Complexation, adsorption and reduction of palladium-dimethylglyoxime: Analytical considerations

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Abstract

Electroanalysis offers an interesting tool for palladium quantification by using adsorptive stripping voltammetry of Pd-dimethylglioxime complex on mercury. Here we show that complexation kinetics and solubility in the homogeneous phase, in addition to surface concentration, are relevant analytical aspects to be considered. Complexation kinetics is first order in both Pd(II) and the ligand ($k = 15$ s^{-1} M^{-1}). This determines the chemical equilibration time after each metal addition: for example when using 1×10^{-4} M dimethylglioxime a non- negligible chemical equilibration time ca. 1 hour should be considered. The upper limit of the linear range is determined by two factors: complex solubility in the solution (ca. 2.5 μM) and surface concentration. The latter should develop a redox charge lower than 30 μC cm^{-2}.

Keywords: Palladium; Dimethylglyoxime; Adsorption; Stripping voltammetry

1. Introduction

Platinum group metals, PGM (platinum, palladium and rhodium) are present in the environment only at low levels, ca. 0.4 ng g^{-1} in the Earth crust [1]. However the use of catalytic converters to reduce gaseous automobile emissions is increasing the presence of these metals in the environment. PGM have been found in soil [2], sediments [2, 3] and even in snow samples from remote unexposed places [4, 5] and it has been proved that PGM may transform into bioavailable species [2, 6-8]. Palladium is of special concern because it has greater mobility in the environment than the other PGM [7]. The release of this metal has been estimated as 250 ng of palladium per kilometer for new diesel engines [11]. In humans, urinary Pd has been correlated with traffic density [12]. Even though nowadays environmental PGM concentrations are low (typically in the pM range [9]), its levels are predicted to rise [2, 10]. Therefore it is important to have analytical techniques that allow palladium qunatification in a variety of matrices and in a wide range of concentrations.

For the determination of palladium traces several sensitive and selective spectrometric techniques have been used [13-18]. Usually direct application of these techniques to the detection of metals in complex matrices such as environmental (road dust, car exhaust fumes), biological (plants) and clinical (blood, urine) samples is limited by numerous interferences. Thus a separation/preconcentration procedure prior to detection is required [14, 19-22]. Recently, dimethylglyoxime (H_2DMG) has been applied as a solid phase extractor due to its ability to form a stable complex (log $\beta_2 = 34.3$) [22]. This complexing agent has been used for quite a long time in the determination of nickel, cobalt and palladium in combination with electroanalytical techniques.

Dimethylglyoxime reacts with a variety of metals (Me) such as nickel, cobalt and palladium to form 1:2 complexes, $Me(HDMG)_2$, which adsorbs on mercury [23-27] and bismuth [28-30]. In the case of Pd(II) reported experimental conditions are very similar, except in the case of Zhao and Gao [31]. For example, Wang and Varugese [32] reported that optimal conditions require acetate buffer solution (pH 5.15) containing 2×10^{-4} M dimethy1glyoxime; the accumulation potential was -0.20 V vs

Ag/AgCl. The height of the stripping peak was found to be linearly dependent on Pd(II) solution concentration (up to 0.16 μM) and preconcentration time (in the range 0-300 s). Full mercury surface coverage (4.98×10^{-10} mol cm^{-2}) was obtained from exposure to a 0.5 μM palladium solution, after stirring for 300 s. A detection limit of 2.1×10^{-10} M was achieved after l0 minutes preconcentration. Using a silver amalgam film electrode, Bobrowski et al, have estimated a detection limit of 1.4×10^{-9} M after l minute preconcentration [27].

The effect of pH and the preconcentration potential on the stripping response for Pd(HDMG)$_2$ concentrations ranging from ca. 5 μM to ca. 200 μM was studied by Georgieva and Pihlar [25]. They recommended the use of a 0.1M sodium acetate/acetic acid buffer solution (pH 4.5) and adsorption potential in the range 0 to -0.3V vs Ag|AgCl.

