Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.826616

52 (2014) 1101–1108
January

Taylor & Francis
Taylor & Francis Group

Solvent extraction of palladium(II) from acidic chloride solutions using tri-octyl/decyl ammonium chloride (Aliquat 336)

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Received 23 March 2013; Accepted 5 May 2013

ABSTRACT

In this study, the effect of different operating conditions including on the extraction of palladium (II) from HCl solution by using tri-n-octylmethylammonium chloride (Aliquat 336)/kerosene was evaluated at 25°C. Different stripping reagents such as $AlCl_3$, KCl, NaCl, NH_4Cl, HCl, and thiourea were evaluated. The results indicate that the mixture of chloride and thiourea would lead to the highest stripping conversion for palladium (II) (i.e. >99%). The extraction distribution ratios were found to increase with the increase in the extractant concentration and decrease with the concentration of chloride ion. In addition, the compositions of palladium complexes in organic phase and equilibrium constant of recovered extraction reaction were estimated. Furthermore, the recovery efficiency of palladium(II) in acidic chloride solution was performed and compared.

Keywords: Solvent extraction; Aliquat 336; Palladium; Stripping

1. Introduction

Platinum group metals (PGMs: Pt, Pd, Rh, Os, Ir, Ru) have a broad range of industrial applications. They are mainly used in the automotive, electronics, petroleum, medical prosthetics, dental, pharmaceutical, chemical, and jewelry industries. Among these, the automotive industry uses a relatively large amount of PGMs as automotive catalysts [1]. Palladium and platinum catalysts are indispensable to the modern automotive industry and cannot be replaced by other materials or metals. Global industrial demand forecasts predict a significant increase in the use of palladium and platinum for use in fuel cell technology, automotive technology, and the development of fuel cell vehicles. Because the natural availability of PGMs in the earth's crust is extremely low, the likelihood of consumption to the point of depletion in the near future is high [2]. Thus, developing effective means for recycling and reusing PGMs has become an increasingly important issue to provide for resource reuse and the reduction in environmental problems. According to the findings reported by Meskers [3], the manufacture of 300 million notebook and desktop computers consumed approximately 24 tons of palladium, 66 tons of gold, 300 tons of silver, 9,100 tons of cobalt (Li-ion batteries for laptops),

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Presented at the Fifth Annual International Conference on "Challenges in Environmental Science & Engineering—CESE 2012" Melbourne, Australia, 9–13 September 2012

and 150,000 tons of copper in 2008. The 1,300 million new units of mobile phones produced consumed 12 tons of palladium, 31 tons of gold, 325 tons of silver, 4,900 tons of cobalt, and 12,000 tons of copper. These waste materials are usually toxic. Therefore, recycling some of the metals consumed during these processes can ensure the continued use of these limited resources. Solvent extraction is a commonly used and easy method for recycling PGMs. Studies have reported that the chlordion-complexes of PGMs $[MCl_6]^{2-}$ can be selectively extracted by neutral and amine extractants [4]. Because of the chemical properties of chloride media and the abundance of chemical species that form in it, the separation and purification of PGMs from chloride media are difficult processes. Solvent extraction has proven to be a relatively effective and inexpensive method for recovering PGMs from low concentration sources.

Aliquat 336 is a water-insoluble quaternary ammonium salt produced by the methylation of mixed tri-octyl/decyl ammonium chloride. Quaternary ammonium halides are more efficient than the corresponding secondary or tertiary amines for extracting metal ions from aqueous halide media. Aliquat 336 is composed of a large organic cation associated with a chloride ion. Because its ammonium structure has a permanent positive charge, Aliquat 336 can form oil-soluble salts with various anions over a wider pH range compared to primary, secondary, or tertiary amines, rendering it suitable for environments with acidic or slightly alkaline pH levels. This study investigates the effectiveness of using Aliquat 336 as an extractant for palladium (II). In addition, the reaction between the extractant and chloride ions was determined by employing the slope analysis. Several studies contain extraction data on recovering Pd using Aliquat 336 [5,6].Various reagents for extracting PGMs have been proposed and examined, including TIBPS [7,8], TBP [9,10], phosphonic acid [11,12], thiophosphoric acid [13], thiophosphinic acid [14,15], oximes [16–18], sulphoxides [19,20], and amines [21–23]. The solvents regularly used to extract solvents include kerosene [24,25], n-hexane [26], xylene [27], toluene [28], benzene [6], and chloroform [29]. This study uses kerosene as a solvent for two reasons: it is (1) relatively inexpensive compared to other solvents such as n-hexane and benzene and (2) relatively environmentally friendly and non-toxic.

