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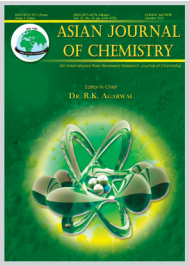

Solvent Extraction of Palladium(II) with 2-Ethylhexyl Benzothiazolyl Sulfide

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A new 2-ethylhexyl benzothiazolyl sulfide was synthesized and used in the extraction of Pd(II) from hydrochloric acid solution. Palladium(II) was extracted quantitatively with 2-ethylhexyl benzothiazolyl sulfide in xylene. Thiourea solution could be used as stripping agent. Extraction parameters of Pd(II), including 2-ethylhexyl benzothiazolyl sulfide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio, thiourea concentration and hydrochloric acid concentration of aqueous phase, were studied. 2-Ethylhexyl benzothiazolyl sulfide and Pd(II) form a 2:1 adduct as $Pd(EHBTS)_2Cl_2$ in the extraction. X-ray crystal structure determination revealed $Pd(EHBTS)_2Cl_2$ square-planar complex in which 2-ethylhexyl benzothiazolyl sulfide acts as a neutral unidentate ligand coordinated with palladium(II) *via* the thiazolyl N atom.

Key Words: Palladium, Solvent extraction, 2-Ethylhexyl benzothiazolyl sulfide.

INTRODUCTION

Various hydrometallurgical processes such as solvent extraction, ion exchange and precipitation have been accomplished for the recovery of palladium in chloride media[1-3]. Solvent extraction has been considered as a most efficient technique for the recovery and separation of platinum-group metals (PGM) from hydrochloric acid solutions[4-10]. One coordination chemistry property of Pd(II) is that it prefers to coordinate most strongly with polarizable atoms, a fact that has pushed the development of extractants bearing donor atoms such as sulfur, phosphorus and nitrogen. These ligands are soft-bases according to the hard-soft acid-base concept[11]. Sulfides are known to be highly selective for extraction of Pd(II) and have been widely used in the extraction of this species. So far, most sulfides reported for this purpose are dialkyl sulfides. In the present work, a new sulfide extractant bearing a heterocyclic substituent, 2-ethylhexyl benzothiazolyl sulfide was synthesized and its extraction behaviour towards Pd(II) from hydrochloric acid solution was also studied, by controlling important parameters like extractant concentration, acidity, contact time, phase ratio and concentration of stripping agent. The crystal structure of $Pd(EHBTS)_2Cl_2$ showed that 2-ethylhexyl benzothiazolyl sulfide (EHBTS) acts as a neutral unidentate ligand coordinated with Pd(II) *via* the benzothiazolyl N atom. This is quite different from general Pd(II) dialkyl sulfide complexes in which sulfides are coordinated with palladium *via* the S atoms of the ligand[12-17].

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corpotation, Japan) was used to measure the concentration of Pd(II). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Pd 247.6 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Pd(II) stock solution (1 g L^{-1}): A weighed portion of palladium metal was dissolved in aqua regia (120 mL). When the metal was completely dissolved, the solution was evaporated to nearly dryness. Residual HNO_3 was removed by adding 30 mL of 6 mol L^{-1} HCl and evaporated to nearly dryness again and this was repeated 3 times. The solution was transferred into a 250 mL of volumetric flask and the final volume was adjusted by adding 0.1 mol L^{-1} HCl solution. The organic phases with desired extractant concentration were obtained by dissolving a definite volume of 2-ethylhexyl benzothiazolyl sulfide (EHBTS) in xylene.