In a previous article we studied the voltammetric reduction of Pd^{II}(HDMG)$_2$ complex preadsorbed on mercury in 0.2 M acetic/acetate buffer (pH 4.85) focusing on surface stages and reaction mechanism [33]. As preconcentration proceeds, molecules adsorb parallel to the electrode surface, but at high surface concentration interactions between adsorbed molecules lead to bilayer or even multilayer formation. Consequently the shape of the voltammetric peak changes dramatically. This is an important aspect to consider because it may limit the conditions under which the procedure is valid.

Besides surface conditions, we have observed a slow Pd(HDMG)$_2$ homogeneous formation kinetics not previously reported. This is an important aspect to be considered when performing the analysis.

Given the relevance of Pd and considering the attractive simplicity of adsorptive stripping techniques for palladium quantification, we center on homogeneous kinetics, surface stages and reaction mechanism in relation to the electroanalytical quantification procedure.

2. Experimental

Adsorption of Pd(HDMG)$_2$ on mercury was performed at controlled potential (-0.3 V vs Ag|AgCl 3.5 M in all experiments) for different adsorption times and complex concentrations. Experiments were performed in 0.2 M acetate buffer solution (pH 4.85). Buffer solutions were prepared dissolving 2.726 g sodium acetate trihydrate and 0.455mL concentrated glacial acetic acid and made up to 100 mL solution. Pd(II) concentration ranged within $2 \times 10^{-7} – 2 \times 10^{-6}$ M, the upper limit to avoid precipitation of the complex. H$_2$DMG concentration ranged within $1 \times 10^{-4} – 3 \times 10^{-4}$ M.

Water (18.2 MΩ) from a MilliQ Water System was used to prepare the solutions used throughout this work. Pd(II) standard solution (1000ppm) was prepared by weighing 0.0216 g PdCl$_2$ (Merck, 59% Pd, anhydro); 1mL concentrated HCl and water were added to the total volume of 10 mL. All other chemicals were analaR grade (Merck, Fluka or similar).

Voltammetric measurements were performed with a Princeton Applied Research 273A potentiostat. A PAR 303A mercury electrode in hanging drop mode was used as working electrode. Platinum wire was used as counter electrode. N$_2$ was used to degas the solution in the cell; gas flow was maintained above the solution to prevent O$_2$ reabsorption. All measurements were performed at 25 ± 1 ºC.

3. Results and Discussion

The electric signal obtained in adsorptive stripping voltammetry is the result of the application of a two-step procedure. The first one is a preconcentration step performed at constant potential for a fixed adsorption time, t_{ads}. In the case of Pd(II) determination preconcentration is performed at -0.3 V [25] and corresponds to the adsorption of Pd(HDMG)$_2$ from the solution. It is required that all species in the solution be in thermodynamic equilibrium. At the end of this preconcentration step the surface and bulk concentration, Γ and C respectively, are related by [32]:

$$\Gamma = k_{ads} \, C \, t_{ads} \qquad (1)$$

where k_{ads} is an adsorption rate constant.

At the second step, a linear sweep is applied (LSV) and potential is scanned in negative direction. A current peak is obtained due to the reduction of the adsorbed specie and is directly related to its surface concentration, Γ. At low coverage, preadsorbed Pd(HDMG)$_2$ leads to a single well defined voltammetric peak [32, 33]. Under this surface condition the voltammetric response is typical of an irreversible surface redox process, being the peak current, i_p, proportional to the surface concentration [33]:

$$i_P = \frac{F}{eRT} \nu Q = \frac{nF^2}{eRT} \nu \Gamma \qquad (2)$$

where F, R, T and e have the usual meaning, ν is the potential sweep rate and Q is the charge transferred from the electrode and obtained by integration of the voltammetric current. As long as Γ is proportional to the bulk concentration, then i_p as well as Q are expected to be a measure of the bulk complex concentration, although usually i_p is preferred over Q in electroanalysis. As has been stated, equation 2 is valid as long as the condition of low surface coverage is fulfilled. However as Γ increases equation 2 may no longer be valid, especially when interactions among adsorbed molecules become relevant. In fact, these interactions modify the characteristics of the surface redox process [23, 33].

Considering that solution thermodynamic equilibrium and adequate surface conditions are required, two basic aspects need to be considered from an analytical point of view. First, the kinetics of homogeneous complexation affects the whole dynamic range. Second, the complex solubility in the buffer solution and the characteristics of the surface process influence the upper limit of the dynamic range. These features may also affect the sensitivity.

