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Recovery of palladium(II) from acidic chloride solution using kerosene containing tri-n-octyl/decyl amine (Alamine 336)

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ABSTRACT

This study employed a tri-n-octyl/decyl amine (Alamine 336) as an extractant dissolved in kerosene to extract palladium(II) from HCI solution at 25˚C. The experiments of different stripping reagents such as HCI, NaCl, KCl, $BaCl_2$, $AlCl_3$, and thiourea were compared, respectively; and the optimal status was determined. The results showed that the extraction distribution ratios are proportional to the extractant concentration and disproportional to chloride ion concentration. By graphical analysis, the compositions of palladium complexes in organic phase and equilibrium constant of recovered extraction reaction were examined. Finally, the recovery efficiency of palladium(II) in acidic chloride solution was determined.

Keywords: Solvent extraction; Stripping; Alamine 336; Palladium

1. Introduction

The platinum group metals (PGMs: Pt, Pd, Rh, Os, Ir, and Ru) are used extensively in automobiles, chemicals, jewelry, medical prostheses, and dental and extrusion devices. The PGMs demand projections show a significant increase in the use of these metals for current fuel cell technology, automotive technology, and the development of fuel cell vehicles. Due to the characteristics such as resistance to oxidation and corrosion, catalytic activity, electrical conductivity, and high melting points, PGMs are extremely useful in different industries. In automobiles, demand for platinum(IV) and palladium(II) in the autocatalyst sector has risen up by 5% each year [1]. PGMs are used in catalytic converters to reduce harmful emissions. Approximately 60% [1] of the annual world production of palladium(II) and platinum(IV) was used in automotive exhaust catalysts [2], but the amount of PGMs currently being recycled from used autocatalysts remains around 20% [3,4]. For the automotive industry, technology that uses the platinum(IV) and palladium(II) catalysts cannot be substituted by other metals. The recovery of palladium from waste solutions as well as preconcentration techniques to facilitate their determination at very low levels is important environmental and economical issues.

The traditional PGM recovery methods are costly and complex because of the chemical separation, acid dissolution, physical treatment, and refining processes [5,6]. During the PGM recovery operations, the separation technique of classical precipitation methods [7–9] is relatively low and costly because of the number of operations required. By contrast, the use of

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solvent extraction reduces the costs while offering better selectivity. Palladium is the most commonly used PGM. Recently, the price of palladium has rised, thus recycling of palladium can reduce costs and the impact on environment.

The solvents commonly used for extraction include xylene [10], toluene [11], benzene [12], chloroform [13], n-hexane [14], and kerosene [15–17]. To improve safety and protect the environment during the extraction process, environmental friendly and renewable solvents for metal recovery is extremely vital. Kerosene is nontoxic and inexpensive, this study employed it as a solvent to conduct extraction.

Alamine 336 (tri-octyl/decyl amine) is a basic extractant, also called an anionic exchanger. The existing basic extractants are primary amines (RNH_2), secondary amines (R_2NH), tertiary amines (R_3N), and quaternary ammonium (R_4N^+). C_8–C_{10} saturated aliphatic tertiary amines (e.g. Alamine 300; 308; 336) dissolved in organic solvents and are effective extractants for carboxylic acids [18–20]. Alamine 336 (tertiary amine, R_3N, $R = CH_3(CH_2)_7$) has been used in extracting PGMs [21]. Alamine 336 is a water insoluble tri-octyl/decyl amine, which is capable of forming oil soluble salts of anionic species at low pH levels. Since tri-octyl/decyl amine contains a basic nitrogen atom, it can react with variety of inorganic and organic acids to form amine salts, which are capable of undergoing ion exchange reactions with many other anions. Alamine 336 is a purifying organic and inorganic species, which is capable of forming anions using a solvent extraction process. Alamine 336 is transformed into amine salts, which then undergoes anion exchange between chloride and the negative metallic complex. The general reactions can be described in two steps—protonation and ion exchange—which are shown below [22].

$$\text{Protonation}: R_3N_{(org)} + H^+_{(aq)} + Cl^-_{(aq)} \leftrightarrows R_3NH^+Cl^-_{(org)}$$

$$\text{Exchange}: 2R_3NH^+Cl^-_{(org)} + PdCl^{2-}_{4(aq)} \leftrightarrows PdCl_4(R_3NH)_{2,(org)} + 2Cl^-_{(aq)}$$

where the subscripts (org) and (aq) represent the organic and aqueous phases, respectively. The extent to which $PdCl_4^{2-}$ will exchange with Cl^- is a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase.

