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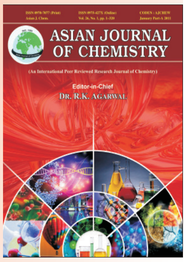

Solvent Extraction of Pd(CN)$_4^{2-}$ from Alkaline Cyanide Solution with Dodecyl Trimethylammonium Bromide

LEI CHEN, ZHANGJIE HUANG*, JING CHEN and MINHONG LIU

Department of Chemistry, Yunnan University, Kunming 650091, P.R. China

*Corresponding author: Fax: +86 871 5032180; Tel: +86 871 6688875; E-mail: zhjhuang@ynu.edu.cn

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The solvent extraction of Pd(CN)$_4^{2-}$ from alkaline cyanide solution by using dodecyltrimethylammonium bromide diluted in benzene was investigated. It has been indicated that Pd(CN)$_4^{2-}$ extraction percentage increases by increasing dodecyltrimethylammonium bromide concentration. Extraction parameters of Pd(CN)$_4^{2-}$, including appropriate diluting agent, dodecyltrimethylammonium bromide concentration, contact time of aqueous and organic phases, pH of the aqueous solution and organic/aqueous phase ratio, were studied. Octanol has an obvious synergistic effect on Pd(CN)$_4^{2-}$ extraction with dodecyltrimethylammonium bromide. It was indicated that at dodecyltrimethyl ammonium bromide concentration 0.01 mol L^{-1}, contact time of 10 min, octanol concentration 40 % (v/v), organic/aqueous phase ratio 1, the optimal pH of the aqueous phase11.5, almost all of the Pd(CN)$_4^{2-}$ (> 99 %) was transferred from the aqueous phase into the organic phase. Ammonium thiocyanate solution could be used as stripping agent. Most of the Pd(CN)$_4^{2-}$ in the organic phase can be stripped with aqueous solutions of ammonium thiocyanate.

Keywords: Palladium, Dodecyltrimethylammonium bromide, Alkaline cyanide solution.

INTRODUCTION

Recovery of palladium from various resources is restricted to leaching in cyanide or hydrochloric acid media[1]. From the leaching solutions, various procedures have been developed for the separation and obtention of this precious metal. Solvent extraction is a thrilling option for separation and recovery of palladium from primary and secondary leaching solutions. Various solvent systems have been used worldwide for palladium recovery[2-6]. Usually, these extraction systems can extract palladium from hydrochloric acid solution. Most of the reported palladium extractants were only effective in hydrochloric acid solution[7-13].

In recent years, some new extraction systems to recover Au(I) directly from the alkaline cyanide leaching solution have been introduced[14-18]. Quaternary ammonium salts have also been used to partition Au(CN)$_2^-$ due to their high loading capacity and their broad application pH range. Extraction of KAu(CN)$_2$ from cyanide solutions was done by using quaternary ammonium tetra-decyldimethyl-benzyl-ammonium chloride (TDMBAC) with the addition of tri-*n*-butylphosphate (TBP). The results indicated that the organic phase has a high extraction capacity. Almost all of the Au(CN)$_2^-$ (> 95 %) was transferred from the aqueous phase into the organic phase, from which elemental gold could potentially be recovered[19]. The extraction of KAu(CN)$_2$ from alkaline cyanide solutions was done using quaternary ammonium cetylpyridinium bromide as an extractant with the addition of tributylphosphate as a modifier. The extraction was found to be nearly quantitative and almost all of the Au(I) (> 98 %) was extracted into the organic phase[20]. The extraction of KAu(CN)$_2$ from alkaline cyanide solutions was done using quaternary ammonium cetyltrimethylammonium bromide as an extractant, almost all of the gold (> 99 %) in the aqueous phase could be selectively extracted and transferred into the organic phase. The Au(CN)$_2^-$ in the loaded organic phase could be easily replaced by ClO$_4^-$ due to the stronger association of ClO$_4^-$ anion with quaternary ammonium salt cation than that of Au(CN)$_2^-$. Most of the Au(CN)$_2^-$ in the organic phase can be stripped with NaClO$_4$ aqueous solutions[21].