Basic extractants can be classified into four categories: quaternary ammonium (R_4N^+), tertiary amines (R_3N), secondary amines (R_2NH), and primary amines (RNH_2). C_8–C_{10} saturated aliphatic quaternary amines (for example, Aliquat 336; 464) dissolved in organic solvents are effective extractants for carboxylic acids [30]. Aliquat 336 (quaternary ammonium, $R_4N^+Cl^-$) analkaline extractant, is commonly used in the packing materials for anionic exchanger.

With regard to Aliquat 336, the extractant reacts as an anion-exchanger forming an ion-pair with the metal species from the acidic aqueous solution. The speciation of the Pd–Cl complexes in solution [A1] affects the reaction as follows [31,32]:

$$2[R_4N^+Cl^-]_{(org)} + PdCl^{2-}_{4(aq)} \rightleftharpoons [(R_4N^+)_2PdCl_4^{2-}]_{(org)} + 2Cl^-_{(aq)}$$

The subscripts (org) and (aq) refer to organic and aqueous phases, respectively. Using UV–Vis spectrometry, Tait and Shillington [33] and Foulon et al. [34] determined stoichiometry and proposed a reaction mechanism.

Generally, the characteristics of a good extractant include an excellent extraction rate, high stripping efficiency, high selectivity, no toxicity, and low cost. This study experiments with various combinations of stripping reagents to achieve a stripping percentage over 99%. On the other hand, Lee et al. [24,35] also investigated the stripping efficiency with various stripping agents and investigated Aliquat 336 as an extractant for platinum, which the maximum efficiency achieved was 96.7% by single-stage stripping. This study investigates the following stripping agents: HCl, $(NH_2)_2CS$ with HCl, $(NH_2)_2CS$ with NaCl, $(NH_2)_2CS$ with KCl, $(NH_2)_2CS$ with $AlCl_3$, and $(NH_2)_2CS$ with NH_4Cl. We found that $(NH_2)_2CS$ with a chloride ion compound-like HCl provided stripping efficiencies above 99%.

2. Materials and methods

2.1. Reagents and solutions

Aliquat 336 (tri-octyl/decyl ammonium chloride; average molecular weight: 0.442 kg/mol; density: 880 kg/m^3) was used without purification. Aliquat 336 is a mixture of C8 (octyl) and C10 (capryl) chains, with C8 predominating. Aliquat 336 was obtained from ACROS Corporation (USA) and mixed with kerosene (supplied by Chinese Petroleum Co., Taiwan). An organic phase composed of 90% (v/v) Aliquat 336 and 10% (v/v) l-octanol (FERAK, purity of 99%) was used as the extractant. Thiourea (VETEC, at a purity of 99%) was used as the stripping agent. The diluent kerosene (boiling point: 180–270˚C; density: 800 kg /m^3) was obtained from Union Chemical Co., Taiwan.

Analytical grade palladium chloride (PdCl2, Merck, Germany) was dissolved in 10 MHCl to prepare a 0.02 M aqueous solution. This stock solution was then diluted to desired concentrations with distilled water and HCl for use throughout the study.

Standard solutions were prepared from 1,000 mg L^{-1} of palladium atomic absorption standard (Merck, Germany). NaCl, KCl, $AlCl_3$, NH_4Cl, and HCl were obtained from ACROS (USA). All chemicals were analytical reagent grade.

