.3	0.2
1.0	4.1	0.3	0.3	0.2
3.0	4.8	0.3	0.3	0.2
5.0	4.4	0.4	0.2	0.2
7.0	4.2	0.8	0.2	0.1
9.0	4.6	1.8	0.1	0.2

Figure 2 shows the effect of the 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 the Pd existed as $PdCl_4^{2-}$ when the HCl concentration was

higher than 0.1 mol/L [12], and this Pd(II) could be extracted even by single Alamine 336. Therefore, the complete extraction of Pd(II) was obtained by this mixture of Cyanex 301 and Alamine 336.
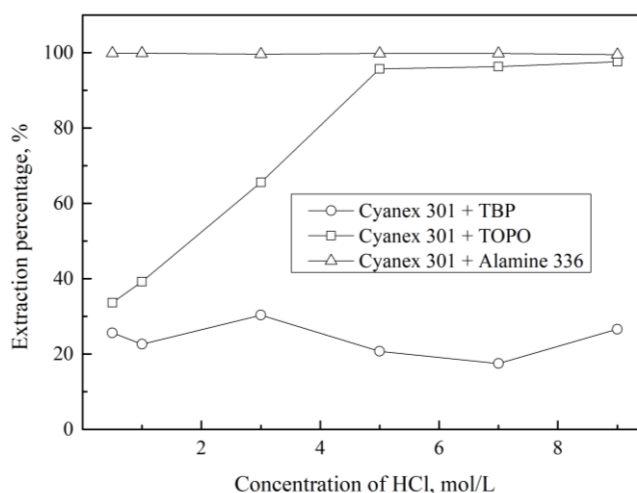
Figure 2. Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5–9 mol/L. Organic: 0.01 mol/L Cyanex 301 + 0.1 mol/L TBP, 0.01 mol/L Cyanex 301 + 0.01 mol/L TOPO, 0.01 mol/L Cyanex 301 + 0.02 mol/L Alamine 336. O/A = 1. Diluent: kerosene.

When Cyanex 301 was mixed with TOPO, the extraction percentage of Pd(II) increased rapidly from 34% to 97% as the HCl concentration increased from 0.5 to 5 mol/L and then was kept as a constant with the further increase in the HCl concentration up to 9 mol/L. 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. Moreover, the distribution ratio of Pd(II) with these mixtures, such as Cyanex 301 + TBP, Cyanex 301 + TOPO, and Cyanex 301 + Alamine 336, is displayed in Table 3. It is certain that there was strong interaction in the mixture of Cyanex 301 + Alamine 336, while that of Cyanex 301 + TBP was negligible. In the case of Cyanex 301 + TOPO, the *D* value increased significantly from 0.5 to 29.9. Compared to Cyanex 301 + Alamine 336, the extraction of Pd(II) by Cyanex 301 + TOPO was less varied.

Table 3. Distribution ratio of Pd(II) with Cyanex 301 + TBP, Cyanex 301 + TOPO, and Cyanex 301 + Alamine 336.

[HCl], M	$D_{\text{Cyanex 301+TBP}}$	$D_{\text{Cyanex 301+TOPO}}$	$D_{\text{Cyanex 301+Alamine 336}}$
0.5	0.3	0.5	833.2
1.0	0.3	0.6	1000.0
3.0	0.4	1.9	262.4
5.0	0.3	19.3	555.1
7.0	0.2	25.9	499.5
9.0	0.4	29.9	191.5

Table 4 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 the HCl concentration increased from 5 to 9 mol/L, and the highest enhancement coefficient of 6.4 was obtained at 9 M HCl. As shown in Table 4, the coefficient *R* of these extractants with Cyanex 301 was less than 1, except with TOPO at a HCl concentration higher than 3 mol/L. This means that the addition of organophosphorus extractants (D2EHPA, PC 88A, and Cyanex 272), TBP, and Alamine

336 caused antagonism during the extraction of Pd(II). Moreover, it is difficult to indicate the reaction mechanism of Pd(II) with Cyanex 301 and its mixture. The reaction of Pd(II) with Cyanex 301 might occur by chelate formation [11].

Table 4. Synergistic enhancement coefficient (*R*) of Pd(II) with mixture of Cyanex 301 and various extractants.

