Study of the Reduction of Palladium(II) on a Mercury Electrode in the Presence of Dimethylglyoxime

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Abstract
The adsorptive behavior of Pd^{II} ions in the presence of dimethylglyoxime (DMG) was investigated using voltammetric techniques. It was found that the bis-dimethylglyoximato palladium(II) complex is adsorbed strongly between pH 3 and 5 and between the potentials 0 and -0.3 V (vs. Ag/AgCl). The peak current is proportional to the Pd-DMG surface concentration, and increases linearly with scan rate ($\partial \log i_p / \partial \nu = 0.97$). The adsorptive stripping response was evaluated with respect to pH, the concentration of the electrolyte, the addition of surfactants and the preconcentration potential. From the results a general scheme for the reduction process is given.

Keywords: Palladium, Adsorptive stripping voltammetry, Dimethylglyoxime, Reduction process

1. Introduction

High sensitivity is commonly difficult to attain when determining low concentrations of palladium by electro-analytical techniques. The main reasons for this are the low solubility of palladium in mercury and the irreversibility of the electrochemical process. However, a significant enhancement in the sensitivity of voltammetric methods can be achieved by adsorptive preconcentration of the analyte [1, 2].

Determination of palladium by adsorptive stripping voltammetry (AdSV) on the hanging mercury drop electrode (HMDE) was first described by Wang and Varughese [3]. The use of dimethylglyoxime (DMG) as a complexing ligand in slightly acidic media (pH 5.15) was recommended for the accumulation of the palladium–dimethylglyoxime complex (Pd-DMG). Zhao and Gao [4] who investigated the polaro-graphic behavior and adsorption of Pd-DMG complexes in strong alkaline media found that $Pd(HDMG)_2OH^-$ is the adsorbed species on the mercury electrode and determined the stability constant of the ternary complex ($\log \beta' = 7.76$). The same authors [5] also investigated the reduction of Pd-DMG in acidic media (pH 2) using single sweep polarography. The addition of the anionic surfactant sodium dodecylbenzene-sulfonate, was proposed to increase the solubility of the analyte and thus improve the sensitivity of the polarographic measure-ments. Xu and Zeng [6] used furil α-dioxime in ammoniacal media for the determination of palladium by differential pulse polarography (DPP) and applied this to the analysis of charcoal containing Pd catalysts. Basu and Rajagopalan [7] used DMG for the enhancement of the nickel peak by simultaneously determining palladium and nickel in electroplating baths. They established that the palladium DPP peak in ammoniacal ammonium chloride buffer is not affected by DMG. Also other ligands like crown ethers [8] have been used for the adsorptive modification of the graphite electrode and anodic stripping determination of palladium.

From previous studies of the voltammetric determination of palladium [1–8] it is evident that by replacing the dropping mercury electrode with a stationary mercury drop electrode [3] a hundred fold increase in the detection limit is achievable. As in the case of other analytes [1, 2] there is no doubt that the full potentialities of AdSV, in trace analysis, can only be achieved

when a stationary electrode is used for the accumulation of the reactants. In our previous investigations [9, 10] dimethyl-glyoxime and other oximes were used for the adsorptive preconcentration of palladium on the stationary mercury electrode. From an analytical point these studies agree with the data published by Wang and Varughese [3]. This detailed study aims at explaining the reduction process of the Pd-DMG complex in acidic media.

2. Experimental

All reagents were of analytical purity or suprapur quality. Deionized water was additionally purified using the Milli-Q system. Acetate buffer of pH 3.6 was used as the supporting electrolyte. This was prepared by mixing the appropriate amounts of 0.1 M acetic acid and 0.1 M sodium acetate. An ethanolic solution of 0.1 M dimethylglyoxime was prepared by dissolving DMG (butane-2,3-dione dioxime, Merck, Darmstadt, Germany) in absolute ethanol. A palladium standard stock solution (1.00 mg/mL) was prepared by dis-solving palladium(II) chloride (Merck) in 6 M HCl, and standardized gravimetrically (precipitation with DMG). Work-ing standards were prepared by serial dilution of the stock solution with 0.1 M HCl. A combined glass electrode and a pH meter were used for the pH measurement.

