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**Journal of Chemical and Pharmaceutical Research, 2014, 6(6):2634-2640**

**Research Article**

**ISSN : 0975-7384**
**CODEN(USA) : JCPRC5**

# Solvent extraction of palladium(II) with 2-hexyl-5-methyl benziminazole sulfide

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## ABSTRACT

*A new extractant of 2-hexyl-5-methyl benziminazole sulfide (HMBMS) was synthesized and used in the extraction of Pd(II) from hydrochloric acid solution. Pd(II) was extracted quantitatively with HMBMS in kerosene. Thiourea solution could be used as stripping agent. Extraction parameters of Pd(II), including 2-hexyl-5-methyl benziminazole sulfide (HMBMS) concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio and hydrochloric acid concentration of aqueous phase, were studied in detail. The extraction saturation capacity of Pd(II) was determined from 0.1mol $L^{-1}$ HCl solution with 30% (v/v) HMBMS and its experimental value exceeded 10 g $L^{-1}$ under the experimental conditions. Pd(II) and Pt(IV) could be separated effectively and the separation coefficient of Pd(II) and Pt(IV) ($\beta_{Pd/Pt}$) reached $1.5\times10^{4}$ when HMBMS and HC1 concentration were fixed at 20% (V/V) and 0.1 mol $L^{-1}$, respectively. Stripping of Pd(II) from loaded organic phase was performed using thiourea solution.*

**Keywords:** Palladium, Solvent Extraction, 2-Hexyl-5-Methyl Benziminazole Sulfide, Separation

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## INTRODUCTION

The conventional method for the separation of palladium from other platinum group metals (PGMs) is by chemical precipitation[1,2]. Precipitation process has inherent problems, such as high chemical consumption and high labor requirements involved in the repeated process, slow kinetics, and solid-liquid separation. The chemical precipitation process increases environmental pollution due to use of toxic chemicals [3]. Feasible hydrometallurgical techniques need to be developed to replace the conventional chemical precipitation method. Solvent extraction has been considered as a most efficient technique for the recovery and separation of platinum-group metals (PGM) from hydrochloric acid solutions [4,5]. Early studies on the solvent extraction of palladium mainly involved the extraction of palladium in aqueous acid solution. Chloride is the most common media into which all the precious metals, except silver, can be efficiently brought into solution. A number of studies on the extraction of palladium from hydrochloric acid solution have been carried out, and many different extraction systems have been examined, including oxime [6,7], alkyl derivative of 8-hydroyquinoline[8], phosphonium [9] and so on.

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. 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 [10-12]. In the present work, a new sulfide extractant bearing a heterocyclic substituent, 2-hexyl-5-methyl benziminazole sulfide (HMBMS) was synthesized and its extraction behavior 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.

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## EXPERIMENTAL SECTION

2.1 Major materials and equipments

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) and Pt(IV) stock solution(1.000 g $L^{-1}$): A weighed portion of palladium or platinum 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 $L^{-1}$ HCI 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 norm volume was adjusted by adding 0.1 mol $L^{-1}$ HCI solution.

A new extractant of 2-hexyl-5-methyl benziminazole sulfide (HMBMS) was synthesized in our laboratory. The organic phases with desired extractant concentration were obtained by dissolving a definite volume of 2-hexyl-5-methyl benziminazole sulfide (HMBMS) in kerosene.

2.2 Experimental methods

2.2.1 General extraction procedure

Equal volumes (20 mL) of both phases were mixed and vigorously shaken for 20 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.

Percentage extraction of Pd(II) or Pt(IV) was calculated according to Eq. (1):

$$E = \frac{[M]_{(0)}}{[M](aq)} \times \mathbf{100} \tag{1}$$

Where $[M]_{(o)}$ is metal ion concentration of organic phase, $[M]_{(aq)}$ is the metal concentration of stock solution before extraction.

