POLAROGRAPHIC DETERMINATION OF PALLADIUM ION

V. Dumitrescu*, Dana Popa and A. Tudorache

abstract: There was studied the polarographic behavior of palladium ion in presence of the reagent α - nitroso - β - naphtol and the solvent hexamethylphosphotriamide (HMPA). The method can be used for quantitative determinations of palladium into the domain $(0.5 \div 2.5) \cdot 10^{-4}$M. Polarograms were well defined and reproductible.

key words: polarographic, determination, palladium

Introduction

Polarographic determination of many species can be achieved using aqueous or non-aqueous mediums. A large variety of inorganic and organic substances that are not soluble in water requires a proper solvent or a mixture of solvents so that the polarographic waves should be well defined for a quantitative determination. In this study is presented a method of polarographic determination of palladium in presence of α - nitroso - β - naphtol as reagent and HMPA solvent.

HMPA is a colorless liquid miscible which water in any ratio and with other polar and non-polar organic solvents. HMPA has been used in polarographic determination of Pd^{+2} complexes [1,2].

In the specialty literature a series of electrometric determination of Pd^{+2} is mentioned [3÷15].

In this paper the solvents influence on polarographic waves and the optimal conditions for quantitative determination of palladium were established.

Experimental

Apparatus and reagents

Polarographic determinations were accomplished with the aid of a polarograph LP72 and a recorder TZ213S. The electrochemical cell was composed of dropping mercury electrode as working electrode and a electrode with large surface of mercury as (simultaneously)

* Department of Analytical Chemistry, University of Bucharest, 90 road Panduri, Bucharest, ROMANIA

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counter electrode and reference electrode. The glass capillary had a diameter of 0,07 mm and the dropping rate was 2 drops/second.

For the determinations the following (basic) solutions were used:

- $PdCl_2$ solution 10^{-3} M in 1% HCl ; $PdCl_2$ (solid substance) was provided by Fluka;
- $(CH_3)_4NCl$ (tetramethylamonium chloride) 1M; $(CH_3)_4NCl$ (solid substance) was used as support electrolyte and was provided by Merck;
- gelatine solution 0,1%, used as a suppresor for polarographic maxims;
- α - nitroso - β - naphtol solution 10^{-3} M in 50% ethanol; α - nitroso - β - naphtol (solid substance) provided by Merck;
- HMPA solution 99%; HMPA (solid substance) provided by Merck;

All reagent used in our studies were of analytical purity. The solutions were obtained in bidistilled water. Sample volume was 5 mL.

Results and Discussion

The polarographic study of palladium ion in presence of HMPA was made using the following solutions: $(CH_3)_4NCl$ $2 \cdot 10^{-1}$ M; gelatine 0,02%; HMPA 20%; Pd^{2+} $2{,}5 \cdot 10^{-4}$M; α - nitroso - β - naphtol 10^{-3}M. In Fig. 1 the polarogram obtained is shown. The polarogram obtained was well defined and reproducible. It shows two reduction steps. We discussed and analyzed during this study only the second polarographic wave, for which $E_{1/2}$= –1,465 V.

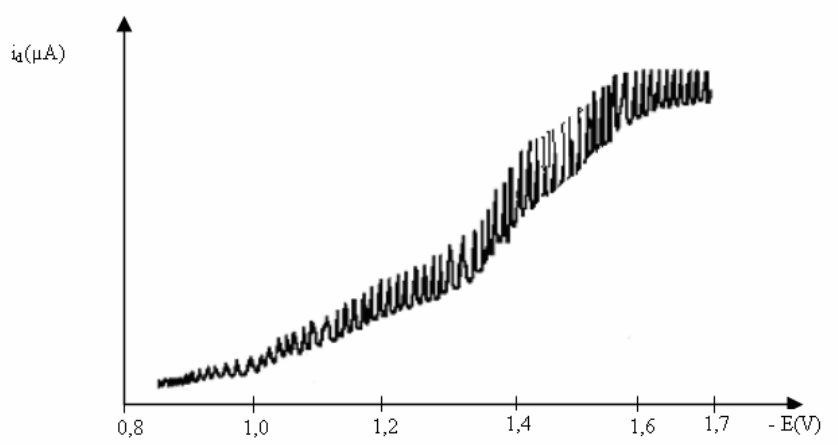

Fig. 1 *Polarogram for a solution containing the complex between Pd^{2+} and α - nitroso - β - naphtol in presence of HMPA*

In these conditions (Pd^{2+}+HMPA+ α - nitroso - β - naphtol) the influences of various components of the solution were studied.

a) Influence of suppresser

The presence of maxims on polarograms has a drawback of incorrect evaluation of parameters of polarographic wave. Removing of these maxims could be fulfilled by adding to the solution to be polarographically determined an active superficial substance in a low concentration.

Gelatine in different concentrations was used as a suppresser for polarographic maxims maintaining the concentrations of other substances constant.

The polarographic wave becomes less defined and its height decreases with the increase of gelatine concentration. It was established that 1 mL gelatine/5 mL sample was enough for obtaining well defined and reproductible polarograms.

b) Influence of reagent concentration

Concentrations of $(CH_3)_4NCl$ 10^{-1} M; gelatine 0,02%; HMPA 20%; Pd^{2+} $2{,}5\cdot10^{-4}$ M were kept at a constant value. It was observed that by adding α - nitroso - β - naphtol with a higher concentration than 10^{-3} M the half-wave potential is constant. At smaller concentrations the polarographic wave is less defined and $E_{1/2}$ takes more positive values. At higher reagent concentrations the height of the polarographic waves decreases (we consider only the second polarographic wave).

c) Influence of support electrolyte

As a support electrolyte in our polarographic determinations a solution of tetramethylamonium chloride 10^{-1} M was used. At this concentration the polarographic waves are well defined and reproductible. Support electrolyte is in excess than the concentration of palladium.

d) Influence of the height of Hg column

This study was accomplished using the following solutions: Pd^{2+} $2\cdot10^{-4}$ M ; $(CH_3)_4NCl$ 10^{-1} M; gelatine 0,02%; HMPA 20%; α - nitroso - β - naphtol 10^{-3} M, at different mercury column heights within 300-600 mm. It was noticed that the height of the polarographic waves increased with the increase of the mercury column height.

