*Polish Journal of Chemical Technology, 9, **2**, 99 — 101, 2007, 10.2478/v10026-007-0037-4*

Extraction of Palladium(II) Ions from Chloride Solutions with Phosphonium Ionic Liquid Cyphos®IL101

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The extraction of palladium(II) from hydrochloric acid solutions of various concentrations in the presence of different amounts of sodium chloride with phosphonium ionic liquid Cyphos®IL101 in toluene was investigated. The extraction of Pd(II) is very effective. The percentage extraction of Pd(II) from 0.1 mol dm-3 HCl solution amounts to 97% with Cyphos®IL101. Both the increase in HCl concentration and the presence of NaCl have a negative influence on the extraction. The extent of extraction from 0.1 mol dm-3 HCl solution in the presence of 0.5 mol dm^{-3} NaCl is about 80% and from 3 mol dm^{-3} HCl is lower and amounts to 56%. The extraction of Pd(II) from aqueous 0.1 mol dm^{-3} HCl and from 0.1 mol dm^{-3} HCl in the presence of 0.5 mol dm^{-3} NaCl with this phosphonium ionic liquid is rapid and the equilibrium is achieved after 1 – 2 minutes. The extraction of Pd(II) from aqueous 3 mol dm^{-3} HCl is slower and the equilibrium is achieved after 5 – 6 minutes.

Keywords: extraction of palladium(II), hydrochloric acid, phosphonium ionic liquids.

Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

At present noble metals have a wide range of industrial applications. They are used in electronic, chemical, pharmaceutical and petroleum industries, also in instrument and jewelry making. A demand for these metals has increased in recent years, whereas the natural sources are limited[1]. Both the recovery of noble metals, especially palladium, from waste solutions as well as preconcentration techniques to facilitate their determination at very low levels are important economical and ecological issues.

In recent years extraction has became a suitable and powerful method for metal recovery from low concentrated sources, including palladium. Various extractants have been used for the extraction of palladium(II): hydroxyoximes[2, 3], dialkyl sulphides[4], hydrophobic amines[5, 6], and pyridinecarbox-amides[7, 8], alpha benzoim oxime[9], α-amino phosphonate[10] and Aliquat 336[11].

The kinetics of palladium(II) extraction with dialkyl sulphides from hydrochloric acid solutions is very slow and a few hours are needed to achieve equilibrium. This slow process results not only from symmetrical palladium(II) chlorocomplex ($PdCl_4^{2-}$) but also from high hydrophobicity of the proposed extractants and their surface activity[4].

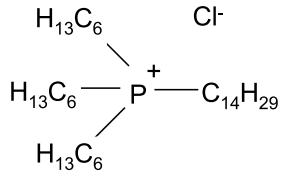
In the last ten years there have appeared many publications and patents about the synthesis and the applications of ionic liquids (ILs), which are classified as 'green' organic solvents due to their immeasurably low vapor pressure[12]. Moreover, ILs have many other attractive properties, such as wide liquid range, good chemical and thermal stability, hydrophobic or hydrophilic character, nonflammability, high ionic conductivity and a wide electrochemical potential window, and because of that they have found many different applications[12, 13].

ILs are used as solvents and catalysts in organic reactions, electrolite in alternate sources of energy, microbicides, fungicides, antielectrostatics, plasticizers, greases, extractants of sulphur compounds from diesel oil and the modifing agents of the silica surface[12]. There also have appeared publications concerning the new applications of ionic liquids as solvents for the extraction of metals and organic compounds[14 – 18], for membranes productions[19 – 20], biodiesel recovery processes[21] as well as spent nuclear fuel purification[22].

Looking for an extractant allowing the fast extraction of palladium(II), the authors have used a phosphonium ionic liquid. It is the aim of the work to extract palladium(II) from hydrochloric acid solutions of various concentrations and various sodium chloride contents with tetradecyl(triheksyl)phosphonium chloride.

EXPERIMENTAL

Commercialy pure tetradecyl(triheksyl)phosphonium chloride (96% purity, Cyphos®IL101, produced by Cytec Industries Inc.) was used as an extractant. Its structure is presented below.



tetradecyl(triheksyl)phosphonium chloride

The extraction were carried out in a typical way with five millimolar solutions of Cyphos®IL101 in toluene as an organic phase. The aqueous feeds contained $5 \cdot 10^{-3}$ mol dm^{-3} of palladium(II) chloride in 0.1 – 3 mol dm^{-3} HCl and 0.1 mol dm^{-3} HCl in the presence of 0.05 – 0.5 mol dm^{-3} NaCl. 5 cm^3 of both phases were mechanically shaken for a period of time between 30 seconds and 30 minutes at room temperature and left to stand for phase separation. Palladium(II) concentrations were determined in the

initial aqueous solutions and in the aqueous phases after extraction by the spectrophotometric method at 408 nm, using potassium iodide as a reagent[23]. The percentage extraction (%) was calculated from the contents of palladium ions in the aqueous phases before (c_0) and after (c) the extraction:

$$\%E = \frac{c_0 - c}{c_0} \cdot 100\% \quad (1)$$

The volumes of the phases did not change.