[HCl], M	$R_{Cyanex\ 272}$	$R_{PC\ 88A}$	R_{D2EHPA}	R_{TBP}	R_{TOPO}	$R_{Alamine\ 336}$
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

Figure 2 shows that the extraction of Pd(II) by the mixture of Cyanex 301 and TOPO rose rapidly with the increase in the HCl concentration. Therefore, the low acid concentration would be favorable for the stripping of Pd(II) from this mixture. Some hard–soft ligands such as SCN^-, CO_3^{2-}, and $RCOO^-$ were chosen for stripping experiments. In the recovery of the PGMs, the concentration of the acid is often controlled to 6 mol/L in the presence of oxidizing agents [1,5]. A synthetic solution containing 100 mg/L Pd(II) was prepared, and the HCl concentration was adjusted to 5 mol/L HCl for the stripping experiments. These solutions were contacted with the mixture of Cyanex 301 and TOPO. After the extraction by the combination of 0.01 mol/L Cyanex 301 and 0.01 mol/L TOPO, the concentration of Pd(II) in the loaded organic phase was 97 mg/L Pd(II), and this loaded organic phase was employed for the stripping experiments. Table 5 shows the stripping percentage of Pd(II) by several agents. The stripping percentage was negligible by the stripping agents used in this work, which could be ascribed to the strong interaction between Pd(II) and sulfur in Cyanex 301 [6,11].

Table 5. Stripping of Pd(II) in loaded mixture phase of Cyanex 301 and trioctylphosphine oxide (TOPO) using various reagents.

Stripping Reagent	Pd(II) Stripping (%)
0.5 mol/L HCl	0.5
5.0 mol/L HCl	1.0
0.5 mol/L NaSCN	0.5
0.1 mol/L $Na_2S_2O_3$	0.5
0.5 mol/L $(NH_2)_2CS$	2.0
0.5 mol/L Na_2CO_3	0.5
0.5 mol/L Oxalic acid	0.5
0.5 mol/L $(NH_2)_2CS$ + 5.0 mol/L HCl	1.0

Loaded organic phase: 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 performed by using single LIX 63 and its mixture with other extractants. The concentration of LIX 63 was fixed at 0.01 mol/L, and that of Cyanex 272/PC 88A/D2EHPA/TBP was 0.1 mol/L, whereas that of TOPO/Alamine 336 was 0.01 mol/L. Figure 3 shows the extraction of Pd(II) by single LIX 63 and its mixtures at several HCl concentrations. As the HCl concentration increased from 0.5 to 9 mol/L, the extraction percentage of Pd(II) by single LIX 63 decreased from 83% to 9%.
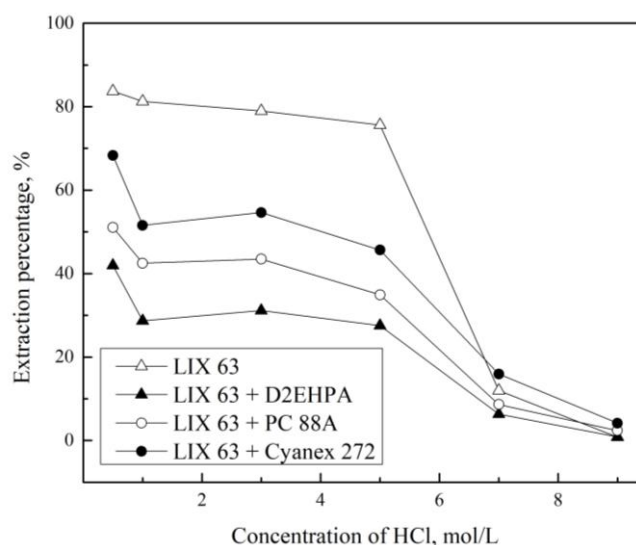
Figure 3. Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5–9 mol/L. Organic: 0.01 mol/L 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63), 0.01 mol/L LIX 63 + 0.1 mol/L Cyanex 272/PC 88A/D2EHPA. O/A = 1. Diluent: kerosene.

Similarly to LIX 63, the extraction of Pd(II) by its mixture with D2EHPA, PC 88A, and Cyanex 272 fell rapidly with the increase in the 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 the three mixtures might be related to their structures [21]. Further, the acidity of these organophosphorus extractants was ordered as follows: D2EHPA (pKa = 3.24) > PC 88A (pKa = 4.51) > Cyanex 272 (pKa = 6.37). Whewell et al. reported that LIX 63 is protonated by acid media and easily degraded at a high acid concentration, leading to a reducing complexation of metals with oxime [22].

Table 6 shows the *D* value of Pd(II) with LIX 63 and its mixture. The variation in the extraction of Pd(II) with single LIX 63 decreased rapidly, while that of its mixtures was negligible.