Up to now, no report has been found to extract palladium from alkaline cyanide solution. In this work, the solvent extraction of Pd(CN)$_4^{2-}$ from alkaline cyanide solution by dodecyltrimethylammonium bromide has been investigated. Various parameters, such as the concentrations of dodecyltrimethylammonium bromide, influences of aqueous solution pH on Pd(CN)$_4^{2-}$ extraction, contact time of aqueous and organic phases and influences of the diluents, were studied. Octanol was added in the organic phase to improve palladium extraction efficiency. The stripping of Pd(CN)$_4^{2-}$ with ammonium thiocyanate was also investigated.

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 determined with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Dodecyltrimethylammonium bromide (DTAB), ammonium thiocyanate (NH_4SCN), octanol and benzene (analytical grade) were purchased from Beijing Chemical Reagent Co. $Pd(CN)_4^{2-}$ was supplied by Yunnan Gold Group Co. Other chemicals were all commercially available reagents of analytical grade.

Octanol was chosen as a synergic agent. Dodecyl-trimethylammonium bromide solutions were made by dissolution in calculated volumes of octanol (40 % ,v/v) and benzene. Stock solution of palladium was prepared by diluting $Pd(CN)_4^{2-}$ in ultra-pure water. The pH of the aqueous solution was adjusted with 0.1 mol L^{-1} KOH.

General extraction procedure: Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 10 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 diluents: In order to choose an appropriate diluting agents for the $Pd(CN)_4^{2-}$ extraction system, various diluting agents were studied, such as kerosene, methylbenzene, dimethylbenzene, chloroform and benzene. Their experiments were performed as the following parameters were fixed: Initial $Pd(CN)_4^{2-}$ concentration in the aqueous phase 0.1 g L^{-1}, organic-to-aqueous (O/A) phase ratio 1, initial pH in aqueous solution 11.5, DTAB 0.01 mol L^{-1}, dodecyltrimethylammonium bromide solutions were made by dissolution in calculated volumes of octanol (40 %, v/v) and benzene and mixing time 10 min. The results are shown that the solubility for dodecyltrimethyl-ammonium bromide decreased in the following sequence: benzene > dimethylbenzene > methylbenzene > kerosene. Finally, benzene was selected as the appropriate diluting agents.

Influences of extractant and octanol concentration: To investigate the effect of octanol and dodecyltrimethylammonium bromide concentration on the extraction performances of $Pd(CN)_4^{2-}$, the parameters of experiments were fixed: Initial $Pd(CN)_4^{2-}$ concentration in the aqueous phase 0.1 g L^{-1}, organic-to-aqueous phase ratio 1, initial pH in aqueous solution 11.5 and mixing time 10 min. The percentage extraction of $Pd(CN)_4^{2-}$ increases by increasing octanol concentration in the organic phase from 0 to 40 % (v/v). When its content in the organic phase is 40 % (v/v), the percentage extraction of $Pd(CN)_4^{2-}$ remains essentially unchanged. In addition, pure octanol cannot extract $Pd(CN)_4^{2-}$ by itself even with the addition of surfactant, but it can positively improve $Pd(CN)_4^{2-}$ extraction with dodecyltrimethylammonium bromide. Furthermore, it has been observed that the separation of organic and aqueous phases was very difficult and more than 24 h were needed for the complete separation of two phases. By comparison, when 40 % (v/v) octanol is added in the organic phase, the $Pd(CN)_4^{2-}$ extraction percentage increases rapidly.

Fig. 1 showed that the dodecyltrimethylammonium bromide dissolved in benzene with the extractant concentration varying from 0.0003 to 0.010 mol L^{-1}. The percentage extraction of Pd(II) increased in the range from 3.2 to 99.2 % by increasing dodecyltrimethyl-ammonium bromide concentration from 0.0003 to 0.010 mol L^{-1}. Further increasing dodecyltrimethylammonium bromide concentration from 0.01 to 0.014 mol L^{-1}, the percentage extraction of Pd(II) kept constant. 0.010 mol L^{-1} dodecyltri-methylammonium bromide was needed for quantitative extraction of Pd(II) from a alkaline cyanide solution solution containing 0.1 g L^{-1} palladium.

