

Cyclic voltammetric, EQCM and impedance study of the 1-octanol- β -cyclodextrin-electrodeposited platinum system in perchloric medium

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Abstract

The system of 1-octanol- β -cyclodextrin in 0.5 M HClO₄ at Pt electrodeposited on an Au/quartz crystal (Pt/Au/Q) has been studied by cyclic voltammetry (CV), the electrochemical quartz crystal microbalance (EQCM) and impedance measurements. β -Cyclodextrin (β -CD), a cyclic oligomer of seven α -D-glucopyranose units, was chosen for this study because it forms an inclusion complex with primary alcohols and because of its hydrophilic exterior. Previous cycling in 1-octanol profoundly affected ("aged") the electrodeposited Pt, as is readily seen in subsequent CVs and mass curves in 0.5 M HClO₄. Since adsorbed 1-octanol and β -CD would tend to render the Pt surface hydrophobic and hydrophilic, respectively, these opposite tendencies should be detectable by the EQCM. Effectively, in a positive potential scan, 1-octanol and β -CD added at -0.22 V produced a mass decrease and increase, respectively, of aged Pt/Au/Q, owing to a decrease and increase of the amount of adsorbed water and/or ions, which was attributed to physisorption of these compounds. With freshly deposited Pt/Au/Q, 1-octanol added at open circuit produced a mass decrease over the whole potential cycle, again evidence of adsorption of a hydrophobic compound.

The potential at which the aged Pt/Au/Q electrode immersed in an 1-octanol solution was held while β -CD was added to the electrolyte crucially affected the subsequent voltammogram and mass curve. If β -CD and 1-octanol were added together at -0.22 V, the current in a subsequent positive scan was the same as in 1-octanol added at -0.22 V, but the mass was higher, both at -0.22 V and over the whole positive scan. This mass increase was probably due to physisorption (since the current was unaffected) of the inclusion complex, since β -CD alone did not affect the mass at -0.22 V. On the contrary, if β -CD was added at open circuit to an electrolyte already containing 1-octanol, also added at open circuit, both the H desorption and Pt oxidation currents were lower than in 1-octanol, indicating a strong interaction of β -CD with the Pt surface, and the mass was also lower over most of the positive scan. Most probably this strong interaction of β -CD involves adsorbed residues formed in the dissociative chemisorption of 1-octanol at open circuit.

Keywords: 1-Octanol electrooxidation; β -Cyclodextrin; EQCM; Platinum electrode

1. Introduction

The understanding of the poisoning of the electrode surface during the electrooxidation of organic compounds is of crucial importance due to its relevance in

the development of new materials and/or new combustibles for fuel cells. It is usually accepted that the oxygen atoms required for the formation of oxygenated species in the electrooxidation of organic molecules arise, not from water in solution, but from surface metal oxides, formation of which necessarily involves H₂O molecules, which have to compete for the electrochemical surface sites with the anions of the electrolyte, the organic molecule and, in the case of dissociative chemisorption of the organic compound, some or all of its dissociation products [1].

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In previous studies it was found that C4 to C8 primary alcohols [2] can physisorb on electrodeposited Pt, physisorption increasing with the alcohol size, in parallel with the decrease of its solubility in water (i.e., increasing hydrophobicity). One way of changing the adsorption of an alcohol is by addition of other species such as cyclodextrins (CDs), which are cyclic oligomers of six, seven, or eight α -D-glucopyranose units, denoted as α , β and γ CDs, respectively. Their molecular structures resemble a “truncated cone” with a relatively non-polar cavity as compared with water, while the exterior is hydrophilic [3]. The most used cyclodextrin is β -CD, due to the size of its cavity (0.78 nm internal diameter and 0.78 nm height) [4] and its electrochemical stability [5]. CDs are also known for their ability to form inclusion complexes with a variety of guests [6–8], especially with n -alcohols, since the cavity of β -CD is somewhat larger than the diameter of the methyl group, 0.4 nm [9].

Hydrophobic interactions play a significant role in the complexation. Thus, with data from [10], we have found that there is a linear correlation between the log of the formation constant of the inclusion complexes of β -CD with the alcohol, K_a , and the number of carbon atoms in the alcohol, Z , as follows: $\log K_a = -0.694 + 0.495Z$. For these complexes ΔH and ΔS are both positive, indicating a predominance of the entropy factor, as is characteristic of systems with hydrophobic interactions [10]. While 1-butanol and 1-pentanol are completely inside the CD cavity, the polar head of 1-hexanol and longer alcohols would stick outside the CD cavity [10].