Distribution coefficient (D) of metal ion in organic and aqueous phase was calculated by:

$$\mathbf{D} = \frac{[M]_{(o)}}{[M]_{(a)}} = \frac{E}{1 - E} \tag{2}$$

Where $[M]_{(a)}$ is residual metal concentration of aqueous phase after extraction, $[M]_{(o)}$ is metal ion concentration of organic phase.

Separation coefficient of Pd(II) and Pt(IV) ($\beta_{Pd/Pt}$) was expressed as:

$$\beta_{Pd/Pt} = \frac{D_{Pd}}{D_{Pt}} = \frac{E_{Pd}(1 - E_{Pt})}{E_{Pt}(1 - E_{Pd})} \tag{3}$$

2.2.2 Synthesis of 2-hexyl-5-methyl benziminazole sulfide (HMBMS)

HMBMS was synthesized according to the following procedure: 2-Mercapto-5-methyl benzimidazole (7.5g) , acetone (50 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 about 30 min. hexyl bromide (7.5 mL) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 5 hours. 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 HMBMS was obtained. Its structure (Fig. 1) was verified by $^1H$ NMR, $^{13}C$ NMR, and mass spectra.

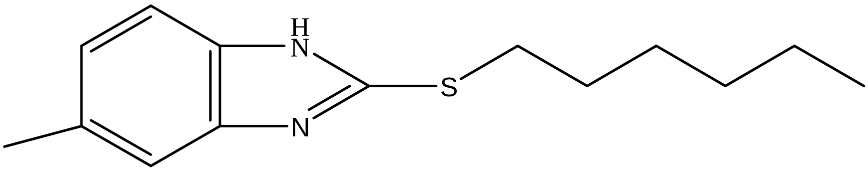

**Fig.1. Structure of 2-hexyl-5-methyl benziminazole sulfide (HMBMS)**

$^1$H NMR（500MHz，CDCl3），δ 7.47（d，J=7.6Hz, 1H），7.36（s，1H），7.05（d，J=8.1 Hz, 1H），3.33（t，J=7.3 Hz, 2H），2.94（s, 3H）,1.77～1.74（m, 2H），1.38～1.35 (m, 2H）,1.28～1.21(m, 4H）,0.86（t，J=6.6 Hz, 3H）ppm;

$^{13}$C NMR (125 MHz，CDCl3) δ 150.90, 132.34, 123.91, 114.03, 33.25, 31.70, 30.04, 28.80, 22.90, 22.00,14.37 ppm;

HRMS (ESI) m/z found : 249.1417 $(M+H)^+$; calc: 249.1419 $(M+H)^+$

## RESULTS AND DISCUSSION

### 3.1 Influences of the extractant concentration

To investigate the effect of HMBMS 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, HMBMS dissolved in kerosene with the extractant concentration varying from 1% to 8% (v/v). The percentage extraction of Pd(II) increased in the range from 37.5% to 99.1% by increasing HMBMS concentration from 1% to 5% (v/v). Further increasing HMBMS concentration from 5% to 8% (v/v), the percentage extraction of Pd(II) kept constant. 5% (v/v) HMBMS was needed for quantitative extraction of Pd(II) from a 0.1 mol $L^{-1}$ HCI aqueous solution containing 100 mg $L^{-1}$ palladium.

