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Recovery of Pure Pd(II) from Spent Electroplating Solutions by Solvent Extraction with Ionic Liquids from Sulfuric Acid Leaching Solution of Cemented Pd

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Abstract: Palladium (Pd) electroplating is widely practiced in the manufacture of advanced electronic devices. The Pd(II) present in spent electroplating solutions is treated by cementation with zinc (Zn) metal powder. In order to recover pure Pd from the cemented Pd, a process that consisted of leaching followed by solvent extraction was investigated. For this purpose, solvent extraction experiments using synthesized ionic liquids (ILs) with organic and inorganic anions were performed to find separation conditions at which selective extraction of Pd(II) over Zn(II) from synthetic H₂SO₄ leaching solutions is possible. The concentration of sulfuric acid was varied from 0.5 to 9 M. The complete separation of Pd(II) over Zn(II) by ILs such as ALi-CY301 (*N*-methyl-*N,N,N*-trioctylammonium bis(2,4,4-trimethylpentyl) dithiophosphinic), ALi-SCN (*N*-methyl-*N,N,N*-trioctylammonium thiocyanate), ALi-I (*N*-methyl-*N,N,N*-trioctylammonium iodide) and ALi-Br (*N*-methyl-*N,N,N*-trioctylammonium bromide) depends on H₂SO₄ concentration, while ALi-LIX63 (*N*-methyl-*N,N,N*-trioctylammonium 5,8-diethyl-7-hydroxydodecane-6-oxime) and ALi-LIX84 (*N*-methyl-*N,N,N*-trioctylammonium 2-hydroxy-5-nonylacetophenone oxime) can completely separate Pd(II) irrespective of H₂SO₄ concentration. Additionally, the mixture of HCl and thiourea, aqua regia solution, NH₃ solution and the mixture of NH₄Cl and NH₃ are powerful stripping agents for Pd(II) from the loaded ALi-LIX63/ALi-LIX84, ALi-CY301, ALi-Br/ALi-I and ALi-SCN, respectively. However, application of the separation conditions to the real 5 M sulfuric acid leaching solutions of cemented Pd indicated that it was difficult to separate the two ions by extraction with ALi-LIX63 and ALi-LIX84. Use of NaClO as an oxidizing agent during the sulfuric acid leaching of real cemented Pd resulted in an enhancement of Zn(II) extraction by ALi-LIX63 and ALi-LIX84. Therefore, removal of chloride ions from the sulfuric acid leaching solutions is necessary to apply the separation conditions obtained from synthetic sulfuric acid leaching solutions.

Keywords: separation; extraction; stripping; synthesized ionic liquid; palladium



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1. Introduction

Palladium electrodeposition has some advantages, such as easy control, versatile operating conditions, good throwing power and crack-free smooth and adherent coatings with high purity, and thus is employed in the manufacture of electronic devices and advanced materials [1,2]. The concentration of Pd(II) in the spent electroplating solutions depends on the electroplating conditions. In practice, there are many kinds of ions in the diverse spent electroplating solutions, and the concentration of Pd(II) in these solutions is not high. In order to recover Pd(II) in the spent electroplating solutions, cementation with zinc (Zn) metal powder is generally practiced in order to concentrate Pd(II) [2]. In cementation, zinc metal powders with fine size are employed for the cementation kinetics. Therefore, it is necessary to recover pure palladium (Pd) metal from the cemented Pd. The surface of the cemented Pd is covered with Pd metal, while zinc metals exist in the interior of the cemented Pd. Leaching of the cemented Pd can be considered as a means to

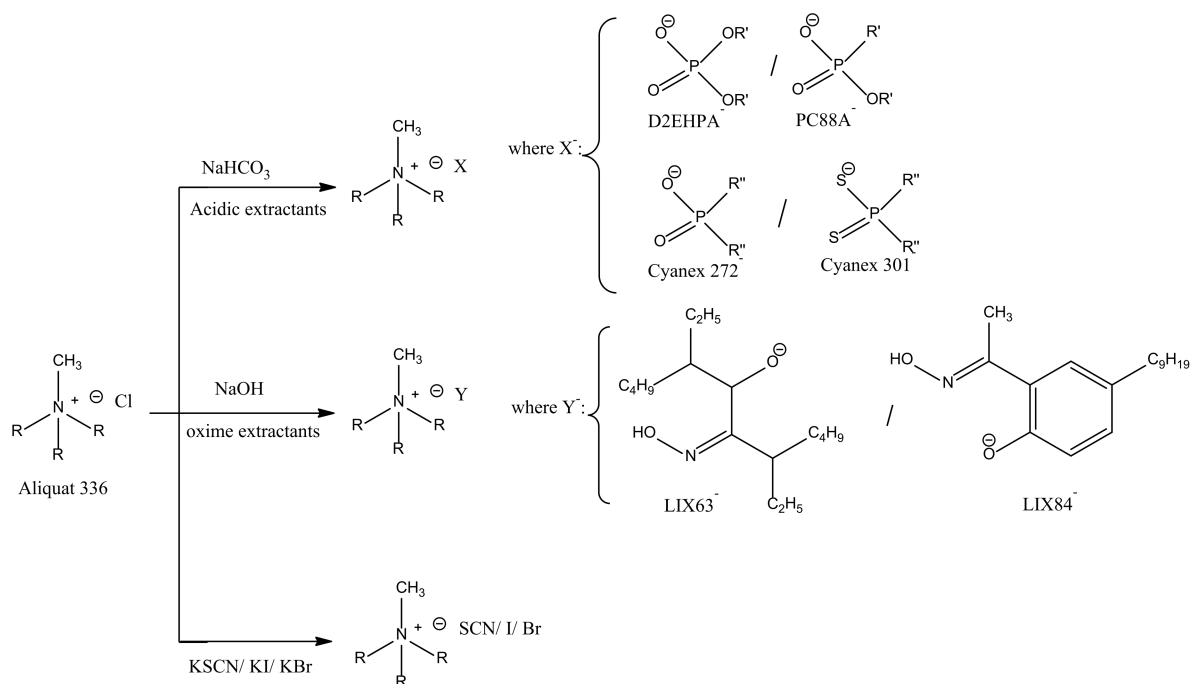
recover Pd from the cemented Pd. Since there is a lot of difference in the standard reduction potential between Pd(II) and Zn(II), leaching in the presence of oxidizing agents would lead to the complete dissolution of the Pd and Zn metal in the cemented Pd. Once Pd(II) and Zn(II) are completely dissolved, it is necessary to separate these two metal ions to recover Pd(II) with high purity.

Solvent extraction [3–6], ion exchange [7] and precipitation [8] are generally employed to separate Pd(II) over impurities from the leaching solution. Among these methods, solvent extraction is favorable for separation of Pd(II) due to the high selectivity and the purity of the obtained metal ion in the solution [3,9,10]. There are several commercial extractants that can selectively extract Pd(II) from hydrochloric acid solutions, such as 5,8-diethyl-7-hydroxydodecane-6-oxime (LIX 63), Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) [4], 2-hydroxy-5-nonylaceto-phenone oxime (LIX 84-IC) [6,11,12], dibutyl sulfoxide (DBSO) [13], *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) [14], tri-*n*-octyl amine (Alamine 300) [15] and di-octylsulfide (DOS) [16]. However, solvent extraction of Pd(II) by these extractants has some drawbacks, as follows: The stripping of Pd(II) from the loaded Cyanex 301 is difficult [4], and the expensive price of DOS makes its application to the industrial scale difficult. Pd(II) extraction percentage by LIX 63 depends on the acidity of the solution [3,4].