Table 6. Distribution ratio of Pd(II) with single 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63), LIX 63 + Cyanex 272, LIX 63 + PC 88A, and LIX 63 + D2EHPA.

[HCl], M	$D_{LIX\ 63}$	$D_{LIX\ 63+Cyanex\ 272}$	$D_{LIX\ 63+PC\ 88A}$	$D_{LIX\ 63+D2EHPA}$
0.5	5.2	2.2	1.0	0.7
1.0	4.3	1.1	0.7	0.4
3.0	3.8	1.2	0.8	0.5
5.0	3.1	0.8	0.5	0.3
7.0	0.1	0.2	0.1	0.1
9.0	0.0	0.0	0.0	0.0

In the case of the mixture of LIX 63 and TOPO, the extraction of Pd(II) increased from 58% to 90% as the HCl concentration increased from 0.5 to 5 mol/L and then declined rapidly with the further increase in the HCl concentration to 9 mol/L (see Figure 4).
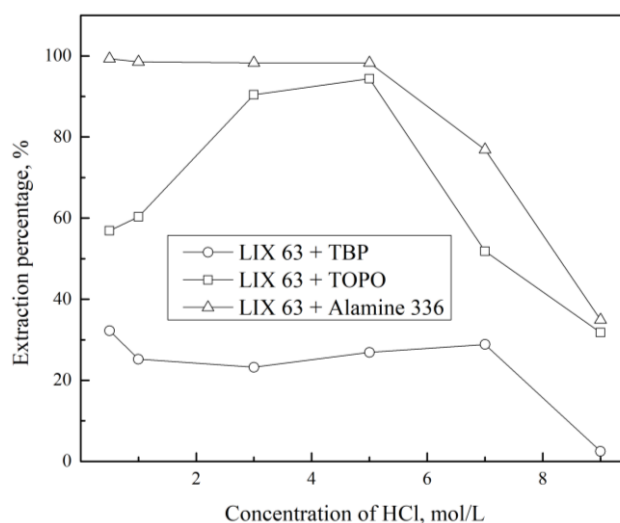
Figure 4. Effect of HCl concentration on extraction of Pd(II). Aqueous: [Pd] = 100 mg/L, [HCl] = 0.5–9 mol/L. Organic: 0.01 mol/L LIX 63 + 0.1 mol/L TBP, 0.01 mol/L LIX 63 + 0.01 mol/L Alamine 336/TOPO. O/A = 1. Diluent: kerosene.

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 mol/L and reduced to zero at 9 mol/L 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 [23]. The mixture of LIX 63 and Alamine 336 extracted completely Pd(II) in the HCl concentration range from 0.5 to 5 mol/L, and the extraction percentage decreased sharply with the further increase in the HCl concentration up to 9 mol/L. 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 [24]. As can be seen in Table 7, the highest *D* value of Pd(II) was obtained by mixing LIX 63 and Alamine 336 at 0.5 mol/L HCl, and then this declined significantly with an increase in the HCl concentration range from 1.0 to 9.0 mol/L, whereas the change by LIX 63 + TBP was very small. Compared to Cyanex 301 + TOPO, the extraction of Pd(II) with LIX 63 + TOPO was remarkably different when the HCl concentration was higher than 5.0 mol/L. This might be attributed to the formation of oxidation products during solvent extraction [25].

Table 7. Distribution ratio of Pd(II) with 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63) + TBP, LIX 63 + trioctylphosphine oxide (TOPO), and LIX 63 + Alamine 336.

[HCl], M	$D_{\text{LIX 63+TBP}}$	$D_{\text{LIX 63+TOPO}}$	$D_{\text{LIX 63+Alamine 336}}$
0.5	0.4	1.3	140.4
1.0	0.3	1.5	66.6
3.0	0.3	9.5	57.9
5.0	0.4	16.9	57.1
7.0	0.4	1.1	3.3
9.0	0.0	0.5	0.5

The synergistic coefficient during the extraction of Pd(II) with mixtures of LIX 63 and the above extractants is shown in Table 8.

