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ISSN: 1844-0401

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POLAROGRAPHIC DETERMINATION OF PALLADIUM ION IN PRESENCE OF α,α'- DIPYRIDYL AND HEXAMETHYLPHOSPHOTRIAMIDE

V. Dumitrescu* **and Oana-Lucia Terteleac**

abstract The polarographic behavior of palladium ion in the presence of α, α'- dipyridyl reagent and HMPA solvent was studied. The method can be used for quantitative determination of palladium into the domain $2 \cdot 10^{-5} – 10^{-4}$ M. Polarograms were well defined and reproducible.

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, α'- dipyridyl and hexamethyl-phosphotriamide (HMPA) solvent.

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

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

In this paper a polarographic method for determination of palladium is described, in presence of α, α'- dipyridyl reagent and HMPA.

Experimental

Polarographic determinations were accomplished with the aid of a polarograph LP7e coupled with a recorder TZ213S. The electrochemical cell was composed of dropping mercury electrode as working electrode and an electrode with large surface of mercury as (simultaneously) counter electrode and reference electrode. The glass capillary had a diameter of 0,07 mm and the dropping rate was 2 drops/second.

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For the determinations the following (basics) 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 suppressor for polarographic maxims;

– α,α'- dipyridyl solution 10^{-2} M in 50% ethanol; α,α'- dipyridyl (solid substance) provided by Merck;

– HMPA solution 99%; HMPA solution 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 discussions

In Fig. 1 is shown the polarogram obtained in the following conditions: $(CH_3)_4NCl$ 10^{-1} M; gelatine 0.01%; HMPA 20%, Pd^{2+} 10^{-4} M; α,α'- dipyridyl 10^{-3} M.

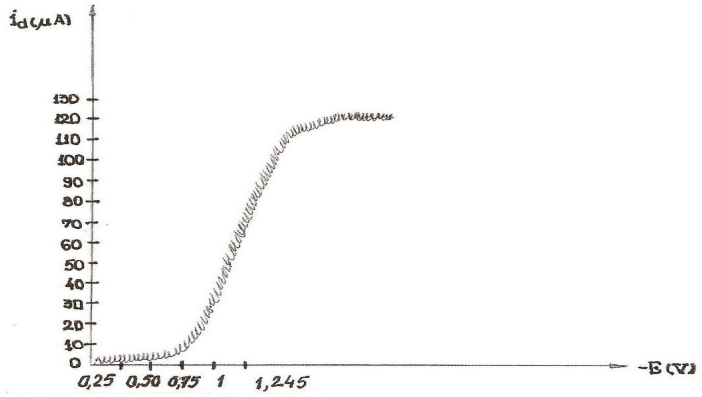

Fig. 1 *Polarogram for a solution containing the complex between Pd^{2+} and α, α'- dipyridyl in presence of HMPA*

The polarogram obtained is well defined, reproducible and the half-wave potential is $E_{1/2} = -1.245$ V.

In these conditions (Pd^{2+} + HMPA + α,α'- dipyridyl) 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 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 0.5 mL gelatine/5 mL sample was enough for obtaining well defined and reproductible polarograms.

b) Influence of α, α'- dipyridyl concentration

Concentrations of $(CH_3)_4NCl$ 10^{-1} M; gelatine 0.01%; HMPA 20%; Pd^{2+} 10^{-4} M were kept at a constant value. It was observed that by adding α,α'- dipyridyl 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.

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 reproducible. 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+} $3 \cdot 10^{-5}$ M; $(CH_3)_4NCl$ 10^{-1} M; gelatine 0.01%; HMPA 20%; α,α'- dipyridyl 10^{-3} M, at different mercury column heights within 400-600 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.

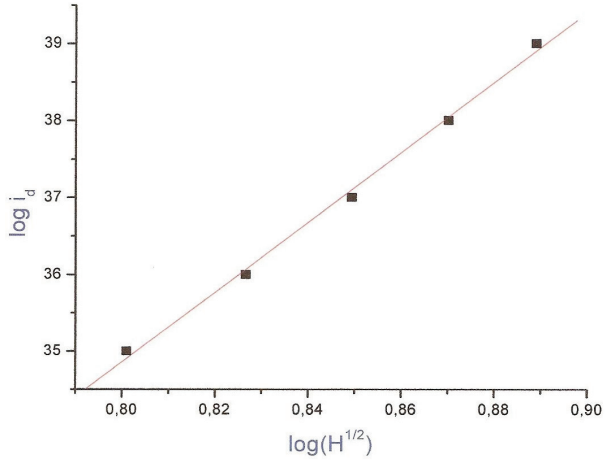

Fig. 2 *Dependence log $i_d = f$ (log $H^{1/2}$).*

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.

Cyclic voltammetry of Pd^{2+} sample solution performed with a CV-50W voltametric analyzer, using a three electrodes system (carbon paste as working, carbon paste as counter, and $Hg/Hg_2Cl_2/Cl^-_{(s)}$ as reference electrode) showed that the reaction is irreversible.

