



Solvent Extraction of Palladium(II) with 2-Ethylhexyl Benzimidazole Sulfide from Hydrochloric Acid Media

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The solvent extraction of Pd(II) from hydrochloric acid solutions were investigated using 2-ethylhexyl benzimidazole sulfide (EHBMS) in presence of toluene. Pd(II) was strongly extracted by a lower concentration 2-ethylhexyl benzimidazole sulfide in a lower concentration hydrochloric acid solution. Extraction parameters of Pd(II), including 2-ethylhexyl benzimidazole sulfide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio and H^+ concentration of aqueous phase, were studied. The optimal extraction parameters were obtained and summarized, 2-ethylhexyl benzimidazole sulfide concentration 0.005 mol L^{-1} , organic/aqueous (O/A) phase ratio 1.0, H^+ concentration of aqueous phase 0.2 mol L^{-1} and contact time of two phases 15 min. Stripped of Pd(II) from loaded organic phase was performed using thiourea solution (1.0 mol L^{-1}).

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

INTRODUCTION

Palladium is one of the important rare metals indispensable for high-technology industries as a raw material of catalysts, electronic materials and so on¹⁻³. As Pd(II) can form a number of complexes which are soluble in organic solvents, solvent extraction has become an effective technique in the recovery and separation of palladium from aqueous solutions. Various reagents have been studied on the solvent extraction of Pd(II), for example, cyanamides⁴, trialkyl amines⁵, 8-hydroxyquinoline^{6,7}, Schiff base⁸, ketones⁹ and sulphur-containing extractants¹⁰⁻¹². Palladium, according to Pearson theory, belongs to the group of soft acids, thus forms complexes with ligands containing sulfur donor atoms. Sulfide extractants contain sulfur atom and can coordinate with palladium ions *via* S atom. Sulfides are known to be highly selective for extraction of Pd(II) and have been widely used in the extraction of this species¹³⁻¹⁷. So far, most sulfides reported for this purpose are dialkyl sulfides. In this work, a new 2-ethylhexyl benzimidazole sulfide extractant bearing a heterocyclic substituent was synthesized and used in the extraction of Pd(II) in hydrochloric acid media.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, 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 (1.0 g L^{-1}): A weighed amount 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 benzimidazolyl sulfide in toluene.

Synthesis of 2-ethylhexyl benzimidazole sulfide (EHBMS): 2-Ethylhexyl benzimidazole sulfide was synthesized according to the following procedure: 2-mercaptobenzimidazole (0.1 mol), acetone (150 mL) and KOH (0.1 mol) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for *ca.* 20 min, 2-ethylhexyl bromide (0.1 mol) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 3 h. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether (50 mL), washed with water two times and dried with anhydrous Na_2SO_4 . The

ether was evaporated and 2-ethylhexyl benzimidazole sulfide (EHBMS) was obtained. The precipitate was recrystallized from ethyl acetate to give a yield of 75 %. Melting point of the obtained product was 76-78 °C. Its structure (Fig. 1) was verified by elemental analysis, ^1H NMR, ^{13}C NMR and mass spectra. The results of elemental analysis are listed below: $\text{C}_{15}\text{H}_{22}\text{N}_2\text{S}$, calcd. (found) (%) C 68.66 (68.76), H 8.46 (8.26), N 10.68 (10.62); ^1H NMR (500 MHz, CDCl_3) δ 7.55-7.53 (m, 2H), 7.18-7.17 (m, 2H), 3.40-3.36 (m, 2H), 1.67-1.64 (m, 1H), 1.40-1.30 (m, 4H), 1.18-1.17 (m, 4H), 0.81-0.78 (m, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 151.81, 139.48, 122.13, 114.22, 39.13, 37.13, 32.26, 28.65, 25.50, 22.90, 13.98, 10.65 ppm; HRMS (ESI) m/z , calcd. (%): 263.1576 ($\text{M} + \text{H}^+$); found (%): 263.1569 ($\text{M} + \text{H}^+$).