Table 8. Synergistic enhancement coefficient (*R*) of Pd(II) with mixture of 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63) and various extractants.

| [HCl], M	$R_{Cyanex\ 272}$	$R_{PC\ 88A}$	R_{D2EHPA}	R_{TBP}	R_{TOPO}	$R_{Alamine\ 336}$
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

Table 8 shows that the enhancement coefficient by the mixture of LIX 63 and organophosphorous extractants was less than 1, except for 7 and 9 mol/L for the mixture of LIX 63 and Cyanex 272, and at 9 mol/L for the mixture of LIX 63 and PC 88A/D2EHPA. Therefore, the addition of Cyanex 272 into the LIX 63 system would reduce synergism during the extraction of Pd(II) when the concentration of HCl is less than 7 M while those of PC 88A and D2EHPA are less than 9 M. 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 mol/L by the mixture with TOPO, the HCl concentration was very high. Among the tested mixtures, the mixture of LIX 63 and Alamine 336 was suitable for the extraction of Pd(II). Thus, this combination was selected for further experiments.

The reaction of Pd(II) with the mixture of TBP/TOPO/Alamine 336 can be represented as a solvating reaction [16]:

$$PdCl_4{}^{2-}{}_{aq} + HB_{org} + S_{org} = PdCl_2(HB) \cdot S_{org} + 2Cl^- \tag{1}$$
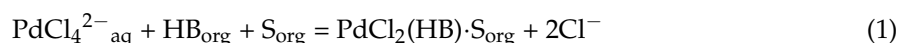
where S represents TBP, TOPO, and Alamine 336.

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 mol/L while keeping the total concentration of the mixture at 0.02 mol/L. The concentration of HCl in the synthetic Pd(II) solution was fixed at 5 mol/L. 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. Further, there was not much difference in the *D* value obtained by the mixture of LIX 63 + Alamine 336 (see Table 9). As a result, the extraction efficiency of Pd(II) was similar in these ranges studied.
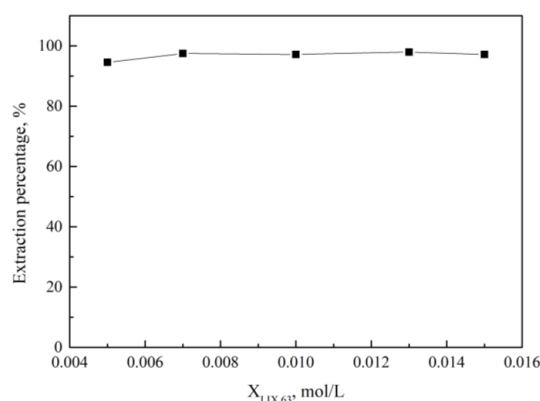
Figure 5. The effect of 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63) + Alamine 336 concentration on extraction of Pd(II). Aqueous: Pd = 100 mg/L, [HCl] = 5 mol/L. Organic: [LIX 63] + [Alamine 336] = 0.02 mol/L. O/A = 1. Diluent: kerosene.

Table 9. Distribution ratio of Pd(II) by varying the concentration of 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63) and Alamine 336.

| Extractant	*D*
0.005 mol/L Alamine 336 + 0.015 mol/L LIX 63	34.6
0.007 mol/L Alamine 336 + 0.013 mol/L LIX 63	35.6
0.01 mol/L Alamine 336 + 0.01 mol/L LIX 63	34.6
0.013 mol/L Alamine 336 + 0.007 mol/L LIX 63	34.7
0.015 mol/L Alamine 336 + 0.005 mol/L LIX 63	17.4

The stripping behavior of Pd(II) from the loaded mixture phase of LIX 63 and Alamine 336 was investigated. For this purpose, the loaded organic phase was prepared by extraction with a mixture of 0.01 mol/L LIX 63 and 0.01 mol/L Alamine 336. The concentration of Pd in the loaded mixture phase 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) can be quantitatively stripped by acidic aqueous solutions containing thiourea [17]. Therefore, several agents, such as HCl, NaSCN, $Na_2S_2O_3$, $(NH_2)_2CS$, and $(NH_2)_2CS$ + HCl, were used in the stripping experiments. Table 10 shows the stripping percentage of Pd(II) by the reagents. The Pd(II) in the loaded organic phase was completely stripped by $(NH_2)_2CS$. Moreover, the addition of HCl to $(NH_2)_2CS$ had a negative effect on the stripping of Pd(II) owing to the decrease in the activity of $(NH_2)_2CS$ in the presence of HCl during the stripping experiments. Except for $(NH_2)_2CS$, the stripping percentage of Pd(II) by HCl, NaSCN, and $Na_2S_2O_3$ was very low. Therefore, $(NH_2)_2CS$ was selected for the stripping of Pd(II) from the loaded mixture phase of LIX 63 and Alamine 336.