3.1. *Homogeneous complexation and complex solubility*

Slow Pd(HDMG)$_2$ homogeneous formation kinetics is reflected in the fact that the peak current slowly increases after the addition of Pd(II) to a solution containing H$_2$DMG in the buffer (Figure 1). This proves that under our experimental conditions chemical equilibrium is not quickly established.
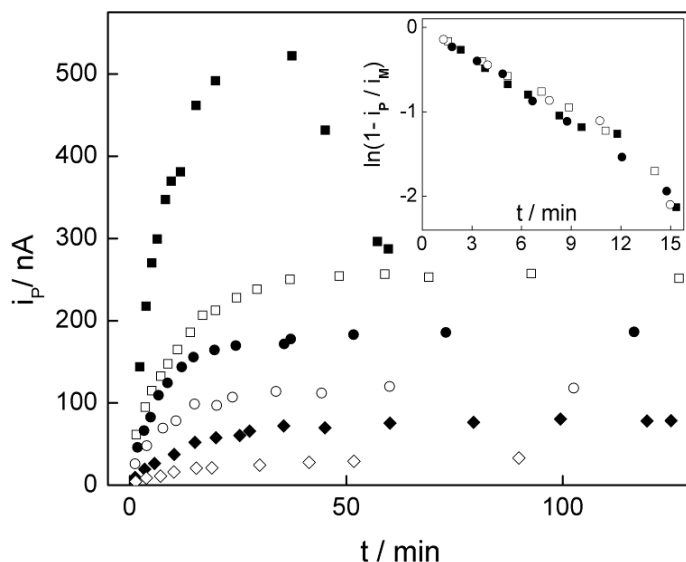

Figure 1. Evolution of peak current after addition of palladium to an acetate buffer (pH 4.85) solution containing 1×10^{-4} M H$_2$DMG. Total palladium concentration: (◊) 2.6×10^{-7} M, (◆) 5.3×10^{-7} M, (○) 8.2×10^{-7} M, (●) 1.1×10^{-6} M, (□) 2.1×10^{-6} M and (■) 4.3×10^{-6} M. The insert shows that peak current results fit a first order kinetics. i_M represents the maximum value of peak current obtained from each curve.

The kinetics of the formation of the complex was studied. In a first set of experiments different total Pd(II) concentrations were used, C_0, while H$_2$DMG concentration remained unchanged (1×10^{-4} M). Once the homogeneous chemical equilibrium is reached the complex concentration in the solution must be practically equal to nominal Pd(II) concentration because of the non-complexing nature of the buffer, the pH and the stability constant of Pd(HDMG)$_2$. A pseudo-first order kinetic law was obtained. Thus the concentration of the complex in the solution is given by:

$$C(t) = C_0 [1 - \exp(-kt)]$$

where k is the pseudo-first order kinetic constant. Thus, in our experiments $k = k_1$ [H$_2$DMG] remains practically unchanged throughout the experiments. $k = 0.09$ min^{-1} is obtained as a mean value in our experimental conditions (Figure 1). This value assures that more than 99.5 % of the reaction has been completed in an hour regardless of the total palladium concentration. Consequently, a chemical

equilibration time must be carefully considered when applying this method. In our case, for $[H_2DMG]$ = 1×10^{-4} M, this time is ca. 1 hour.