Voltammetric measurements were conducted using a Model 174 and a Model 374 microprocessor controlled polarograph (EG&G PARC) in combination with a stationary mercury electrode (SMDE Model303A, PARC). Square wave measure-ments were performed with a M273 Potentiostat/Galvanostat (EG&G PARC) coupled to a personal computer. An Ag/AgCl electrode filled with a saturated KCl solution was used as a reference electrode and a platinum wire as an auxiliary. Oxygen was removed by purging with pure argon (99.9%). After which the samples were stirred (magnetic stirrer at 750 rev/min), the palladium chelate was preconcentrated for two minutes at medium drop size (0.025 cm^2) and allowed to equilibrate for 15 seconds. Measurements were made in a DPP mode with a polarizing voltage of 8 mV/s scanned in a negative (cathodic) direction.

3. Results and Discussion

3.1. The Effect of pH on Voltammetric Behavior of Pd^{II}

From the literature it is known that the reduction of palladium on mercury is irreversible in weak acidic and in neutral media. However very little data exists about the adsorptive properties of palladium hydroxo complexes on the Hg electrode. Therefore, we investigated the behavior of palladium(II) in various media, including hydrochloric acid, acetate, phosphate and ammonium buffer (Table 1). Due to the low solubility of palladium hydroxide ($K_{sp} = 3.2 \times 10^{-29}$, [11]), the measurements were carried out at low concentrations of Pd^{II} using preconcentration on SMDE, and applying a DPP mode of measurement. Since both palladium and DMG can be reduced, we investigated the behavior of palladium, DMG and a combination of palladium and DMG. Voltammetric peaks for the reduction of palladium appear at approximately $-0.35\,V$ in $0.1\,M$ HCl and at $-0.90\,V$ in the ammonia buffer (Table 1). DMG (measured in DPP mode) is reduced at $0.3\,V$ and $0.65\,V$ more negative potentials in acidic and alkaline media, respectively. The peak height of palladium-DMG complex depends on pH, the time taken for preconcentration, and the accumulation potential. The asymmetric shape of the voltammetric peak obtained by linear-sweep (LS) mode indicates an adsorptive character [12]. The reduction process of Pd^{II}-DMG was irreversible over the time scale of DPP and LS techniques ($5\,mV/s < v < 1\,V/s$) and showed no anodic response, as found by Wang and Varughese [3].

In all cases when the pH value was increased (Table 1), the reductionpotentials shifted in a negative direction. The palladium(II)-aqua, or hydroxo complexes already present in the acidic medium are also adsorbed *viz.* preconcentrated on mercury electrode. This peak is also observed in neutral and weakly alkaline media but only at very low concentrations of palladium ($< 10\,mg/L$). The adsorption of the palladium hydroxo complexes is significantly weaker than the adsorption of the dimethylglyoximate complex. In an acidic medium the ratio between corresponding adsorptive peak heights at $2\,min$ of preconcentration is approximately 1:5. Peak potentials of both the palladium-aqua and Pd-DMG complexes in the observed pH range do not differ significantly ($\Delta E_p < 50\,mV$).

The pH of the medium also affects the voltammetric peak heights. The following relation can be written for the main Pd^{II} species present in the aqueous phase:

$$C_{Pd} = [Pd^{2+}] + [PdOH^+] + [Pd(OH)_2] + [Pd(HD)_2]$$
$$+ [Pd(OH)(HD)^{2-}],$$

where C_{Pd} represents the total (analytical) concentration of Pd^{II} in solution and HD singly deprotonated DMG. From the stability constants of the corresponding complexes [11, 13], we can calculate the concentration of the individual species at different pH values. In the absence of DMG the molecular $Pd(OH)_2$ represents the main palladium species in solution above pH 2. Pd^{2+} predominate only in strong acid media below pH 1. The presence of DMG changes substantially the distribution of palladium species. As shown in Figure 1, below pH 8.4, bis-dimethylglyoximato palladium(II) complex is the main component and at higher pH values ternary complex $Pd(HD)_2(OH)^-$ prevails. In the whole pH range ($0 < pH < 14$) both the hydroxo complexes and free Pd^{II} represents a negligible fraction of the total concentration. Of the noncomplexed DMG species (not shown in the diagram), H_2D represents the main fraction below pH 10 and a fraction of the complex forming species HD^- decreases in this region linearly with a decrease in pH.