RESULT AND DISCUSSION

The extraction from 0.1 mol dm^{-3} HCl, 3 mol dm^{-3} HCl and 0.1 mol dm^{-3} HCl in the presence of 0.5 mol dm^{-3} NaCl was studied. The equilibrium of palladium(II) extraction from aqueous 0.1 mol dm^{-3} HCl and from 3 mol dm^{-3} HCl is achieved after 1 – 2 minutes. The extraction of palladium(II) from aqueous 0.1 mol dm^{-3} HCl in the presence of 0.5 mol dm^{-3} NaCl is slower and the equilibrium is achieved after 5 – 6 minutes (Fig. 1). The extraction of palladium(II) with this phosphonium ionic liquid is rapid. The initial extraction rates amount to 1.35 · 10^{-4} mol dm^{-3} s^{-1}, 1.03 · 10^{-4} mol dm^{-3} s^{-1} and 0.87 · 10^{-4} mol dm^{-3} s^{-1} for palladium in 0.1 mol dm^{-3} HCl, 0.1 mol dm^{-3} HCl in the presence of 0.5 mol dm^{-3} NaCl and in 3 mol dm^{-3} HCl, respectively.

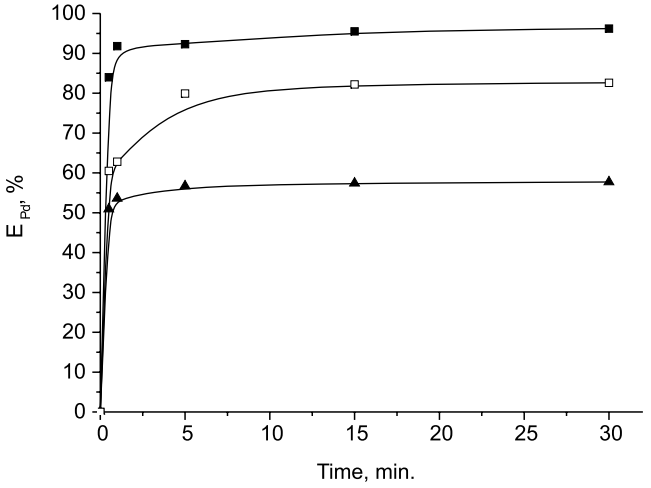


Figure 1. Extraction of Pd(II) vs. the time of extraction with Cyphos®IL101 from 0.1 mol dm^{-3} HCl solution (■), 3 mol dm^{-3} HCl solution (▲) and 0.1 mol dm^{-3} HCl solution in the presence of 0.5 mol dm^{-3} NaCl (□), [Pd(II)] = 5 • 10^{-3} mol dm^{-3}, [IL101] = 5 • 10^{-3} mol dm^{-3}

The extraction of palladium(II) from the chloride media depends upon hydrochloric acid concentration and the contents of the added sodium chloride and it is very effective. The percentage extraction of palladium(II) at equilibrium from 0.1 mol dm^{-3} HCl solution amounts to 97% with Cyphos®IL101. The increase in HCl concentration and the presence of NaCl have a negative influence on the extraction. The extent of palladium(II) extraction from 0.1 mol dm^{-3} HCl solution in the presence of 0.5 mol dm^{-3} NaCl is 83% and from 3 mol dm^{-3} HCl is lower and amounts to 56% (Fig. 2).

The isotherms of palladium(II) extraction from 0.1 mol dm^{-3} HCl, 3 mol dm^{-3} HCl and from 0.1 mol dm^{-3} HCl in the presence of 0.5 mol dm^{-3} NaCl with

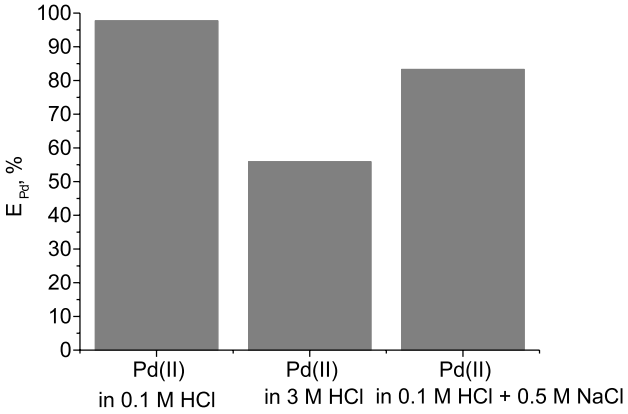


Figure 2. Extraction of Pd(II) with Cyphos®IL101 from HCl solutions of various concentrations with the addition and without NaCl, [Pd(II)] = 5 • 10^{-3} mol dm^{-3}, [IL101] = 5 • 10^{-3} mol dm^{-3}