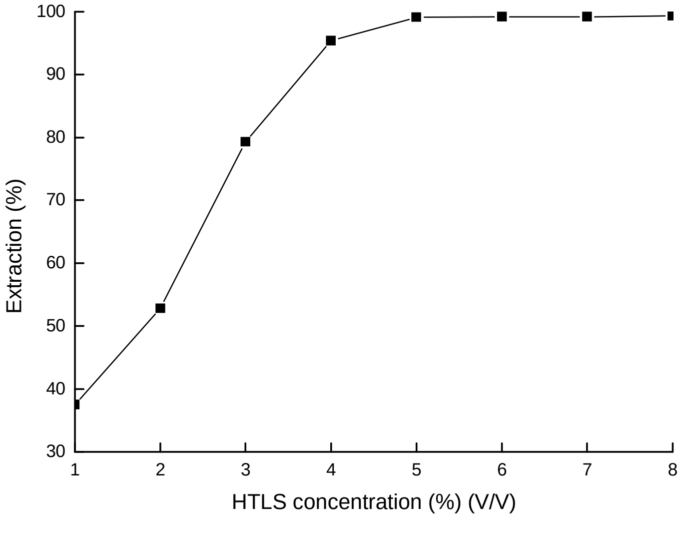

**Fig.2. Effect of extractant concentration on the extraction of Pd(II).**
*$C_{Pd(II)}$: 100 mg $L^{-1}$,$C_{HCl}$ : 0.1 mol $L^{-1}$,O/A: 1.0, contact time: 20 min*

### 3.2 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. Nearly all of the Pd(II) (＞99%) was transferred from the aqueous phase into the organic phase when HCI concentration in the range from 0.1 to 0.5mol $L^{-1}$.The percentage extraction of Pd(II) decreased in the range from 99.1% to 64.3% by increase of HCI concentration from 0.5 mol $L^{-1}$ to 4.0 mol $L^{-1}$. Therefore, 0.1 mol $L^{-1}$ HCI was adopted in all subsequent experiments.

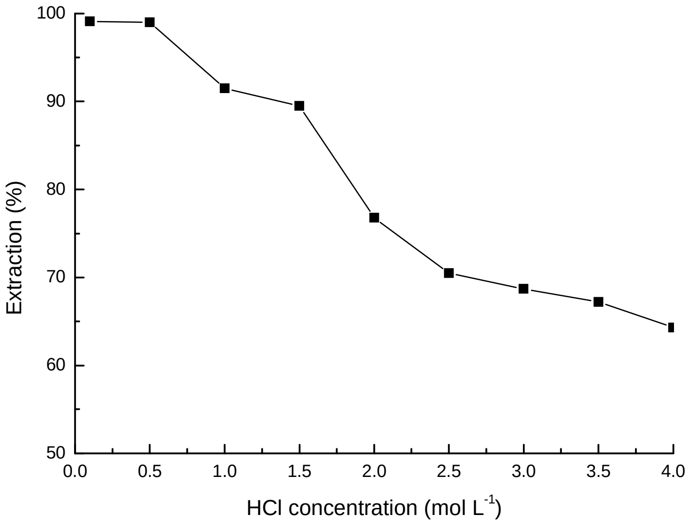

**Fig.3. Effect of HCl concentration on the extraction of Pd(II)**
*$C_{Pd(II)}$: 100 mg $L^{-1}$,$C_{HMBMS}$: 5 % (v/v), O/A: 1.0, contact time: 20 min*

3.3 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 30 min. The percentage extraction of Pd(II) increased in the range from 47.6.0% to 99.1% by in increased of contact time from 5 min to 20 min. Further increasing contact time from 20 min to 30 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 20 min.

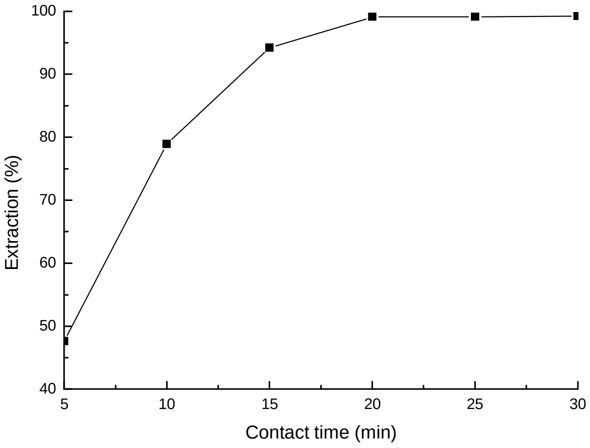

**Fig.4. Effect of contact time on the extraction of Pd(II)**
*$C_{Pd(II)}$: 100 mg $L^{-1}$, $C_{HMBMS}$: 5 % (v/v) ,O/A: 1.0, $C_{HCl}$ : 0.1 mol $L^{-1}$*

3.4 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 0.2 to 1.0, the percentage extraction of Pd(II) increased from 47.8 to 99.1%. By further increasing O/A from 1.0 to 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.