Synthesis of 2-ethylhexyl benzothiazolyl sulfide (EHBTS): 2-Ethylhexyl benzothiazolyl sulfide was synthesized according to the following procedure: 2-mercaptobenzothiazole (7.5 g), acetone (150 mL) and KOH (2.8 g) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for *ca.* 0.5 h. 2-Ethylhexyl bromide (9 mL) was then added gradually with stirring through a

dropping funnel and the reaction mixture was refluxed for 6 h. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether (20 mL), washed with water two times and dried with anhydrous Na_2SO_4. The ether was evaporated and EHBTS was obtained. Its structure (Fig. 1) was verified by ^1H NMR, ^{13}C NMR and mass spectra. ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz 1H), 7.76 (d, *J* = 7.39 Hz 1H), 7.45-7.39 (m,1H), 7.32-7.27 (m, 1H), 3.44-3.39 (m, 2H), 1.83-1.77 (m, 1H), 1.56- 1.35 (m,8H), 1.00 - 0.92 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.80, 153.38, 135.17, 125.96, 124.05, 121.40, 120.89, 39.19, 37.80, 32.50, 28,81, 25.78, 22.94, 14.11, 10.90 ppm; HRMS (ESI) m/z found :280.1193 $(M+H)^+$; calc.: 280.1188 $(M+H)^+$.

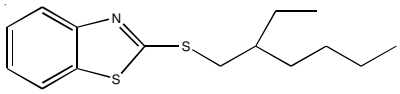

Fig. 1. Structure of 2-ethylhexyl benzothiazolyl sulfide (EHBTS)

General extraction procedure: Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 40 min, which was sufficient enough to attain equilibrium in a preliminary experiment. After phase separation, the concentration of Pd(II) in aqueous solution was determined by an atomic absorption photometer. These results were further used to estimate the extraction efficiency of metal. The amount of extracted metal ion was calculated according to the differences in the metal concentrations of the aqueous phase between, before and after the extraction.

RESULTS AND DISCUSSION

Influences of the extractant concentration: To investigate the effect of 2-ethylhexyl benzothiazolyl sulfide (EHBTS) concentration on the extraction performances of Pd(II), the experiments were performed at the fixed conditions. The results are shown in Fig. 2. As can be seen from Fig. 2, EHBTS dissolved in xylene with the extractant concentration varying from 1 to 9 % (v/v). The percentage extraction of Pd(II) increased in the range from 58.8 to 99.6 % by increasing 2-ethylhexyl benzothiazolyl sulfide concentration from 1 to 7 % (v/v). Further increasing EHBTS concentration from 7 to 9 % (v/v), the percentage extraction of Pd(II) only had a slight increase (from 99.6 to 99.9 %). 7 % (v/v) EHBTS was needed for quantitative extraction of Pd(II) from a 0.1 mol L^{-1} HCl aqueous solution containing 100 mg L^{-1} palladium.

Influences of hydrochloric acid concentration: In industrial application for extraction of Pd(II), the acidity of stock solution usually influences significantly. The effect of hydrochloric acid concentration on the extraction of Pd(II) is shown in Fig. 3. The extraction curve indicated the percentage of extraction of Pd(II) decreased drastically with the increase of HCl concentration. The percentage extraction of Pd(II) decreased in the range from 99.6 % to 44.2 % by increase of HCl concentration from 0.1 mol L^{-1} to 2.0 mol L^{-1}. Quantitative extraction of palladium occurred at 0.1 mol L^{-1} HCl. Therefore, 0.1 mol L^{-1} HCl was adopted in all subsequent experiments.