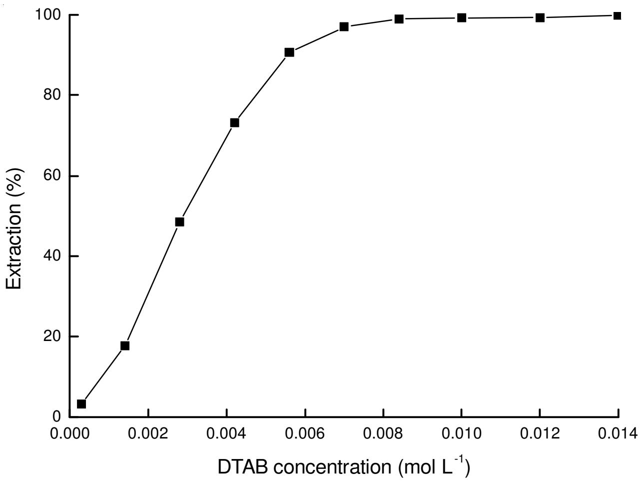

Fig. 1. Effect of extractant concentration on the extraction of $Pd(CN)_4^{2-}$; $C_{Pd(II)}$: 0.1g L^{-1}, O/A:1, contact time: 10 min, pH:11.5

Influences of contact time: To investigate the effect of contact time of organic and aqueous phases on $Pd(CN)_4^{2-}$ extraction, the parameters of experiments were fixed: Initial Pd(II) concentration in the aqueous phase 0.1 g L^{-1}, organic-to-aqueous phase ratio 1, initial pH in aqueous solution 11.5, octanol was chosen as a synergic reagent and the organic phase used 40 % (v/v) octanol in benzene and the organic phase containing 0.01 mol L^{-1} dodecyltrimethylammonium bromide.

To extract $Pd(CN)_4^{2-}$ 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. 2. 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 1 to 20 min. The percentage extraction of Pd(II) increased in the range from 97 to 99 % by increased of contact time from 1 to 10 min. Further increasing contact time from 10 to 20 min, the percentage extraction of

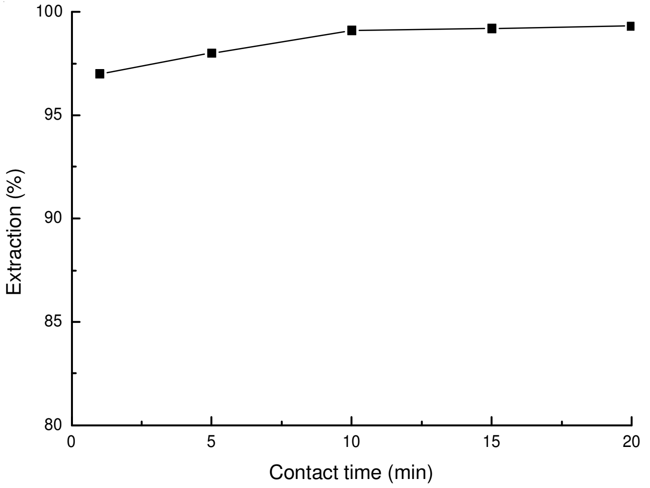

Fig. 2. Effect of contact time on extraction of $Pd(CN)_4^{2-}$; $C_{Pd(II)}$: 0.1g L^{-1}, O/A:1, C_{DTAB} 0.01 mol L^{-1}, pH:11.5

$Pd(CN)_4^{2-}$ kept constant. Extraction equilibrium can be established within 10 minutes. Therefore, the minimum period of equilibration required for the quantitative extraction of palladium was found to be about 10 min.