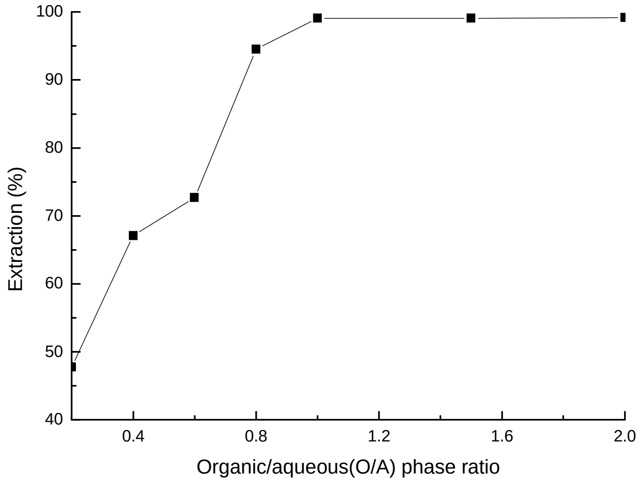

**Fig.5. Effect of O/A on the extraction of Pd(II)**

*$C_{Pd(II)}$: 100 mg $L^{-1}$, $C_{HMBMS}$: 5 % (v/v) , contact time: 20 min , $C_{HCl}$: 0.1 mol $L^{-1}$*

3.5 Determination of extraction saturation capacity of Pd(II)

The above experiments demonstrated that HMBMS had strong extraction for Pd(II) at a lower acidity. The following experiments were carried out to determine the extraction saturation capacity of Pd(II) at the following fixed parameters: Pd(II) concentration of aqueous solution, 1.000 g $L^{-1}$; O/A ,1.0; contact time of two phases, 20 min; $H^+$ concentration of aqueous phase, 0.1 mol $L^{-1}$. Eleven shares of the stock solutions were extracted in turn using the same organic phase with 30% (v/v) HMBMS. After eleven extractions, for partial organic phase lost severely, the experiment could not be carried out further. The results are shown in Table 1. According to Table 1, the Pd(II) concentration of organic phase exceeded 10 g $L^{-1}$,which suggested that the extraction saturation capacity of Pd(II) was over 10 g $L^{-1}$ under the experimental conditions.

**Table 1.The determination data of extraction saturation capacity of Pd(II)**

| Number | Percentage extraction of Pd(II) (%) | Pd(II) concentration in organic phase (g $L^{-1}$) |
|---|---|---|
| 1 | 99.3 | 0.993 |
| 2 | 99.2 | 1.985 |
| 3 | 99.0 | 2.975 |
| 4 | 98.9 | 3.964 |
| 5 | 98.7 | 4.951 |
| 6 | 98.5 | 5.936 |
| 7 | 98.2 | 6.918 |
| 8 | 97.7 | 7.895 |
| 9 | 97.4 | 8.869 |
| 10 | 97.3 | 9.842 |
| 11 | 96.8 | 10.81 |

3.6 Verification separation of Pd(II) and Pt(IV)

The as-obtained extraction parameters need to be verified if they are or not workable in practical application for the separation of Pd(II) and Pt(IV) from hydrochloric acid solution. A synthetically mixed stock solution containing Pd(II) and Pt(IV), Pd(II) concentration 992 mg $L^{-1}$ and Pt(IV) concentration 987 mg $L^{-1}$, respectively. The stock solution was prepared by dissolving each solutes in 0.1 mol $L^{-1}$ HCl solution. The mixed solution was contacted with equal volume of organic phase with 20% (v/v) HMBMS for 20 min. The results revealed that 99.1% Pd(II) but only 0.7% Pt(IV) were extracted to the organic phase. The results are shown in Table 2. According to Table 2, the separation coefficient of Pd(II) and Pt(IV) ($\beta_{Pd/Pt}$) reached $1.5\times10^4$, indicating Pd(II) and Pt(IV) were separated completely.