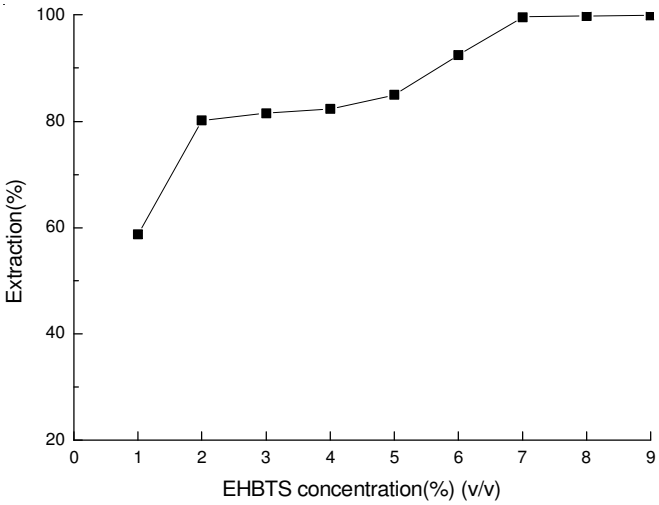

Fig. 2. Effect of extractant concentration on the extraction of Pd(II); $C_{Pd(II)}$: 100 mg L^{-1}, C_{HCl}: 0.1 mol L^{-1}, O/A: 1.0, contact time: 40 min

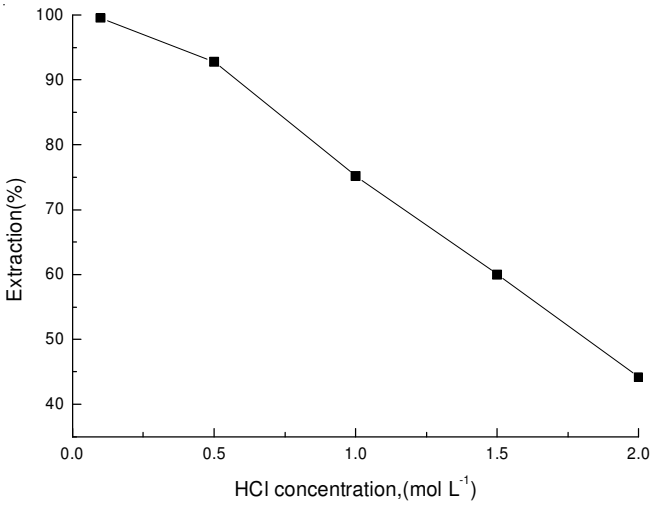

Fig. 3. Effect of HCl concentration on the extraction of Pd(II); $C_{Pd(II)}$: 100 mg L^{-1}, C_{EHBTS}: 7 % (v/v), O/A: 1, contact time: 40 min

Influences of contact time: To extract Pd(II) efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 4. Contact time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 5 to 60 min. The percentage extraction of Pd(II) increased in the range from 30 to 99.6 % by increased of contact time from 5 to 40 min. Further increasing contact time from 40 to 60 min, the percentage extraction of Pd(II) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of palladium was found to be about 40 min.

Influences of organic/aqueous (O/A) phase ratio: To obtain optimal O/A for extraction of Pd(II), the following experiments were performed at other fixed extraction parameters. The results are shown in Fig. 5. As can be seen from Fig. 5, by increasing O/A from 0.4 to 1.0, the percentage extraction of Pd(II) increased from 70.2 to 99.6 %. By further increasing O/A from 1.0 to 1.6, the percentage extraction of

Pd(II) kept constant. Therefore, Pd(II) can be extracted efficiently by controlling organic/aqueous (O/A) phase ratio, 1.0.

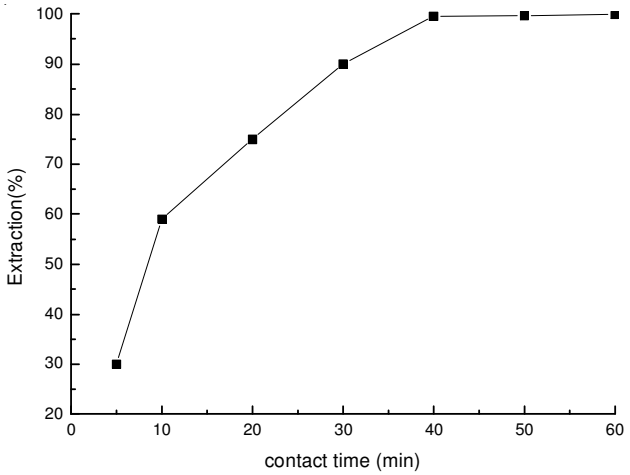

Fig. 4. Effect of contact time on the extraction of Pd(II); $C_{Pd(II)}$: 100 mg L^{-1}, C_{EHBTS}: 7 % (v/v), O/A: 1.0, C_{HCl}: 0.1 mol L^{-1}