If we want to achieve an optimal concentration of the $Pd(HD)_2$ complex in solution, pH must be below 8. The high stability of $Pd(HD)_2$ chelate ($\log \beta_2 = 10^{34.3}$, [13]) and a higher total concentration of DMG than palladium ($C_{DMG} \gg C_{Pd}$), ensure its predominance in acidic media. Throughout, the conditional stability constant of Pd-DMG complex decreases proportionally with an increase in the acidity of the solution.

The maximum adsorption of the Ph-hydroxo and Pd-DMG complexes was found experimentally to be between pH 3 and 6. In more acidic or more alkaline media the adsorptive peaks decreased. The decrease in the voltammetric peak height with an increase in the acidity of the medium, in the absence of the DMG, can be explained by the decrease in the concentration of adsorbable $Pd(OH)_2$ complexes.

Figure 2 shows the dependence of peak potential (a) and the peak current (b) of the Pd-DMG on pH in the acetate buffer. It was found that for a ten-fold decrease in the hydrogen ion concentration the voltammetric peak was shifted by approximately $90\,mV$ in a cathodic direction. The height of the peak in the observed pH range shows a parabolic profile which reaches its maximum at about pH 3.6. A similar pH dependence of the

Table 1. Voltammetric peak potentials (in V vs.Ag/AgCl) of Pd^{II} in different supporting electrolytes [a].

Electrolyte	pH	E_p^{Pd-OH}	E_p^{DMG}	E_p^{Pd-DMG}
1.0 M HCl	0.1		-0.444	
0.5 M HCl	0.44		-0.63	
0.1 M HCl	1.1	-0.352	-0.652	-0.360
0.1M HCl/KCl	1.2	-0.360	-0.688	-0.368
	1.5	-0.368	-0.748	-0.370
	1.8	-0.370	-0.764	-0.372
	2.0	-0.380	-0.768	-0.384
	2.2	-0.398	-0.792	-0.400
	2.5	-0.410	-0.860	-0.412
0.1 M CH_3COOH (HAc)	2.9	-0.444	-1.086	-0.446
0.1M HAc/ NaAc	3.6	-0.514	-1.26	-0.556
0.2 M Na_2HPO_4/NaH_2PO_4	6.8	-0.772	-1.356	-0.776
	7.5	-0.80	-1.384	-0.80
	8.2	-0.84		-0.84
	9.1	-0.89		-0.92
0.1 M NH_3/NH_4Cl	9.5	-0.90	-1.568	-0.90

[a] $C_{Pd} = 15\,mg/L$, $C_{DMF} = 1 \times 10^{-4}\,M$, $t_a = 1\,min$ at $-0.3\,V$.
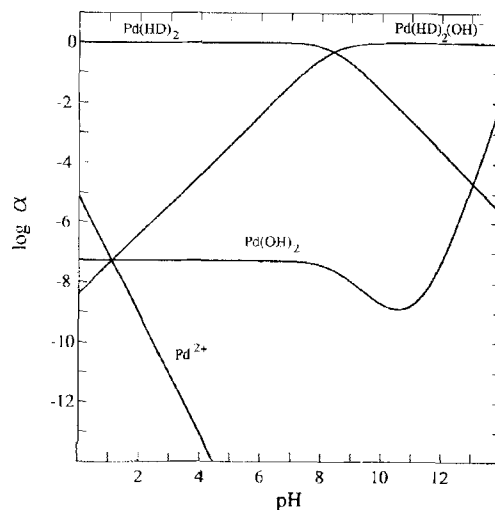
Fig. 1. Distribution of the main palladium-hydroxo and palladium-dimethylglyoximato species depending on pH; $C_{DMG} = 1 \times 10^{-4}\,M$.
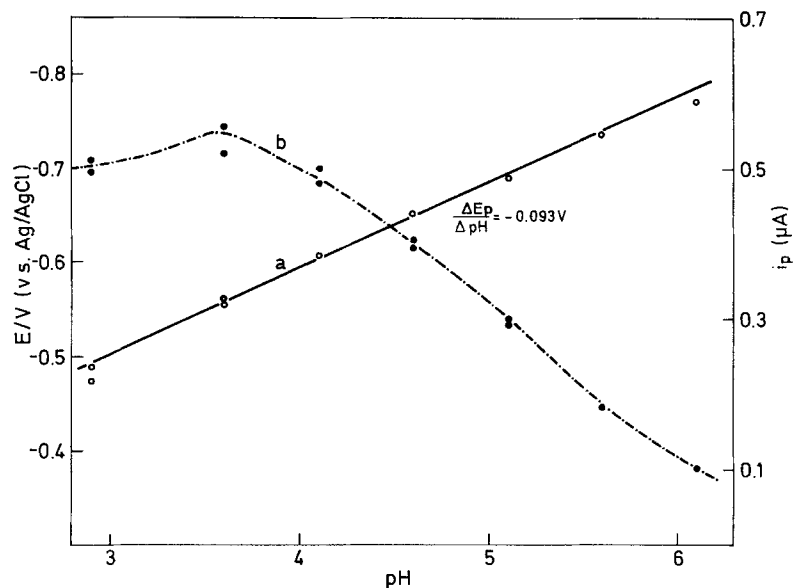
Fig 2. Dependence of the peak potential (a) and peak current (b) on pH in 0.1 M acetate buffer, 1×10^{-4} M DMG, 15 mg Pd^{2+}/L, deposition time: 2 min at -0.3 V, electrode area: 0.025 cm^2.