**Table 2. Residual concentration and percentage extractions of Pd(II) and Pt(IV)**

| Metal ion | Pd(II) | Pt(IV) |
|---|---|---|
| Mixed stock solution concentration (mg $L^{-1}$) | 992 | 987 |
| Residual concentration (mg $L^{-1}$) | 9 | 980 |
| Percentage extraction (%) | 99.1 | 0.7 |

3.7 Stripping properties of palladium

Palladium(II) stripping experiments were performed using thiourea solution as the stripping system. The stock palladium-loaded organic phase ($C_{Pd}$=100 mg $L^{-1}$) was prepared by the same extraction procedure as described above.

The following parameters were fixed: palladium(II) concentration in loaded organic phase 100 mg $L^{-1}$, organic-to-aqueous (O/A) phase ratio 1.0, and mixing time of two phases 5 minutes. The effects of thiourea concentration on palladium striping are presented in Fig.6. As seen in Fig.6, by the increasing of thiourea concentration, the stripping percentage increases markedly at first and then only slightly. When the thiourea concentration reaches 0.5 mol $L^{-1}$, the stripping percentage is leveled. Maximum stripping was 99.0 %, which suggests that thiourea is also one of the efficient stripping agents for the separation of Pd(II). The stripping was quantitative when 0.5 mol $L^{-1}$ thiourea solution was used.

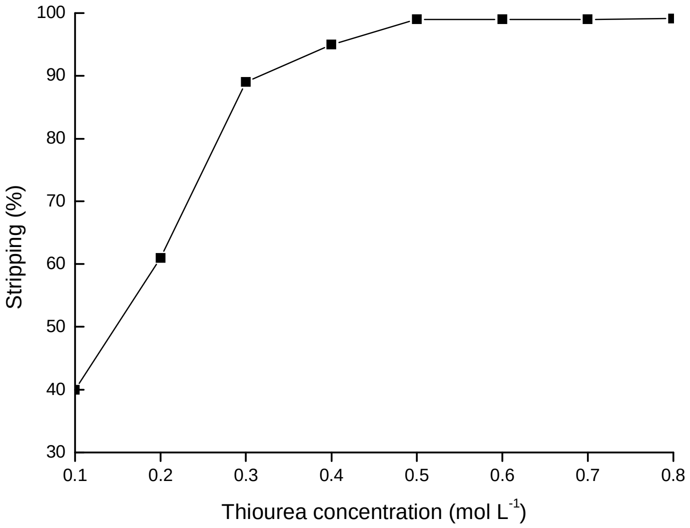

**Fig.6. Effect of stripping reagent concentration on the stripping of Pd(II)**

*$C_{Pd(II)}$: 100 mg $L^{-1}$, O/A: 1.0, contact time: 5 min*

## CONCLUSION

The solvent extraction of Pd(II) from hydrochloric acid solutions were investigated using 2-hexyl-5-methyl benziminazole sulfide (HMBMS) diluted in kerosene. Extraction parameters of Pd(II) were obtained and summarized as the following: HMBMS concentration, 5% (v/v); organic/aqueous (O/A) phase ratio ,1.0; hydrochloric acid concentration of aqueous solution, 0.1 mol $L^{-1}$; contact time of two phases 20 min. The saturation extraction capacity of Pd(II) was determined with 30% (v/v) HMBMS and its experimental value exceeded 10 g $L^{-1}$. Pd(II) and Pt(IV) could be separated completely and the separation coefficient of Pd(II) and Pt(IV) ($\beta_{Pd/Pt}$) reached $1.5\times10^4$ when HMBMS and HC1 concentration were fixed at 20% (V/V) and 0.1 mol $L^{-1}$, respectively. Pd(II) loaded in organic phase could be stripped efficiently using an aqueous solution containing thiourea. The percentage stripping of Pd(II) was 99.0 % using 0.5 mol $L^{-1}$thiourea solution.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (51264038) and Science and Technology Support Program of China (2008BAB32B10)

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