Unlike commercial molecular extractants, ionic liquids (ILs) can overcome the above-mentioned disadvantages. Indeed, ILs such as Cyphos IL 101, Aliquat 336 and their synthesized ILs have been employed for metal ion extraction because of their advantages in terms of kinetics as well as extraction efficiency [9,10,17–21]. Since ILs can extract metal ions through both ion exchange and ion pair formation mechanisms [20,22], they have been applied for metal extraction from various leachates. Pd(II) can form stable complexes with diverse anions, such as I^- , Br^- , Cl^- , SCN^- and HSO_4^- [23,24], which can be extracted into ILs phase. It has been reported that synthesized ILs such as ALi-Br and ALi-I (ALi represents Aliquat 336) are efficient to extract Pd(II) from chloride solutions [9]. The mixture of protic ionic liquids trioctylammoniumbis(trifluoromethanesulfonyl)amide ([TOAH][NTf₂]) and trioctylammonium nitrate ([TOAH][NO₃]) shows a selectivity for Pd(II) and Pt(IV) [25]. Two kinds of commercial ILs, such as Cyphos IL 101 and 104 (triethyl(tetradecyl)phosphonium chloride and triethyl(tetradecyl)phosphonium bis-2,4,4-trimethylpentylphosphinate) diluted by toluene, are employed for selective extraction of Pd(II) from a solution containing Ni(II), Cu(II), Pb(II), Fe(III), Rh(III), Ru(III) and Pt(IV) [10]. The undiluted imidazolium-based ILs with Tf₂N⁻ as anions can extract Pd(II), and the extraction performance depends on the concentration of chloride ion [26]. Betainium bis-(trifluoromethanesulfonyl) imide IL exhibits higher extraction efficiency of Pd(II) than Rh(II) and Ru(III) from nitric acid solutions [27].

Extensive research has been reported on the solvent extraction and separation of Pd(II) from hydrochloric acid solutions containing platinum group metals and other base metal ions by using commercial extractants. Compared to hydrochloric acid medium, few works have been reported on the solvent extraction behavior of Pd(II) in sulfuric acid solution. Since commercial extractants and ILs have their characteristic advantages and disadvantages in their extraction performance, the extraction and separation behavior of Pd(II) by both commercial extractants and ILs is necessary for developing an optimum process for the recovery of Pd(II). Therefore, the objective of this study was to find appropriate IL extractants and then to develop a suitable separation process for the recovery of Pd(II) in the sulfuric acid leachate of cemented Pd from spent electroplating solutions. For this purpose, synthetic sulfuric acid leaching solutions containing Pd(II) and Zn(II) were employed in the experiments. Two kinds of ILs with organic (ALi-D2, ALi-PC, ALi-CY301, ALi-CY272, ALi-LIX63, ALi-LIX84) and inorganic species as anions (ALi-I, ALi-Br, ALi-SCN) were employed to separate Pd(II) and Zn(II) from the synthetic sulfuric acid leaching solutions. These ILs were prepared by reacting Aliquat 336 (*N*-Methyl-*N,N,N*-trioctylammonium chloride) with anionic group of organophosphorus acids, such as D2EHPA (di(2-ethylhexyl)phosphoric acid), PC 88A (2-ethylhexyl hydrogen-

2-ethylhexylphosphonate), Cyanex 301, Cyanex 272 (bis(2,4,4-triethylpentyl)phosphinic acid), LIX 63, LIX 84, as well as the anions of inorganic salts (KI, KBr, KSCN) (see Scheme 1). The extraction and separation behavior of the two metal ions was investigated by varying the acidity of the synthetic sulfuric acid solutions. From the obtained results, the advantages and disadvantages of the separation of Pd(II) by these synthesized ILs were discussed. The stripping behavior of each loaded organic phase was also explored. Based on the obtained results, some suitable ILs were proposed for the selective extraction of Pd(II) from the leaching solution of cemented Pd.



Scheme 1. The synthesis of ILs with organic and inorganic anions.

2. Experimental

2.1. Reagents and Chemicals

Aliquat 336 (93%) and LIX 84 (99%) were supplied by BASF Co., Ludwigshafen, Germany, PC 88A (95%), Cyanex 272 (85%) and Cyanex 301 (70%) were provided by Cytec Inc., Saddle Brook, NJ, USA, and D2EHPA (95%) and LIX 63 (70%) were products of Daihachi Chem., Osaka, Japan, and IS Chem. Co., Seoul, Korea, respectively. All extractants were used without further purification. Organic phases were prepared by diluting the extractants with kerosene (Daejung Co., Shiheung, Korea, >90%). Decanol (Daejung Co., Shiheung, Korea, >98%) was added into organic solution (10% *v/v*) as a modifier to avoid the formation of a third phase.

The synthetic leaching solutions containing 100 mg/L of Pd(II) and 500 mg/L of Zn(II) were prepared by dissolving the corresponding amount of metal sulfates, such as PdSO₄ (Sigma-Aldrich Co., St. Louis, MO, USA, 99.9%) and ZnSO₄ (Duksan Co., Kyungki-do, Korea, 99%), in H₂SO₄ solution. The acidity of the synthetic solution was controlled from 0.5 to 9 M by adding H₂SO₄ (Daejung Co., Shiheung, Korea, 95%) solution. HCl (Daejung Co., Shiheung, Korea, 35%), HNO₃ (Daejung Co., Shiheung, Korea, 60%) and H₂SO₄ solutions were diluted by distilled water to desired concentrations for stripping experiments. Thiourea ((NH₂)₂CS, Daejung Co., Shiheung, Korea, >96%) and NH₃ (Junsei Co., Tokyo, Japan, 28%) solutions were used as stripping agents, and all the employed chemicals were of analytical grade.

2.2. Synthesis of Ionic Liquids

Ionic liquids such as ALi-D2, ALi-PC, ALi-CY and ALi-CY301 ($R_3CH_3N \cdot A$) were prepared according to the method reported in the literature [28]: an equimolar concentration of Aliquat 336 and acidic extractants in kerosene were mixed in a beaker, and then 0.5 M $NaHCO_3$ solution was added. The mixtures were stirred to expel CO_2 gas and to promote the formation of bi-functional ILs. ALi-SCN ($R_3CH_3N \cdot SCN$) was synthesized by contacting Aliquat 336 and the aqueous solution of 1.6 M KSCN several times for the complete replacement of chloride with thiocyanate [19,22]. ALi-LIX63/LIX 84 were obtained by mixing an equimolar concentration of Aliquat 336 and LIX 63/LIX 84 in kerosene, and then 2 M NaOH was added. These organic mixtures were contacted four times with NaOH solution for the complete formation of ILs. These synthesized ILs were washed many times with distilled water and then filtered.

In the case of ALi-SCN, chloride precipitation using $AgNO_3$ was performed to verify the transfer of the chloride ions from the organic phase to the aqueous phase. ALi-I and ALi-Br were prepared according to the literature [9], in which the complete replacement of chloride with iodide or bromide was achieved by reacting Aliquat 336 and 3 M KI or KBr solutions. After contacting of the organic phase three times with the fresh KBr or KI solution at the same experimental conditions, the synthesized ILs were washed many times with water to remove chloride and impurities. The structure and synthesis of these ILs are exhibited in Scheme 1.

In order to investigate the formation of ILs, the FT-IR spectra (FT-IR-Vertex 80 V, Bruker, Leipzig, Germany) of individual extractants and synthesized ILs were analyzed. The ILs were synthesized when the interaction occurred in functional groups of a single extractant such as LIX 63/LIX 84/Cyanex 301 and Aliquat 336, leading to some changes in the characteristic groups. Therefore, the changes in the characteristic bands of the acidic/oxime extractants before and after being mixed with Aliquat 336 were recorded and are shown in Figure 1 and Table 1. The region of $3500\text{--}500\text{ cm}^{-1}$ spectra was analyzed in more detail, where changes were observed. The data show that there was a significant change in the characteristic bands of the synthesized ILs, denoting that LIX 63/LIX 84 and Cyanex 301 reacted with Aliquat 336 to form ILs. The evidence is the occurrence of a significant change in the range of P-S, P=S, S-H (thiophosphinic group) and C-O, C-OH, C=N (oxime group). It is easier to observe the transformation of the C-OH group of LIX 84 than that of LIX 63 because this functional group (-OH) directly links to the benzene cycle, which makes this hydroxyl group more active and easier to participate in chemical reaction. Moreover, the drastic decrease in the intensities or even disappearance of the $(CH_3)^+N$ peak at 1463 cm^{-1} of Aliquat 336 was observed after synthesis of ILs, indicating the occurrence of strong and effective interaction at that position. This also agrees well with the reported spectra data [29]. From the evidence of significant changes on characteristic bands, it can be verified that the targeted ILs were successfully synthesized from the reactants.

Table 1. Frequencies of characteristic vibrational bands of single extractants and corresponding synthesized IL.