Influences of organic/aqueous phase ratio: To obtain optimal organic/aqueous for extraction of Pd(II), the parameters of experiments were fixed: initial Pd(II) concentration in the aqueous phase 0.1 g L^{-1}, contact time: 10 min, initial pH in aqueous solution 11.5, Octanol was chosen as a synergic reagent and the organic phase used 40 % (v/v) octanol in benzene and the organic phase containing 0.01 mol L^{-1} DTAB. The results are shown in Fig. 3. Fig. 3 showed that by increasing organic/aqueous phases from 0.5 to 1, the percentage extraction of Pd(II) increased from 98 to 99 %. By further increasing organic/aqueous phases from 1 to 2, the percentage extraction of Pd(II) kept constant. Therefore, Pd(II) can be extracted efficiently by controlling organic/aqueous phase ratio 1.

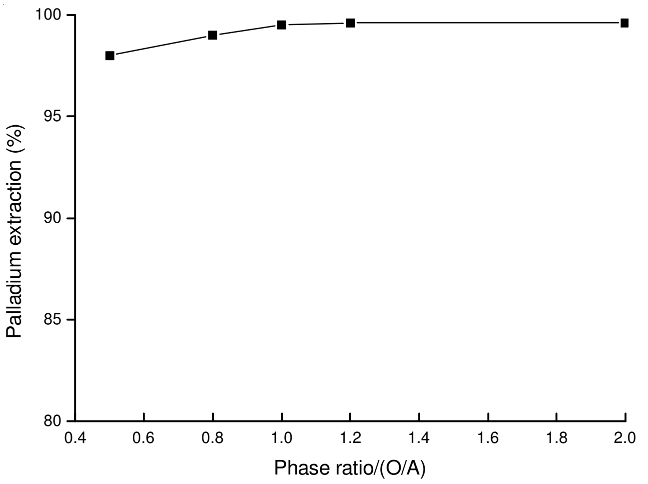

Fig. 3. Effect of organic/aqueous phases on the extraction of Pd(II); $C_{Pd(II)}$: 0.1 g L^{-1}, contact time: 10 min, dodecyltrimethylammonium bromide 0.01 mol L^{-1}, pH:11.5

Influences of aqueous solution pH on palladium extraction: Experiments were conducted to investigate the effect of aqueous solution pH on palladium extraction for initial Pd(II) concentration 0.1 g L^{-1}, contact time: 10 min, octanol was chosen as a synergic reagent and the organic phase used contain 40 % (v/v) octanol in benzene and the organic phase containing 0.01 mol L^{-1} dodecyltrimethylammonium bromide. The results are shown in Fig. 4. Fig. 4 suggested that by increasing pH from 7 to 11.5, the percentage extraction of Pd(II) increased from 98 to 99 %. If the pH of aqueous phase further increases, the percentage extraction decreases dramatically. The initial pH of the aqueous phase was selected in this study to be 11.5.

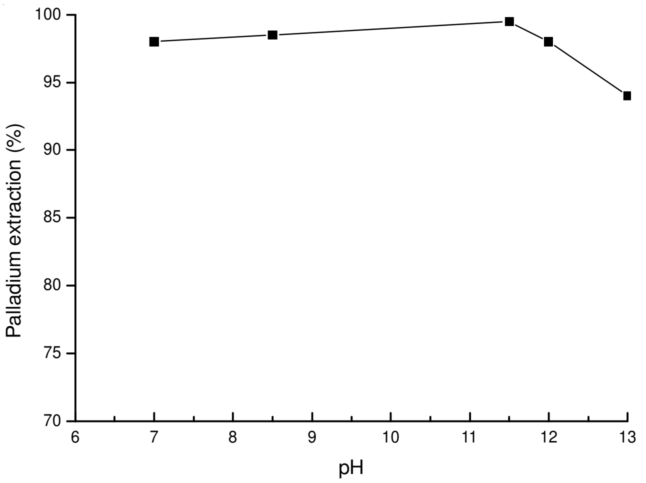

Fig. 4. Effect of pH on the extraction of Pd(II); $C_{Pd(II)}$: 0.1g L^{-1}, contact time: 10 min, dodecyltrimethylammonium bromide 0.01 mol L^{-1}, O/A:1