In the electrochemical quartz crystal microbalance (EQCM) experiments, mass changes and the corresponding cyclic voltammograms (CVs) are obtained simultaneously, which in many cases gives an insight into the phenomena occurring at the interface [11]. In this work we have used the EQCM to study the adsorption of 1-octanol, a very sparingly (about 2 mM) soluble molecule, in the presence and absence of β -CD, with the aim of understanding the role of a large molecule, β -CD, in the structuring of the interface. Since adsorbed 1-octanol and β -CD would tend to render the Pt surface hydrophobic and hydrophilic, respectively, these opposite tendencies should be detectable by the EQCM. The results obtained, together with impedance measurements, allowed some insight into the effect of β -CD on the 1-octanol-Pt system.

2. Experimental

2.1. Reagents and equipment

Solutions were prepared by injection with a syringe of the required volume of 1-octanol (Aldrich, analytical grade) and/or β -CD (Merck, for Biochemistry) aqueous

solution(s) in the 0.5 M HClO₄ supporting electrolyte. All the solutions were freshly prepared with twice distilled water (conductivity near 2 μ S cm⁻¹). The experiments were carried out at room temperature under a nitrogen atmosphere.

An electrochemical quartz crystal microbalance (EQCM-501-Elchema) with 10 MHz AT-cut quartz oscillators, together with an Elchema PS 205 potentiostat with suitable software for fully automated control of the experiments and data acquisition, was used. The calibration constant was $dm/df = 4.4 \text{ ng cm}^{-2} \text{ Hz}^{-1}$.

The impedance spectra in the frequency range between 10⁴ and 10⁻² Hz were recorded at selected constant potentials with an Autolab frequency response analyzer, using a 10-mV rms sinusoidal modulation. An SCE was used as the reference electrode, the contact with the solution being effected through a Luggin capillary with a Pt-Pyrex seal.

2.2. Electrodes

Black Pt/Au/Q electrodes were obtained by Pt electrodeposition at 1 mA cm⁻² from 2 mM H₂PtCl₆ (Aldrich, about 10% acid solution) in 0.5 M H₂SO₄ on the Elchema 10 MHz AT-cut Au/Q quartz crystal supplied with a thin film of gold deposited on both sides (0.25 cm² geometric area for voltammetry and 0.24 cm² for mass change measurements). The mass electrodeposited (near 7 μ g) was controlled by the EQCM, and the roughness factor (R_F) of the Pt/Au/Q electrodes was calculated from the hydrogen desorption charge, taking a value of 0.224 mC cm⁻² for the H monolayer [12,13]. With the exception of the electrode used for the CVs shown in Fig. 2, in all cases, the electrodeposited Pt/Au/Q electrodes had already been cycled in the presence of 1-octanol, which considerably changed their CVs and mass curves, and these electrodes are, hereafter, referred to as aged electrodes. They were subjected to 10 repetitive cyclic voltammograms (RCV) in 0.5 M HClO₄ prior to each experiment, which very much improved the reproducibility of the results. Bright Pt/Q electrodes (with the same geometric area as Au/Q) and Pt wire electrodes (0.24 cm² geometric area, $R_F = 5.5$), both supplied by Elchema, were also used. Current densities and mass changes are referred to the geometric area. Potentials were measured against, and are referred to, a saturated calomel electrode (SCE).

3. Results

3.1. Voltammetric determination of the formation constant of the 1-octanol- β -cyclodextrin inclusion complex

As noted above, β -CD forms an inclusion complex with 1-octanol [10]. Zhao et al. [14] deduced the fol-

lowing equation for cyclic voltammetry and differential pulse voltammetry, based on the equation for current titration:

$$\frac{1}{c} = K \frac{(1-A)}{1-I/I_0} - K, \quad (1)$$

where c is the concentration of β -CD, K is the apparent binding constant, I_0 and I are the peak currents of 1-octanol electrooxidation in the absence and presence of β -CD, respectively, and A is a constant. This equation applies only if a 1:1 association complex is formed and if the concentration of β -CD is much larger than that of 1-octanol.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out with smooth platinum electrodes in a 1 M HClO₄ solution, 1 mM in 1-octanol and with β -CD concentrations between 0 and 6 mM. Similar results were obtained with both techniques. Fig. 1 shows the DPV curves (Fig. 1(a)), where only one peak of 1-octanol electrooxidation near 1.0 V is observed. The plot of $1/c$ vs. $1/(1-I/I_0)$ (Fig. 1(b)) obtained with these DPV data yields a straight line with an intercept $-K = -550 \pm 130 \text{ M}^{-1}$, which is 39% higher than the value of 396 M^{-1} obtained by non-electrochemical methods [15].

