Efficiency and Mechanism of Palladium(II) Extraction from Chloride Media with *N*-Hexadecylpiperidinium Chloride

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Abstract

N-hexadecylpiperidinium chloride ([PIP16]Cl) has been synthesized and examined as a reagent for extractive recovery of palladium(II) from hydrochloric acid solutions. The effect of the contact time between the two phases, temperature and the concentration of palladium(II) ions, the extractant and HCl, were also evaluated. The anion-exchange mechanism of palladium(II) extraction with [PIP16]Cl was confirmed by Job's method, UV–VIS, IR and ¹H NMR analysis. The extraction of palladium(II) from 0.1 mol·L^{−1} HCl solution with [PIP16]Cl in toluene was very effective and amounted to almost 100%. Increases in both HCl and NaCl concentrations and increasing temperature had negative effects on the effectiveness of palladium(II) extraction. [PIP16]Cl also exhibited selectivity to extraction of palladium(II) over some other metals: rhodium(III), iron(III), aluminium(III), copper(II) and lead(II). From among the examined stripping solutions the most effective were 0.5 mol·L^{−1} aqueous solution of ammonia and 0.1 mol·L^{−1} thiourea in 0.1 or 1 mol·L^{−1} HCl. The percentage of palladium(II) stripped from loaded organic phase reached nearly 100%. The feasibility of regeneration of [PIP16]Cl and its reuse in subsequent extractions was also investigated.

Keywords Palladium · Extractive recovery · Solvent extraction · Stripping · *N*-hexadecylpiperidinium chloride

1 Introduction

Demand for precious metals such as palladium(II), platinum(IV), gold(III) and rhodium(III) is still high as they are widely used in the automotive, chemical, electrical, glass, petroleum, jewelry, medical and biomedical industries. In 2018, the global consumption of palladium was 314.7 tons, platinum 243.3 tons, gold 4,345.1 tons and rhodium 31.5 tons [1–3]. As the natural resources of these metals are limited and depleting, the effective recycling of spent materials containing these precious metals, e.g. waste electronic and electrical equipment, is required. Both pyrometallurgical and hydrometallurgical methods are

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used for the recovery of precious metals from natural and secondary raw materials [2–5]. Solvent extraction is one of the methods commonly used for recovery of metals from aqueous solutions. Therefore, the reagents exhibiting the ability to extract these metals have recently become a subject of interest to many researchers in the world and the synthesis of new extractants is a top priority. The choice of extractant, providing maximum efficiency of extraction requires consideration of a number of parameters, including the type of metal species, pH of solution and temperature. A perfect extractant should show the following characteristics [6, 7]:

- The ability to make a permanent chemical bond with the extracted metals in reversible reactions;
- Chemical stability and the overall solubility of the active ingredient in the free form and bound to metal, poor solubility in aqueous phase, and lack of tendency to form a third intermediate stage;
- The ability to reach the extraction equilibrium in a short time, i.e. have a high rate of extraction;
- High extraction capacity defining the maximum concentration of the metal in the organic phase;
- Low viscosity and not too low interfacial surface tension (these features allow easy mixing, rapid phase separation and lack of propensity to form emulsion);
- Low vapor pressure, non-toxicity, non-flammability, corrosive inactivity, no odor, rapid natural biodegradation, etc. (elements to ensure safe use and preserve the environment).

Classical solvent extraction has been the subject of many scientific papers. Because of increasing demand for recovered precious metals, the search for new effective precious metals extractants has gained significance. Until now many different extractants have been studied and proposed for recovery and separation of precious metals, e.g. hydrophobic amines [8–13], organophosphorus extractants [12–15], different derivatives of amides [16–21], pyridine [22, 23] and piperidine [24]. Ionic liquids are also an important group of extractants, e.g. ammonium [8, 12, 13, 25–28], phosphonium [29–33], imidazolium, pyridinium, piperidinium, pyrrolidinium [34–36] and betainium ionic liquids [37]. Looking for a fast and efficient extractant for recovery of palladium ions, we proposed to synthesize and test *N*-hexadecylpiperidinium chloride ([PIP16]Cl). The aim of our study is to examine the extraction capabilities of the synthesized [PIP16]Cl for palladium(II) ions from hydrochloric acid solutions of various concentrations. The mechanism and thermodynamics of palladium(II) extraction have been also investigated.