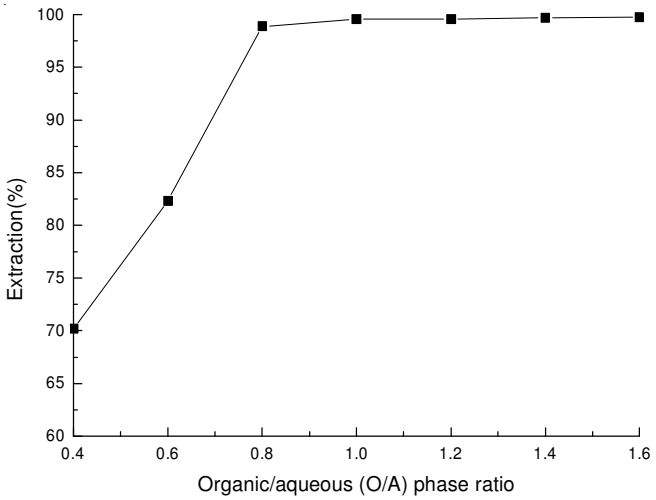

Fig. 5. Effect of O/A on the extraction of Pd(II); $C_{Pd(II)}$: 100 mg L^{-1}, C_{EHBTS}: 7 % (v/v), contact time: 40 min, C_{HCl}: 0.1 mol L^{-1}

Stripping properties of palladium: Palladium loaded in the organic phase was stripped with various stripping agents, such as thiourea, hydrochloric acid, nitric acid, sodium hydroxide, ammonia and sodium sulfite as stripping agents. In the following experiments, the organic phase loaded with 100 mg L^{-1} Pd(II) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 60 min; organic/aqueous (O/A) phase ratio, 1. The results show that palladium can not be stripped from organic phase with acid solution and sodium hydroxide. Thiourea solution can be used as the effective stripping agent. As can be seen from Fig. 6, by increasing thiourea concentration from 0.1 to 0.7 mol L^{-1}, the percentage stripping of Pd(II) increased from 74.9 to 98.7 %. By further increasing concentration of thiourea from 0.7 to 1.2 mol L^{-1}, the percentage stripping of Pd(II) kept constant. The stripping was quantitative when 0.7 mol L^{-1} thiourea solution was used.

X-Ray crystallography of $Pd(EHBTS)_2Cl_2$: The crystal structure of $Pd(EHBTS)_2Cl_2$ is shown in Fig. 7. Crystallographic data and some experimental conditions used to obtain the intensity data are given in Table-1. As expected, in Pd(II)-EHBTS complex, EHBTS acts as neutral unidentate ligand coordinating to palladium via the thiazolyl N atom. The complex is of *trans*-conformation and Pd(II) is coordinated by two Cl atoms and two EHBTS at opposite position. Two opposite Pd-N and Pd-Cl bond distances are equivalent respectively. The Pd-atom and two N-atoms are coplanar (N(1)-Pd(1)-N(1)# =180.00º). Thus, the palladium-EHBTS complex as a whole is in complete symmetry with palladium atom at the symmetry center of the square-planar complex.