In Fig. 2 we show the dependence between log i_d and log $H^{1/2}$, where i_d is the limiting current intensity and H is the mercury column height (for the second polarographic wave).

We reached the conclusion that the dependence log $i_d = f(\log H^{1/2})$ is linear which means that current intensity is a diffusion-controlled process.

In Fig. 3 is presented the logarithmic analysis of the second polarographic wave for a more accurate determination of half-wave potential.

From this representation we obtained $E_{1/2}$= - 1,465 V.

We accomplished the quantitative determination of Pd^{2+} in presence of α - nitroso - β - naphtol and HMPA. We established the optimal conditions for polarographic determination of Pd^{2+} : $(CH_3)_4NCl$ 10^{-1} M; gelatine 0,02%; HMPA 20%; α - nitroso - β - naphtol 10^{-3} M. Palladium concentration was taken within the domain $0{,}5\cdot10^{-4}$ M-$2{,}5\cdot10^{-4}$ M.

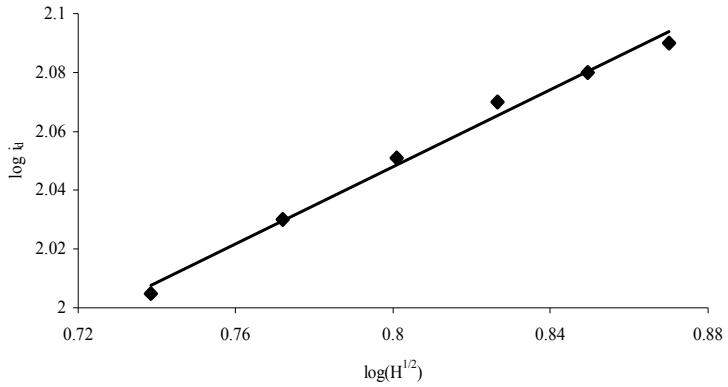

Fig. 2 *Dependence* $\log i_d = f(\log H^{1/2})$

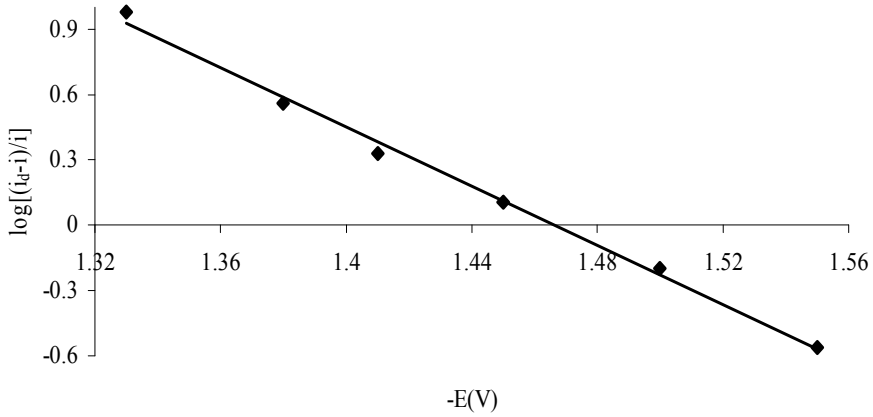

Fig. 3 *Diagram of logarithmic of the second polarographic wave*

In Fig. 4 the calibration curve for quantitative determination of palladium ion is given, taking into account the second polarographic wave.

It was ascertained that Pd^{2+} could be determined within the domain $0{,}5 \cdot 10^{-4}$ M-$2{,}5 \cdot 10^{-4}$ M.

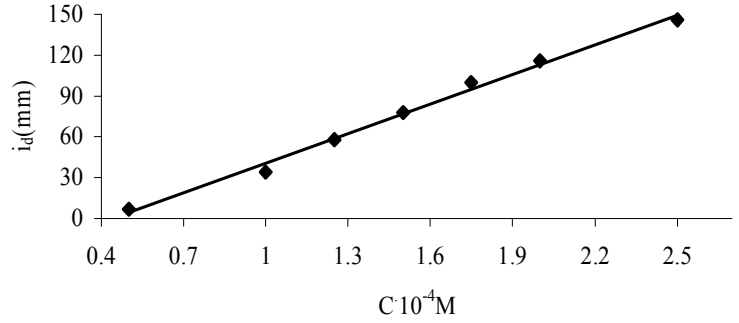

Fig. 4 *Calibration curve for palladium polarographic determination in presence of* α *- nitroso -* β *- naphtol and HMPA*

Conclusions

In this paper the condition of polarographic determination of palladium ion in presence of α - nitroso - β - naphtol and HMPA solvent were established. This solvent influenced the diffusion current intensity and the value of the half-wave potential ($E_{1/2}$). This effect is due to the solvation modification of the ions and to different diffusion coefficients.

Polarograms were well defined and reproducible. The results lead us to the conclusion that this method can be applied to the quantitative determination of palladium ion within the concentration domain $0{,}5\cdot10^{-4}$ M – $2{,}5\cdot10^{-4}$ M in presence of α - nitroso - β - naphtol and HMPA solvent. The whole study was made for the second polarographic wave.

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