peak current was also observed by Wang and Varughese [3] but the reported maximum peak current was at pH 5.15.

The decrease of the peak height with a decrease in pH is caused by a lower fraction of HD$^-$ and a correspondingly lower equilibrium concentration of the Pd(HD)$_2$ in solution. The decrease of the peak height at pH values greater than 4 is opposite to that expected, since according to the distribution diagram (Fig. 1), at higher pH values the voltammetric peak should increase proportionally to the increase in the HD$^-$ concentration (not shown in the diagram). This can be explained by the precipitation of Pd(HD)$_2$(s), and/or the formation of Pd(OH)(HD)$_2^-$ ($K_f = 3.2 \times 10^5$, [13]) at higher pH values. The adsorption of the latter was not observed. This agrees with the statement made by Basu and Rajagopalan [7]), who found that in ammoniacal media there was no enhancement of the peak current for Pd^{II} in the presence of DMG.

Similar behavior of Pd-DMG was observed in the 0.1 M phtalate buffer. The peak potential was linearly proportional to pH between pH 3.5 and 6.5. For a unit pH increase, E_p is shifted approximately 100 mV in a cathodic direction. It was found that i_p-pH dependence expressed a similar parabolic profile as in the acetate buffer, but with a maximum peak height around pH 5. The dependence of the peak potential on the pH of the media indicates that protons participate in the rate determining step (rds) of the electrode process.

3.2. Effect of Reactant Concentrations

Figure 3 shows the effect of the DMG concentration on peak height in an acetate buffer of pH 3.6 at different Pd^{II} concentrations. The DMG concentration in solution has a noticeable effect on the peak height. When the concentration of DMG increases from 1×10^{-5} M to 1×10^{-4} M, the voltammetric peak height increases rapidly but then declines and begins to decrease at concentrations higher than 3×10^{-4} M. The decrease in the peak height at higher DMG concentrations is caused either by the precipitation of the Pd(HD)$_2$(s) at the electrode surface or to the formation of multimolecular films of the adsorbate at the electrode surface which cannot be reduced completely. Also the competitive adsorption of free H$_2$D may be

the reason for the decrease in the surface concentration of Pd(HD)$_2$ and the subsequent decrease in the Pd peak height. Figure 3 shows that 1×10^{-4} M DMG, at pH 3.6 and a preconcentration time of 2 minutes, gives a linear response at a palladium concentration below 5 μg/L. At higher concentrations of palladium a shorter preconcentration time, accumulation in the nonstirred solution, and/or a buffer of lower pH should be used to obtain the linear response.