In a second set of experiments H_2DMG concentration was varied from 1×10^{-4} M to 3×10^{-4} M while total Pd(II) concentration remained unchanged (1.1 μM). As can be observed in Figure 2 results of the second set of experiments can be fitted to a pseudo first order kinetics. Furthermore i_p slowly increases reaching always the same steady value. This fact is not surprising since peak current (i_p) should not depend on H_2DMG concentration as long as Pd(II) is the limiting reactant. However, in previous papers where complexation kinetics was not considered, steady value was not observed and a H_2DMG concentration effect was reported [25, 27].
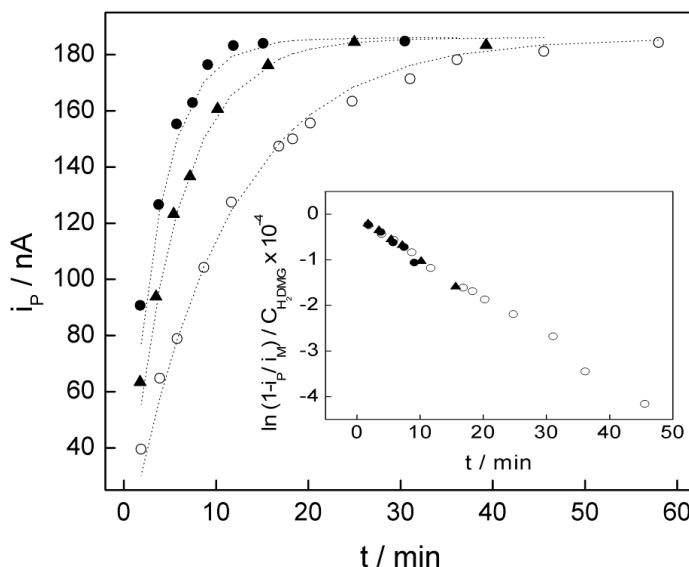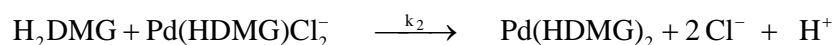

Figure 2. Evolution of peak current after addition of dimethylglyoxime to an acetate buffer (pH 4.85) solution containing 1.1×10^{-6} M Pd(II). Total H_2DMG concentration: (O) 1×10^{-4} M, (▲) 2×10^{-4} M and, (●) 3×10^{-4} M. The insert shows that peak current results fit a first order kinetics. i_M represents the maximum value of peak current obtained from each curve.

Finally, the complexation reaction results to be first order in both reactants, Pd(II) and H_2DMG.

Ellefsen and Gordon [34] have proposed that complex formation involves two kinetic steps:

$$H_2DMG + PdCl_4^{2-} \xrightarrow{k_1} Pd(HDMG)Cl_2^- + 2\,Cl^- + H^+$$

$$H_2DMG + Pd(HDMG)Cl_2^- \xrightarrow{k_2} Pd(HDMG)_2 + 2\,Cl^- + H^+$$

where the first reaction is the rate determining step. $Pd(HDMG)Cl_2^-$ was postulated as an intermediary product. This mechanism is in agreement with our experimental results. In our case $PdCl_4^{2-}$ is initially present since $PdCl_2$ is dissolved in concentrated HCl when preparing standard solutions.

Also complex solubility has been considered. During stabilization and for the highest palladium concentration used in this study (Figure 1) the peak current slowly decreases after reaching a maximum. This effect may be explained by the aggregation of molecules of the complex in the solution prior to precipitation. However this phenomenon was not visually noticed.

Complex solubility ca. 2.5 μM can be estimated from studies of the precipitation from homogeneous solution [35]. This solubility value is consistent with our results. Thus, while i_p clearly diminishes for $C_o = 4.2$ μM during chemical equilibration, it exhibits a constant value for $C_o = 2.1$ μM. The signal increment above the steady value could be originated in the tendency to supersaturation [35]. Thus solubility establishes the upper limit of the analytical window in Pd(II) determination.

3.2. *Characteristics of the surface process*

Preadsorbed $Pd(HDMG)_2$ undergoes an irreversible reduction process when potential is scanned in negative direction (Figure 3). A single asymmetric peak is obtained and no anodic peak is observed. The peak potential, E_P, is linearly dependent on the logarithm of the scan rate, $\ln(v)$, for constant adsorption time and scan rates within the range $0.010 - 25$ V s^{-1}. A shift towards more negative values is observed when incresing adsorption time.