Swain et al. used Alamine 300 as an extraction solvent to extract palladium and platinum [15]. To derive a suitable stripping agent, HCl, $(NH_2)_2CS$ with HCl, $(NH_2)_2CS$ with NaCl, $(NH_2)_2CS$ with KCl, $(NH_2)_2CS$ with $BaCl_2$, and $(NH_2)_2CS$ with $AlCl_3$ were used at different concentrations. $(NH_2)_2CS$ with HCl was the best stripping agent for palladium. However, few data have been reported on the stripping of PGMs from the loaded amines [23].

2. Materials and methods

2.1. Reagents and solutions

Tri-octyl/decyl amine, marketed as Alamine 336 (M.W. 392 g/mol), was used without further purification. Alamine 336 is a mixture of saturated and straight chain trialkylamines with carbon chains C_8 and C_{10}, in which the proportion of the carbon chain C_8 is about 2 to 1 [25]. Alamine 336 was obtained from Cognis Corporation (USA) and it was mixed with kerosene (supplied by Chinese Petroleum Co., Taiwan). Modifiers l-Octanol (FERAK, Germany, 99%) was added at 10% (v/v) concentration to the kerosene to maintain the solubility of the Alamine 336.

Stock solutions of 0.02 M palladium chloride were prepared by dissolving analytical grade chemical, $PdCl_2$ (Merck, Germany), in 10 M of HCl. The synthetic aqueous solutions containing palladium were used for each solvent extraction by diluting the stock solutions to the desired concentration and then mixing them.

Standard solutions were prepared from 1,000 $mg\,L^{-1}$ of palladium atomic absorption (Merck, Germany). Thiourea, NaCl, KCl, $BaCl_2$, $AlCl_3$, and HCl (analytical grade) were obtained from ACROS (USA). All other chemicals were of an analytical reagent grade. Working solutions of palladium were prepared by sampling the appropriate volumes of the stock solution and diluting them with distilled water.

2.2. Procedure

Twenty milliliters of the organic solution and an equal volume of aqueous solution were mixed in glass flasks with ground glass stoppers, and shaken by a mechanical shaker for at least 30 min at 25.0 ± 0.2°C until equilibrium was attained. Preliminary experiments had shown that the time needed to reach equilibrium was less than 15 min. The organic solutions contained 0.02–0.5 M Alamine 336 dissolved in kerosene. The concentration of palladium(II) ions in the initial aqueous solutions ranged from 1×10^{-4} to 2×10^{-2} M. The two phases got separated after they had been allowed to settle for over 6 h at 25.0 ± 0.2°C.

After phase separation, the equilibrium chloride ion concentration was measured by Automatic Potentiometric Titator (Metrohm). The concentration of palladium(II) in the aqueous phase was analyzed by a GBC SenseAA atomic absorption spectrophotometer (AAS).

Before measuring the Pd concentration in the organic phase, a stripping experiment was conducted. Stripping experiments were performed with all the loaded extractants while keeping the aqueous to organic phase ratio at 2:1 at a temperature of 25.0 ± 0.2 °C for 30 min. Palladium in the organic phase was stripped with either HCl, $(NH_2)_2CS$ with HCl, $(NH_2)_2CS$ with NaCl, $(NH_2)_2CS$ with KCl, $(NH_2)_2CS$ with $BaCl_2$, or $(NH_2)_2CS$ with $AlCl_3$; the metal concentration in the acidic solutions was analyzed by AAS.

This process has been shown to be quantitative, and the mass balance for the metal was always fulfilled in the extraction-stripping procedure within ±2%.

3. Results and discussion

3.1. Extraction equilibrium of palladium

When the chloride ion concentration is higher than 1 M, palladium and chloride ions form stable chlordion complexes—$PdCl_4^{2-}$ [24]. When Alamine 336 to extract the palladium in aqueous phase was fully loaded, the complexes formed by Alamine 336 and Pd may further react and form a polymeric species [25]. Thus, assuming that the extraction of palladium(II) with Alamine 336 causes the formation of an m-merized complex, it can be represented by the following general reaction:

$$m\mathrm{PdCl_4^{2-}} + m(p+q)\overline{\mathrm{R_3NHCl}} \rightleftharpoons \overline{(\mathrm{PdCl_4(R_3NH)}_p(\mathrm{R_3NHCl})_q)_m} + mp\mathrm{Cl^-} \qquad (1)$$

The bar indicates the species in the organic phase.