Extractant	C-O (cm^{-1})	C-O-H (cm^{-1})	C=N (cm^{-1})	N-O-H (cm^{-1})	P-S (cm^{-1})	P=S (cm^{-1})	S-H (cm^{-1})	C-H (cm^{-1})	$(CH_3)^+N$ (cm^{-1})
Aliquat 336	-	-	-	-	-	-	-	1378	1463.6
LIX 84	1025.6	1375	1620	3370	-	-	-	-	-
LIX 63	998	1382	1706	3370	-	-	-	-	-
Cyanex 301	-	-	-	-	804	608	≈ 2500	1365	-
ALi-LIX84	1096	1409	1620	3370	-	-	-	-	-
ALi-LIX63	1014	1377	1668	3370	-	-	-	-	1463.6
ALi-CY301	-	-	-	-	814	613.9	-	1365	1479.7

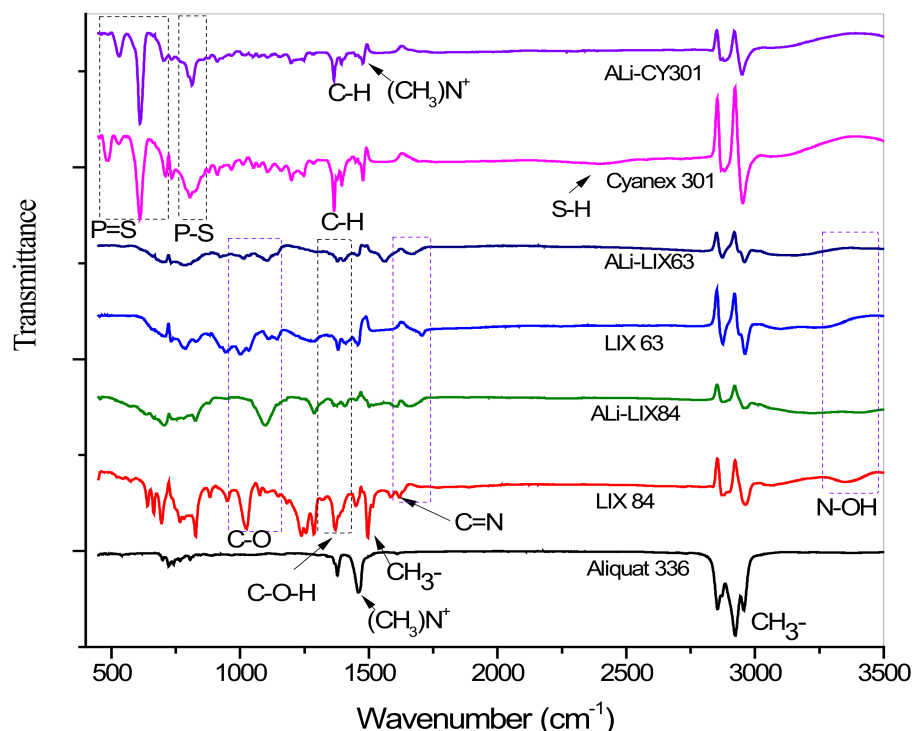


Figure 1. Comparison on FT - IR spectra of single extractants and the synthesized ILs, such as ALi-LIX63, ALi-LIX84 and ALi-CY301.

2.3. Experimental Procedure and Analytical Methods

The solvent extraction experiments were performed by mixing equal volume of the aqueous and organic phase (10 mL each) in a screwed cap bottle. The mixtures were stirred for 30 min using a Burrell wrist action shaker (model 75, Pittsburgh, PA 15205, USA) at ambient temperature (22 ± 1 °C). After shaking, the two phases were disengaged by keeping them in a glass separatory funnel for 30 min. The extraction percentage (%E) and stripping percentage (%S) of metals are defined as:

$$\%E = \frac{m_M}{m} \times 100, \quad (1)$$

$$\%S = \frac{m_M^*}{m_M} \times 100, \quad (2)$$

where m and m_M are the mass of a metal in the aqueous phase before extraction and in the loaded organic phase respectively, while m_M^* is the mass of metal in the aqueous phase after stripping from the loaded organic phase.

The mass of metals was calculated according to volume and the concentration of metal ions in the aqueous phase before and after extraction/stripping. The concentration of metal ions was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos). The experiments were performed in triplicate and the errors associated with the extraction and stripping percentages were within $\pm 5\%$.

3. Results and Discussion

3.1. Effect of H_2SO_4 Concentration on the Separation of Pd(II) over Zn(II)

In our previous work, the concentration of both Pd(II) and Zn(II) in the sulfuric acid leaching solution was the same (1000 mg/L) [2]. However, the concentration of these two ions in the leaching solution depends on the size, composition and pulp density of the cemented Pd in the leaching. Considering that Pd metal is much more expensive than Zn metal, excess Zn metal would be present in the cemented Pd. Therefore, the

concentration of Zn(II) was controlled to five times that of Pd(II) in this work. Namely, the concentrations of Pd(II) and Zn(II) in the synthetic leaching solution were fixed at 100 and 500 mg/L, respectively. Moreover, the excess Zn(II) was used in these experiments in order to investigate the effect of Zn(II) on selective separation of Pd(II). The H₂SO₄ concentration was varied from 0.5 to 9 M in this study. Once the suitable range of H₂SO₄ concentration was discovered, the selective extraction of Pd(II) from such real leaching solution of cemented Pd would be performed.

Dissociation of sulfuric acid occurs in two steps, and the second dissociation of hydrogen sulfate depends on the concentration of sulfuric acid. As the concentration of sulfuric acid increases, the existence of hydrogen ions depresses the second dissociation of hydrogen sulfate. Therefore, hydrogen sulfate is the dominant species of sulfuric acid in concentrated sulfuric acid solution. The complex formation constants of Pd(II) with hydrogen sulfate and sulfate ions are represented in Equations (3) and (4) [24]:



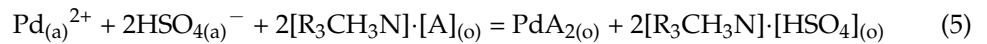
Compared to the complex formation constants of Pd(II) with sulfate/hydrogen sulfate ions, the complex formation constants with SCN[−], I[−] and Br[−] are large, as represented in Table 2 [23,24,30–34], and these complexes can be extracted by the ammonium cation of the corresponding ILs owing to their affinity. In addition, Pd(II) has a stronger tendency to form stable complexes with these inorganic anions than that of Zn(II), thus the selective separation could be obtained on the basis of the difference in formation of extracted complexes. Preliminary experimental data indicated that Pd(II) was well-extracted by both ILs with organic anions (ALi-CY 301, ALi-LIX63, ALi-LIX84) and ILs with inorganic anions (ALi-SCN, ALi-I, ALi-Br). In these experiments, the concentration of ILs was fixed at 0.1 M. The volume ratio of organic to aqueous phase was unity.

Table 2. The stability constants of metal complexes at 25 °C [30–34].

Reaction	logK	Reaction	logK
Pd ²⁺ + Cl [−] = PdCl ⁺	4.47	Pd ²⁺ + 2SCN [−] = Pd(SCN) ₂ ⁰	15.46
Pd ²⁺ + 2Cl [−] = PdCl ₂ ⁰	7.74	Pd ²⁺ + 3SCN [−] = Pd(SCN) ₃ [−]	21.94
Pd ²⁺ + 3Cl [−] = PdCl ₃ [−]	10.2	Pd ²⁺ + 4SCN [−] = Pd(SCN) ₄ ^{2−}	27.42
Pd ²⁺ + 4Cl [−] = PdCl ₄ ^{2−}	11.5	Zn ²⁺ + Cl [−] = ZnCl ⁺	0.43
Pd ²⁺ + Br [−] = PdBr ⁺	5.17	Zn ²⁺ + 2Cl [−] = ZnCl ₂ ⁰	0.61
Pd ²⁺ + 2Br [−] = PdBr ₂ ⁰	9.42	Zn ²⁺ + 3Cl [−] = ZnCl ₃ [−]	0.5
Pd ²⁺ + 3Br [−] = PdBr ₃ [−]	12.72	Zn ²⁺ + 4Cl [−] = ZnCl ₄ ^{2−}	0.2
Pd ²⁺ + 4Br [−] = PdBr ₄ ^{2−}	14.94	Zn ²⁺ + Br [−] = ZnBr ⁺	−0.57
Pd ²⁺ + I [−] = PdI ⁺	6.08	Zn ²⁺ + I [−] = ZnI ⁺	−1.50
Pd ²⁺ + 2I [−] = PdI ₂ ⁰	22.00	Zn ²⁺ + SCN [−] = ZnNSC ⁺	0.90
Pd ²⁺ + 3I [−] = PdI ₃ [−]	≈25.80	Zn ²⁺ + 2SCN [−] = Zn(NSC) ₂ ⁰	0.70
Pd ²⁺ + 4I [−] = PdI ₄ ^{2−}	28.30	Zn ²⁺ + 3SCN [−] = Zn(NSC) ₃ [−]	0.60
Pd ²⁺ + SCN [−] = PdSCN ⁺	8.14	Zn ²⁺ + 4SCN [−] = Zn(NSC) ₄ ^{2−}	0.30