2.2. Extraction/stripping procedure

Extraction/stripping was conducted by shaking equal volumes (20 mL) of organic and aqueous phases (O: A) in separate funnels using a mechanical shaker at a temperature of 25 ± 0.2˚C for 12 h. Preliminary experiments indicated that the reaction time required to reach equilibrium was less than 1 h. The concentration of palladium (II) ions in the initial aqueous solutions ranged from 1×10^4 to 2×10^2 M, and the concentration of chloride ions in the solutions ranged from 1 to 10 M. The organic solutions contained 0.02–0.5 M Aliquat 336 dissolved in kerosene. Each organic solution also contained 10% l-octanol. Preliminary experiments indicated that adding 10% l-octanol could ensure that the Aliquat 336 completely dissolved in the kerosene.

After reaching equilibrium and phase disengagement, the equilibrium chloride ion concentration was determined using an automatic potentiometric titrator (Metrohm). The concentration of palladium (II) in the aqueous phase after appropriate dilution was analyzed using a GBC Sense AA atomic absorption spectrophotometer (AAS). For each AAS analysis, the blank tests and spike tests were performed to meet the QA/QC requirement.

Because AAS cannot be used to measure palladium concentration in the organic phase, a stripping experiment must be performed to measure the palladium concentration in the aqueous phase. Stripping experiments were also conducted with the loaded extractants while maintaining an aqueous to organic phase ratio of 2:1 at a temperature of 25.0 ± 0.2˚C for 12 h. All temperatures during the experiments were controlled within ± 0.2˚C.

Palladium in the organic phase was stripped using either HCl, $(NH_2)_2CS$ with HCl, $(NH_2)_2CS$ with $AlCl_3$, $(NH_2)_2CS$ with NaCl,$(NH_2)_2CS$ with KCl, or $(NH_2)_2CS$ with NH_4Cl. The palladium concentrations in the acidic solutions were analyzed using the AAS.

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

2.3. Determination of distribution ratio

After equilibrium, the palladium concentration removed by the extractant in the organic phase must be stripped so that an aqueous solution can be obtained and measured. The palladium concentration in the aqueous phase after equilibrium can be determined directly by diluting with water to reach desired proportions. These concentrations are then used to obtain the percentage of extraction ($\%E = \frac{[D \times 100]}{[D+1]}$), the distribution ratio 'D' ($D = [M_{\text{org}}/M_{\text{aq}}]$, where M = palladium concentration [M], and the stripping efficiency S ($\%S = M_{\text{aq}}/M_{\text{org}} \times 100\%$).

3. Results and discussion

3.1. Extraction equilibrium of palladium

When HCl or chloride ion concentrations are higher than 1 M, as shown by Levitin et al. [36], palladium and chloride ions form stable chlordion complexes, such as $PdCl_4^{2-}$. Regarding the use of Aliquat 336 dissolved in kerosene to extract the palladium in aqueous phase, when Aliquat 336 was fully loaded, the complexes formed by Aliquat 336 and palladium can further react and form a polymeric species [5,37]. Thus, assuming that the extraction of palladium (II) with Aliquat 336 causes the formation of an m-mer-ized complex, it can be represented by the following general reaction:

$$m\mathrm{PdCl}_4^{2-} + m(p+q)\overline{\mathrm{R_4NCl}} \leftrightharpoons \overline{\mathrm{PdCl_4(R_4N)}_p(\mathrm{R_4NCl})_q)_m} + mp\ \mathrm{Cl}^- \tag{1}$$

The bar indicates the species in the organic phase. The absence of a bar indicates the aqueous phase.

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

$$K_{mpq} = \frac{[\overline{(\mathrm{PdCl_4(R_4N)}_p)(\mathrm{R_4NCl})_q)_m}][\mathrm{Cl}^-]^{mp}}{[\mathrm{PdCl}_4^{2-}]^m[\overline{\mathrm{R_4NCl}}]^{m(p+q)}} \tag{2}$$

The extraction equilibrium constant for hydrochloric solutions with kerosene included 10% (v/v) l-octanol as the diluent.