The extraction equilibrium constant (K_{mpg}) can be expressed as:

$$K_{mpq} = \frac{[\overline{(\mathrm{PdCl_4(R_3NH)}_p)(\mathrm{R_3NHCl})_q)_m}][\mathrm{Cl^-}]^{mp}}{[\mathrm{PdCl_4^{2-}}]^m[\overline{\mathrm{R_3NHCl}}]^{m(p+q)}} \qquad (2)$$

The extraction equilibrium constant for hydrochloric solutions with kerosene as the diluent.

The distribution ratio of Palladium is defined as:

$$D_{\mathrm{Pd}} = \frac{[\overline{\mathrm{Pd(II)}}]}{[\mathrm{Pd(II)}]} \qquad (3)$$

Substituting Eq. (2) into (3), we obtain:

$$\begin{aligned} D_{\mathrm{Pd}} &= \frac{m[\overline{(\mathrm{PdCl_4(R_3NH)}_p(\mathrm{R_3NHCl})_q)_m}]}{[\mathrm{PdCl_4^{2-}}]} \\ &= mK_{mpq}[\mathrm{PdCl_4^{2-}}]^{m-1}[\overline{\mathrm{R_3NHCl}}]^{m(p+q)}[\mathrm{Cl^-}]^{-mp} \end{aligned} \qquad (4)$$

Therefore, at a low distribution ratio and constant concentrations of Alamine 336, $[\mathrm{PdCl_4^{2-}}]^{m-1}$ $[\overline{\mathrm{R_3NHCl}}]^{m(p+q)}$ will be approximately constant. Thus, a plot of $\log D_{\mathrm{pd}}$ vs. $\log[\mathrm{Cl^-}]$ will give a straight line with a slope of mp. The experimental results are shown in Fig. 1. The straight lines have slopes of −2, or $mp = 2$. Substituting Eq. (3) into (4) and rearranging Eq. (4), it follows that:

$$[\overline{\mathrm{Pd(II)}}][\mathrm{Cl^-}]^2 = mK_{mpq}[\mathrm{PdCl_4^{2-}}]^m[\overline{\mathrm{R_3NHCl}}]^{m(p+q)} \qquad (5)$$

At constant concentrations of Alamine 336, the degree of aggregation of the Pd-Alamine 336 complex in the organic phase, m, is obtained from the plot of $\log[\overline{\mathrm{Pd(II)}}][\mathrm{Cl^-}]^2$ vs. $\log[\mathrm{PdCl_4^{2-}}]$. As shown in Fig. 2, the straight lines have unit slopes. Therefore, the extracted species is monomeric, or $m = 1$ and $p = 2$. Thus, Eqs. (2) and (4) can be simplified to:

$$K_{2q} = \frac{[\overline{(\mathrm{PdCl_4(R_3NH)_2(R_3NHCl)}_q}][\mathrm{Cl^-}]^{-2}}{[\mathrm{PdCl_4^{2-}}][\overline{\mathrm{R_3NHCl}}]^{2+q}} \qquad (6)$$

And:

$$D_{\mathrm{Pd}} = K_{2q}[\overline{\mathrm{R_3NHCl}}]^{2+q}[\mathrm{Cl^-}]^{-2} \qquad (7)$$

