POLAROGRAPHIC BEHAVIOR OF PALLADIUM ION IN PARTIAL AQUEOUS MEDIUMS

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abstract : There was studied the polarographic behavior of palladium ion in   presence of the reagent 1,10-phenantroline and the solvent hexamethylphosphotriamide (HMPA). The method can be used for quantitative determinations of palladium into the domain $5 \cdot 10^{-5}$ M-$2 \cdot 10^{-4}$ M. Polarograms were well defined and reproductible.

keywords: 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 1 , 10-phenantroline and HMPA solvent.

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

In the specialty literature a series of electrometric determination of Pd^{+2} is mentioned [3-14].

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

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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 cathode and a electrode with large surface of mercury as anode. 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 ; $PdCl_2$ solution was provided by Fluka ;
> * $(CH_3)_4NCl$ (tetramethylamonium chloride) 1M; $(CH_3)_4NCl$ was used as support electrolyte and was provided by Merck;
> * gelatine solution 0,1% , used as a suppresor for polarographic maxims;
> * 1,10-phenantroline solution 10^{-2} M in 50% ethanol provided by Merck;
> * HMPA solution 99% 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

I. The polarographic study of palladium ion in presence of HMPA (without reagent) was made using the following solutions: $(CH_3)_4NCl$ 10^{-1} M; gelatine 0.01%; HMPA 20%; Pd^{2+} $5 \cdot 10^{-5}M-2 \cdot 10^{-4}M$. The polarograms obtained were well defined and reproductible. We mention that these are the optimal conditions. The polarograms height increases with the increase of the concentration of the $PdCl_2$ solution. We made the logarithmic analysis of the polarographic wave. We also made the calibration curve. We made polarographic determinations of Pd^{2+} in presence of HMPA and 1,10-phenantroline reagent, using solutions with the same concentrations as we mentioned above and phenantroline $10^{-3}M$ and Pd^{2+} $2 \cdot 10^{-4}M$. In fig.1 the polarogram obtained is shown.
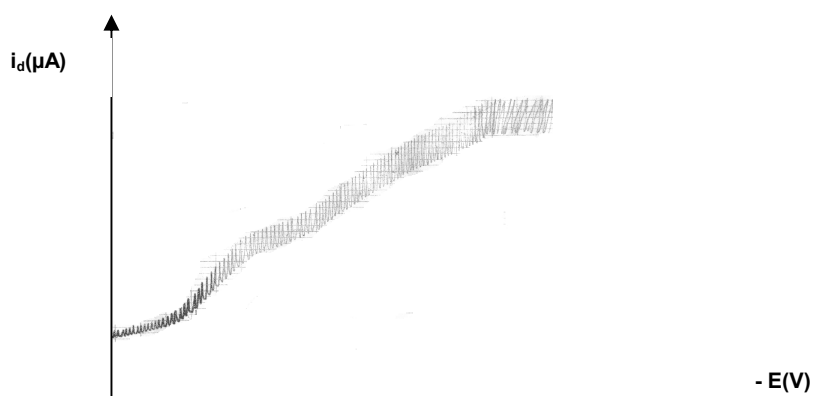

Fig. 1. *Polarogram for a solution containing the complex between Pd^{2+} and 1,10-phenantroline in presence of HMPA*

The polarogram is also obtained in optimal conditions for polarographic determination of palldium. It shows two reduction steps. We discussed and analyzed during this study only the second polarographic wave, for which $E_{1/2}$= -1.32 V.

In these conditions (Pd^{2+}+HMPA+1,10-phenantroline) 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 0.5 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 0,1%; HMPA 20%; Pd^{2+} $2 \cdot 10^{-4}$ M were kept at a constant value. It was observed that by adding 1,10-phenantroline with a higher concentration than 10^{-3} M the semiwave 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).

In polarographic determination the optimal reagent concentration must be at least 20 times higher than that of Pd^{2+} .

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+} $15 \cdot 10^{-5}$ M ; $(CH_3)_4NCl$ 10^{-1} M; gelatine 0,1%; HMPA 20%; 1,10-phenantroline 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 h and log $H^{1/2}$, where h is the limit current intensity and H is the mercury column height (for the second polarographic wave).

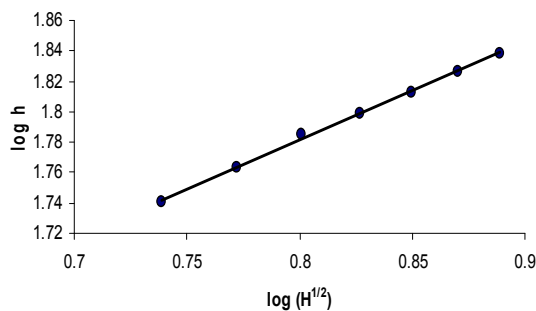**Fig.2**: *Dependence log h = f(log H$^{1/2}$)*

We reached the conclusion that the dependence log h = f(logH$^{1/2}$) 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 semiwave potential.
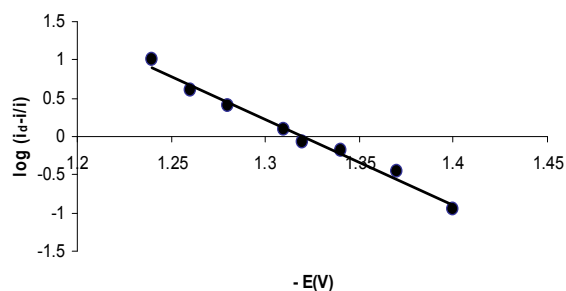

Fig. 3: *Diagram of logarithmic of the second polarographic wave*

From this representation we obtained E$_{1/2}$= - 1.32 V.

We also accomplished the quantitative determination of Pd^{2+} in presence of 1,10-phenantroline and HMPA. We established the optimal conditions for polarographic determination of Pd^{2+} : (CH$_3$)$_4$NCl 10^{-1} M; gelatine 0,1%; HMPA 20%; 1,10-phenantroline 10^{-3} M. Palladium concentration was taken within the domain 5·10^{-5} M-2·10^{-4} M.

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 5·10^{-5} M-2·10^{-4} M.
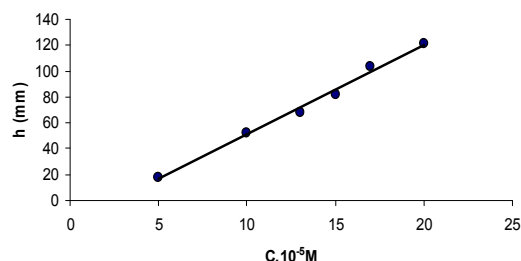
Fig.4: *Calibration curve for palladium polarographic determination in presence of 1,10 phenantroline and HMPA*

Conclusions

In this paper the condition of polarographic determination of palladium ion in presence of 1,10- phenantroline and HMPA solvent were established. This solvent influenced the diffusion current intensity and the value of the semiwave potential ($E_{1/2}$). This effect are due to the solvation modification of the ions and to different diffusion coefficients.

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 with in the concentration domain $5 \cdot 10^{-5}$ M-2$\cdot$ 10^{-4} M in presence of 1,10-phenantroline and HMPA solvent. In presence of 1,10-phenantroline reagent the semiwave potential takes more negative values than in its absence. The whole study was made for the second polarographic wave.

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