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 nitrosobenzene and the following solvents: hexamethylphosphortriamide (HMPA), dimethylphormamide (DMFA), dimethylsulfoxide (DMSO). 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 reproducible.

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 nitrosobenzene reagent and HMPA, DMFA, DMSO solvents.

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+} complex with *p*-nitrosodimethylaniline [1].

In the mid '60 there was established that one of the most important solvents in polarographic studies is DMFA [2]. In the presence of DMFA the polarographic reduction of Sn (II) was studied with very good results [3].

DMSO is a very good solvent in polarographic determinations of many cations in aqueous or partially aqueous solutions.

In the specialty literature a series of electrometric determination of Pd^{2+} is mentioned [4÷13].

In this paper the solvents influence on polarographic waves and the optimal (experimental) conditions for quantitative determinations 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$_3$)$_4$NCl (tetramethylammonium chloride) 1M; (CH$_3$)$_4$NCl was used as support electrolyte and was provided by Merck;

–   gelatine solution 0.1%, used as a suppresser for polarographic maxims;

–   nitrosobenzene solution 10^{-2}M in 50% ethanol, provided by Merck;

–   HMPA solution 99% provided by Merck;

–   DMFA solution 99.8% provided by Merck;

–   DMSO solution 99.8% provided by Schuchardt.

All reagents 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$_3$)$_4$NCl 10^{-1}M; gelatine 0.01%; HMPA 20%; Pd^{2+} $5 \cdot 10^{-5}$M÷$10 \cdot 10^{-5}$M. The polarograms obtained were well defined and reproducible. 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. From this we obtained $E_{1/2} = -1.34$ V. We also made the calibration curve. We made polarographic determinations of Pd^{+2} in presence of HMPA and nitrosobenzene reagent, using solutions with the same concentrations as we mentioned above and nitrosobenzene $2 \cdot 10^{-3}$M and Pd^{2+} $10 \cdot 10^{-5}$M. In Fig. 1 the polarogram obtained is shown.

This polarogram is also obtained in optimal conditions for polarographic determination of palladium. It shows two reduction steps. We discussed and analyzed during this study only the second polarographic wave, for which $E_{1/2} = -1.468$ V.

Comparing the polarograms we noticed that in presence of nitrosobenzene the semiwave potential ($E_{1/2}$) moves towards "more negative" values.

In these conditions (Pd^{2+}+HMPA+nitrosobenzene) the influences of various components of the solution were studied.
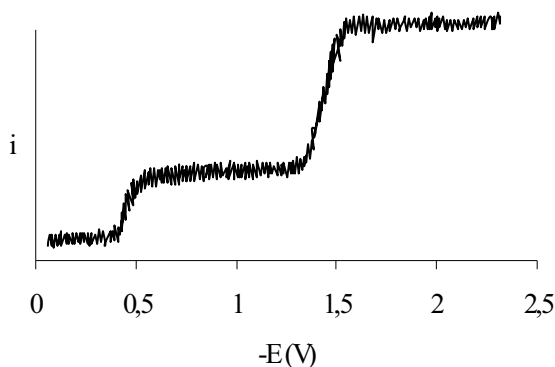
Fig. 1: *Polarogram for a solution containing the complex between* Pd^{2+} *and nitrosobenzene, in presence of HMPA.*

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 reproducible polarograms.

b) Influence of reagent concentration

Concentrations of $(CH_3)_4NCl$ $10^{-1}M$; gelatine 0.01%; HMPA 20%; Pd^{2+} $10 \cdot 10^{-5}M$ were kept at a constant value. It was observed that by adding nitrosobenzene with a higher concentration than $2 \cdot 10^{-3}M$ 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 determinations 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 tetramethylammonium chloride $(CH_3)_4NCl$ $10^{-1}M$ 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+} $10 \cdot 10^{-5}M$; $(CH_3)_4NCl$ $10^{-1}M$; gelatine 0.01%; nitrosobenzene $2 \cdot 10^{-3}M$; HMPA 20%, at different mercury column