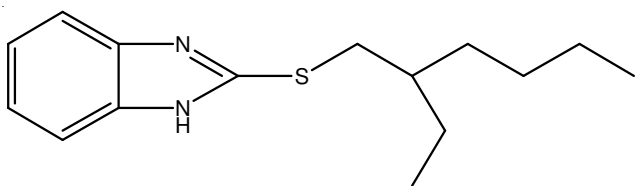


Fig. 1. Structure of 2-ethylhexyl benzimidazole sulfide (EHBMS)

General extraction procedure: All the experiments were carried out at room temperature (25 ± 1 °C). Experiments were out by shaking equal volumes (10 mL) of the aqueous and organic phases in 100 mL of separatory funnel for a stipulated time under vigorous shaking, leading to attain extraction equilibrium. After phase separation, the concentration of metal ion 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 benzimidazole sulfide 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, EHBMS dissolved in toluene with the extractant concentration varying from 0.001-0.01 mol L^{-1} . The percentage extraction of Pd(II) increased in the range from 59.9-99.2 % by increasing 2-ethylhexyl benzimidazole sulfide concentration from 0.001-0.05 mol L^{-1} . Further increasing the concentration of 2-ethylhexyl benzimidazole sulfide from 0.05-0.10 mol L^{-1} , the percentage extraction of Pd(II) only had a slight increase (from 99.2-99.6 %). 0.005 mol L^{-1} EHBMS was needed for quantitative extraction of Pd(II) from a 0.2 mol L^{-1} HCl aqueous solution containing 100 mg L^{-1} palladium.

Influences of concentration of H^+ : In industrial application for extraction of Pd(II), the acidity of stock solution usually influences significantly. The effect of H^+ 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 H^+ concentration. Quantitative

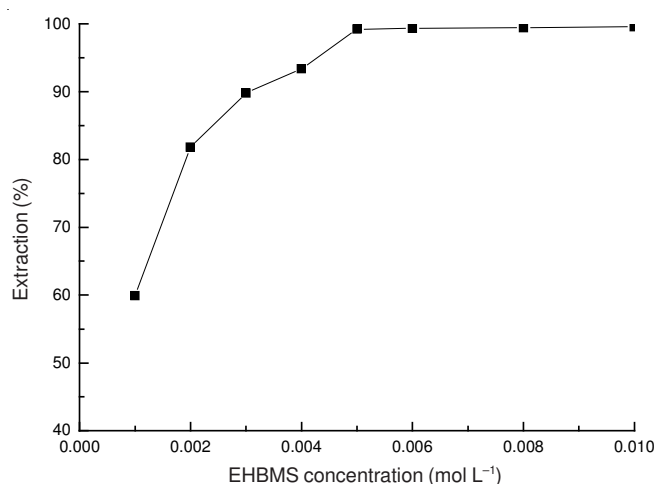


Fig. 2. Effect of extractant concentration on the extraction of Pd(II). $C_{\text{Pd(II)}}$: 100 mg L^{-1} , C_{HCl} : 0.2 mol L^{-1} , O/A: 1.0, contact time: 15 min