Table 10. Stripping of Pd(II) in loaded mixture phase of 5,8-diethyl-7-hydroxyldodecane-6-oxime (LIX 63) and Alamine 336 using various reagents.

Stripping Reagent	Pd(II) Stripping (%)
0.5 mol/L HCl	0.0
5.0 mol/L HCl	2.0
0.5 mol/L NaSCN	3.0
0.1 mol/L $Na_2S_2O_3$	0.9
0.5 mol/L $(NH_2)_2CS$	100.0
0.5 mol/L $(NH_2)_2CS$ + 5.0 mol/L HCl	27.0

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

Because $(NH_2)_2CS$ can strip Pd(II) in the loaded organic phase, the effect of the $(NH_2)_2CS$ concentration was investigated. As is shown in Figure 6, Pd(II) was entirely stripped by $(NH_2)_2CS$ in the concentration range from 0.05 to 0.7 mol/L.
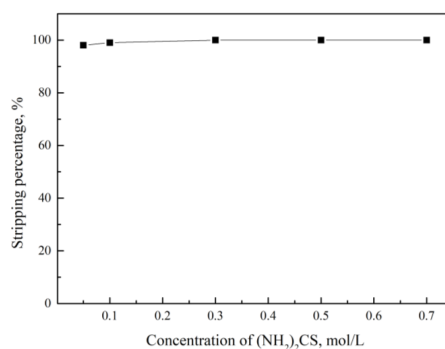
Figure 6. Effect of thiourea concentration on stripping of Pd(II).

It can be said that the synergism and antagonism caused by the mixtures employed in the current work provide valuable information for understanding the effect of mixtures. This information would lead to further study on the extraction of Pd(II) in the presence of other metals using extractant mixture systems.

4. Conclusions

The extraction of Pd(II) with mixtures of either Cyanex 301 or LIX 63 and some extractants, such as cationic, anionic and neutral extractants, was investigated in the HCl concentration range from 0.5 to 9 mol/L. In the case of the mixture with Cyanex 301, only its mixture with TOPO showed a synergistic effect on the extraction of Pd(II) when the HCl concentration was higher than 7 mol/L. However, it was very difficult to strip Pd(II) from the loaded mixture phase of Cyanex 301 and TOPO. On the contrary, the mixture of LIX 63 and Alamine 336 showed a synergistic effect in the whole HCl concentration range, and the mixture of LIX 63 and TOPO was favorable for the extraction only when the HCl concentration was higher than 3 mol/L. 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.

Author Contributions: Man Seung Lee designed the research and helped to analyze the data. Hoai Thanh Truong performed the 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.

References

1. Jimenez de Aberasturi, D.; Pinedo, R.; Ruiz de Larramendi, I.; Ruize de larramendi, J.I.; Rojo, T. Recovery by hydrometallurgical extraction of the platinum-group metals from car catalytic converters. *Miner. Eng.* **2011**, *24*, 505–513. [CrossRef]
2. Nikoloski, A.N.; Ang, K.L. Review of the application of ion exchange resins for the recovery of platinum group metals from hydrochloric acid solutions. *Miner. Process. Extr. Metall. Rev.* **2014**, *35*, 369–389. [CrossRef]
3. Rovira, M.; Cortina, J.L.; Amaldos, J.; Sastre, A.M. Recovery and separation of platinum group metals using impregnated resins containing Alamine 336. *Solvent Extr. Ion Exch.* **1998**, *16*, 1279–1302. [CrossRef]
4. Anticó, E.; Hidalgo, M.; Masana, A.; Salvadó, V.; Muñoz, M.; Valiente, M. Study of a palladium mass accelerate transfer through a solid supported liquid membrane containing Kelex 100. *Process. Metall.* **1992**, *7*, 1505–1510.
5. Barakat, M.A.; Mahomoud, M.H.H.; Mahrous, Y.S. Recovery and separation of palladium from spent catalyst. *Appl. Catal. A* **2006**, *301*, 182–186. [CrossRef]
6. Kakoi, T.; Goto, M.; Nakashio, F. Solvent extraction of palladium with bis(2,4,4,-trimethylpentyl)dithiophosphinic acid and bis(2,4,4,-trimetylpentyl)monothiophosphinic acid. *Solvent Extr. Ion Exch.* **1994**, *12*, 541–555. [CrossRef]
7. Chen, M.; Wu, S.; Huang, Z.; Chen, J.; Chen, M.J. Separation and recovery of Pd(II) and Pt(II) from cyanide liquors of Pd-Pt flotation concentrate via solvent extraction. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 1699–1709. [CrossRef]
8. Lee, S.H.; Chung, K.S. Synergistic extraction of palladium(II) with thenoyltrifluoroacetone and tri-n-octylphosphine oxide. *Bull. Korean Chem. Soc.* **1995**, *16*, 479–483.
9. Cieszynska, A.; Wisniewski, M. Selective extraction of palladium(II) from hydrochloric acid solutions with phosphonium extractants. *Sep. Purif. Technol.* **2011**, *80*, 385–389. [CrossRef]
10. Swain, B.; Jeong, J.K.; Kim, S.K.; Lee, J.C. Separation of platinum and palladium from chloride solution by solvent extraction using Alamine 300. *Hydrometallurgy* **2010**, *104*, 1–7. [CrossRef]
11. Truong, H.T.; Lee, M.S. Separation of Pd(II) and Pt(IV) from hydrochloric acid solutions by solvent extraction with Cyanex 301 and LIX 63. *Miner. Eng.* **2018**, *115*, 13–20. [CrossRef]