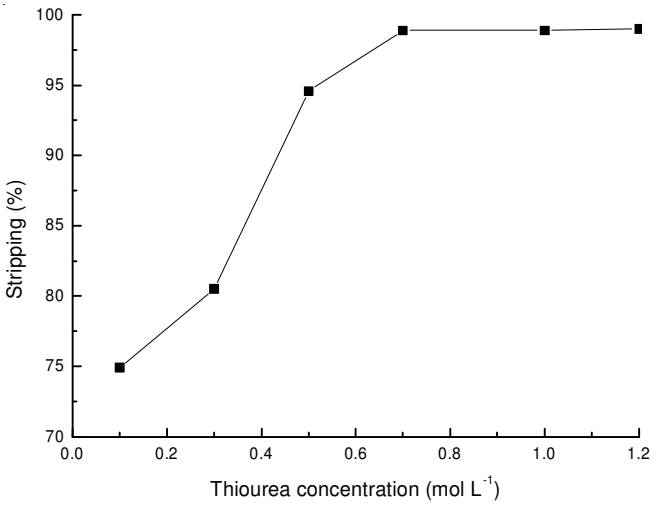

Fig. 6. Effect of stripping reagent concentration on the stripping of Pd(II); $C_{Pd(II)}$: 100 mg L^{-1}, C_{EHBTS}: 7 % (v/v), O/A: 1, contact time: 60 min

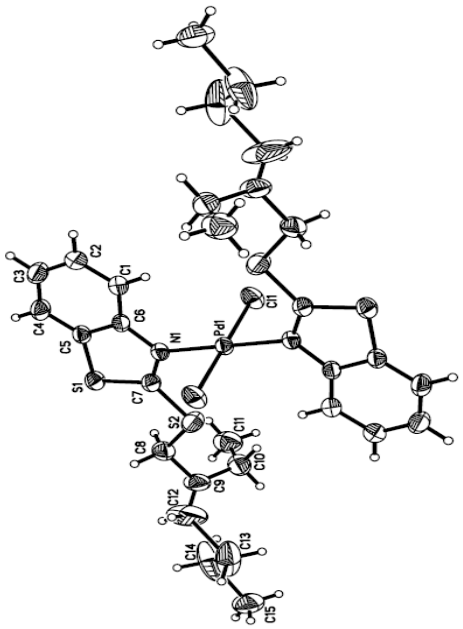

Fig. 7. Crystal structure of $Pd(EHBTS)_2Cl_2$

Conclusion

The solvent extraction of Pd(II) from hydrochloric acid solutions were investigated using 2-ethylhexyl benzothiazolyl sulfide (EHBTS) diluted in xylene. Extraction parameters of Pd(II) were obtained and summarized as the following:

TABLE-1
CRYSTAL DATA AND STRUCTURE PARAMETERS FOR EHBTS-Pd(II)

Parameters	Data
Empirical formula	$C_{30}H_{40}N_2PdS_4Cl_2$
Formula weight	734.18
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.638(5) Å α = 90º
	b = 9.159(5) Å β= 113.128(17)º
	c = 18.571(5) Å γ = 90º
Volume	1664.0 (13) $Å^3$
Z	2
Calculated density	1.465 mg/m^3
Absorption coefficient	0.992 mm^{-1}
F(000)	756
Crystal size	0.23 × 0.17 × 0.12 mm^3
θ Range for data collection	2.08 to 28.50º
Reflections collected	11095
Goodness-of-fit on F^2	1.037
Final R indices [I>2σ(I)]	R_1 = 0.0534, wR_2 = 0.1271
R indices (all data)	R_1 = 0.0972, wR_2 = 0.1465
Largest diff. peak and hole	0.975 and -1.036 e. $Å^{-3}$

2-ethylhexyl benzothiazolyl sulfide (EHBTS) concentration, 7 % (v/v); organic/aqueous (O/A) phase ratio,1; hydrochloric acid concentration of aqueous solution, 0.1 mol L^{-1}; contact time of two phases 40 min. Pd(II) loaded in organic phase could be stripped efficiently using an aqueous solution containing thiourea. X-ray crystal structure determination revealed $Pd(EHBTS)_2Cl_2$ square-planar complex in which EHBTS acts as a neutral unidentate ligand coordinated with palladium(II) via the thiazolyl N atom, which is quite different from general alkyl sulfide which is coordinated with Pd(II) *via* S atoms of the ligands.

ACKNOWLEDGEMENTS

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