2 Experimental

2.1 Reagents

Commercial palladium chloride PdCl_2 (99%, Avantor Performance Materials Poland S.A., Poland), platinum chloride PtCl_4 (99%, Avantor Performance Materials Poland S.A., Poland), rhodium chloride RhCl_3 (98%, Aldrich, Poland), gold chloride AuCl_3 (99%, Aldrich, Poland), copper chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (analytically pure, Chempur, Poland), lead chloride PbCl_2 (analytically pure, Avantor Performance Materials Poland S.A., Poland), iron chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (analytically pure, Chempur, Poland), aluminum chloride

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (analytically pure, Chempur, Poland), hydrochloric acid (analytically pure, 35–38%, Chempur, Poland), sulfuric acid (analytically pure, 95%, Chempur, Poland), nitric acid (analytically pure, 65%, Avantor Performance Materials Poland S.A., Poland), ammonium thiocyanate (pure, Chempur, Poland), thiourea (analytically pure, Chempur, Poland) and aqueous ammonia (analytically pure, 25%, Chempur, Poland) were used to prepare aqueous solutions. Toluene (analytically pure, Chempur, Poland) was used as diluent of the extractant. Piperidine (Chemat, Poland), 1-bromohexadecane (Chemat, Poland), hydrochloric acid (standard solution, Chemat, Poland) and diethyl ether (Chempur, Poland) were used for the synthesis.

2.2 Procedure

2.2.1 Synthesis and Characterization of *N*-Hexadecylpiperidinium Chloride

N-hexadecylpiperidine was obtained by the reaction described in Cieszyńska and Wieczorek [23]. Liquid *N*-hexadecylpiperidine was obtained by reacting 2 mol of piperidine with 1 mol of alkyl bromide in diethyl ether for several hours. Subsequently (0.1 mol) *N*-hexadecylpiperidine was suspended in 15 mL of hot water (70.0 ± 1.0 °C) while stirring. Then (0.1 mol) 1 mol·L⁻¹ hydrochloric acid was added. The reaction was carried out for 24 h in ambient temperature (20.0 ± 1.0 °C), then the solvent was evaporated (Fig. 1). Solid product was purified by recrystallization in water–ethanol (1:1). A crystalline product was filtrated in vacuum and dried in a vacuum desiccator.

The obtained *N*-hexadecylpiperidinium chloride was characterized by ¹H NMR and ¹³C NMR (Varian Merkury, Gemini + 300VT), IR (Jasco FT/IR-4700) and elemental analysis (Elementar Analyser Vario EL III). Melting points were determined with a DigiMelt MPA161, SRS.

The characteristics of *N*-hexadecylpiperidinium chloride is given below:

¹H NMR (CDCl_3): $\delta = 0.74$ (m, 3H, CH_3), 1.11–1.19 (m, 26H, CH_2), 1.35 (m, 2H, $(\text{CH}_2)_2$), 1.71–1.72 (m, 6H, CH_2), 2.12–2.15 (m, 2H, CH_2N), 2.64–2.67 (m, 2H, CH_2N), 2.81–2.85 (m, 2H, CH_2N), 3.35–3.38 (m, 1H, NH^+).

¹³C NMR (CDCl_3): $\delta = 14.00$, 21.95, 22.53, 22.55, 23.46, 26.78, 26.89, 28.04, 28.63, 28.94, 29.22, 29.27, 29.36, 29.45, 29.51, 29.53, 29.55, 29.57, 31.79, 52.89, 57.39.

IR = 719, 949, 1461, 2493, 2848, 2917 cm^{-1} .

Fig. 1 Synthesis of *N*-hexadecylpiperidine chloride ([PIP16]Cl)

Analysis calc.: C, 72.94; H, 12.74; N, 4.05 found: C, 71.52; H, 12.67; N, 3.38.
mp. = 164 °C, yield: 96%

2.2.2 Solvent Extraction

Aqueous feed for single extractions contain 0.1–1 mmol·L⁻¹ of palladium(II) ions and the stock solutions for the selectivity experiments contain 0.5 mmol·L⁻¹ palladium(II) ions and 0.5 mmol·L⁻¹ of other metal such as rhodium(III), platinum(IV), gold(III), copper(II), lead(II), iron(III) or/and aluminum(III). Stock solutions were prepared by dissolving appropriate amounts of their suitable chlorides in double distilled water containing a minimum amount of the corresponding mineral acid. The acidity of the solution was controlled by HCl solutions (0.1–5 mol·L⁻¹). Hydrochloric acid and chloride concentrations were also determined by potentiometric titration. The organic phases were 0.2–100 mmol·L⁻¹ solutions of [PIP16]Cl in the presence of toluene.