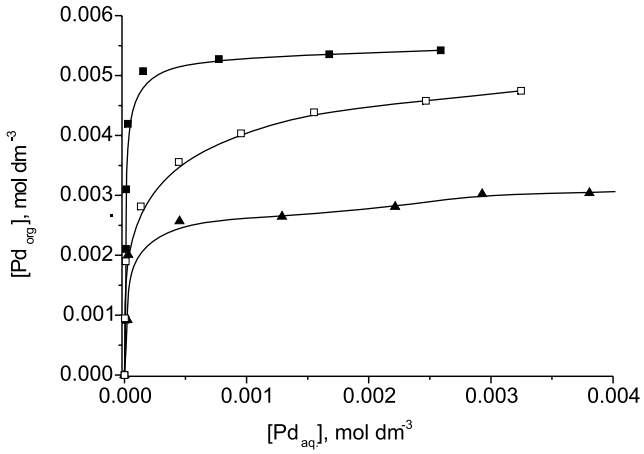


Figure 3. The isotherms of palladium(II) extraction from 0.1 mol dm^{-3} HCl (■), 3 mol dm^{-3} HCl (▲) and from from 0.1 mol dm^{-3} HCl in the presence of 0.5 mol dm^{-3} NaCl (□) with Cyphos®IL101, [Pd(II)] = 1 • 10^{-3} - 5 • 10^{-3} mol dm^{-3}, [IL101] = 5 • 10^{-3} mol dm^{-3}

Cyphos®IL101 were investigated (Fig. 3). There is a visible difference between the extraction from 0.1 mol dm-3 HCl and 3 mol dm^{-3} HCl. In the acidic system the most probable extraction mechanism is anion-exchange, which is analogous to the extraction with quartenary ammonium salts. The authors have proposed a mechanism proceeding according to the following equations:

– at 0.1 mol dm^{-3} HCl

$$2H^+_{(w)} + PdCl^{2-}_{4(w)} + [R_3R'P^+][Cl^-]_{(o)} = [R_3R'P^+][PdCl^-_3]_{(o)} + 2Cl^-_{(w)} + 2H^+_{(w)} \quad (2)$$

– at 3 mol dm^{-3} HCl

$$2H^+_{(w)} + PdCl^{2-}_{4(w)} + 2[R_3R'P^+][Cl^-]_{(o)} = [R_3R'P^+]_2[PdCl^{2-}_4]_{(o)} + 2Cl^-_{(w)} + 2H^+_{(w)} \quad (3)$$

The complexes with the molar ratio of palladium(II) to the extractant equal 1:1 ([R_3R'P$^+$][$PdCl_3^-$]) from 0.1 mol dm^{-3} HCl and 1:2 ([R_3R'P$^+$]$_2$[$PdCl_4^{2-}$]) from 3 mol dm^{-3} HCl are extracted. The extraction of these two complexes is confirmed by the extraction data given in Fig. 4, presenting the relationship of log D_{Pd} vs. [IL101]/[Pd(II)] ratio. The intersection points of the ligand/palladium ratio

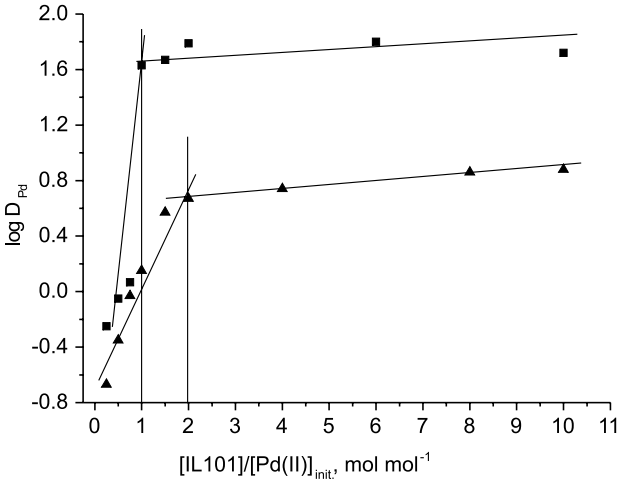


Figure 4. The effect of IL101/Pdini. molar ratio distribution on the ratio of Pd(II), [Pd(II)] = 5 • 10^{-3} mol dm^{-3} in 0.1 HCl (■) and in 3 mol dm^{-3} HCl (▲), [IL101] = 1.25 • 10^{-3} - 5 • 10^{-2} mol dm^{-3}

equal 1 and 2 are observed, which corresponds to the complexes in the organic phase mentioned above.

CONCLUSIONS

The extraction of palladium(II) from the chloride media with tetradecyl(triheksyl)phosphonium chloride (Cyphos®IL101) depends upon the content of hydrochloridc acid and the concentration of added sodium chloride. Both the increase in HCl concentration and the presence of NaCl have a negative influence on the extraction. The percentage extraction of palladium(II) from 0.1 mol dm^{-3} HCl, 0.1 mol dm^{-3} in the presence of 0.5 mol dm^{-3} NaCl and from 3 mol dm^{-3} HCl at equilibrium is 97, 83 and 56%, respectively. The equilibium is achieved in 1 – 6 minutes and it depends upon the concentration of HCl and added NaCl. These results presended here prove that Cyphos®IL101 is an effective extractant for palladium(II) separation from the chloride media.

ACKNOWLEDGEMENT

This work was supported by the grant No. 32-139/2007 DS.

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