Figure 2 shows that the extraction percentage of Pd(II) by ALi-CY 272, ALi-D2 and ALi-PC was lower than 25%, while that of Zn(II) was less than 5%. Compared to other ILs with organophosphorus anions, ALi-CY 301 can completely extract Pd(II) from H₂SO₄ in the concentration range between 0.5 and 9 M, while the extraction percentage of Zn(II) gradually decreased from 74.7% to 8.2% as H₂SO₄ concentration increased from 0.5 to 9 M. The higher extraction percentage of Pd(II) by ALi-CY 301 can be ascribed to the difference in functional groups of organic anions (CY 272[−], D2EHPA[−], PC 88A[−] and CY 301[−] anions), which affects the interaction degree with Pd(II). Since Pd(II) is a soft acid according to hard soft acid base principle (HSAB), it has a stronger tendency to interact with soft bases such as sulfur atoms, rather than oxygen atoms (hard base). Along these lines, it can be deduced that CY301[−] anions could have a weaker link with the ammonium cation center of ILs

(where nitrogen atoms act like a hard base) compared to CY272^- , D2EHPA^- and PC 88A^- anions. This could facilitate the interaction between CY301^- anion Pd(II) . The decrease in Zn(II) extraction by ALi-CY 301 with the increase of H_2SO_4 concentration could be due to the competition in the extraction with H_2SO_4 , which can lead to the regeneration of Cyanex 301 and the formation of ILs such as $\text{ALi}\cdot\text{HSO}_4$. Besides, the high concentration of H_2SO_4 was able to depress the extraction ability of Cyanex 301 for Zn(II) [35]. The extraction reaction of Pd(II) by ALi-CY 301 can be expressed as:



where $[\text{R}_3\text{CH}_3\text{N}]\cdot[\text{A}]$ denotes ALi-CY 301 , and the subscripts (a) and (o) represent the aqueous and organic phases, respectively.

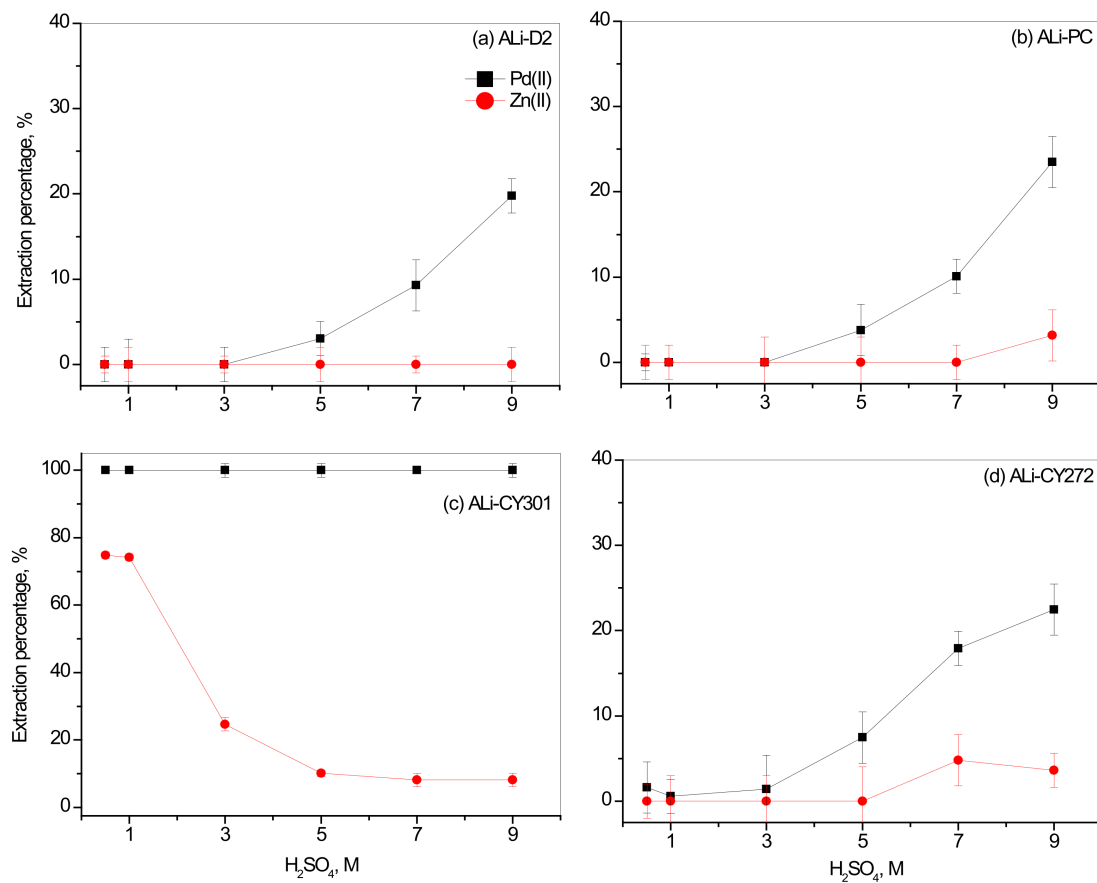


Figure 2. Effect of H_2SO_4 concentration on extraction of Pd(II) and Zn(II) by ILs: (a) ALi-D2 , (b) ALi-PC , (c) ALi-CY301 and (d) ALi-CY272 . Conditions: $[\text{Pd(II)}] = 100 \text{ mg/L}$ and $[\text{Zn(II)}] = 500 \text{ mg/L}$; [extractant] = 0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/O = 1.

In Figure 3, Pd(II) was completely extracted by ALi-LIX63 and ALi-LIX84 , while Zn(II) extraction was negligible in the H_2SO_4 concentration range of 0.5 to 9 M. Zn(II) extraction by ALi-LIX84 increased from zero to 5.1% when H_2SO_4 concentration increased from 7 to 9 M. The extraction reaction of Pd(II) by ALi-LIX63 and ALi-LIX84 can be proposed as:



where $[\text{R}_3\text{CH}_3\text{N}]\cdot[\text{A}] = \text{ALi-LIX63}/\text{ALi-LIX84}$ IL.

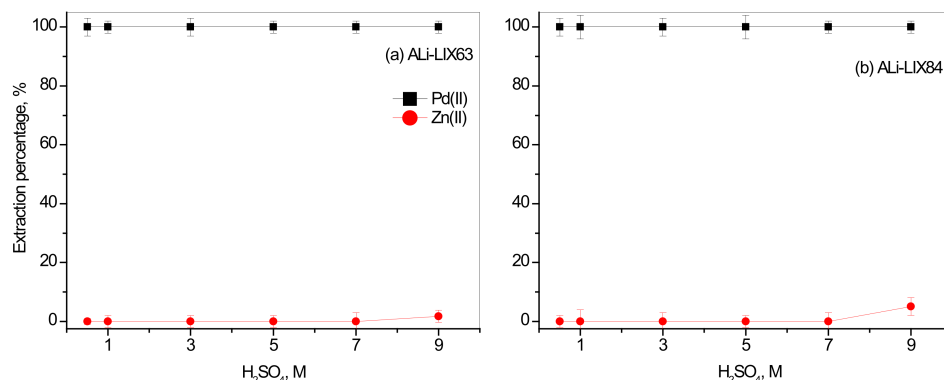
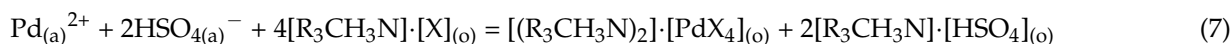


Figure 3. Effect of H₂SO₄ concentration on extraction of Pd(II) and Zn(II) by ILs: (a) ALi-LIX63 and (b) ALi-LIX84. Conditions: [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L; [extractant] = 0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/O = 1.