Both phases were mechanically shaken in glass separatory funnels and then left to stand. When both phases were clear and transparent, they were separated. Unless otherwise described, all extractions were carried out for 10 min at room temperature (20 ± 1.0 °C). The volume ratio of the aqueous phase to the organic phase was equal to 1 (A/O = 1). The percentage extraction (*E*), distribution ratio (*D*) and separation factor (*SF*_{Pd/M}) were calculated using the following equations:

$$E = \frac{[M]_{(i)} - [M]_{(aq)}^*}{[M]_{(i)}} \cdot 100\% \quad (1)$$

$$D = \frac{[M]_{(org)}^*}{[M]_{(aq)}^*} \quad (2)$$

$$SF_{Pd/M} = \frac{D_{Pd}}{D_M} \quad (3)$$

where: $[M]_{(i)}$ represents the concentration of metal ions in the aqueous phases before extraction and $[M]_{(aq)}^*$ and $[M]_{(org)}^*$ are the metal ion concentrations in the aqueous and organic phase after extraction.

The volumes of phases did not change. Each experiment was carried out three times and the error did not exceed 5%.

2.2.3 Stripping

The loaded organic phase with palladium(II) was stripped with water, 0.1 mol·L⁻¹ EDTA, 0.1 mol·L⁻¹ thiourea in 0.1 or 1.0 mol·L⁻¹ HCl, 0.5 mol·L⁻¹ aqueous ammonia, 0.5 mol·L⁻¹ NH₄SCN, 5.0 mol·L⁻¹ HCl, 5 mol·L⁻¹ HNO₃ and 6 mol·L⁻¹ H₂SO₄ (A/O = 1).

2.2.4 Analytical Techniques

Microwave plasma-atomic emission spectroscopy (4210 MP AES, Agilent, USA) was used for metal determination in the initial aqueous solutions and in the aqueous phases after extraction and stripping. Then the concentrations of metals in the organic phases

were calculated based on mass balance. The organic phase loaded with palladium(II), after extraction, was separated from the aqueous phase and completely evaporated. The obtained sample of complex [PIP16]–Pd was analyzed by UV–VIS (MeterTech, SP-8001 Spectrophotometer), ^1H NMR (Varian Mercury, Gemini + 300VT) and IR using the ATR technique (Jasco FT/IR-4700).

3 Discussion of Results

3.1 Effect of HCl and NaCl Concentration

The effect of hydrochloric acid concentration and sodium chloride concentration on palladium(II) extraction with [PIP16]Cl was investigated. The increase in both HCl and NaCl concentration had an unfavorable influence on palladium(II) extraction. The extent of palladium(II) extraction from $0.1\text{ mol}\cdot\text{L}^{-1}$ HCl amounted to nearly 100%, while from $8\text{ mol}\cdot\text{L}^{-1}$ HCl it decreased to approximately 10% (Fig. 2a). The increase in HCl concentration would favor the back reaction (Eq. 4), thus the extraction efficiency of palladium(II)

Fig. 2 Effect of HCl and NaCl concentration in the feed on the extraction of palladium(II) ions. Initial aqueous phase: (a) $[\text{Pd(II)}] = 0.5\text{ mmol}\cdot\text{L}^{-1}$ in $0.1\text{--}8\text{ mol}\cdot\text{L}^{-1}$ HCl or (b) $[\text{Pd(II)}] = 0.5\text{ mmol}\cdot\text{L}^{-1}$ in $0.1\text{ mol}\cdot\text{L}^{-1}$ HCl with $0\text{--}5\text{ mol}\cdot\text{L}^{-1}$ NaCl; organic phase: $2\text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl in toluene; A/O = 1

decreases. The addition of sodium chloride in the amount of 3 and 5 mol·L⁻¹ caused a decrease in the percentage of palladium(II) extraction to 15 and 7%, respectively (2b). The efficiency of palladium(II) extraction decreased due to competition between PdCl₄²⁻ and Cl⁻ to bind with [PIP16]⁺ as a result of the anion-exchange reaction [6]. The mechanism of palladium(II) extraction with *N*-hexadecylpiperidinium chloride is described in Sect. 3.3.

