Liquid-Liquid Extraction of Palladium(II) from Hydrobromic Acid Media by Hexadecylpyridinium Bromide

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A simple and rapid liquid-liquid extraction of palladium has been studied involving ion-pairing of bromocomplexes of palladium(II) with hexadecylpyridinium bromide (HDPB) dissolved in chloroform. The stoichiometry and distribution of \((\text{HDP})_2\text{PdBr}_4\) between the aqueous and organic phase was investigated by spectrophotometric mole ratio method. The extraction efficiency of palladium(II) by HDPB was studied as a function of several variables: acid, salt, surfactant concentration and equilibrium time. The results showed that \(\text{PdBr}_4^{2-}\) extraction could be explained by assuming the formation of \((\text{HDP})_2\text{PdBr}_4\) complexes in the aqueous solution and transfer to organic phase. The extraction was fast and the shaking time was only a few min. The average recovery of palladium(II) from an aqueous solution containing 10 \(\mu\)g/ml of analyte was 99% with an RSD% of 0.95. The percentage recovery of 0.2 \(\mu\)g/ml palladium(II) was 96%.

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Introduction

Liquid-liquid extraction is one of the most efficient methods used to separate, concentrate and purify metal ions and organic compounds. Extraction has become a technique used to recover and separate noble metals, including palladium(II). Several reagents have been proposed, including hydroxoyximes, alkyl derivatives of 8-hydroxyquinoline and hydrophobic amines. Some of them are used in industry. However the extraction occurs very slowly; this is caused by the nature of the hydrophobic extractant and the symmetrical palladium chlorocomplex. The drawback can be overcome by the addition of thiocyanate ions, which disturb the symmetry of palladium(II) chlorocomplex, or the use of a phase transfer catalyst.

Surfactants have been employed with great success in photometric, fluorometric and phosphorimetric determinations because they tend to enhance the solubility and detection sensitivity of analytes. Surfactants also play an important role in separation science. For example, aqueous micellar solutions are used as the mobile phase in micellar liquid chromatography as well as in the electro lytic mobile phase of micellar electrokinetic capillary chromatography. A well-known phase separation method, namely, the cloud point extraction, has been successfully used in the extraction preconcentration, separation and purification of various species, ranging from metal chelates, organic compounds of environmental concern as well as a number of proteins and related biochcmicals. Many investigators have studied the separation of metals by liquid surfactant membranes. In recent years, we have studied the influence of different conditions on the micellization of hexadecylpyridinium bromide (HDPB) using a membrane electrode selective to the surfactant and conductometric method.

In the present study, we found the stoichiometry and extraction mechanism of palladium(II) with HDPB in chloroform by a spectrophotometric method and separation of palladium from hydrobromic acid media.

Experimental

Reagents and chemicals

Hexadecylpyridinium bromide (HDPB) and other reagents were purchased from Merck Chemical Company and were used as received. Reagent grade chloroform (Fluka) was used as the organic phase. A stock solution of 0.01 M palladium(II) was prepared by dissolving \(\text{PdCl}_2\) (Merck) in 0.1 M hydrobromic acid. The solution was standardized gravimetrically with dimethylglyoxime.

Apparatus

A Shimadzu UV-VIS 2100 spectrophotometer and a Shimadzu AA-670 atomic absorption spectrophotometer (acetylene-air flame) were used to determine metal ion concentrations in aqueous phases. The pH measurements were made with a Metrohm 692 pH/ion meter using a combined glass electrode. X-Ray studies were made with a Philips WDXRF Spectrometer Model PW2404.

Extraction procedure

An aqueous solution (5 ml) containing 50 \(\mu\)g of palladium(II) at 0.1 M hydrobromic acid and 0.15 M NaBr was transferred to a glass funnel. Chloroform (5 ml) containing a 0.003 M

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Surfactant was added to the funnel and the contents were shaken for 5 min. The two phases were allowed to settle and separate. The absorbance of aqueous and organic phase was measured at 331 and 347 nm, respectively against reagent blank. The amount of palladium(II) present was determined from the calibration curve and calculated extraction efficiency. Palladium(II) from organic phase was stripped with 1.2 M hydrochloric acid and 0.01 M thiourea and determined with the atomic absorption spectrophotometer. The limit of detection, which was calculated as the concentration that gives a reading equal to three-times the standard deviation of a series of the procedural blank signals (n = 4), was found to be 0.72 ppm.

Results and Discussion

Bromocomplexes of palladium(II)

The optimum concentration of bromide ion for complete formation of PdBr$_4^{2-}$ species in 10 µg/ml palladium(II) solution was studied with various concentrations of bromide ion from 0 to 0.3 M at 331 nm. The resulting data show that maximum absorbance is attained when the concentrations of bromide ions are approximately 0.15 M or higher (Fig. 1). The absorption spectrum of bromo complex in 0.15 M bromide ion is shown in Fig. 2.

Stoichiometry and ion-association complexes

Figure 3 shows the absorbance of 10 µg/ml of palladium(II) in the presence of increasing amounts of HDPB in solutions. The absorbance vs. HDPB/Pd mole ratio plots obtained at 320 and 432 nm show two distinct breaks at the mole ratios of about 1 and 2, emphasizing the successive formation of 1:1 and 2:1 (HDPB-to-palladium) species in solution (Fig. 3).

Optimum extraction conditions

The optimum extraction conditions were established by the studies of the effects of pH, surfactant concentration, ionic strength and shaking time.