The formation kinetics of Pd(II)-hydrogen sulfate complexes is fast and depends on the concentration of sulfuric acid due to the nucleophilicity of HSO₄[−] as an oxygen-donor ligand towards the d orbital of Pd(II) [24]. This may promote the selective extraction of Pd(II) over Zn(II).

Since anions such as SCN[−], Br[−] or I[−] are more hydrophobic than HSO₄[−], the complexes can be stabilized in the organic phase according to Hofmeister series [36]. Hence, synthesized ILs such as ALi-SCN, ALi-I and ALi-Br can provide the anions with which Pd(II) can form complexes such as PdX₄^{2−} species (X: SCN/I/Br), and these species can be selectively extracted to the IL organic phase. Consequently, these synthesized ILs can selectively extract Pd(II) over Zn(II) from sulfuric acid solution. As expected, Pd(II) was completely extracted regardless of the concentration of H₂SO₄. Zn(II) extraction by ALi-I and ALi-Br was quite similar (see Figure 4). When H₂SO₄ concentration was less than 3 M, no Zn(II) was extracted by ALi-I. However, the extraction percentage of Zn(II) sharply increased from zero to completeness as H₂SO₄ concentration increased from 3 to 9 M. This may be attributed to the effect of HSO₄[−] on the extraction of Zn(II) by ILs. Therefore, control of sulfuric acid concentration is important to separate Pd(II) and Zn(II) by ALi-I and ALi-Br.

In the extraction with ALi-SCN, Zn(II) was completely extracted when H₂SO₄ concentration was less than 3 M, but rapidly decreased to negligible as H₂SO₄ concentration increased from 5 to 9 M. The high extraction percentage of Zn(II) in the H₂SO₄ concentration range from 0.5 to 3 M may be related to the formation of Zn(SCN)₄^{2−} complexes that can be extracted to the organic phase [37,38]. However, the competitive extraction of hydrogen ions by ALi-SCN [39] may reduce the extraction of Zn(II) from concentrated H₂SO₄ solution. The extraction of hydrogen ions can lead to a decrease in the effective concentration of IL. The extraction reaction of Pd(II) by ALi-SCN, ALi-I and ALi-Br is proposed as Equation (7):



where X represents SCN, I and Br.

Among some ILs tested in this work, the selective extraction of Pd(II) over Zn(II) by ALi-I and ALi-Br was possible when H₂SO₄ concentration was less than 3 M, while that by ALi-SCN and ALi-CY 301 was possible when H₂SO₄ concentration was higher than 7 M. Therefore, it might be concluded that ALi-LIX63 and ALi-LIX84 are the best candidates to separate Pd(II) over Zn(II) in the H₂SO₄ concentration range from 0.5 to 9 M.

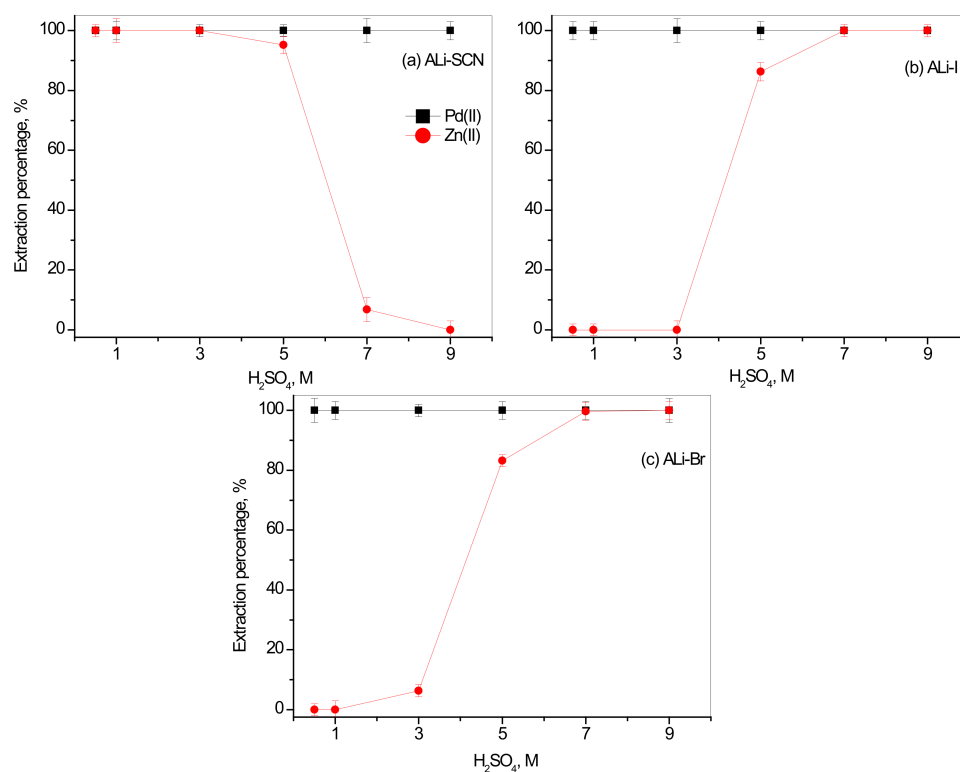


Figure 4. Effect of H₂SO₄ concentration on extraction of Pd(II) and Zn(II) by ILs: (a) ALi-SCN, (b) ALi-I and (c) ALi-Br. Conditions: [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L; [extractant] = 0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/O = 1.

3.2. Effect of Synthesized ILs Concentration on the Separation of Pd(II) over Zn(II)

3.2.1. Effect of Concentration of Synthesized ILs with Organic Anions

To investigate the effect of IL concentration on the selective extraction of Pd(II) over Zn(II), the concentration of ILs was varied from 0.001 to 0.1 M. The synthetic leaching solution contained 100 mg/L of Pd(II) and 500 mg/L of Zn(II). Based on the data in Section 3.1, H₂SO₄ concentration was adjusted for the complete separation of Pd(II) and Zn(II): namely, 7 M H₂SO₄ for ALi-CY301, and 0.5 M H₂SO₄ for ALi-LIX63 and ALi-LIX84. In these experiments, the volume ratio of organic to aqueous phase was unity. Figure 5a shows that Pd(II) was completely extracted by ALi-CY301, while the extraction of Zn(II) increased from zero to 8.1% with the increase of ALi-CY301 concentration from 0.001 to 0.1 M. Therefore, 0.001 M ALi-CY301 was selected for complete separation of Pd(II) over Zn(II). The increase of Zn(II) co-extraction might be related to the strong affinity of Zn(II) toward CY301[−] anions according to Lewis acid base theory [35], since Zn(II) ion is an electron-pair acceptor which has a strong tendency to accept the nonbonding electron pairs from the functional group of CY301[−]. Furthermore, their effective interaction can be accelerated by the increase of ALi-CY301 concentration. Therefore, it is essential to control ALi-CY301 concentration for the selective extraction of Pd(II).

Figure 5b,c display selective extraction of Pd(II) over Zn(II) by ALi-LIX63 and ALi-LIX84 from 0.5 M H₂SO₄ solution. The extraction percentage of Pd(II) sharply increased from 23.7% to 100% and from 6.3% to 100% when the concentration of both ALi-LIX63 (Figure 5b) and ALi-LIX84 (Figure 5c) increased from 0.001 to 0.005 M. Zn(II) was not extracted at all by either ALi-LIX63 or ALi-LIX84 in this condition. Hence, among three synthesized ILs with organic anions, ALi-LIX63 and ALi-LIX84 exhibited selectivity and high efficiency for the separation of Pd(II) and Zn(II). This was explained by the selectivity of the organic anions of LIX 63 and LIX 84 for Pd(II) compared to the Cyanex 301 anion. It can be verified from the reported data that these cationic extractants show selectivity for Pd(II) extraction [4,6,12]. When the concentration of LIX 84 and ALi-LIX84 was the

same (0.1 M), the extraction percentage of Pd(II) was 80%, while complete extraction was possible by ALi-LIX84. Therefore, it might be said that the synthesized ILs can enhance the extraction of Pd(II) compared to the cationic extractants.