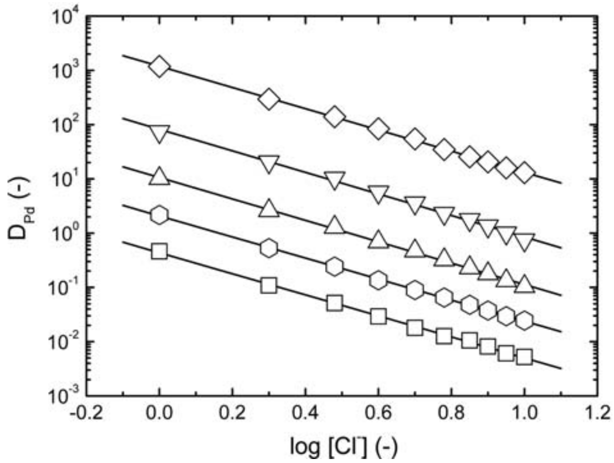

Fig. 1. Plots of $\log D_{\mathrm{Pd}}$ vs. $\log[\mathrm{Cl^-}]$ at equilibrium for various Alamine 336 concentrations in kerosene at 25 °C. (1) □ $[\overline{\mathrm{R_3N}}] = 0.02$ M, slope = −1.93; (2) ⬡ $[\overline{\mathrm{R_3N}}] = 0.05$ M, slope = -1.94; (3) △ $[\overline{\mathrm{R_3N}}] = 0.1$ M, slope = −1.97; (4) ▽ $[\overline{\mathrm{R_3N}}] = 0.2$ M, slope = −1.98; and (5) ◇ $[\overline{\mathrm{R_3N}}] = 0.5$ M, slope = −1.96.

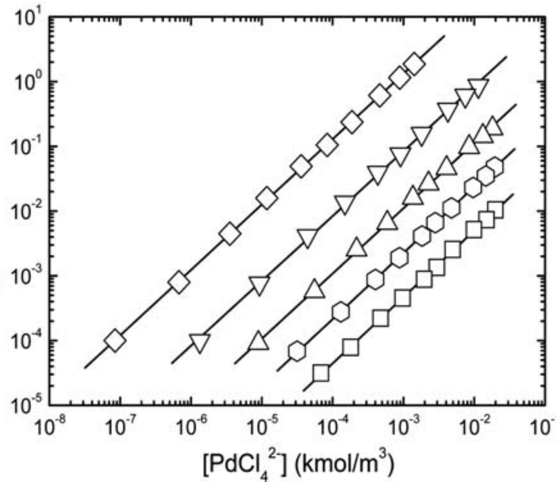

Fig. 2. Plots of $\log D_{Pd}[Cl^-]^2$ vs. $\log[PdCl_4^{2-}]$ at equilibrium for various Alamine 336 concentrations in kerosene at 25° C. (1) □ $[\overline{R_3N}] = 0.02\,M$, slope = 1.03; (2) ⬡ $[\overline{R_3N}] = 0.05\,M$, slope = 1.02; (3) △ $[\overline{R_3N}] = 0.1\,M$, slope = 1.00; (4) ▽ $[\overline{R_3N}] = 0.2\,M$, slope = 1.00; and (5) ◇ $[\overline{R_3N}] = 0.5\,M$, slope = 1.01.

Rearranging Eq. (7), it follows that:

$$\log D_{Pd} = \log K_{2q} + (2+q)\log[\overline{R_3NHCl}] - 2\log[Cl^-] \tag{8}$$

First, it could be assumed that only species of the type $\overline{(PdCl_4(R_3NH)_2(R_3NHCl)_q}$ are formed. Thus, a plot of $\log(D_{Pd}[Cl^-]^{-2})$ vs. $\log[\overline{R_3NHCl}]$ would give a straight line with an intercept equal to K_{2q} and a slope equal to $(2+q)$.

The concentrations of Alamine 336 were 0.02, 0.05, 0.1, 0.2, and 0.5 M. In Fig. 3, a straight line with a slope of 2.50 is obtained, or $q = 0.5$. This phenomenon implies that more than one species is formed.

Before calculating the experimental results, this study assumed a low distribution ratio (D_{Pd} approximately smaller than 0.1). The distribution ratio and the concentration of Alamine 336 are related. Under suitable conditions, the distribution ratio and Alamine 336 are positively correlated. When considering recycling efficiency, a higher D_{Pd} leads to greater efficiency. Therefore, when calculating m and p values, this study considered the low distribution ratio. Next, this study used a graphic method to discuss the composition of the complexes.