The voltammetric peak height and peak potential is also influenced by the concentration of the supporting electrolyte, i.e., ionic strength. The peak height was doubled and peak potential shifted approximatelly 70 mV in a cathodic direction when the concentration of the acetate buffer was increased from 0.01 M to 0.1 M. At still higher ionic strength peak height
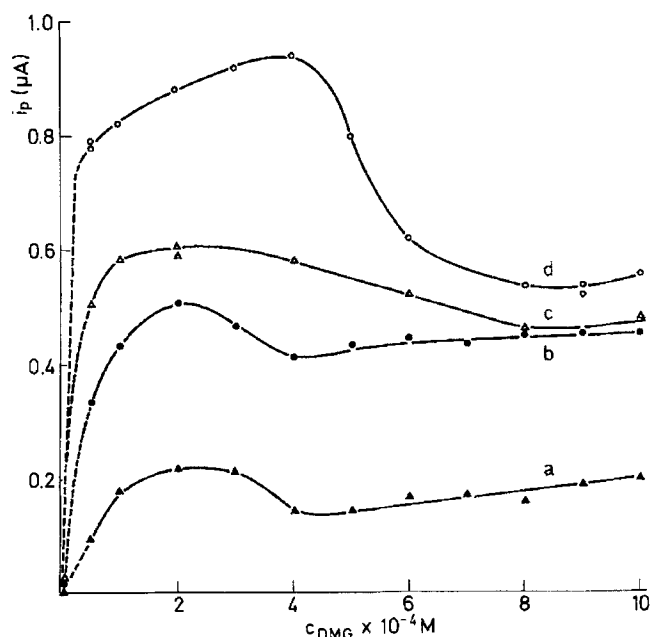

Fig. 3. Effect of the DMG concentration on peak height in an acetate buffer of pH 3.6 at different concentrations of Pd: a)–d): 5, 10, 15 and 20 mg Pd^{2+}/L; deposition time: 2 min at -0.3 V, electrode area: 0.025 cm^2.

decreases and is reduced by 20% when the buffer concentration is increased to 0.5 M. The influence of the ionic strength on the Pd-DMG height can be explained by the changes in the composition of the double layer. As a result, the adsorption of the Pd-DMG at higher concentrations is hindered. For voltammetric measurement a 0.1 M solution of acetic acid and sodium acetate was recommended as the optimal buffer concentration.

3.3. Effect of Surfactants

From the adsorptive accumulation of the Pd-DMG on the Hg electrode we would expect that different surface active substances and anions, which are specifically adsorbed on Hg electrode, may inhibit the adsorption of Pd-DMG, and therefore affects the voltammetric response. Curve a in Figure 4 shows the dependence of the Pd-DMG peak height in the absence of other adsorbable compounds at different preconcentration potentials. The Pd-DMG is adsorbed over a wide potential range from 0 to −0.35 V during which the voltammetric peak height remains constant. At more positive potentials, the adsorption is inhibited due to electrode surface oxidation. At more negative potentials than −0.35 V, the peak decreases due to an instantaneous reduction of the Pd-DMG complex arriving from the bulk of the solution to the electrode surface. For adsorptive preconcentration of Pd-DMG a potential between 0 and −0.3 V should be used.

The presence of Triton X-100 has a severe effect on the peak height (curve b). Considering the fact that the Triton X-100 is a nonionic detergent, its effect becomes more pronounced as the potential of zero charge (pzc) is approached. The influence of the iodide ions on the palladium peak height is related to their specific adsorption on the mercury electrode. The Pd-DMG adsorption is strongly inhibited which can be seen from the plots c and d (Fig. 4). This inhibition is stronger at greater positive potentials, because the adsorption of iodide is stronger with a higher excess of positive charge on the electrode. Additionally we may expect with iodide a further peak height decrease due to the competitive complexation of palladium ($\log \beta_4 = 10^{24.5}$, [11]).
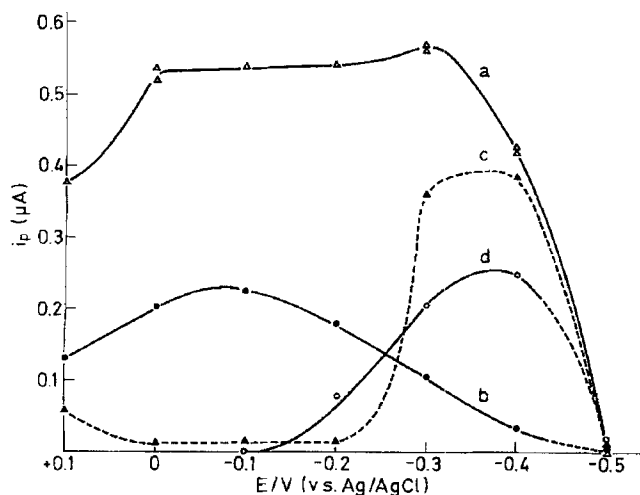