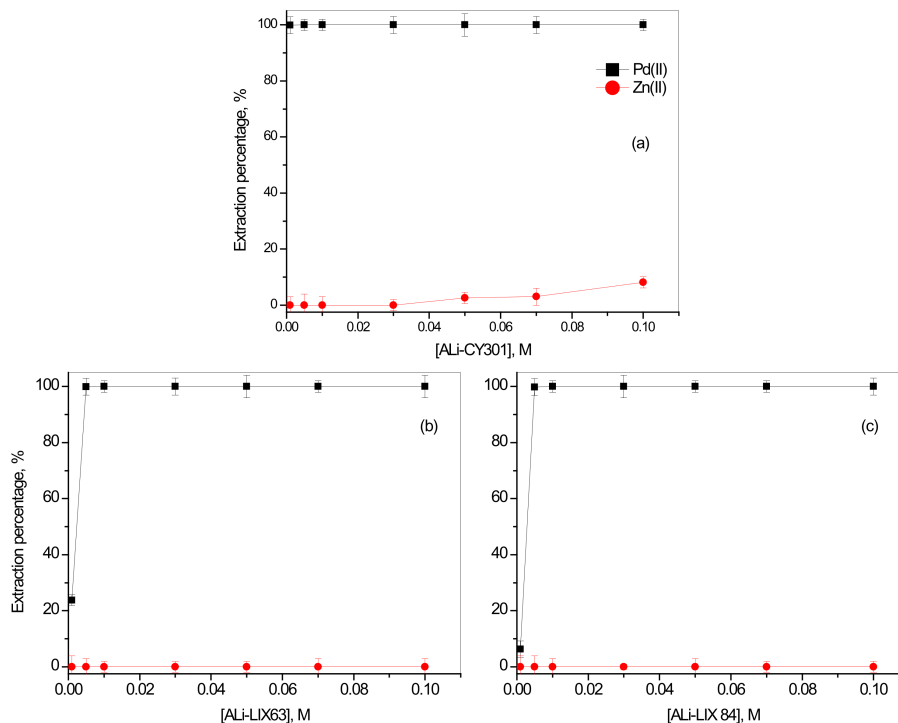


Figure 5. Effect of (a) ALi-CY301, (b) ALi-LIX63 and (c) ALi-LIX84 concentration on extraction of Pd(II) and Zn(II). Conditions: [extractant] = 0.001–0.1 M, diluent: kerosene; modifier: decanol 10% *v/v*. A/O = 1, (a) 7 M H₂SO₄, (b,c) 0.5 M H₂SO₄ [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L.

3.2.2. Effect of Concentration of Synthesized ILs with Inorganic Anions

In these experiments, IL concentration was varied from 0.001 to 0.1 M and the concentration of H₂SO₄ in synthetic leaching solution was controlled for each employed IL (0.5 M H₂SO₄ for ALi-I and ALi-Br and 9 M for ALi-SCN). The concentrations of Pd(II) and Zn(II) in the synthetic leaching solution were 100 and 500 mg/L, respectively. The volume ratio of the organic to aqueous phase was kept at unity. The results indicated that Pd(II) extraction percentage is a function of ALi-SCN concentration. As seen in Figure 6a, the extraction percentage of Pd(II) increased from 64% to 100% when the concentration of ALi-SCN increased from 0.001 to 0.005 M, and then remained constant with the increase of ALi-SCN. Zn(II) was not extracted at all in these conditions.

Figure 6b,c show that the extraction percentage of Pd(II) increased from 63.6% to 100% and from 39.9% to 100% when the concentration of ALi-I and ALi-Br increased from 0.001 to 0.005 M, then remained constant with the increase of ILs concentration. In these conditions, no Zn(II) was extracted and complete separation of Pd(II) and Zn(II) was possible. Our results indicate that both the synthesized ILs with organic (ALi-CY301, ALi-LIX63 and ALi-LIX84) and inorganic anions (ALi-SCN, ALi-I and ALi-Br) are effective in separating Pd(II) and Zn(II) from sulfuric acid solutions. Herein, ALi-I and ALi-Br are the best as an extractant for separating Pd(II) and Zn(II) when H₂SO₄ concentration is lower than 3 M, while ALi-CY301 and ALi-SCN are good when H₂SO₄ concentration is higher than 7 M. Especially, ALi-LIX63 and ALi-LIX84 can selectively extract Pd(II) from H₂SO₄ concentration in the range from 0.5 to 9 M, while Zn(II) was not extracted at all.

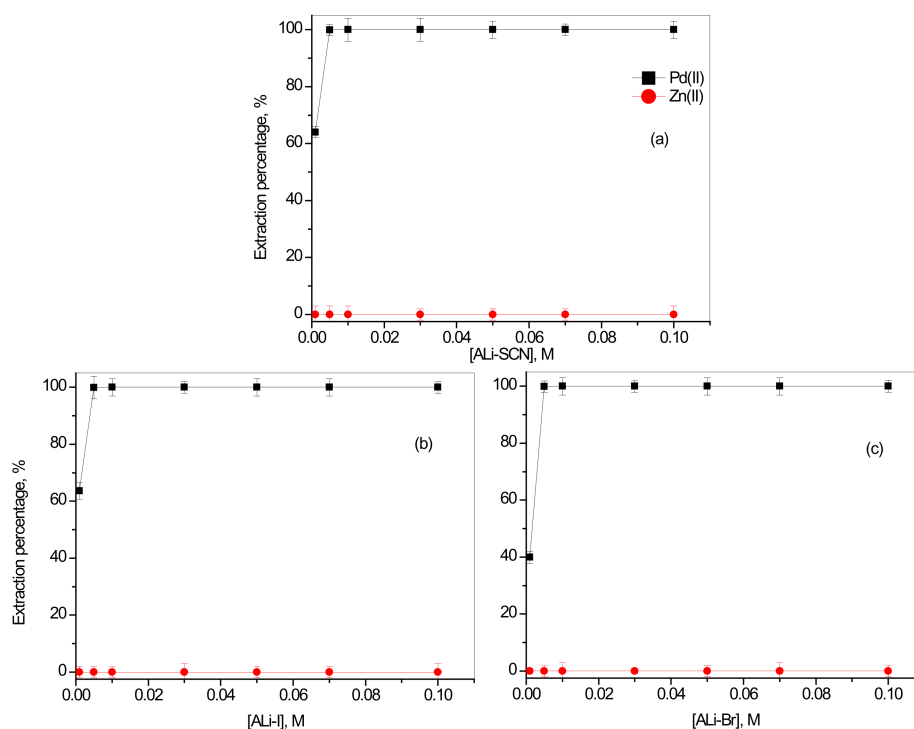


Figure 6. Effect of (a) ALi-SCN, (b) ALi-I and (c) ALi-Br concentration on extraction of Pd(II) and Zn(II). Conditions: [extractant] = 0.001–0.1 M, diluent: kerosene; modifier: decanol 10% *v/v*. A/O = 1, (a) 9 M H₂SO₄, (b,c) 0.5 M H₂SO₄; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L.

3.3. Stripping of Pd(II)

3.3.1. Preliminary Stripping Experiments

Stripping is one of the important steps in the solvent extraction process, and thus several stripping agents were tested to recover Pd(II) from the loaded IL phases. The Pd(II) in the loaded synthesized ILs was obtained by contacting 0.005 M ILs, except for ALi-CY301, to the aqueous solution containing 100 mg/L of Pd(II) and 500 mg/L of Zn(II) at certain H₂SO₄ concentrations. In the case of ALi-CY301, its concentration was controlled to 0.001 M. Based on the best condition for complete separation of Pd(II) over Zn(II), the concentration of H₂SO₄ in synthetic leaching solution was adjusted for each employed IL as follows: 7 M H₂SO₄ for ALi-CY301, 0.5 M H₂SO₄ for ALi-LIX63, ALi-LIX84, ALi-I and ALi-Br and 9 M for ALi-SCN. The volume ratio of organic to aqueous phase was unity. The concentration of Pd(II) in the loaded organic phase of the ILs was 100 mg/L, and no Zn(II) was extracted at these conditions.