12. Upadhyay, A.K.; Lee, J.C.; Kim, E.Y.; Kim, M.S.; Kim, B.S.; Kumar, V. Leaching of platinum group metals (PGMs) from spent automotive catalyst using electro-generated chlorine in HCl solution. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 1991–1999. [CrossRef]

13. Rane, M.V.; Venugopal, V. Study on the extraction of palladium(II) and platinum(IV) using LIX 84I. *Hydrometallurgy* **2006**, *84*, 54–59. [CrossRef]

14. Bandekar, S.V.; Dhadke, P.M. Solvent extraction separation of platinum(IV) and palladium(II) by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A). *Sep. Purif. Technol.* **1998**, *13*, 129–135. [CrossRef]

15. Sun, P.P.; Lee, M.S. Separation of Pt(IV) and Pd(II) from the loaded Alamine 336 by stripping. *Hydrometallurgy* **2011**, *109*, 181–184. [CrossRef]

16. Foulon, C.; Pareau, D.; Durand, G. Thermodynamic and kinetic studies of palladium(II) extraction by extractant mixtures containing LIX 63. Part I. Thermodynamic study. *Hydrometallurgy* **1999**, *51*, 139–153. [CrossRef]

17. Nguyen, T.H.; Sonu, C.H.; Lee, M.S. Separation of Pt(IV), Pd(II), Rh(III), and Ir(IV) from concentrated hydrochloric acid solutions by solvent extraction. *Hydrometallurgy* **2016**, *164*, 71–77. [CrossRef]

18. Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*; John Wiley & Sons: Milton, Australia, 1986.

19. Grigorieva, N.A.; Pavlenko, N.I.; Pashkov, G.L.; Flritlikh, I.Y.; Nikiforova, L.K. Investigation of the state of bis(2,4,4-trimethylpentyl)dithiophosphinic acid in nonane in the presence of electron-donar additives. *Solvent Extr. Ion Exch.* **2010**, *28*, 510–525. [CrossRef]

20. Batchu, N.K.; Sonu, C.H.; Lee, M.S. Solvent extraction equilibrium and modeling studies of manganese from sulfate solutions by mixture of Cyanex 301 and TBP. *Hydrometallurgy* **2014**, *144–145*, 1–6. [CrossRef]

21. Banda, R.; Min, S.H.; Lee, M.S. Selective extraction of Hf(IV) over Zr(IV) from aqueous H_2SO_4 solutions by solvent extraction with acidic organophosphorus based extractants. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 1712–1719. [CrossRef]

22. Whewell, R.J.; Foakes, H.J.; Hughes, M.A. Degradation in hydroxyoxime solvent extraction systems. *Hydrometallurgy* **1981**, *7*, 7–26. [CrossRef]

23. Watson, E.K.; Rickelton, W.A. A review of the industrial and recent potential applications of trioctylphosphine oxide. *Solvent Extr. Ion Exch.* **1992**, *10*, 879–889. [CrossRef]

24. Liu, Y.; Jeon, H.S.; Lee, M.S. Solvent extraction of Pr and Nd from chloride solution by mixtures of acidic extractants and LIX 63. *Korean J. Met. Mater.* **2016**, *54*, 592–597.

25. Nguyen, T.H.; Lee, M.S. Effect of HCl concentration on the oxidation of LIX 63 and subsequent separation of Pd(II), Pt(IV), Ir(IV) and Rh(III) by solvent extraction. *Korean J. Met. Mater.* **2016**, *54*, 768–774.