The distribution ratio of palladium is defined as:

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

Substituting Eq. (2) into Eq. (3), we can obtain the following equation:

$$D_{\mathrm{Pd}} = \frac{m[\overline{(\mathrm{PdCl_4(R_4N)}_p(\mathrm{R_4NCl})_q)_m}]}{[\mathrm{PdCl_4^{2-}}]} = mK_{mpq}[\mathrm{PdCl_4^{2-}}]^{m-1}[\overline{\mathrm{R_4NCl}}]^{m(p+q)}[\mathrm{Cl^-}]^{-mp} \quad (4)$$

Therefore, at a low distribution ratio ($D_{\mathrm{pd}} < 0.1$) and constant concentrations of Aliquat 336, $[\mathrm{PdCl_4^{2-}}]^{m-1}[\overline{\mathrm{R_4NCl}}]^{m(p+q)}$ are approximately constant because the concentration of Aliquat 336 exceeds the concentration of palladium, and the percentage of Aliquat 336 consumed is sufficiently minimal to be disregarded. A plot of log D_{pd} vs. log [Cl⁻] will show a straight line with a slope of *mp*. The experimental results are shown in Fig. 1. The straight lines have average slopes of approximately −2, or $mp = 2$. Substituting Eq. (3) into Eq. (4), Eq. (4) can be rearranged as

$$[\overline{\mathrm{Pd(II)}}][\mathrm{Cl^-}]^2 = m\,K_{mpq}[\mathrm{PdCl_4^{2-}}]^m[\overline{\mathrm{R_4NCl}}]^{m(p+q)} \quad (5)$$

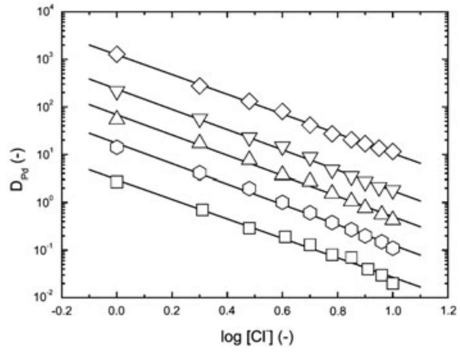

Fig. 1. Plots of log D_{Pd} vs. log [Cl⁻] at equilibrium for various Aliquat 336 concentrations in kerosene at 25℃: (1) □ $[\overline{\mathrm{R_4N^+}}] = 0.02$ M, slope = −2.04; (2) ⬡ $[\overline{\mathrm{R_4N^+}}] = 0.05$ M, slope = −2.12; (3) △ $[\overline{\mathrm{R_4N^+}}] = 0.1$ M, slope = −2.13; (4) ▽ $[\overline{\mathrm{R_4N^+}}]$=0.2 M, slope = −2.13; and (5) ◇ $[\overline{\mathrm{R_4N^+}}] = 0.5$ M, slope = −2.07.

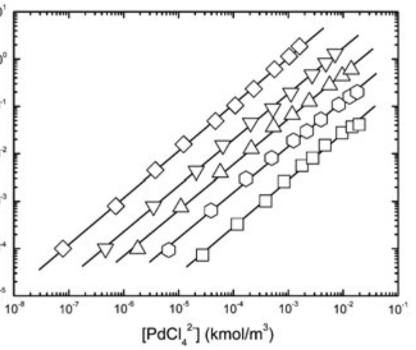

Fig. 2. Plots of log $[\overline{\mathrm{Pd(II)}}][\mathrm{Cl^-}]^2$ vs. log $[\mathrm{PdCl_4}^{2-}]$ at equilibrium for various Aliquat 336 concentrations in kerosene at 25℃: (1) □ $[\overline{\mathrm{R_4N^+}}] = 0.02$ M, slope = 0.99; (2) ⬡ $[\overline{\mathrm{R_4N^+}}] = 0.05$ M, slope = 0.96; (3) △ $[\overline{\mathrm{R_4N^+}}] = 0.1$ M, slope = 0.96; (4) ▽ $[\overline{\mathrm{R_4N^+}}] = 0.2$ M, slope = 0.97; and (5) ◇ $[\overline{\mathrm{R_4N^+}}] = 0.5$ M, slope = 0.99.