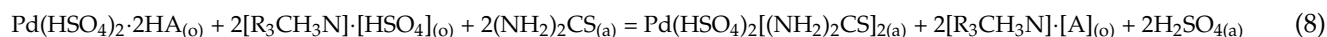
It has been reported that NH₃ solution and the mixture of HCl and thiourea are efficient stripping agents for Pd(II) from the loaded phases of ALi-I and ALi-Br, as well as LIX 63 [4,9]. Therefore, these agents and single thiourea as well as acidic solutions (HCl, H₂SO₄) were employed to investigate Pd(II) stripping efficiency. Table 3 displays the stripping percentage of Pd(II) from the corresponding loaded IL phase. Among the tested stripping agents, NH₃ solution exhibited the highest stripping capacity for Pd(II) from ALi-SCN (5%), ALi-I (89.7%) and ALi-Br (100%), whereas a mixture of 0.1 M HCl and 0.5 M thiourea showed a quantitative stripping of Pd(II) from the loaded ALi-LIX63 and ALi-LIX84. However, the stripping of Pd(II) from the loaded ALi-CY 301 was very difficult (<1%). This can be attributed to the strong affinity between Pd(II) and sulfur atoms of Cyanex 301 on the basis of the HSAB principle. The limited stripping of Pd(II) with NH₃ solution from the loaded ALi-SCN may be related to the co-extraction of hydrogen ions from concentrated H₂SO₄ solution [39].

Table 3. Stripping efficiency of Pd(II) using diverse reagents ([IL] except ALi-CY301 = 0.005 M, [ALi-CY301] = 0.001 M, A/O = 1, [Pd] in the loaded phase was 100 mg/L).

Stripping Agent	Loaded Organic Phase, Stripping Percentage (%S)					
	ALi-C301	ALi-LIX63	ALi-LIX84	ALi-I	ALi-Br	ALi-SCN
5% NH ₃	0.6	0.0	2.1	89.7	100.0	5.0
0.1 M HCl	0.0	0.0	0.0	0.3	2.4	0.0
0.1 M H ₂ SO ₄	0.0	0.0	0.1	0.0	0.0	0.0
0.5 M thiourea	0.5	2.9	2.2	2.5	9.0	1.1
0.1 M HCl + 0.5 M thiourea	0.8	13.5	14.1	11.4	17.9	1.2
0.1 M H ₂ SO ₄ + 0.5 M thiourea	0.2	0.3	0.3	0.0	1.0	0.6

3.3.2. Stripping of Pd(II) from Loaded Organic Phase of Synthesized ILs with Organic Anions

To investigate the effect of HCl and thiourea concentration on stripping of Pd(II) from the loaded ALi-LIX63 and ALi-LIX84 phases, their concentrations were varied from 0.1 to 5 M and 0.1 to 0.5 M, respectively. The results in Table 4 reveal that the mixture of 0.5 M HCl and 0.5 M thiourea can completely strip Pd(II) from the loaded ALi-LIX63, while complete stripping of Pd(II) from the loaded ALi-LIX84 was possible by the mixture of 0.5 M HCl and thiourea, whose concentration was in the range from 0.1 to 0.5 M. The stripping percentage of Pd(II) decreased when HCl concentration in the mixture was higher than 1 M. This phenomenon may be related to the stability of the Pd(II)-chloro complexes in the concentrated HCl solution, resulting in the extraction of Pd-chloro complexes to the organic phase. The stripping reaction of Pd(II) from the loaded ILs using a mixture of HCl and thiourea can be represented as follows:



where HA denotes LIX 63/LIX 84.

Table 4. Effect of HCl and thiourea concentration on stripping of Pd(II) from ALi-LIX63 and ALi-LIX84 loaded phases ([IL] = 0.005 M, A/O = 1, [Pd] in the loaded phase was 100 mg/L).

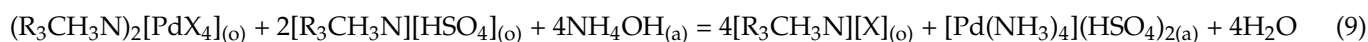
Stripping Agent	Pd(II) Stripping Percentage (%S)		Stripping Agent	Pd(II) Stripping Percentage (%S)	
	ALi-LIX63	ALi-LIX84		ALi-LIX63	ALi-LIX84
0.1 M HCl + 0.5 M thiourea	13.5	14.1	0.5 M HCl + 0.1 M thiourea	81.8	100
0.5 M HCl + 0.5 M thiourea	100	100	0.5 M HCl + 0.2 M thiourea	91.0	100
1 M HCl + 0.5 M thiourea	100	100	0.5 M HCl + 0.3 M thiourea	94.1	100
3 M HCl + 0.5 M thiourea	65.3	65.9	0.5 M HCl + 0.4 M thiourea	96.9	100
5 M HCl + 0.5 M thiourea	34.4	45.0	0.5 M HCl + 0.5 M thiourea	100	100

Since stripping of Pd(II) from the loaded ALi-CY 301 was difficult, aqua regia solutions with several dilution degrees were employed, and 90% of Pd(II) was stripped from the loaded ALi-CY301 by aqua regia diluted 1.5 times.

3.3.3. Stripping of Pd(II) from Loaded Organic Phase of Synthesized ILs with Inorganic Anions

According to preliminary stripping experiments, NH₃ solution is appropriate to strip Pd(II) from the loaded phase of ILs with inorganic anions. To investigate the effect of NH₃ concentration on the stripping of Pd(II) from the loaded ALi-I and ALi-Br phases, the concentration of NH₃ was changed from 0.5 to 3 M (see Table 5). The stripping percentage of Pd(II) from the loaded ALi-Br was higher than that from the loaded ALi-I phase. Pd(II) from ALi-Br was completely stripped by 0.5 M NH₃, while only 91.4% of Pd(II) was

stripped from the loaded ALi-I. The stripping reaction of Pd(II) from the loaded ALi-I and ALi-Br with NH₃ solution can be proposed as:



where X denotes Br and I.

Table 5. Effect of NH₃ concentration on stripping of Pd(II) from ALi-I and ALi-Br loaded phases ([IL] = 0.005 M, A/O = 1, [Pd] in the loaded phase was 100 mg/L).

Stripping Agent NH ₃ , M	Loaded Organic Phase, %S	
	ALi-I	ALi-Br
0.5	91.4	100
1	89.6	100
2	88.5	100
3	86.5	100

The stripping percentage of Pd(II) by a single NH₃ solution from the loaded ALi-SCN was low (5%), however, the use of a concentrated NH₃ solution as a stripping agent is unfavorable owing to the probable decomposition of ILs [40]. Therefore, NH₄Cl was added to 5% NH₃ solution to enhance the stripping of Pd(II). The obtained results show that 98.4% of Pd(II) was stripped from the loaded ALi-SCN by the mixture of 1 M NH₄Cl and 5% NH₃ solution. When the concentration of NH₄Cl was higher than 1 M, the excess concentration of chloride ions in the stripping solution adversely affected the stripping of Pd(II) due to the extraction of the Pd(II)-chloro complex.

Table 6 shows that synthesized ILs such as ALi-CY301, ALi-LIX63, ALi-LIX84, ALi-SCN, ALi-I and ALi-Br can be considered as potential extractants for separation of Pd(II) over Zn(II) from sulfuric acid solutions. The selective extraction efficiency of Pd(II) over Zn(II) by ILs depends on H₂SO₄ concentrations. It is noticeable that both ALi-LIX63 and ALi-LIX84 can selectively extract Pd(II) regardless of H₂SO₄ concentration in the range from 0.5 to 9 M. On the other hand, the difference in the complex formation degree between Pd(II) and Zn(II) with inorganic anions (SCN⁻, I⁻, Br⁻) significantly contributes to the complete separation of two metal ions from sulfuric acid solutions by ILs such as ALi-SCN, ALi-I and ALi-Br. The complete stripping of Pd(II) from the loaded ILs was possible by employing either the mixture of HCl and thiourea or NH₃ solution. These data indicated that a simple solvent extraction process using the synthesized ILs can be applied for the separation of Pd(II) and Zn(II) from the sulfuric acid leaching solutions of cemented Pd.