Influences of ammonium thiocyanate concentration on stripping of Pd(II): Fig. 5 shows the effect of ammonium thiocyanate concentration in the aqueous solution on the stripping of Pd(II). The following parameters were fixed: palladium concentration in loaded organic phase, 0.1 g L^{-1}; and mixing time of two phases, 10 min. The effects of ammonium thiocyanate concentration on palladium striping are presented in Fig. 5. As Fig. 5, for the same A/O phase ratio (A/O = 1), by the increasing of NH_4SCN concentration, the stripping percentage increases markedly at first and then only slightly. When the NH_4SCN concentration reaches 0.1 mol/L, the stripping percentage is leveled. Maximum stripping was 99 %, which suggests that NH_4SCN is also one of the efficient stripping agents for the separation of Pd(II).

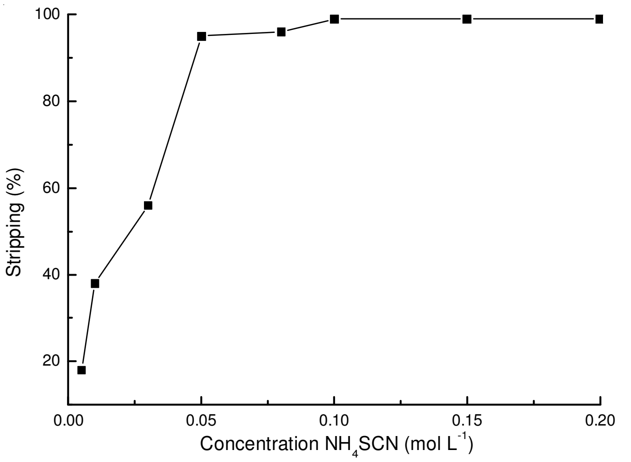

Fig. 5. Effect of stripping reagent concentration on the stripping of Pd(II); $C_{Pd(II)}$: 0.1g L^{-1}, contact time: 10 min, O/A:1

For continuous operation, the organic phase should be reproduced after a stripping process. To investigate the reuse of DTAB-benzene-octanol, an organic phase that had been stripped with a 0.1 mol L^{-1} NH_4SCN aqueous solution was used to extract another alkaline cyanide solution with 0.1 g L^{-1} palladium(II). The results show that most of palladium(II) could be extracted into the recycled organic phase. It is concluded that the reuse of the organic phase for industrial application is possible.

Conclusion

The solvent extraction of $Pd(CN)_4^{2-}$ from alkaline cyanide solution with dodecyltrimethylammonium bromide and octanol was investigated. The percentage extraction of palladium increases with increasing dodecyltrimethylammonium bromide concentration in organic phase. Octanol cannot extract palladium by itself but can positively assist dodecyltrimethylammonium bromide in extracting palladium. The optimum extraction parameters of $Pd(CN)_4^{2-}$ were obtained and summarized as:

Dodecyltrimethylammonium bromide concentration, 0.01 mol L^{-1}; octanol concentration, 40 % (v/v), organic/aqueous phase ratio, 1. The optimal pH of the aqueous phase,11.5; contact time of two phases, 10 min. Octanol has an obvious synergistic effect on $Pd(CN)_4^{2-}$ extraction with dodecyltrimethylammonium bromide. The percentage extraction of $Pd(CN)_4^{2-}$ reaches 99 % using 0.01 mol L^{-1} dodecyltrimethylammonium bromide and 40 % (v/v) octanol in the organic phase. The palladium-laden organic phase can be stripped efficiently using an ammonium thiocyanate (NH_4SCN) solution. Almost all of the $Pd(CN)_4^{2-}$ (> 99 %) was stripped from the organic phase into the aqueous phase. The proposed method could be applied potentially for the direct extraction of $Pd(CN)_4^{2-}$ from alkaline cyanide solution.

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