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

$$\mathrm{K}_{2q} = \frac{[\overline{(\mathrm{PdCl_4(R_4N)_2(R_4NCl)}_q)}][\mathrm{Cl^-}]^{-2}}{[\mathrm{PdCl_4^{2-}}][\overline{\mathrm{R_4NCl}}]^{2+q}} \quad (6)$$

and

$$D_{\mathrm{Pd}} = K_{2q}[\overline{\mathrm{R_4NCl}}]^{2+q}[\mathrm{Cl^-}]^{-2} \quad (7)$$

Eq. (7) can be rearranged as

$$\log D_{\mathrm{Pd}} = \log K_{2q} + (2+q)\log[\overline{\mathrm{R_4NCl}}] - 2\log[\mathrm{Cl^-}] \quad (8)$$

Initially, we can assume that only type $\overline{\mathrm{PdCl_4(R_4N)_2(R_4NCl)}_q}$ species are formed. Thus, a plot of $\log(D_{\mathrm{Pd}}[\mathrm{Cl^-}]^2)$ vs. $\log[\overline{\mathrm{R_4NCl}}]$ would show a straight line with an intercept equal to $K_{2\mathrm{q}}$ and a slope equal to $(2+q)$.

Aliquat 336 concentrations were 0.02, 0.05, 0.1, 0.2, and 0.5 M. Fig. 3 shows a straight line with a slope of 1.87, which can be regarded as near to a slope of 2, or $q = -0.13$. That the value of *q* is a negative number with no physical value can be considered an

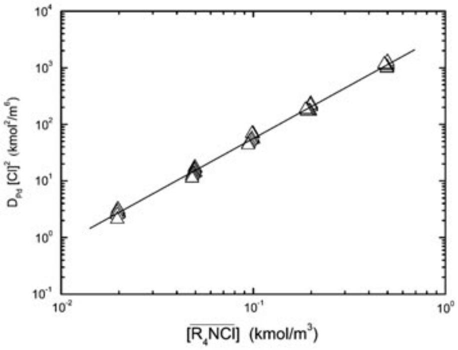

Fig. 3. Plots of log $D_{\mathrm{Pd}}[\mathrm{Cl^-}]^2$ vs. log $[\overline{\mathrm{R_4NCl}}]$ at equilibrium for various Aliquat 336 concentrations in kerosene at 25℃. Slope = 1.87.

experimental error. Because $q \doteq 0$ the polymeric species is represented by $\overline{(\mathrm{PdCl_4(R_4N)_2}}$.

Before calculating the experimental results, we had to assume a low distribution ratio (D_{Pd} smaller than approximately 0.1). Having a $D_{\mathrm{Pd}} < 0.1$ is required in order to fit the logic of the study and work within its hypothetical conditions (namely a low distribution ratio and constant concentrations of Aliquat 336). The distribution ratio and concentration of Aliquat 336 are related. Under suitable conditions, the distribution ratio and Aliquat 336 are positively correlated. The experimental portions of the study included that D_{Pd} was smaller than 0.1 thereby resulting in a greater recycling efficiency. Therefore, when calculating *m* and *p* values, we only considered a low distribution ratio; this range fulfilled our hypothesized equation. We also conducted graphic analysis to explore the possible compositions of the complexes.