3.2. Cyclic voltammetry and mass curves of electrodeposited Pt/Au/Q electrodes

3.2.1. Cyclic voltammetry and mass curves of a fresh Pt/Au/Q electrode in the absence and presence of 1-octanol admitted at open circuit

CVs and mass curves recorded at 0.02 V s^{-1} with a fresh Pt/Au/Q electrode, $R_F = 12.7$, in 0.5 M HClO₄ without (dashed line) and with 2 mM *n*-octanol (solid

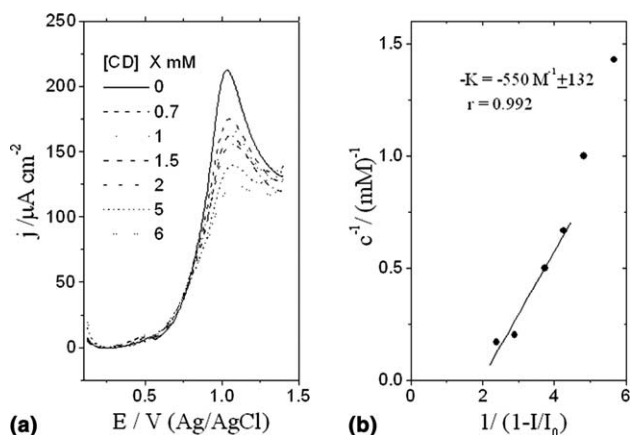
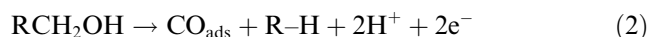


Fig. 1. (a) Differential pulse voltammetry of a smooth Pt electrode in 1 M HClO₄ + 1 mM octanol + 0–6 mM β -CD. (b) Plot of the reciprocal of the β -CD concentration, c , vs. $1/(1-I/I_0)$ (where I_0 and I are the peak currents in the absence and presence, respectively, of β -CD), which allows the apparent binding constant of the 1-octanol- β -CD inclusion complex to be obtained.

line) admitted at open circuit are shown in Fig. 2. The experiment in 0.5 M HClO₄ was recorded after 10 potential cycles, in order to obtain a reproducible CV. After this, 1-octanol was added at open circuit and the first experiment was recorded.

The CV in 0.5 M HClO₄ is typical of polycrystalline Pt, with a $Q_{\text{ox}}/Q_{\text{H}}$ ratio of 2.2. In 1-octanol, a small anodic peak appeared at 0.0 V (Fig. 2(a)). It is due to the electrooxidative dehydrogenation of physisorbed 1-octanol, yielding a chemisorbed species, probably CO, according to the reaction of primary alcohols [2,16]:



With electrodeposited platinum electrodes, as is the case here, this reaction of primary alcohols occurs even with alcohol addition at open circuit, but with smooth Pt electrodes this peak is observed only if the alcohol is added at a controlled potential of -0.22 V (about 0 V vs. the reversible hydrogen electrode) [2].

The onset potential of the anodic current in the Pt oxide region was shifted positively by 1-octanol, indicating that the adsorbed alcohol inhibited the electrooxidation of Pt. This inhibition of the Pt oxidation could be partly responsible for the decrease of the platinum oxide reduction current observed in the negative scan (Fig. 2(a)), which, however, should stem mainly from the simultaneous occurrence of Pt oxide electroreduction and 1-octanol electrooxidation, or from the chemical reduction of the Pt oxide by the alcohol as proposed by Chen and Schell [17] in order to explain the excitability (large changes brought about by small perturbations) they observed in the electrooxidation of primary alcohols on Pt. Effectively, the mass

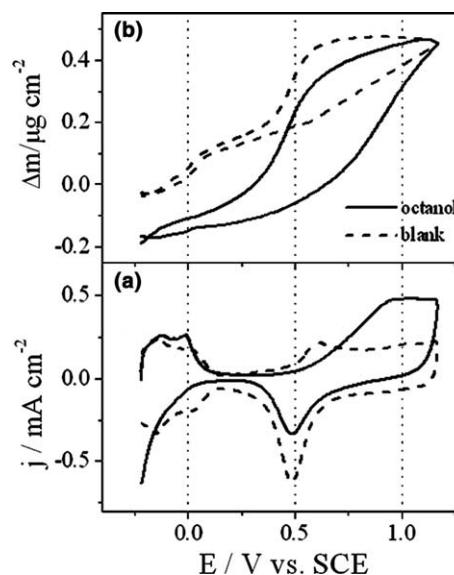


Fig. 2. First scan at 0.02 V s^{-1} of a freshly electrodeposited Pt/Au/Q electrode in 0.5 M HClO₄ in the presence (solid line) and the absence (dashed line) of 2 mM 1-octanol added at open circuit. (a) Cyclic voltammograms. (b) Simultaneously recorded mass changes. $R_F = 12.7$.