An interesting effect is the significant narrowing of the voltammetric peak when Q approaches 38 μC cm^{-2}. The comparison of peaks in Figure 3 shows that while Q increases almost two times, peak current increases almost 12 times. This behaviour is the consequence of interactions between adsorbed molecules. Interactions become evident as surface charge approaches the redox charge of a monolayer (ca. 38 μC cm^{-2}), value that can be overcome since adsorbed molecules can build up a multilayer [33]. Peak widths from a number of experiments (for different adsorption times and Pd(II) concentrations) are summarized in the Figure 3. Each datapoint in that plot has been obtained from experiments where different adsorption times and solution concentrations were used, thus exploring different Γ; despite this differences, all datapoints lie in the same curve. Thus, our results are good evidence that in this system peak width depends exclusively on surface coverage (which is equivalent to the measured Q).
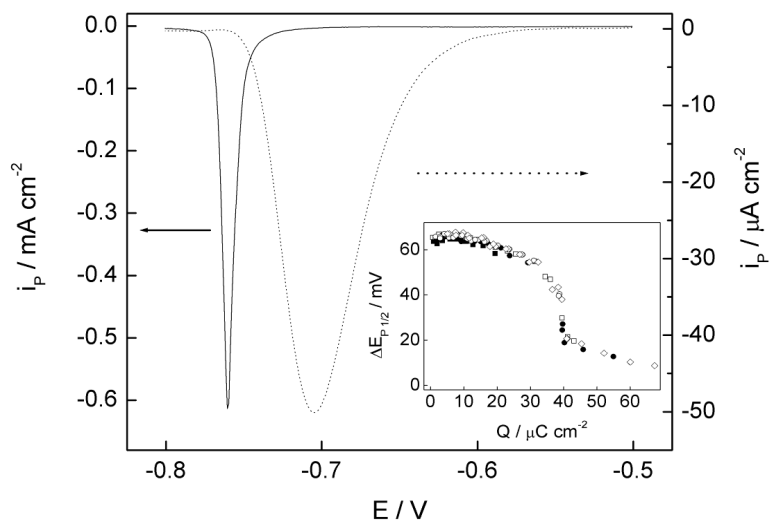

Figure 3. Voltammetric response of Pd(HDMG)$_2$ adsorbed on mercury at -0.3 V for C$_o$ = 1.1 μM. Adsorbed charges Q$_1$(t$_{ads}$ 240 s) = 31 μC cm^{-2} (dot line) and Q$_2$(t$_{ads}$ 720 s) = 72 μC cm^{-2} (solid line). Insert: Behaviour of half peak width with increasing adsorbed charge. Total palladium concentration: (■) 2.6 × 10^{-7} M, (□) 5.3 × 10^{-7} M, (●) 8.2 × 10^{-7} M, (O) 1.1 × 10^{-6} M, (◊) 2.1 × 10^{-6} M.

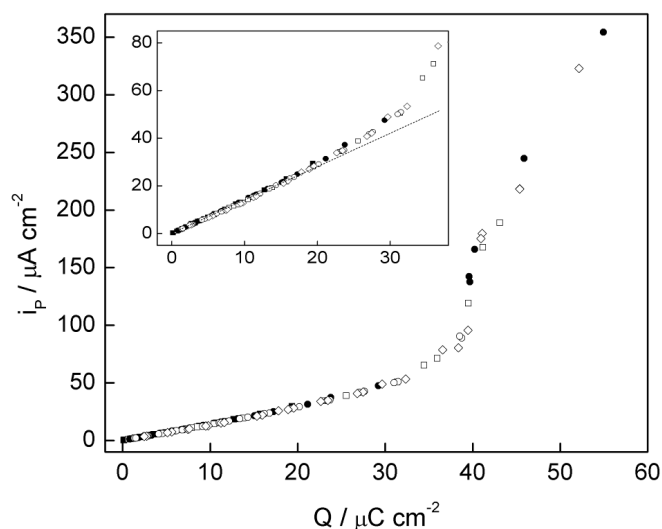**Figure 4.** Peak current vs adsorbed charge. Total palladium concentration: (■) 2.6 × 10^{-7} M, (□) 5.3 × 10^{-7} M, (◇) 1.1 × 10^{-6} M, and (●) 2.1 × 10^{-6} M. Acetate buffer solution (pH 4.85), 1 × 10^{-4} M H$_2$DMG, 0 < t$_{ads}$ < 600 s.