3.2. Reconfirmation of extraction equilibrium formation by slope analysis

When $q \doteq 0$, considering the species that may form during the organic phase, such as $\overline{\mathrm{PdCl_4(R_4N)_2}}$, Eq. (3) can be expressed as

$$D_{\mathrm{Pd}} = \frac{[\overline{\mathrm{PdCl_4(R_4N)_2}}]}{[\mathrm{PdCl_4^{-2}}]} \tag{9}$$

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

$$D_{\mathrm{Pd}}[\mathrm{Cl^-}]^2 = K_{20}[\overline{\mathrm{R_4NCl}}]^2 \tag{10}$$

Plotting $D_{\mathrm{Pd}}[\mathrm{Cl^-}]^2$ against $[\overline{\mathrm{R_4NCl}}]^2$ would theoretically achieve a straight line with a slope of K_{20} and an intercept = 0. Fig. 4 shows a straight line with a slope of $K_{20} = 7503.41$ and an intercept = −14289.17 (k mol/m^3)^2. Because the intercept was theoretically 0, an intercept with a negative number indicates an experimental error, with no physical value; thus, they are not discussed further.

3.3. The effect of Aliquat 336 on the recovery of palladium (II)

We examined the effect of an Aliquat 336 extractant concentration ranging between 0.02 and 0.5 M on the extraction of 0.001 M of palladium (II) from 1.0 M HCl. The recovery percentage of palladium (II) increased when the Aliquat 336 concentration increased. When the Aliquat 336 concentration was higher than 0.1 M, the palladium was nearly completely extracted (>98%) (Fig. 5).

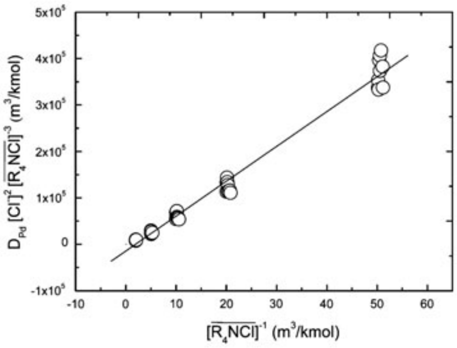

Fig. 4. Plots of $D_{\mathrm{Pd}}[\mathrm{Cl^-}]^2$ $[\overline{\mathrm{R_4NCl}}]^{-3}$ vs. $[\overline{\mathrm{R_4NCl}}]^{-1}$ at equilibrium for various Aliquat 336 concentrations in kerosene at 25˚C. Slope = 7503.41. Intercept = −14289.17.

Previous studies [21] have shown that when Alamine 304 is used to extract platinum, higher concentrations of chloride ions cause lower extraction rates. In addition, Fig. 5 shows that a higher chloride ion concentration caused a lower palladium extraction rate using Aliquat 336. It was noted that both [Cl$^-$] and $\mathrm{PdCl_4^{2-}}$ are negatively charged and may potentially bond with the positively charged amine extractants [24,35]. During the reaction, [Cl$^-$] might be replaced by $\mathrm{PdCl_4^{2-}}$ due to the similar chemical properties between these two species. Therefore, excessive chloride ions negatively impact extraction with $\mathrm{PdCl_4^{2-}}$. In this study, the best extraction results were obtained using a 1 M chloride ion concentration because the higher concentration of chlorine ions would result in a low extraction efficiency, which is in a good agreement with the findings reported in the literature [24].

3.4. Selection of stripping reagents

During any extraction process, the metal must be stripped from the loaded organic phase. To identify a

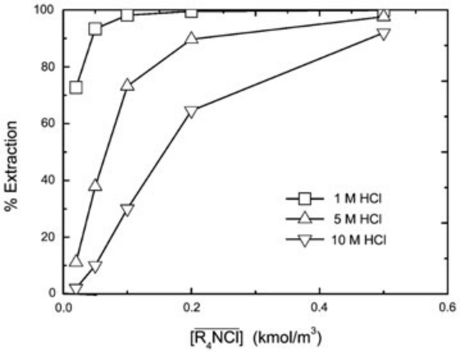

Fig. 5. The effect of Aliquat 336 and HCl concentrations on the extraction of palladium (II). Aliquat 336: 0.02, 0.05, 0.1, 0.2, and 0.5 M. HCl: 1, 5, and 10 M.