decrease observed upon alcohol injection at constant potential [2] clearly shows that 1-octanol chemically reduces at least a fraction of the Pt oxide.

The mass curves are closed both in the absence and presence of 1-octanol (Fig. 2(b)), i.e., no irreversible changes occur in the Pt electrodeposit. Furthermore, in 0.5 M HClO₄ the mass increase between 0.60 V (inflexion in the positive scan) and the positive potential limit is the same as the mass decrease between the positive potential limit and the first inflexion point in the negative scan at 0.39 V, indicating that apparently only the oxidation and reduction of Pt affect the mass curves in this potential region. (This is not the behaviour of *aged* electrodes, as will be shown below). However, the ratio $\Delta m_{\text{O}}F/Q_{\text{O}}$, where Δm_{O} is the mass increase in the Pt oxidation region, Q_{O} the number of moles of electrons transferred in the same region and F Faraday's constant, is 4.4, much lower than the theoretical value of 8.0 g per mole of electrons corresponding to the formation of anhydrous PtO or PtO₂, as has been found experimentally to be the case for sputtered Pt films in 0.1 M NaOH [18].

In the presence of 1-octanol, the mass increase in the Pt oxide region is also nearly the same as the mass decrease in the negative scan down to the first inflexion point (solid line in Fig. 2(b)), which again would seem to indicate that the mass curves in this region also reflect mainly the oxidation and reduction of Pt. However, the mass increase in 1-octanol is *twice* that in 0.5 M HClO₄ and it is difficult to envisage a mechanism by which 1-octanol could enhance the oxidation of Pt. The ratio $\Delta m_{\text{O}}F/Q_{\text{O}}$ in 1-octanol, 5.0, is about the same as in base electrolyte, since the relative increase of the mass and the charge in the Pt oxidation region is about the same. Therefore, we come to the conclusion that 1-octanol decreases the adsorption of water and/or ions on a *fresh* Pt electrodeposit *over the whole potential range* between hydrogen evolution and oxygen evolution, this decrease of the adsorption of water being most probably due to the physisorption of 1-octanol. The mass decrease is highest in the double layer region, as was to be expected for the physisorption of a neutral molecule, and be-

comes progressively lower with increasing oxidation of the Pt surface.

The very small mass increase at 0.0 V in the positive scan (Fig. 2(b)) is probably due to the adsorption of the small amount of CO produced in the anodic peak at 0.0 V.

In order to allow a quantitative comparison of CVs and mass curves reported here, in Table 1 we show the following magnitudes for each experiment: charge density of hydrogen desorption in the positive sweep, Q_{H} ; roughness factor, R_{F} , obtained with a value of 224 $\mu\text{C cm}^{-2}$ for a hydrogen monolayer; charge density in the Pt oxide region in the positive sweep, Q_{O} ; ratio of the oxygen to the hydrogen charge density, $Q_{\text{O}}/Q_{\text{H}}$; and the mass increase per mole of electrons transferred in the Pt oxide region, $m_{\text{O}}F/Q_{\text{O}}$.

3.2.2. Cyclic voltammetry and mass curves of aged Pt/Au/Q electrodes in the absence and presence of 1-octanol admitted at open circuit

As is well known [2], already one potential cycle in the presence of 1-octanol profoundly affects electrodeposited Pt/Au/Q electrodes, "aging" them in two ways: the hydrogen charge decreases by about one-half and the final mass after one potential cycle is higher than the initial mass, even in 0.5 M HClO₄. The Pt oxide region was completely anomalous, both in shape and in the $Q_{\text{ox}}/Q_{\text{H}}$ ratio, which was 4.0 and 4.5 at 0.1 and 0.02 V s^{-1} , respectively. The same aging also appears after cycling in 0.5 M HClO₄, but only after prolonged potential cycling [13]. Similarly, Gloaguen et al. [19] found that a few cycles up to 1.2 V vs. RHE completely changed the mass curve of electrodeposited Pt in the H region.