3.4. The Separation of Pd(II) over Zn(II) from Real Leaching Solution of Cemented Pd

The cemented Pd was obtained from the spent electroplating solutions by cementation with Zn metal powder. The cemented Pd was washed with diluted sulfuric acid solution and then the residues were dissolved at the optimum leaching condition [2], namely, a mixture of 5 M H₂SO₄ and 1.5% NaClO, pulp density: 2 g/L, 1 h, and 25 °C. At this condition, the Pd and Zn metal in the cemented Pd were completely dissolved. The concentrations of Pd(II) and Zn(II) in the real leaching solution were 1926 and 74 mg/L, respectively.

From our data on the separation of Pd(II) and Zn(II) by several ILs, ALi-LIX63 and ALi-LIX84 were selected as extractants and employed to the real leaching solution of the cemented Pd. The concentration of these two ILs was varied from 0.005 to 0.2 M and the volume ratio of the two phases was fixed at unity. Figure 7 shows that both Pd(II) and Zn(II) was extracted by (a) ALi-LIX63 and (b) ALi-LIX84, and the extraction percentage is a function of ILs' concentration. The obtained results indicated that the extraction percentage of Pd(II) and Zn(II) increased from 51.4% (40.5%) to 99.5% (98.7%) and from 22.3% (22.1%) to 100% (100%) respectively, when the concentration of ALi-LIX63 (ALi-LIX84) increased from 0.005 to 0.2 M.

Table 6. Summary on the separation of Pd(II) and Zn(II) from sulfuric acid solution by using synthesized ILs in this work ([Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L).

IL Extractant	[H ₂ SO ₄], M	Extraction Percentage (%E)	Stripping Agents	Stripping Percentage (%S)	Separation Efficiency
0.1 M ALi-D2	9	Pd: 19.8 Zn: 0	-	-	Low extraction percentage Complete separation
0.1 M ALi-CY272	5	Pd: 7.5 Zn: 0	-	-	Low extraction percentage Complete separation
0.1 M ALi-PC	7	Pd: 10 Zn: 0	-	-	As above
0.001 M ALi-CY301	7–9	Pd: 100 Zn: 0	Aqua regia diluted 1.5 times	90.6	High extraction percentage of Pd(II) but control of IL concentration to low is necessary to avoid co-extraction of a small amount of Zn(II). High separation
0.005 M ALi-LIX63	0.5–9	Pd: 100 Zn: 0	Mixture of 0.5 M HCl and 0.5 M Thiourea	100	High extraction and stripping percentage Complete separation
0.005 M ALi-LIX84	0.5–9	Pd: 100 Zn: 0	Mixture of 0.5 M HCl and 0.1 M Thiourea	100	As above
0.005 M ALi-I	0.5–3	Pd: 100 Zn: 0	0.5 M NH ₃	91.4	As above
0.005 M ALi-Br	0.5–1	Pd: 100 Zn: 0	0.5 M NH ₃	100	As above
0.005 M ALi-SCN	9	Pd: 100 Zn: 0	1 M NH ₄ Cl and 5%NH ₃	98.4	As above

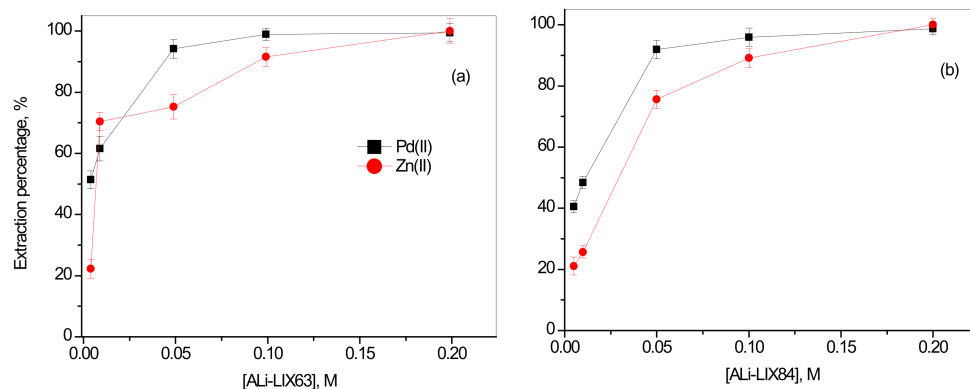
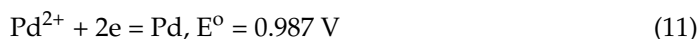


Figure 7. Effect of (a) ALi-LIX63 and (b) ALi-LIX84 concentration on extraction of Pd(II) and Zn(II). Conditions: [extractant] = 0.005–0.2 M, diluent: kerosene; modifier: decanol 10% *v/v*. A/O = 1, real leaching solution of 5 M H₂SO₄ and 1.5% NaClO; [Pd(II)] = 1926 mg/L and [Zn(II)] = 74 mg/L.

The co-extraction of Zn(II) in these experiments was attributed to the use of NaClO as an oxidizing agent during sulfuric acid leaching of the cemented Pd. The standard reduction potentials of Pd(II) and hypochlorite ions at 25 °C are represented as follows [41]:



Equations (10) and (11) indicate that the hypochlorite ions can be reduced to chloride ions during the leaching of the cemented Pd with the mixture of H₂SO₄ and NaClO at 25 °C. According to the HSAB principle, Pd(II) is a soft acid, while Zn(II) is classified as borderline. Since chloride ions are a hard base, Zn(II) has a stronger tendency to form chloro complexes than Pd(II). Compared to pure sulfuric acid solution, the extraction of Zn(II) is enhanced in the real leaching solution owing to the formation of Zn(II)–chloro complexes [34,42]. According to our results on the leaching of Pd and Zn metal, Pd metal would not be dissolved in the sulfuric acid solution when hydrogen peroxide is employed as an oxidizing agent [2], and thus the use of NaClO is necessary.

The extraction data with the real leaching solution indicate that removal of chloride ions is necessary to apply the separation conditions obtained from pure synthetic sulfuric acid solutions.

4. Conclusions

The separation of Pd(II) and Zn(II) from synthetic sulfuric acid leaching solutions of cemented Pd from spent electroplating solutions was investigated by solvent extraction with synthesized ILs. Among the ILs employed in this work, ALi-LIX63 and ALi-LIX84 completely separated Pd(II) over Zn(II) in the H₂SO₄ concentration range from 0.5 to 9 M, whereas the selective extraction of Pd(II) by ILs such as ALi-CY301, ALi-SCN, ALi-I and ALi-Br depended on H₂SO₄ concentrations. Namely, selective extraction of Pd(II) by ALi-I and ALi-Br was possible when H₂SO₄ concentration was low (0.5–3 M), while ALi-CY301 and ALi-SCN were effective in selective extraction of Pd(II) from concentrated H₂SO₄ concentrations (7–9 M). It was found that control of ALi-CY301 concentration was very important to separate Pd(II) over Zn(II). Two kinds of synthesized ILs with organic (ALi-CY301, ALi-CY272, ALi-LIX63, ALi-LIX84) and inorganic anions (ALi-I, ALi-Br, ALi-SCN) were selective for Pd(II) extraction. Pd(II) from the loaded phase of ALi-LIX63 and ALi-LIX84 was completely stripped by the mixture of HCl and thiourea. Aqua regia solutions were effective for stripping of Pd(II) from the loaded ALi-CY301. Stripping of Pd(II) from loaded ALi-I and ALi-Br was possible by the 0.5 M NH₃ solution, while 98.4% of Pd(II) was stripped from the loaded ALi-SCN by using a mixture of NH₄Cl and NH₃ solutions.

Application of the extraction conditions to the real 5 M sulfuric acid leaching solution of cemented Pd indicated that it was difficult to separate Pd(II) and Zn(II) by extraction with ALi-LIX63 and ALi-LIX84. The use of NaClO as an oxidizing agent during the sulfuric acid leaching of real cemented Pd resulted in an enhancement of Zn(II) extraction by ALi-LIX63 and ALi-LIX84. Our results indicate that it is necessary to remove chloride ions from the sulfuric acid leaching solution to apply the separation conditions obtained from synthetic sulfuric acid solutions.

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