The effect of surface interactions on i$_p$ and Q is explored. Plot of experimental results of i$_p$ obtained for a set of concentrations and t$_{ads}$ (Figure 4) show again all datapoints lying in the same

curve, which is a clear demonstration that the correlation between i_p and Q does not depend on such variables. The linear relationship between them as proposed in equation 2 is lost for high surface concentrations regardless of adsorption time. This limit can be set at ca. 25 μC cm^{-2} (Figure 4). Changes in peak shape as charge increases with the consequent loss on i_p-Q linearity point to the fact that i_p and Q may not be equally valid as analytical signal in a wide range of concentrations.

Calibration curves were built measuring both i_p and Q for three t_{ads}: 600 sec (Figure 5) and 180 and 60 sec (Figure 5). Linear plots were obtained for t_{ads} 60 and 180 sec. It is interesting to point out that measured Q values did not exceed 25 μC cm^{-2}. The slopes of Q *vs* C can be converted to i_p *vs* C by a factor equal to 1.43 s^{-1}, as predicted by equation 1. In the case of the t_{ads} 600 sec, where Q exceeds 25 μC cm^{-2}, linearity of both signals is only observed in the low zone of the curve. Comparing both surface conditions it can be concluded that the departure from linear behaviour is more critical in the case of i_p vs C plot and that Q seems to allow an extension of linear behaviour up to 30 μC cm^{-2} at the cost of a smaller slope.
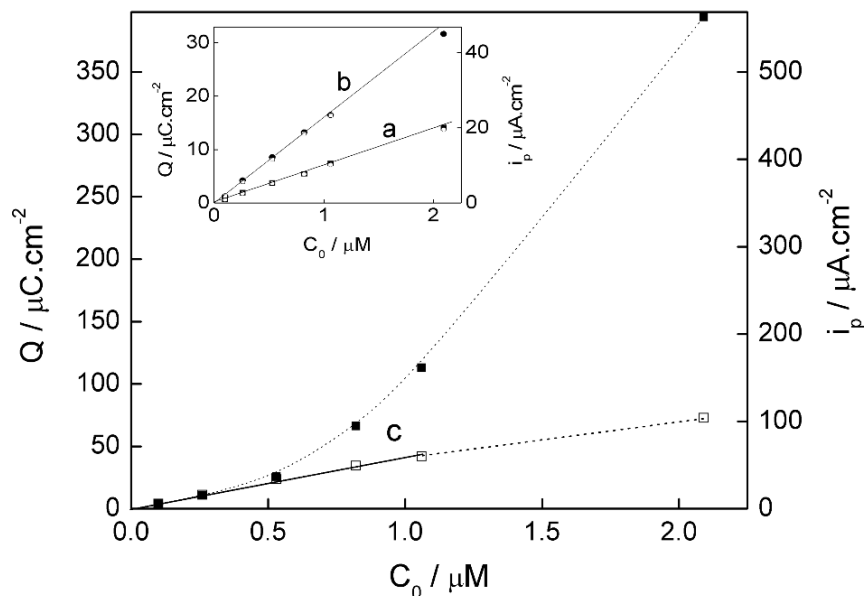

Figure 5. Calibration plots for three different adsorption times. a) 60 s, b) 180 s and c) 600 s. (■) peak current (right y axes); (□) Charge (left y axes).

It is clear that molecular interactions between adsorbed molecules are relevant, and that they affect the linearity of the analytical signal. Thus it is important to pay attention to Q, which should not exceed 30 μC cm^{-2}, below Q obtained for monolayer formation [33]. Considering that Q should be monitored to avoid the effects previously described and that it allows extending the linear behavior to a wider range of concentrations, we favor Q as the analytical signal when experimental conditions require reaching high Q conditions.

Sensitivity (S) is given by the slope of a plot of the analytical signal as a function of analyte concentration. For any analytical procedure, S needs to be adequate for the particular determination. In the low Q region it is adequate to choose i_p since it is more sensitive than Q as can be observed in Figure 5. However in the high Q region the maximum sensitivity is conditioned by the range of solution concentrations to be explored (Figure 6).