The effect of surfactant concentration on the extraction was investigated in the presence of different ionic strengths. The results are shown in Fig. 4.

Quantitative extraction of palladium(II) was attained over 1.0 \times 10^{-3} - 5.0 \times 10^{-3} M concentration range of HDPB (Fig. 5).

The extraction efficiency of palladium(II) was carried out over the pH range 1 - 10. The results (Fig. 6) show that PdBr$_4^{2-}$ can be quantitatively extracted at pH < 5, while at higher pH values the extent of extraction decreases significantly, most probably due to some hydroxide formation in solution.

After extraction of palladium(II) at pH 2 and presence of 0.15 M bromide ion with 0.003 M of HDPB as the extractant, it was stripped with various concentrations of thiourea as the stripping
agent. With 1.2 M hydrochloric acid and 0.01 M thiourea stripping was quantitative (Table 1).

The effect of shaking time on the extraction efficiency is shown in Fig. 7. This result shows that the application of optimum conditions ensures the quantitative extraction of palladium(II) after shaking for 2 min.

**Nature of extracted species**

The probable mechanism of extraction can be summarized as follows:

\[ \text{Pd}^{2+} + 4\text{Br}^{-} \rightleftharpoons \text{PdBr}_4^{2-} \]

bromocomplex formation in aqueous phase

(1)

\[ \text{HDPB}_{\text{org}} \rightleftharpoons \text{HDPB}_{\text{aq}} \]

distribution of surfactant

(2)

\[ \text{HDPB}_{\text{aq}} \rightleftharpoons \text{HDP}^+ + \text{Br}^- \]

dissociation of surfactant in aqueous phase

(3)

\[ \text{PdBr}_4^{2-} + 2\text{HDP}^+ \rightleftharpoons (\text{HDP})_2\text{PdBr}_4 \]

ion-association complex

(4)

\[ [(\text{HDP})_2\text{PdBr}_4]_{\text{aq}} \rightleftharpoons [(\text{HDP})_2\text{PdBr}_4]_{\text{org}} \]

transformation to organic phase

(5)

The extraction equilibrium and extraction constant \( K_{ex} \) can be written as follows:

\[ \text{PdBr}_4^{2-} + 2\text{HDPB}_{\text{org}} \rightleftharpoons (\text{HDP})_2\text{PdBr}_4 + 2\text{Br}^-_{\text{aq}} \]

(6)

\[ K_{ex} = \frac{[(\text{HDP})_2\text{PdBr}_4]_{\text{org}}[(\text{Br}^-)_{2\text{aq}}]}{[\text{PbBr}_4^{2-}]_{\text{aq}}[\text{HDPB}]_{\text{org}}^2} \]

(7)

\[ D \text{ is defined as:} \]

\[ D = \frac{[(\text{HDP})_2\text{PdBr}_4]_{\text{org}}}{[\text{PbBr}_4^{2-}]_{\text{aq}}} \]

(8)

\[ K_{ex} = \frac{D[Br^-]_{2\text{aq}}}{[\text{HDPB}]_{\text{org}}} \]

(9)

\[ \log D = \log K_{ex} + 2\log[\text{HDPB}]_{\text{org}} - 2\log[\text{Br}^-]_{\text{aq}} \]

(10)

The logarithmic values of the distribution ratio of palladium(II), \( D \), are plotted against \( \log[\text{Br}^-] \) in the aqueous phase. The slope of the straight portion of the plots is found to be 1.98 (Fig. 8), indicating that two bromide ions are released throughout the extraction reaction (Eq. (6)). Therefore the probable composition of the extracted species according to mole ratio method and resulting slope of Eq. (10), is 2:1, i.e. \((\text{HDP})_2\text{PdBr}_4\). According to Eq. (10) at constant concentration of HDPB in organic phase, the extraction efficiency decreases with increase in bromide ion concentration in the aqueous phase. A slope of 1.98 obtained for Fig. 8 indicates that the results are in support of Eq. (10).

**Effect of diverse ions**

Various cations were used in order to assess the tolerance of these ions on the extraction of palladium(II). The tolerance limit for the variation was ±2% in recovery of palladium(II).

Palladium(II) was extracted in the presence of different diverse ions (Table 2). The tolerance limit was set as the amount of foreign ion causing ±2% error in recovery of palladium(II). The results showed that in the extraction and determination of 10 µg/ml of palladium(II), these ions did not...
The results of this achieved quantitative analysis by comparing X-ray intensities (silica-alumina) and the standards are close in composition, we the fact that the composition of sample is known (silica-alumia) and the standards are close in composition, we achieved quantitative analysis by comparing X-ray intensities from samples with those from standards. The results of this method were found to be in satisfactory agreement with that determined by XRF (Table 3).

### Conclusions

A cationic surfactant, hexadecylpyridinium bromide (HDPB), was successfully applied to the extraction of palladium. HDPB having C_16 length of the alkyl group is strongly hydrophobic and the pyridinium head group is suitable to be adsorbed at the chloroform/water interface and can act as an ion exchange reagent for exchanging the bromide ions with bromocomplex of palladium. One of the advantages of this reagent is that, the complexation reaction with metal occurred very effectively at the interface and thus the extraction rate was fast. As a consequence of the second advantage, the proposed method is simple, rapid, selective, reproducible and can be compared with favorably the existing methods of separation.

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### References

USSR Academy of Sciences, Moscow, 83.