Fig. 4. Dependence of the Pd-DMG peak current on the potential of adsorption in 0.1 M acetate buffer at pH 3.6; a) 1×10^{-4} M DMG and 15 mg Pd^{2+}/L; b) (a) + 5 mg/L Triton X-100; c) (a) + 1×10^{-4} M KI, and d) (a) + 1×10^{-3} M KI. Other conditions are the same as in Figure 3.

3.4. Effect of the Scan Rate

The effect of the polarization voltage rate v on E_p has been investigated by adsorptive square-wave voltammetry (AdSWV). The rate of the polarization voltage was obtained by altering the frequency f between 10 and 1000 Hz, using a constant scan increment ΔE_s of 5 mV and an amplitude of 50 mV. Because the scan rate in SWV is proportional to the frequency $v = f(\Delta E_s)$, the logarithmic dependence of the peak height on the polarization voltage change rate expresses the change in i_p with f. The slope of the curve below 500 mV/s, i.e., below 100 Hz remains constant (0.97). This indicates that the peak current increases linearly with the scan rate (frequency) and confirms that the reduction of Pd^{II} results from the adsorbed state [14]. At higher scan rates the slope of the curve declines.

By increasing the scan rate (frequency) the voltammetric peak position is also changed. The slope of the ΔE_p-log v curve shows that the peak potential is shifted by 91 mV in a cathodic direction for a tenfold increase in the scan rate. The same shape and gradient also shows a relationship between peak potential and peak current. From the linear part of both curves the charge transfer coefficient α can be calculated [14], and was found to be 0.6 ± 0.05.

3.5. Electrode Process

The current caused by the reduction of palladium in the presence of DMG depends on: (a) the homogeneous equilibria in the solution, (b) the adsorption of the Pd-DMG complex and (c) the rate of the charge transfer process. In a weak acidic noncomplexing medium the following equilibria exist:

$$Pd(H_2O)_n^{2+} \rightleftharpoons Pd(OH)^+ \rightleftharpoons Pd(OH)_2(aq) \rightleftharpoons Pd(OH)_2(s) \quad (1)$$
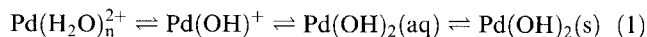
In a strong acid medium (pH < 1), Pd^{II} exists as a tetraaqua complex. If the pH is increased, dihydroxo complexes will predominate in the solution. At higher pH values (and concentrations of Pd^{2+}) molecular Pd(OH)$_2$(aq) will precipitate.

In the presence of the dimethylglyoxime in solution, we have to consider the protolytic reactions of DMG. The equilibrium concentration of complex forming ions HD$^-$ is dependent on the pH. The formation of the Pd-DMG complex between the main species in solution can be presented by the reaction

$$Pd(OH)_2(aq) + 2H_2D \rightleftharpoons Pd(HD)_2 + 2H_2O \quad (2)$$
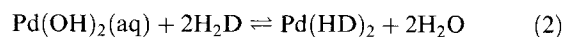
Since the concentrations of both reacting species, i.e., Pd^{2+} and HD$^-$ depend on pH, the stability and the concentration of Pd(HD)$_2$ in solution is conditioned mainly by the pH of the medium.

The adsorptive equilibrium is influenced by the potential and the presence of surface active compounds. The adsorptive equilibrium can be described by the following reaction:

$$Pd(HD)_2(aq) \rightleftharpoons Pd(HD)_2(ads) \quad (3)$$

The adsorption is accelerated by agitation and is inhibited by surface active substances. It is particularly hindered when nonionic surfactants and adsorbable anions are present.