To verify the role of chloride ion concentration on palladium(II) extraction, the experiments of palladium(II) extraction with [PIP16]Cl were carried out at a constant H⁺ ion concentration and Cl⁻ ion concentrations varying in the range 0.1–5 mol·L⁻¹. The concentration of chloride ion was adjusted with sodium chloride. Results are presented in Fig. 3 as plots of log₁₀ *D*_{Pd} against log₁₀[Cl⁻]. The slope of this plot is equal to 3.9, which suggests that 4 mol of chloride ions are involved in the extraction of 1 mol of palladium(II).

3.2 Rate of Palladium(II) Extraction

The effect of contact time on the percentage extraction of palladium(II) with *N*-hexadecylpiperidinium chloride was investigated. The aqueous feed containing palladium(II) ions (0.5 mmol·L⁻¹) in 0.1 mol·L⁻¹ HCl was put in contact with 2 mmol·L⁻¹ [PIP16]Cl in toluene as the organic phase. The contact time was varied from 0.5 to 120 min. The extraction of palladium(II) under these conditions was very efficient, fast and the equilibrium was achieved in 5 min (Fig. 4). Therefore, further extraction experiments were carried out for 10 min. MathCad was used to calculate the initial rate of palladium(II) extraction from the slope at the beginning of the extraction and it amounted to 1.51 × 10⁻⁵ mol·L⁻¹·s⁻¹. Very short times (about few minutes) necessary to achieve the extraction equilibrium are a huge advantage of reagent [PIP16]Cl in comparison with commercial dialkyl sulfides. Kinetics of palladium(II) extraction from acidic chloride solutions with these extractants is very slow and a few hours are needed to achieve equilibrium [38–40]. Pyridine derivatives like pyridinecarboxamides also extract palladium(II) very fast and efficiently. A great disadvantage of these extractants is the impossibility of palladium(II) stripping, while stripping of palladium(II) from the organic phase [PIP16]Cl is very fast and efficient.

It is worth noting that unprompted transfer of palladium(II) ions, without any shaking, to the organic phase is possible. The results obtained are presented in Fig. 5, as a linear relation between the extraction efficiency and contact time, $t^{-0.5}$, indicating that this process is

Fig. 3 Distribution ratio of palladium(II) as a function of chloride ions concentration Initial aqueous phase: [Pd(II)] = 0.5 mmol·L⁻¹ in 0.1 mol·L⁻¹ HCl with 0–5 mol·L⁻¹ NaCl; organic phase: 2 mmol·L⁻¹ [PIP16]Cl in toluene; A/O = 1

Fig. 4 Effect of contact time on (□) palladium(II) extraction and (■) concentration of palladium(II) in the organic phase after extraction. Initial aqueous phase: $[\text{Pd(II)}] = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl; organic phase: $2 \text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl in toluene; A/O = 1

Fig. 5 Spontaneous transfer of palladium(II) ions to the organic phase. Initial aqueous phase: $[\text{Pd(II)}] = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl; organic phase: $2 \text{ mmol}\cdot\text{L}^{-1}$ PIP16]Cl in toluene; A/O = 1

controlled by diffusion. Moreover *N*-hexadecylpiperidine chloride can additionally accelerate extraction, because it is a strong surfactant that reduces the interfacial tension.

3.3 Mechanism of Palladium(II) Extraction

Chlorocomplexes of palladium(II): PdCl^+ , PdCl_2 , PdCl_3^- and PdCl_4^{2-} co-exist in solutions with lower concentration of chloride ions, while in chloride media of Cl^- concentrations of $0.1 - 5 \text{ mol}\cdot\text{L}^{-1}$, the predominant species of palladium(II) is PdCl_4^{2-} [6, 13, 41–43]. According to literature data, palladium(II) extraction with [PIP16]Cl should follow an anion exchange mechanism similar to that of extraction with ammonium salts. To confirm the mechanism of extraction, the nature of palladium–extractant complex was determined and spectral analysis was carried out.