3.2. Reconfirmation of extraction equilibrium formation by slope analysis

When $q = 0.5$, considering the two species that may form in the organic phase, such as $\overline{PdCl_4(R_3NH)_2}$ and $\overline{PdCl_4(R_3NH)_2(R_3NHCl)}$, Eq. (3) can be expressed as:

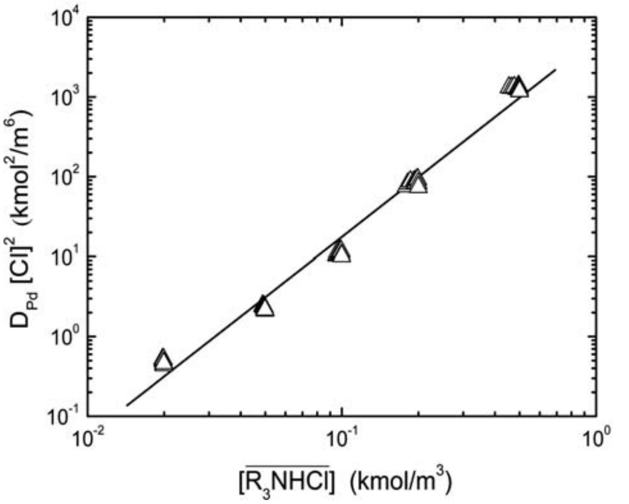

Fig. 3. Plots of $\log D_{Pd}[Cl^-]^2$ vs. $\log[\overline{R_3NHCl}]$ at equilibrium for various Alamine 336 concentrations in kerosene at 25°C. Slope = 2.50.

$$D_{Pd} = \frac{[\overline{PdCl_4(R_3NH)_2}] + [\overline{PdCl_4(R_3NH)_2(R_3NHCl)}]}{[PdCl_4^{2-}]} \tag{9}$$

Using Eq. (7), Eq. (9) becomes:

$$D_{Pd}[Cl^-]^2 = K_{20}[\overline{R_3NHCl}]^2 + K_{21}[\overline{R_3NHCl}]^3 \tag{10}$$

or

$$\frac{D_{Pd}[Cl^-]^2}{[\overline{R_3NHCl}]^{-3}} = K_{20}\frac{1}{[\overline{R_3NHCl}]} + K_{21} \tag{11}$$

Now, a plot of $D_{Pd}[Cl^-]^2[\overline{R_3NHCl}]^{-3}$ vs. $[\overline{R_3NHCl}]^{-1}$ would give a straight line with a slope equal to K_{20} and an intercept equal to K_{21}. In Fig. 4, a straight line with a slope of $K_{20} = 4.23 \times 10^3$ and an intercept $K_{21} = 1.07 \times 10^3$ (kmol/m^3)$^{-1}$ are obtained.

Rovira used resin to impregnate Alamine 336 in a hydrochloric acid solution to extract palladium(II) [25].

3.3. Effect of Alamine 336 on the Recovery of Palladium(II)

The effect of extractant concentration in the range of 0.02–0.5 M of Alamine 336 was studied on the extraction of 0.001 M of palladium(II) from 1.0 M HCl. The recovery percentage of palladium(II) increased with the increase in Alamine 336 concentration. When the Alamine 336 concentration was higher than 0.2 M, the palladium was almost extracted by Alamine 336 (Fig. 5).

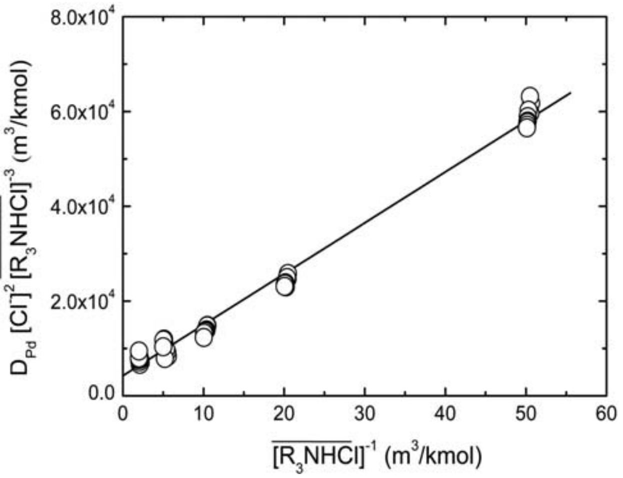

Fig. 4. Plots of $D_{Pd}[Cl^-]^2$ [$\overline{R_3NHCl}^{-3}$] vs. [$\overline{R_3NHCl}^{-1}$] at equilibrium for various Alamine 336 concentrations in kerosene at 25°C. Slope = 4.23 × 10^3 and intercept = 1.07 × 10^3.