Table 1
The stripping of palladium (II) from the loaded Aliquat336 phases by various reagents

[HCl], M	Pd stripping, % ([thiourea], M)	[HCl], M	Pd stripping, % ([thiourea], M)	[NaCl], M	Pd stripping, % ([thiourea], M)
1	7.9 (0)	0.2	99.5 (0.5)	0.2	99.4 (0.5)
2	22.5 (0)	0.2	99. 4(0.2)	0.2	98.9 (0.2)
3	34.1 (0)	0.2	98.9 (0.1)	0.2	98.6 (0.1)
4	41.3 (0)	0.2	98.6 (0.05)	0.2	98.6 (0.05)
5	47.5 (0)	0.2	98.2 (0.02)	0.2	97.9 (0.02)
6	53.7 (0)	0.2	93.5 (0.01)	0.2	93.1 (0.01)
10	72.6 (0)	0.2	86.3 (0.005)	0.2	85.1 (0.005)
		0.5	99.8 (0.5)	0.5	99.7 (0.5)
		0.5	99.7 (0.2)	0.5	99.5 (0.2)
		0.5	99.5 (0.1)	0.5	99.4 (0.1)
		0.5	99.5 (0.05)	0.5	99.3 (0.05)
		0.5	99.1 (0.02)	0.5	98.9 (0.02)
		0.5	94.6 (0.01)	0.5	94.2 (0.01)
		0.5	89.9 (0.005)	0.5	88.2 (0.005)
[KCl], M	Pd stripping, % ([thiourea], M)	[AlCl$_3$], M	Pd stripping, % ([thiourea], M)	[NH$_4$Cl], M	Pd stripping, % ([thiourea], M)
0.2	99.3 (0.5)	0.2	99.0 (0.5)	0.2	99.4 (0.5)
0.2	99.2 (0.2)	0.2	98.8 (0.2)	0.2	99.2 (0.2)
0.2	99.2 (0.1)	0.2	98.5 (0.1)	0.2	90.2 (0.1)
0.2	99.0 (0.05)	0.2	98.0 (0.05)	0.2	98.4 (0.05)
0.2	97.6 (0.02)	0.2	97.8 (0.02)	0.2	97.5 (0.02)
0.2	93.2 (0.01)	0.2	92.0 (0.01)	0.2	93.1 (0.01)
0.2	85.8 (0.005)	0.2	83.4 (0.005)	0.2	86.5 (0.005)
0.5	99.7 (0.5)	0.5	99.6 (0.5)	0.5	99.7 (0.5)
0.5	99.4 (0.2)	0.5	99.2 (0.2)	0.5	99.3 (0.2)
0.5	99.4 (0.1)	0.5	99.1 (0.1)	0.5	99.3 (0.1)
0.5	99.2 (0.05)	0.5	99.0 (0.05)	0.5	99.1 (0.05)
0.5	98.7 (0.02)	0.5	98.1 (0.02)	0.5	98.8 (0.02)
0.5	93.2 (0.01)	0.5	92.5 (0.01)	0.5	93.4 (0.01)
0.5	87.4 (0.005)	0.5	85.2 (0.005)	0.5	88.1 (0.005)

suitable stripping reagent, HCl, $(NH_2)_2CS$ with HCl, $(NH_2)_2CS$ with NaCl, $(NH_2)_2CS$ with KCl, $(NH_2)_2CS$ with $AlCl_3$,and $(NH_2)_2CS$ with NH_4Cl were examined at various concentrations. The loaded organic was generated using 0.5 M of Aliquat 336 (0.005 M Pd). Palladium was stripped from a single-stage loaded organic solvent system. The aqueous phases were separated and, after 12 h, the solution was analyzed.