3.3.1 Determination of the Nature of the Palladium–Extractant Complex

To confirm the mechanism of extraction, the nature of palladium–extractant complex was determined and spectral analysis was carried out. The effect of the [PIP16]Cl concentration on the extraction efficiency at a constant content of palladium(II) of $0.5 \text{ mmol}\cdot\text{L}^{-1}$ was also investigated to determine the nature of extracted species

Fig. 6 Dependence of palladium(II) distribution ratio on the extractant concentration. Initial aqueous phase: $[\text{Pd(II)}] = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl; organic phase: $0.1\text{--}100 \text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl in toluene; A/O = 1

in the organic phase. Figure 6 shows the relation between the distribution ratio of palladium(II) and the concentration of extractant as a straight line of the slope of 2.1. These data suggest that two molecules of extractant take part in extraction of one molecule of palladium.

Job's method was also used to investigate the formation of complexes between PdCl_4^{2-} and [PIP16]Cl [41]. The results obtained indicate that the maximum equilibrium concentration of palladium(II) in the organic phase is achieved when the molar ratio of PdCl_4^{2-} to [PIP16]Cl is equal to 0.5 (Fig. 7). This proves that palladium(II) is extracted from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl to the organic phase of the molar ratio of 1:2, according to the following equation:

The anionic metal chlorocomplex species are extracted from the aqueous to organic phase by an anion-exchange mechanism. This mechanism is compatible with that of palladium(II) extraction with quaternary ammonium or phosphonium salts [8, 12, 13, 25, 30, 33]. The distribution ratio (D) of palladium(II) in the extraction with [PIP16]Cl can be described as follows:

Fig. 7 Job's plot for the Pd–[PIP16]Cl system. The molar ratio of Pd(II) ions concentration to hexadecylpiperidine chloride concentration varies from 0.1 to 2; A/O = 1

Fig. 8 UV–Vis spectra of organic phase (1) before and (2) after extraction of palladium(II).

[Pd(II)] = 0.5 mmol·L⁻¹ in 0.1 mol·L⁻¹ HCl; organic phase: 2 mmol·L⁻¹ [PIP16]Cl in toluene; A/O = 1

Fig. 9 Infrared spectra of [PIP16]Cl and [PIP16]₂PdCl₄ complexes

$$D = \frac{[\text{Pd}]_{(\text{org})}}{[\text{Pd}]_{(\text{aq})}} = \frac{[\text{PIP16}]_2\text{PdCl}_4]_{(\text{org})}}{[\text{PdCl}_4^{2-}]_{(\text{aq})}} \quad (5)$$

3.3.2 Spectrophotometric Analysis of the Palladium–Extractant Complex

The organic phases before and after extraction of palladium(II) from 0.1 mol·L⁻¹ HCl were subjected to UV–Vis analysis in the wavelength range 190–500 nm. Toluene was used as a reference. As shown in Fig. 8, the spectra of organic phases before and after extraction differ. Before extraction, the spectrum of the organic phase shows one ultraviolet absorption peak at 250 nm, while after the extraction its spectrum shows two peaks at 246 and 281 nm. These results suggest that the peak near 250 nm corresponds to [PIP16]Cl, while that at 281 nm corresponds to [PIP16]₂PdCl₄.

The IR spectra of organic phase before and after extraction are presented in Fig. 9. The bands assigned to stretching vibrations appear at 2848, 2916, and 2992 cm⁻¹, so in the same region, and are assigned to the stretching modes of C–H. The band corresponding to the stretching vibrations of the NH⁺ group can be observed at 2494 cm⁻¹.

This band is not present in the spectra recorded after extraction. It is assigned to the protons in the closest neighborhood of the nitrogen donor, therefore, its disappearance indicates that the metals interact with the nitrogen donor. The band at 1460 cm^{-1} is the bending mode of C–H and can be seen on both spectra with no shift. The band at 949 cm^{-1} present in the spectra recorded before and after extraction, corresponds to the stretching modes of C–N.

The NMR chemical shifts before and after extraction of palladium(II) from $0.1\text{ mol}\cdot\text{L}^{-1}$ HCl were examined to study the position of bonding between the metal and the extractant. The NMR spectra are presented in Fig. 10.