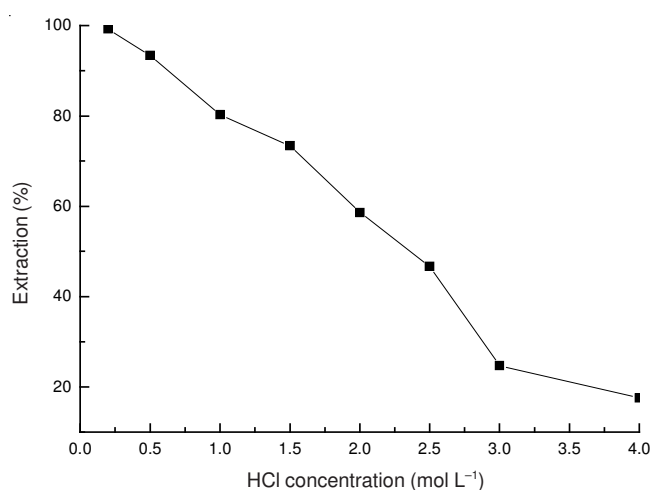


Fig. 3. Effect of HCl concentration on the extraction of Pd(II). $C_{\text{Pd(II)}}$: 100 mg L^{-1} , C_{EHBMS} : 0.005 mol L^{-1} , O/A: 1.0, contact time: 15 min

extraction of palladium occurred at 0.2 mol L^{-1} HCl. Therefore, 0.2 mol L^{-1} HCl was adopted in all subsequent experiments.

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 2-24 min. The minimum period of equilibration required for the quantitative extraction of palladium was found to be about 15 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 0.4-1.0, the percentage extraction of Pd(II) increased from 75.4-99.24 %. By further increasing O/A from 1.0-2.0, 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.

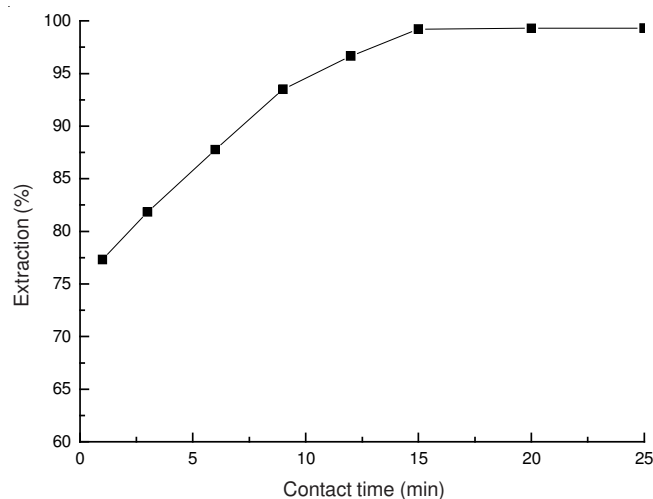


Fig. 4. Effect of contact time on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L⁻¹, C_{EHBMS} : 0.005 mol L⁻¹, O/A: 1.0, C_{HCl} : 0.2 mol L⁻¹

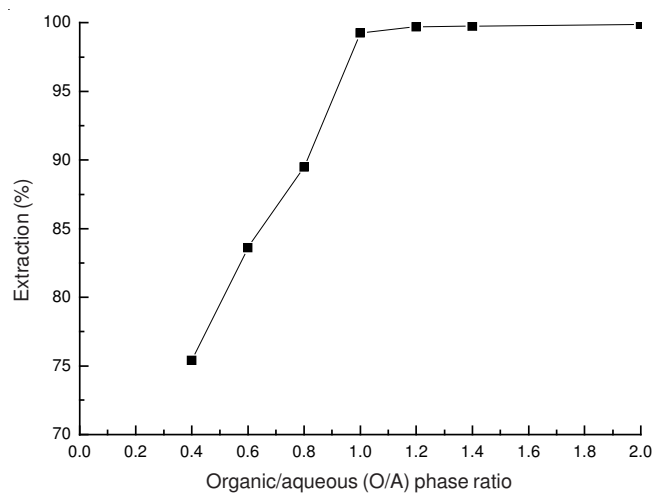


Fig. 5. Effect of O/A on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L⁻¹, C_{EHBMS} : 0.005 mol L⁻¹, contact time: 15 min, C_{HCl} : 0.2 mol L⁻¹