Palladium was stripped from the loaded Aliquat 336 phase (0.005 M Pd) using HCl (1–10 M), NaCl (0.2 and 0.5 M), KCl (0.2, 0.5 M), $AlCl_3$ (0.2, 0.5 M), NH_4Cl (0.2, 0.5 M), and thiourea (0.005–0.5 M). Table 1 shows the results of different chloride concentrations on distribution ratio. When chloride ion concentrations of 0.5 M were matched with 0.5 M of thiourea, the stripping efficiency was > 99%. Previous studies [24,35] have shown that thiourea combined with HCl forms a highly efficient stripping agent for single-stage extractions of amines. We found that, in addition to HCl, other chloride ion compounds can be combined with thiourea to create stripping agents with efficiencies reaching > 99%. Specifically, NH_4Cl can replace HCl to combine with thiourea and form an effective stripping agent. Because NH_4Cl does not contain metal ions, the purification of palladium is unaffected. This indicates that the stripping environment can be controlled at neutral pH levels.

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

$$\overline{(R_4N)_2(PdCl_4)} + 2(NH_2)_2CS \leftrightharpoons 2\overline{R_4NCl} + PdCl_2((NH_2)_2CS)_2 \quad (11)$$

If only palladium complexes are present in the organic phase, palladium is extracted using a coordination–substitution reaction between Cl^- and$(NH_2)_2CS$, which is in good agreement with the findings reported in the literature [24,35]. When palladium complexes are present in the organic phase, the substitution reaction of Cl^- with$(NH_2)_2CS$ occurs competitively and is dependent on the stripping agent and metal ion complex concentrations. The experimental results indicate that the best stripping efficiency was achieved with a thiourea concentration of 0.5 M and a $[Cl^-]$ concentrations of 0.5 M. As shown in Eq. (11), increasing the chloride ion concentration facilitates the formation of $\overline{R_4NCl}$, causing $[Cl^-]$ to replace the $PdCl_4^{2-}$ in the organic phase and enabling $PdCl_4^{2-}$ stripping in the aqueous phase. In addition, it was noted that using Aliquat 336 with thiourea and HCl to strip palladium would result in a higher efficiency [24]. This result was verified using thiourea with NaCl, KCl, $AlCl_3$, and NH_4Cl. Consequently, we infer that the stripping efficiency using thiourea has a higher correlation with chloride ion concentrations than with pH values as indicated in Table 1. Additional chloride ion compounds that could be paired with thiourea to create highly effective stripping agents, thereby eliminating the reliance on HCl would be our future research works. Working solutions for similar experiments can be controlled at neutral pH levels. For industry applications, the findings of this study can reduce the effects of strong acid corrosion on machinery and equipment.

4. Conclusions

In this study, the extraction efficiency of Pd using a chloride solution with Aliquat 336 dissolved in kerosene and 10% l-octanol in a hydrochloric system was investigated. The results show that the distribution ratio (D_{Pd}) and the concentration of extracting reagents have a positive first-order linear correlation; whereas, the D_{Pd} and the concentration of chloride ions exhibit a negative first-order linear correlation In addition, the $\overline{PdCl_4(R_4N)_2}$ complex was identified, and the equilibrium constant (K_{20}) was found to be 7503.41 by slope analysis. On the other hand, the results of the stripping experiment indicated that the 0.5 M $[Cl^-]$ + 0.5 M thiourea system is the optimal method for palladium stripping. Regarding metal recovery, the extraction efficiency of 0.001 M Pd was 99.9% using 0.5 M Aliquat 336 and 1 M HCl, and the recovery efficiency of Pd can reach 99.8%. It was thus concluded that the stripping efficiency using thiourea exhibits a higher correlation with the concentrations of chloride ion than that with pH values. By replacing HCl with other chloride ion compounds (e.g. NH_4Cl), when paired with thiourea, the stripping efficiency was significantly improved, where the NH_4Cl was found to be more effective because it lacks metal ions. Therefore, NH_4Cl does not affect or contaminate the purification of precious metals, and the findings indicated that the working solutions in similar experiments can be controlled at neutral pH levels. For industry applications, the proposed methods in this study could provide a reduction in the corrosion of machinery and equipment by strong acids.

Acknowledgements

The author wishes to recognize Hung-Sheng Tsai, for his collaboration on this research. This work was supported by the National Science Council of the Republic of China, under Grant No. NSC92-2214-E027-006, for which the authors wish to express their thanks.

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