The the NMR peaks at 0.74 and 1.1–1.35 ppm were shifted toward lower magnetic field by 0.15 ppm after the extractions. The peak assigned to the protons of piperidine ring (1.71 ppm) was shifted to a lower magnetic field (by 0.25 ppm) after the palladium loading, which is in agreement with the observation made by Yamaguma et al. concerning the extraction of silver by pyridyl derivative extractant [44]. More significant changes in chemical shifts are observed for the peaks assigned to the protons in the closest neighborhood of the N atom, namely those at 2.15, 2.64, 2.81, 3.35 ppm. After extraction, the peaks were shifted to 2.41, 2.79, 3.15 and 3.68 ppm, respectively. Thus, the changes in the peaks corresponding to the protons neighboring the donor atom include not only their shifts but also deformation of their shapes. Similar observation has been reported by Sasaki et al. who showed that the shifts of the peaks depend on the type of metal extracted. Moreover, the deformation of peak shape is likely due to the paramagnetization of Pd(II) [21].

Fig. 10 ^1H NMR spectra of (a) [PIP16]Cl and (b) [PIP16] $_2$ PdCl $_4$ complex

3.3.3 Effect of Temperature

The effect of temperature in the range 20–70 °C on palladium(II) extraction from 0.1 mol·L⁻¹ HCl was investigated (Fig. 11). The extraction equilibrium constant and thermodynamic parameters were also determined. Increase in temperature causes a negligible decrease in the palladium(II) distribution ratio. According to the equations of extraction mechanism and distribution ratio (Sect. 3.3.1), the extraction constants ($\log_{10}K_{\text{ex}}$) were estimated using the experimental data and the following equations [45]:

$$K_{\text{ex}} = \frac{[\text{PIP16}]_2\text{PdCl}_4]_{(\text{org})} \cdot [\text{Cl}^-]_{(\text{aq})}^2}{[\text{PdCl}_4^{2-}]_{(\text{aq})} \cdot [\text{PIP16Cl}]_{(\text{org})}^2} \quad (6)$$

$$K_{\text{ex}} = D \cdot \frac{[\text{Cl}^-]_{(\text{aq})}^2}{[\text{PIP16Cl}]_{(\text{org})}^2} \quad (7)$$

$$\log_{10}K_{\text{ex}} = \log_{10}D + 2\log_{10}[\text{Cl}^-]_{(\text{aq})} - 2\log_{10}[\text{PIP16Cl}]_{(\text{org})} \quad (8)$$

The values of enthalpies ΔH° and entropies ΔS° were calculated using the Gibbs–Helmholtz equation:

$$\log_{10}K_{\text{ex}} = \frac{-\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (9)$$

The standard enthalpy ΔH° is determined from the slope of the line $\log_{10}K_{\text{ex}}$ against T^{-1} , while the standard entropy ΔS° of the extraction is the coordinate of the intersection point of the plot shown in Fig. 11 with the coordinate axis. The Gibbs energy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ was also calculated. The values of $\log_{10}K_{\text{ex}}$, ΔH° , ΔS° and ΔG° are listed in Table 1. The results obtained indicate that the extraction of palladium(II) with *N*-hexadecylpiperidinium chloride in toluene is an exothermic reaction.

3.4 Stripping of Palladium(II) from the Loaded Organic Phase

Stripping palladium(II) from the loaded organic phase after extraction from 0.1 mol·L⁻¹ HCl with [PIP16]Cl in toluene was examined. Different stripping solutions: water,

Fig. 11 The effect of temperature on the logarithm of palladium(II) extraction constants. Initial aqueous phase: [Pd(II)] = 0.5 mmol·L⁻¹ in 0.1 mol·L⁻¹ HCl; the organic phase: 2 mmol·L⁻¹ [PIP16]Cl in toluene; A/O = 1

Table 1 The values of extraction constant $\log_{10} K_{\text{ex}}$ and thermodynamic parameters: ΔH° , ΔS° and ΔG° of palladium(II) extraction

T [K]	$\log_{10} K_{\text{ex}}$	ΔH° [kJ·mol ⁻¹]	$T\Delta S^\circ$ [kJ·mol ⁻¹]	ΔG° [kJ·mol ⁻¹]
293	5.2	-20.5	8.7	-29.1
303	5.1		9.0	-29.4
313	5.0		9.3	-29.7
323	4.9		9.6	-30.0
333	4.8		9.9	-30.3
343	4.7		10.2	-30.6