S_Q and S_I correlate adsorbed charge or peak current and concentration respectively. Considering the linear relationship between Q and adsorption time observed for low adsorbed charges (data not shown), the following expression can be derived from equation 1:

$$S_Q = \frac{dQ}{dC} = nF k_{ads} t_{ads} \qquad (3)$$

and from equation 2:

$$S_{IP} = \frac{dI_P}{dC} = \frac{nF^2}{eRT} v k_{ads} t_{ads} \qquad (4)$$

Conversion of S_Q into S_{IP} can be done considering equations 3 and 4. From both equations S_{IP} = S_Q 14.3 ν s^{-1}, (ν = 0.1 V s^{-1}). Thus the conversion factor is 1.43 in agreement with our previous observation.
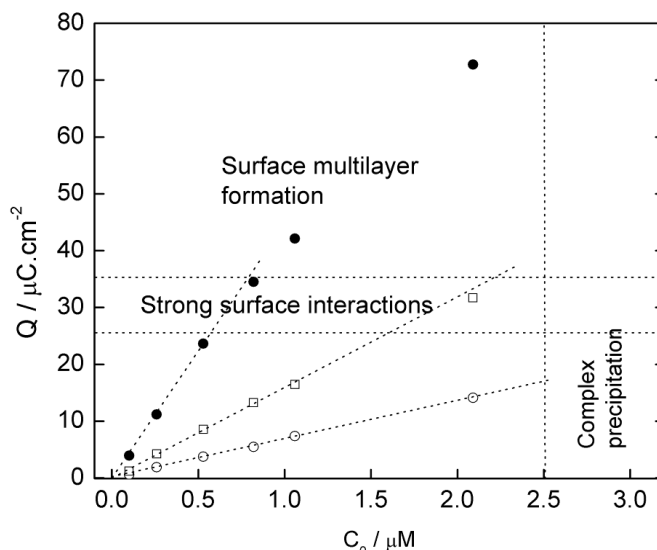

Figure 6: Scheme showing the accesible region of Q and C_o for the determination of Pd(II). t_{ads}: 60 s (O), 180 s (□) and 600 s (●). An increase in t_{ads} favours the sensitivity of the determination, but also the linear range is reduced.

It is evident that if sensitivity needs being improved, longer adsorption times can be used. However, it must be kept in mind that Q should not exceed 30 μC cm^{-2} during the quantification procedure to avoid deviations due to strong surface interactions.

As has been shown through eq. 3 and 4, no matter whether using Q or i_p, sensitivity is clearly limited by Γ. However if sensitivity needs to be improved, it is possible to use a nonlinear potential scan, like square wave voltammetry (SWV), differential pulse voltammetry, etc, during measurement (second step of the procedure). Recently, SWV was applied for palladium determination at a mercury film deposited on a silver electrode ((Hg(Ag)FE) [27]. The use of SWV instead of LSV increased peak current by a factor of ca. 10. After 60 s adsorption at -0.45 V in acetate buffer solution (pH 4.4) containing 50 mg/L Pd(II) and 2×10^{-4} M DMG Ip = 8.8 μA and 1 μA were obtained for SWV (ΔE = 20 mV, f = 100 Hz, step increment = 2 mV) and LSV (ν: 0.020 V s^{-1}) respectively [27]. Comparison of our sensitivity results (ν: 0.1 V s^{-1}) to the sensitivity calculated from the calibration plot [27] also yields a factor ca. 10 in favor of SWV.

As a summary, applicability of adsorption combined with any kind of potential perturbation (LSV, SWV, DPP) depends on two conditions. The first one derives from variables related to the homogeneous phase: solution concentration and chemical equilibration time. The second condition is related to the surface, specifically surface concentration. Solution and surface concentration limits are reflected in Figure 6.

4. Conclusions

Relevant parameters for Pd(II) quantification have been identified. Proper chemical equilibration should be attained before measurement. Solution and surface concentrations are critical because they render the charge transferred due to the reduction of adsorbed Pd(DMGH)$_2$. Strong surface interactions are evidenced in the electrochemical response as surface coverage is close to the monolayer formation. They strongly affect i_p signal. For this reason it is more convenient to use Q as the analytical signal when experimental conditions require reaching the high Q conditions not exceeding 30 μC cm^{-2}. Upper limit for the solution concentration is 2.5 μM to avoid precipitation of the complex.

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