Determination of extraction saturation capacity of Pd(II): Pd(II) concentration of aqueous solution, 1.000 g L⁻¹; O/A, 1.0; contact time of two phases, 15 min; H⁺ concentration of aqueous phase, 0.2 mol L⁻¹. Eight shares of the stock solutions were extracted in turn using the same organic phase with 0.1 mol L⁻¹ 2-ethylhexyl benzimidazole sulfide. After eight extractions, for partial organic phase lost severely, experiment could not be carried out further. The determination data of extraction saturation capacity of Pd(II) is listed in Table-1. According to Table-1, the Pd(II) concentration of organic

Number	Pd(II) concentration in organic phase (g L ⁻¹)	Percentage extraction of Pd(II) (%)
1	0.9987	99.87
2	1.9949	99.62
3	2.9868	99.19
4	3.9725	98.57
5	4.9469	97.44
6	5.9082	96.13
7	6.8471	93.89
8	7.7383	89.12

phase exceeded 7.7 g L⁻¹, which suggested that the extraction saturation capacity of Pd(II) was over 7.7 g L⁻¹ under the experimental conditions.

Stripping properties of palladium: The stripping of Pd(II) from loaded organic phases was investigated using an aqueous solution containing thiourea. In the following experiments, the organic phase loaded with 0.992 g L⁻¹ Pd(II) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 0.5 h; organic/aqueous (O/A) phase ratio, 1.0. The results are shown in Fig. 6. As can be seen from Fig. 6, by increasing thiourea concentration from 0.1-1.0 mol L⁻¹, the percentage stripping of Pd(II) increased from 82.4-97.8%. By further increasing concentration of thiourea from 1.0-1.5 mol L⁻¹, the percentage stripping of Pd(II) kept constant. The stripping was quantitative when 1.0 mol L⁻¹ thiourea solution was used. Hence, 1.0 mol L⁻¹ thiourea solution can be used as the effective stripping agent.

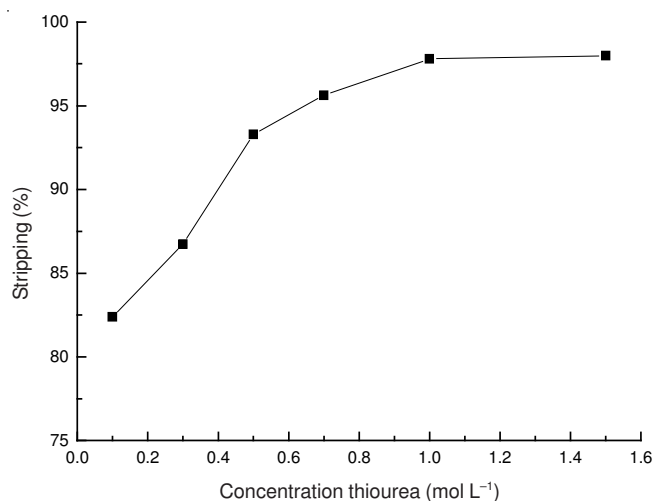


Fig. 6. Effect of stripping reagent concentration on the stripping of Pd(II). $C_{Pd(II)}$: 992.4 mg L⁻¹, C_{EHBMS} : 0.005 mol L⁻¹, O/A: 1.0, contact time: 0.5 h

Conclusion

The solvent extraction of Pd(II) from hydrochloric acid solutions were investigated using 2-ethylhexyl benzimidazole sulfide (EHBMS) diluted in toluene. Extraction parameters of Pd(II) were obtained and summarized as the following: 2-ethylhexyl benzimidazole sulfide concentration, 0.005 mol L⁻¹; organic/aqueous (O/A) phase ratio, 1.0; H⁺ concentration of aqueous solution, 0.2 mol L⁻¹; contact time of two phases 15 min. The saturation extraction capacity of Pd(II) was determined with 0.1 mol L⁻¹ 2-ethylhexyl benzimidazole sulfide and its experimental value exceeded 7.7 g L⁻¹. Pd(II) loaded in organic phase could be stripped efficiently using an aqueous solution containing thiourea.

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