Initial aqueous phase: [Pd(II)]=0.5 mmol·L⁻¹ in 0.1 mol·L⁻¹ HCl; the organic phase: 2 mmol·L⁻¹ [PIP16] Cl in toluene; A/O=1

0.1 mol·L⁻¹ EDTA, 0.5 mol·L⁻¹ aqueous ammonia, 0.5 mol·L⁻¹ NH₄SCN, 6 mol·L⁻¹ H₂SO₄, 5 mol·L⁻¹ HNO₃, 5 mol·L⁻¹ HCl and 0.1 mol·L⁻¹ thiourea in 0.1 or 1 mol·L⁻¹ HCl were used. The stripping was carried out in two stages and the results are presented in Fig. 12. The stripping with water and 6 mol·L⁻¹ H₂SO₄ is ineffective and the efficiency amounts to 0.4 and 5.5%, respectively, in two stages. Better results were achieved using 5 mol·L⁻¹ HNO₃ and 5 mol·L⁻¹ HCl and the percentage of stripping in two stages reached 52 and 59%, respectively. The stripping with 0.1 mol·L⁻¹ EDTA was 60% and with 0.5 mol·L⁻¹ NH₄SCN was near 90%, wherein the first step of stripping was much more efficient than the second. The best results were achieved for stripping with 0.5 mol·L⁻¹ aqueous ammonia and 0.1 mol·L⁻¹ thiourea in 0.1 or 1 mol·L⁻¹ HCl. Palladium(II) ions were transferred in the first stage from the organic phase to all aqueous solutions in 100%.

3.5 Regeneration of the Organic Phase

The regeneration of a spent organic phase is perfectly legitimate, not only because of the impact that the waste organic solutions may have on the environment, but also it is

Fig. 12 Stripping of palladium(II) in (■) first stage and (▒) second stage from loaded organic phase containing Pd(II) in 2 mmol·L⁻¹ [PIP16] Cl after extraction; A/O=1 (M denotes concentration in units of mol·L⁻¹)

economically motivated as it offers the possibility of reusing the organic reagents in subsequent palladium(II) extractions. After extraction of palladium(II) from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl with fresh $2 \text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl, the loaded organic phase was stripped twice with $0.5 \text{ mol}\cdot\text{L}^{-1}$ aqueous ammonia or $0.1 \text{ mol}\cdot\text{L}^{-1}$ thiourea in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl to ensure complete removal of palladium(II) ions. Then the organic phases were regenerated with deionized water and $5 \text{ mol}\cdot\text{L}^{-1}$ HCl and were used again for extraction. This procedure of extraction-stripping-regeneration was repeated six times.

Efficiencies of palladium(II) extraction from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl with both fresh and regenerated extractant are comparable and amount to almost 100% (Fig. 13). It means that *N*-hexadecylpiperidinium chloride is a stable extractant that can be reused for extraction of palladium(II), because regeneration does not change its extractive properties.

3.6 Separation of Palladium(II) from other Metals

Recently, separation of palladium(II), gold(III), rhodium(III) and platinum(IV) from chloride solution has been examined by many researchers [13, 16, 21, 32, 36]. The recovery and separation of palladium(II) e.g. from electronic scraps containing other metals may be processed using the extraction-stripping procedure. Therefore, the possibility of selective extraction of palladium(II) over one chosen metal: platinum(IV), rhodium(III), gold(III), aluminium(III), iron(III), copper(II) and lead(II) was investigated. The results presented in Table 2 indicate that the best palladium(II) separation was observed in the presence of rhodium(III), aluminum(III), iron(III), copper(II) and lead(II). The extraction of palladium(II) amounts to 98–99%, while the extraction efficiency of rhodium(III), aluminum(III), iron(III), copper(II) and lead(II) does not exceed 7%. Separation of palladium(II) from platinum(IV) and gold(III) from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl by extraction with [PIP16]Cl is not possible. The results show that the extraction ability of [PIP16]Cl towards palladium(II), platinum(IV) and gold(III) was similar for two-metal solutions.