The rate of the electrode process depends on the concentration of hydrogen ions (Figure 2). In more acid solutions this is higher and the reaction proceeds at more positive potentials and vice versa. The Pd-DMG complex reduction is described by the following overall reaction:

$$Pd(HD)_2(ads) + Hg + 2H^+ + 2e^- \rightleftharpoons Pd(Hg) + 2H_2D(des)$$

$$(4)$$
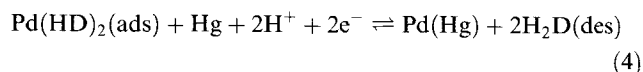
From the kinetic parameter $a(0.6 \pm 0.05)$ it can be assumed that the rds is the transfer of the first electron. Between pH 3 and 5, the voltammetric peak is shifted by $95 \pm 5\,mV$ in a cathodic direction for every tenfold decrease of the H_3O^+ concentration. On this basis it can be presumed that the reaction is first order with respect to the concentration of H_3O^+ ions in the rds. The elementary steps of reaction 4 are therefore closely related to the nickel-DMG complex [15].

Current response during the reduction of the Pd-DMG complex depends on their equilibrium concentration on the electrode surface Γ:

$$i_p = K'A\Gamma_{Pd(HD)_2} = KC_{Pd(HD)_2} = KC_{Pd} \qquad (5)$$

where A represents the electrode area and K and K' are proportionality constants. Equation 5 is valid for low coverage of the electrode surface ($\Theta < 0.8$), i.e., in the linear concentration range [1]. The equilibrium concentration of the $Pd(HD)_2$ in the solution $C_{Pd(HD)_2}$ depends on the pH (1–2). The surface concentration of $Pd(HD)_2$ is dependent on the equilibrium concentration of this species in the solution, the preconcentration time, the rate of the transport towards the electrode and the presence of surface active substances. At a low coverage of the electrode surface ($\Theta \ll 1$), the peak current is linearly proportional to the Pd^{II} concentration in the solution, thus representing the basis for a quantitative analysis. At given experimental conditions ($1 \times 10^{-4}\,M$ DMG, $t_{acc} = 2\,min$) i_p increases linearly with C_{Pd} between 0.05 mg/L (LOQ based on 10 s_{noise}) and 5 mg Pd/L. At higher concentrations of Pd or DMG (Fig. 3) and/or t_{acc}, surface concentration approaches the maximum value of Γ_m ($\Theta \to 1$) and the linearity is lost. It can be recovered by an appropriate modification of the experimental conditions, e.g., a decrease in pH, t_{acc}, C_{DMG} and transport rate or an addition of competitive ligands to the solution.

4. Conclusion

The investigation of the experimental parameters effecting the electrode process rate has pointed out three important stages for the reduction of Pd^{II} ions in solutions containing DMG. These are the dynamic equilibria between hydroxo and dimethylglyoximato species in solution, the adsorption of $Pd(HD)_2$ on the Hg electrode, and the irreversible reduction of the adsorbed component.
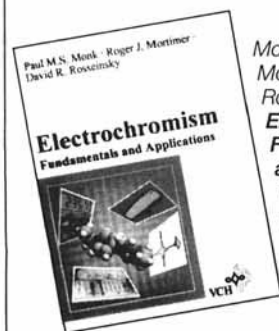
It was found that the palladium hydroxo complexes were also adsorbed on the Hg electrode but the adsorption of these species gave a 5–10 times weaker response than the Pd-DMG adsorption. Pd-DMG is strongly adsorbed on the Hg electrode between pH 3 and 6. The optimum potential range for its accumulation is between 0 and $-0.35\,V$ with respect to the Ag/AgCl electrode. The adsorption of the $Pd(HD)_2$ is inhibited by the presence of those surfactants which also adsorb in this potential range.

For analytical purposes, it is important to ensure an optimum pH value, DMG concentration and not too high a $Pd(HD)_2$ concentration, i.e., to work with a low electrode surface coverage ($\Theta < 0.8$) where i_p shows a linear dependence on $C_{Pd(HD)_2}$. The linear proportionality of the peak current and the scan rate ($\partial \log i_p / \partial \log v = 0.97$) is also important analytically, since by making the correct choice of the excitation signal and the polarization rate [16], the sensitivity of the voltammetric measurements can be increased substantially.

5. References

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