According to the published literature [21], the extraction of palladium will decrease at higher concentrations of hydrochloric acid, owing to the mass action effect of chloride ions. The extraction results in Fig. 5 imply that Pd can be simultaneously extracted by Alamine 336 by adjusting the HCl and Alamine 336 concentrations. The extraction results are shown in Fig. 5. The best extraction effect was obtained at 1 M of chloride ion concentration.

3.4. Selection of stripping regents

In any extraction process, it becomes necessary to re-extract the metal from the loaded organic phase. To discover a suitable stripping regent, HCl, $(NH_2)_2CS$ with HCl, $(NH_2)_2CS$ with NaCl, $(NH_2)_2CS$ with KCl, $(NH_2)_2CS$ with $BaCl_2$, and $(NH_2)_2CS$ with $AlCl_3$ were used at different concentrations. The loaded organic solvent was generated using 0.5 M of Alamine 336. Palladium was stripped from a single stage loaded organic solvent system. The aqueous phases were separated and analyzed.

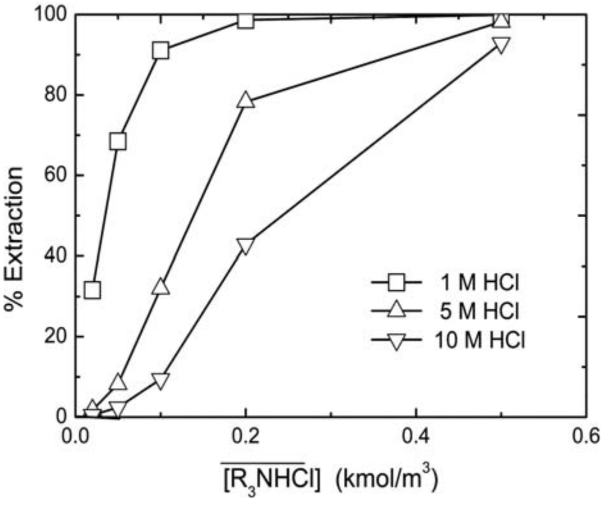

Fig. 5. Effect of Alamine 336 and HCl concentration on the extraction of palladium(II). Alamine 336: 0.02, 0.05, 0.1, 0.2, 0.5 M and HCl: 1, 5, 10 M.

The stripping of palladium from the loaded Alamine 336 phase (0.005 M Pd) was carried out with HCl (1 to 10 M), NaCl (0.2, 0.5 M), KCl (0.2, 0.5 M), $BaCl_2$ (0.2, 0.5 M), $AlCl_3$ (0.2, 0.5 M), and thiourea (0.005 to 0.5 M). The present results demonstrated that a 0.5 M HCl + 0.5 M thiourea system is the best system for stripping palladium. We conducted stripping experiments of palladium from the loaded Alamine 336 solution with several stripping agents, and the results are summarized in Table 1.

The stripping reaction using thiourea with palladium can be represented as follows:

$$\overline{(R_3NH)_2(PdCl_4)} + 2(NH_2)_2CS \rightleftharpoons 2\overline{R_3NHCl} + PdCl_2((NH_2)_2CS)_2 \tag{12}$$

$$\overline{(R_3NH)_2(PdCl_4)(R_3NHCl)} + 2(NH_2)_2CS \rightleftharpoons 3\overline{R_3NHCl} + PdCl_2((NH_2)_2CS)_2 \tag{13}$$

In the case if only palladium complexes are present in the organic phase, it is extracted by a coordination–substitution reaction between $(NH_2)_2CS$ and Cl^- which takes place competitively, and depends upon the concentrations of the metal ion complex and the stripping agent. The experimental results indicate that high stripping efficiency is observed when using thiourea with suitable concentrations of HCI and NaCI. As can be seen in Eqs. (12) and (13), increasing the chloride ion concentration is beneficial to the formation of $\overline{R_3NHCl}$. In other words, the stripping efficiency when using only thiourea is lower than using thiourea with $[CI^-]$. Previous literature has suggested the high efficiency of using thiourea with HCI in Alamine 336 to strip palladium [16]. In this experiment, high stripping efficiency was observed when using thiourea with HCI, and was also observed when using thiourea with NaCl, KCl, $BaCl_2$, and $AlCl_3$. Consequently, this study inferred that the stripping efficiency using thiourea is more highly correlated with chloride ion concentration than pH values. However, recently, less research has explored the correlation between the stripping efficiency and chloride ion concentration.