Extraction of palladium(II) from multi-metal solutions was also studied. The results obtained indicate that in multi-metal system the extraction capacity of [PIP16]Cl towards the tested precious metals from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl is gold(III) > palladium(II) > platinum(IV) > > rhodium(III) (Fig. 14). Separation of palladium(II), platinum(IV) and gold(III),

Fig. 13 Extraction of palladium(II) with fresh (■) and regenerated (■) [PIP16]Cl after stripping with a) $0.5 \text{ mol}\cdot\text{L}^{-1}$ aqueous ammonia and b) $0.1 \text{ mol}\cdot\text{L}^{-1}$ thiourea in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl. Initial aqueous phase: [Pd(II)] = $0.5 \text{ mmol}\cdot\text{L}^{-1}$ in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl; organic phase: $2 \text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl in toluene; A/O = 1

Table 2 Extraction and separation of palladium(II) from two-metal solutions

Feed	$E_{\text{Pd}} (E_{\text{Met}})$, %	$D_{\text{Pd}} (D_{\text{Met}})$	$SF_{\text{Pd/Met}}$
Pd(II)–Pt(IV)	94.5 (83.6)	17.2 (5.10)	3.38
Pd(II)–Au(III)	97.0 (99.4)	32.7 (160.3)	0.204
Pd(II)–Rh(III)	98.7 (6.5)	74.9 (0.07)	1070
Pd(II)–Al(III)	99.5 (3.5)	209 (0.036)	5728
Pd(II)–Fe(III)	99.4 (3.9)	167 (0.04)	4146
Pd(II)–Cu(II)	99.6 (2.8)	237 (0.029)	8094
Pd(II)–Pb(II)	97.8 (1.7)	45.2 (0.017)	2659

Initial aqueous phase: $[\text{Pd(II)}] = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ $[\text{metal}] = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl; organic phase: $2 \text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl in toluene; A/O = 1

Fig. 14 Extraction of palladium(II), platinum(IV), gold(III), rhodium(III), aluminum(III), iron(III), copper(II) and lead(II) from multi-metal solution. Initial aqueous phase: $[\text{metal}] = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl; organic phase: (■) $2 \text{ mmol}\cdot\text{L}^{-1}$ and (▒) $10 \text{ mmol}\cdot\text{L}^{-1}$ [PIP16]Cl in toluene; A/O = 1

which is not possible by extraction, is possible using the stripping process (Table 3). The palladium(II), platinum(IV) and gold(III) were successfully separated and recovered with $0.5 \text{ mol}\cdot\text{L}^{-1}$ aqueous ammonia (Stripping I), $5 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 (Stripping II) and $0.1 \text{ mol}\cdot\text{L}^{-1}$ thiourea in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl (Stripping III), respectively.

4 Conclusions

N-hexadecylpiperidinium chloride in toluene was examined for palladium(II) extraction from hydrochloric acid solutions. The extraction of palladium(II) from chloride media is effective, fast and depends upon HCl and NaCl concentrations, extractant concentration, contact time of the phases and temperature of extraction. The efficient extraction of palladium(II) from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl solution with [PIP16]Cl in toluene amounts to almost 100%. The anion-exchange mechanism of palladium(II) extraction with [PIP16]Cl was confirmed by Job's method, UV–VIS, IR and ^1H NMR analysis, and palladium(II) was extracted to the organic phase as $[\text{PIP16}]_2\text{PdCl}_4$. The thermodynamic parameters of the reaction were obtained and indicate that extraction of palladium(II) from $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl with [PIP16]Cl in toluene is an exothermic reaction. The extractant studied [PIP16]Cl can be reused at least in 6 cycles of extraction-stripping-regeneration process

Table 3 Separation of palladium(II), gold(III) and platinum(IV)

Stripping, %	Pd(II)	Au(III)	Pt(IV)
Stripping I with 0.5 mol·L ⁻¹ aqueous ammonia from loaded organic phase after extraction	100	0	1.5
Stripping II with 5 mol·L ⁻¹ HNO ₃ from organic phase after stripping I	0	0	98
Stripping III with 0.5 mol·L ⁻¹ thiourea in 0.1 mol·L ⁻¹ HCl from organic phase after stripping II	0	100	0

Initial aqueous phase: [metal] = 0.5 mmol·L⁻¹ in 0.1 mol·L⁻¹ HCl; the organic phase: 10 mmol·L⁻¹ [P/P16]Cl in toluene; A/O = 1

without a significant loss in the extraction power. Separation and recovery of palladium(II), platinum(IV) and gold(III) is possible using the extraction-stripping process.

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