heights within 30÷60 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).
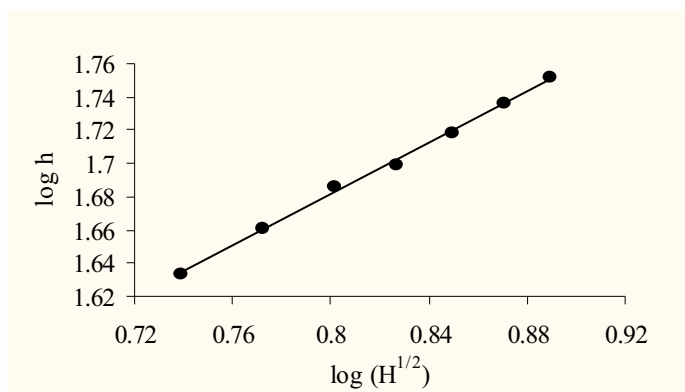

Fig. 2: *Dependence* $\log h = f(\log H^{1/2})$.

We reached the conclusion that the dependence $\log h = f(\log H^{1/2})$ is linear which means that the 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.

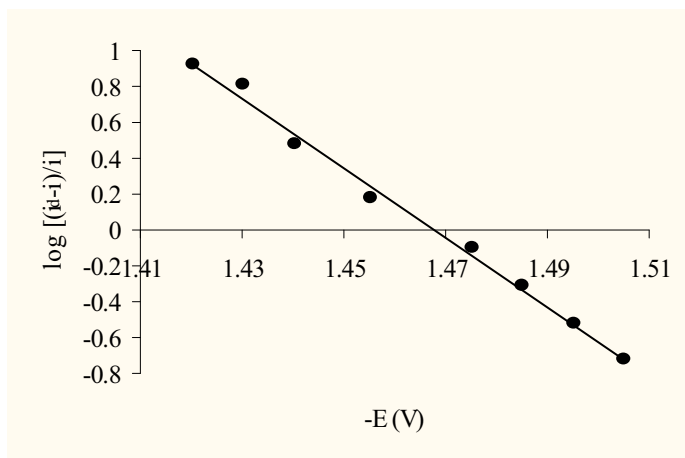From this representation we obtained $E_{1/2} = -1.468$ V.

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

We also accomplished the quantitative determination of Pd^{2+} in presence of nitrosobenzene and HMPA. We established the optimal conditions for polarographic determination of Pd^{2+}: $(CH_3)_4NCl$ 10^{-1}M; gelatine 0.01%; nitrosobenzene $2·10^{-3}$M; HMPA 20%. Palladium concentration was taken within the domain $5·10^{-5}$M÷$20·10^{-5}$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 $5 \cdot 10^{-5}M \div 20 \cdot 10^{-5}M$.
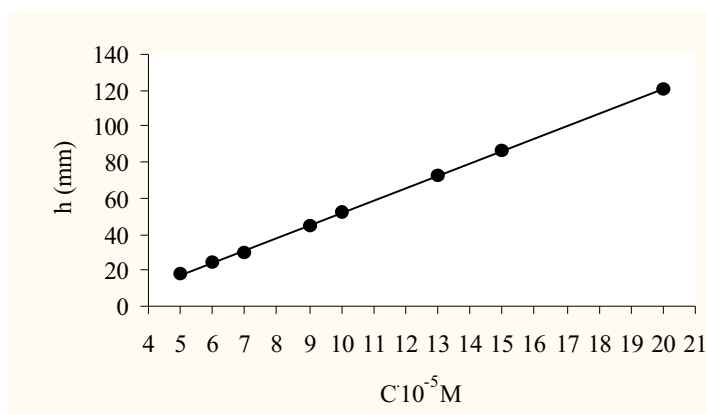

Fig. 4: *Calibration curve for palladium polarographic determination, in presence of nitrosobenzene and HMPA.*

II. We also studied the polarographic behavior of Pd^{2+} in presence of DMFA and nitrosobenzene. The optimal conditions for the polarographic determination: $(CH_3)_4NCl$ $10^{-1}M$; gelatine 0.01%; nitrosobenzene $2 \cdot 10^{-3}M$; DMFA 20%; Pd^{2+} $15 \cdot 10^{-5}M$ were established. We obtained polarographic waves well defined and reproducible just as those obtained in presence of HMPA.