Table 1
Stripping of palladium(II) from the loaded Alamine 336 phases by different reagents

[HCl], M	Pd stripping, % ([Thiourea], M)	[HCl], M	Pd stripping, % ([Thiourea], M)	[NaCl], M	Pd stripping, % ([Thiourea], M)
1	5.6 (0)	0.2	98.9 (0.5)	0.2	98.9 (0.5)
2	17.1 (0)	0.2	98.8 (0.2)	0.2	98.7 (0.2)
3	28.6 (0)	0.2	98.6 (0.1)	0.2	98.5 (0.1)
4	36.5 (0)	0.2	98.5 (0.05)	0.2	98.4 (0.05)
5	42.4 (0)	0.2	97.9 (0.02)	0.2	97.7 (0.02)
6	48.9 (0)	0.2	92.2 (0.01)	0.2	92.0 (0.01)
10	64.7 (0)	0.2	72.3 (0.005)	0.2	71.4 (0.005)
		0.5	99.6 (0.5)	0.5	99.5 (0.5)
		0.5	99.5 (0.2)	0.5	99.4 (0.2)
		0.5	99.4 (0.1)	0.5	99.2 (0.1)
		0.5	99.4 (0.05)	0.5	99.2 (0.05)
		0.5	98.9 (0.02)	0.5	98.5 (0.02)
		0.5	93.5 (0.01)	0.5	93.1 (0.01)
		0.5	76.8 (0.005)	0.5	75.3 (0.005)

[KCl], M	Pd stripping, % ([Thiourea], M)	[$BaCl_2$], M	Pd stripping, % ([Thiourea], M)	[$AlCl_3$], M	Pd stripping, % ([Thiourea], M)
0.2	98.8 (0.5)	0.2	98.6 (0.5)	0.2	97.5 (0.5)
0.2	98.7 (0.2)	0.2	98.6 (0.2)	0.2	97.4 (0.2)
0.2	98.5 (0.1)	0.2	98.5 (0.1)	0.2	97.3 (0.1)
0.2	98.2 (0.05)	0.2	98.1 (0.05)	0.2	97.2 (0.05)
0.2	97.6 (0.02)	0.2	97.6 (0.02)	0.2	96.9 (0.02)
0.2	92.1 (0.01)	0.2	91.7 (0.01)	0.2	88.4 (0.01)
0.2	71.6 (0.005)	0.2	71.1 (0.005)	0.2	67.3 (0.005)
0.5	99.5 (0.5)	0.5	99.5 (0.5)	0.5	99.2 (0.5)
0.5	99.4 (0.2)	0.5	99.3 (0.2)	0.5	99.1 (0.2)
0.5	99.3 (0.1)	0.5	99.3 (0.1)	0.5	99.1 (0.1)
0.5	99.2 (0.05)	0.5	99.1 (0.05)	0.5	98.8 (0.05)
0.5	98.2 (0.02)	0.5	98.0 (0.02)	0.5	97.1 (0.02)
0.5	92.8 (0.01)	0.5	92.2 (0.01)	0.5	90.1 (0.01)
0.5	74.4 (0.005)	0.5	73.7 (0.005)	0.5	68.5 (0.005)

4. Conclusions

For a hydrochloric system, this study extracted Pd via a chloride solution using Alamine 336 dissolved in kerosene. The experimental results reveal that D_{Pd} and the concentration of extracting reagent are positively correlated, whereas D_{Pd} and the concentration of chloride ions are negatively correlated. Through graphical analysis, the complexes $\overline{PdCl_4(R_3NH)_2}$ and $\overline{PdCl_4(R_3NH)_2(R_3NHCl)}$ are indicated, and the equilibrium constants are $K_{20} = 4.23 \times 10^3$ and $K_{21} = 1.07 \times 10^3\ m^3/kmol$.

The results of the stripping experiment indicate that the 0.5 M HCl + 0.5 M thiourea system is the best system for palladium stripping. Regarding metal recovery, the extraction rate of 0.001 M Pd can reach 99.9% when using 0.5 M Alamine 336 and 1 M of HCl, and the recovery rate of Pd can reach 99.6%. Therefore, this study concludes that stripping efficiency using thiourea is more highly correlated with chloride ion concentration than pH values.

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