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

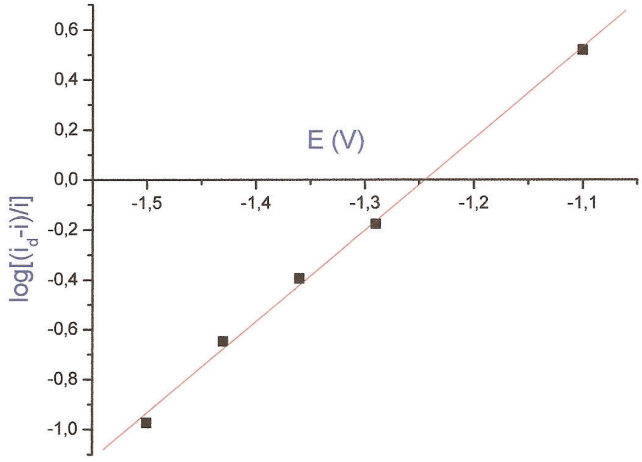

Fig. 3 *Diagram of logarithmic plot of the polarographic wave.*

From this representation we obtained $E_{1/2} = -1.245$ V.

e) Quantitative determination of palladium

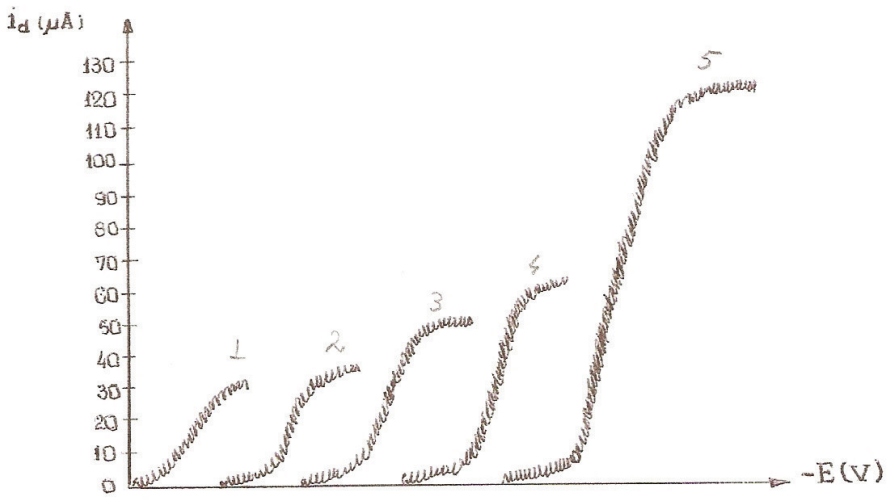

Fig. 4 *Polarograms for palladium solutions with the concentrations:*
1) $2 \cdot 10^{-5}$ M; 2) $3 \cdot 10^{-5}$ M; 3) $4 \cdot 10^{-5}$ M; 4) $5 \cdot 10^{-5}$ M; 5) $1 \cdot 10^{-4}$ M.

We accomplished the quantitative determination of Pd^{2+} in presence of α, α'- dipyridyl and HMPA. We established the optimal conditions for polarographic determination of Pd^{2+}: $(CH_3)_4NCl$ 10^{-1} M; gelatine 0,01%; HMPA 20%; α, α'- dipyridyl 10^{-3} M.

In Fig. 4 some polarograms for different concentrations of palladium are given.

In Fig. 5, the calibration curve is given for quantitative determination of palladium ion. It was ascertained that Pd^{2+} could be determined within the domain $2 \cdot 10^{-5}$ – 10^{-4} M.

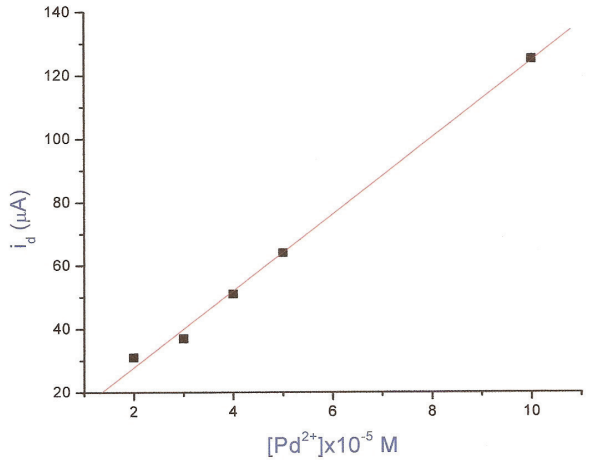

Fig. 5 *Calibration curve for palladium polarographic determination in the presence of α, α'- dipyridyl*

Curve equation is: $y = 3.62887 + 12.07732 \cdot x$

and: s (absolute standard deviation) = 3.1144; s_m (medium standard deviation) = 1.39; RSD (relative standard deviation) = 1.54; R (correlation coefficient) = 0.99826.

Conclusions

In this paper the conditions of polarographic determination of palladium ion in presence of α,α'- dipyridyl and HMPA solvent were established.

Polarograms were well defined and reproductible. The results lead us to the conclusion that this method can be applied to the quantitative determination of palladium ion within the concentration domain $2 \cdot 10^{-5}$ M – 10^{-4} M in presence of α,α'- dipyridyl and HMPA solvent.

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