Using the logarithmic analysis we determined $E_{1/2} = -1.58V$. Data regarding the dependence $\log h = f(\log H^{1/2})$ is given in Fig. 5.
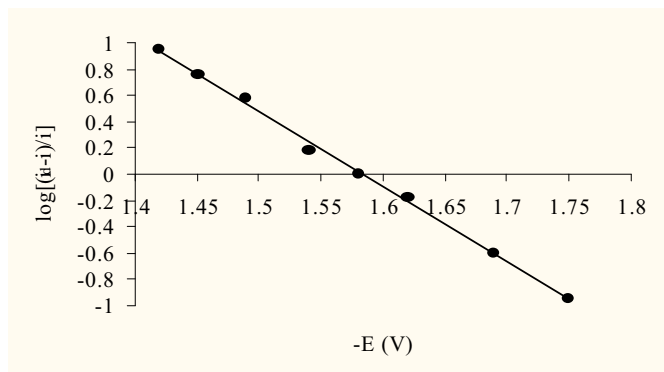

Fig. 5: *Diagram of logarithmic analysis of the second polarographic wave in presence of DMFA and nitrosobenzene.*

We must mention that in presence of DMFA and nitrosobenzene the semiwave potential (for the second wave) takes "more negative" values than in presence of HMPA and nitrosobenzene.

The influence of the height of the mercury column was also studied using solutions with the concentrations mentioned above. The height of the mercury column varied between 30 and 60 mm. The conclusion was the same as in the case of HMPA: the height of the polarographic waves increased with the increase of the mercury column height and the variation is linear, which means that the current intensity is a diffusion - controlled process.

Using nitrosobenzene and DMFA the palladium ion can be polarographically determined within the domain $10 \cdot 10^{-5}$M - $20 \cdot 10^{-5}$M. These determinations were made in the specified conditions, only for the second polarographic wave.

III. The polarographic determination of palladium ion in presence of DMSO and nitrosobenzene was made using the following solutions: $(CH_3)_4NCl$ 10^{-1}M; gelatine 0.01%; nitrosobenzene $2 \cdot 10^{-3}$M; DMSO 20%; Pd^{2+} concentration was taken within the domain $7 \cdot 10^{-5}$M÷$20 \cdot 10^{-5}$M. The polarograms were well defined and reproducible. We considered only the second polarographic wave. The study of the influence of the mercury column height was accomplished with the same conclusion as in the precedent cases (HMPA and DMFA): the polarographic waves increased with the increase of the mercury column height and the dependence $\log h = f(\log H^{1/2})$ is linear, which means that the current intensity is a diffusion controlled process.

Making logarithmic analysis of the second polarographic wave we observed that $E_{1/2} = -1.305$ V. This semiwave potential has a "more positive" value than those obtained in presence of HMPA, respectively DMFA. The palladium ion can be determined by polarography in presence of nitrosobenzene and DMSO within the domain $7 \cdot 10^{-5}$M÷$20 \cdot 10^{-5}$M, in the optimal conditions previously determined.

Conclusions

In this paper the condition of polarographic determination of palladium ion in presence of nitrosobenzene and different non-aqueous solvents (HMPA, DMFA and DMSO) were established. These solvents influenced the diffusion current intensity and the value of the semiwave potential ($E_{1/2}$). These effects are due to the solvation modification of the ions and to different diffusion coefficients. In Table 1 the solvents influence on semiwave potential is presented.

Table 1. The solvents influence on semiwave potential in presence of nitrosobenzene

Pd^{2+} + reactiv + solvent	$-E_{1/2}$(V)
Pd^{2+} + nitrosobenzene + HMPA	1,468
Pd^{2+} + nitrosobenzene + DMFA	1,58
Pd^{2+} + nitrosobenzene + DMSO	1,305

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 $5 \cdot 10^{-5}$M÷$20 \cdot 10^{-5}$M in presence of nitrosobenzene and HMPA, DMFA or DMSO. In presence of nitrosobenzene 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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