Fig. 3 shows the CVs and mass curves obtained in the first scan for an aged (by 10 potential cycles in 0.5 M HClO₄) Pt/Au/Q electrode at 0.10 V s^{-1} (a and c) and at 0.02 V s^{-1} (b and d) in 0.5 M HClO₄ (dashed line) and in a 2 mM 1-octanol + 0.5 M HClO₄ solution (solid line), the octanol having been added at open circuit after one CV in 0.5 M HClO₄ at the same scan rate. The $Q_{\text{O}}/Q_{\text{H}}$ ratio was 4.0 and 4.5 at 0.10 and 0.02 V s^{-1} , respectively, indicating a decreased hydro-

Table 1
Parameters obtained from the cyclic voltammograms appearing in this work

Figure	$Q_{\text{H}}/\text{mC cm}^{-2}$	R_{F}	$Q_{\text{O}}/\text{mC cm}^{-2}$		$Q_{\text{O}}/Q_{\text{H}}$	$(\Delta m_{\text{O}}F/Q_{\text{O}})/\text{g (mole e}^{-})^{-1}$	
			Base	OcOH		Base	OcOH
2	2.89	12.7	6.57	10.5	2.3	4.4	5.0
3(a) (0.1 V s^{-1})	1.05	4.05	4.21	3.11	4.0	6.3	11.5
3(b) (0.02 V s^{-1})	0.88	3.85	4.78	4.62	4.5	6.9	6.6
4	4.35	19.1	12.4	–	2.9	4.0	–
5 and 6	6.39	28.1	10.8	14.3	1.7	3.0	1.7

Q_{H} , charge density of hydrogen desorption; R_{F} , roughness factor calculated from Q_{H} , taking a value of 221 $\mu\text{C cm}^{-2}$ for a hydrogen monolayer on polycrystalline Pt. Q_{O} , charge density of Pt oxide formation; $\Delta m_{\text{O}}F/Q_{\text{O}}$, mass change per mole of electrons transferred in the Pt oxide formation region; and Q_{H} , Q_{O} , and Δm_{O} are referred to the geometrical electrode area.

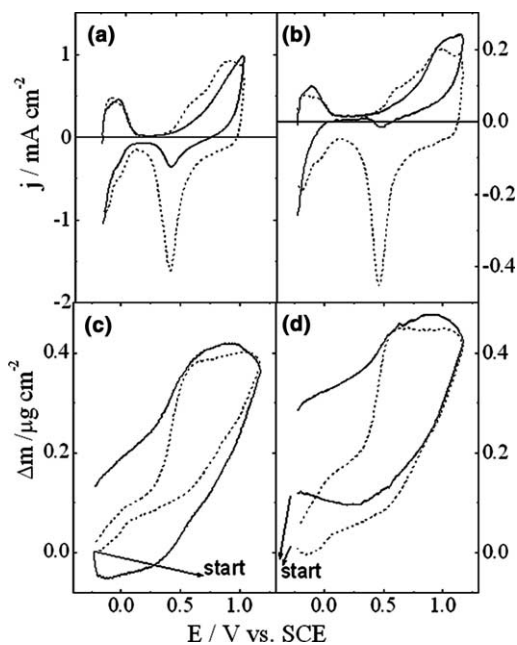


Fig. 3. CVs and mass curves at 0.1 V s^{-1} (a and c) and 0.02 V s^{-1} (b and d) of an aged Pt/Au/Q electrode in 0.5 M HClO_4 (dashed lines) and in a 2 mM (saturated) solution of 1-octanol added at open circuit in 0.5 M HClO_4 after one potential cycle in 0.5 M HClO_4 (solid lines). $R_F = 4.05$ (a and c) and 3.85 (b and d).

gen adsorption in this electrode, as is evident in the CVs of Fig. 3.

Aging did not affect the anodic peak at about 0.0 V in 1-octanol, which appears both with an aged (Fig. 3(a) and (b)) and with a fresh electrode (Fig. 2(a)). However, aging brought about a nearly complete inhibition of the electrooxidation of 1-octanol in the positive scan: at 0.02 V s^{-1} the charge in the Pt oxide region was about the same in 1-octanol as in base electrolyte and at 0.1 V s^{-1} it was even much lower (Table 1). Consequently with this, the current in the negative scan was barely cathodic, especially at the lower scan rate, and only at the potential of the Pt oxide reduction peak. Electroreduction of the alcohol should also contribute to reduction of the cathodic current.

The first-scan mass curves in Fig. 3(c) and (d) were made to coincide at the positive potential limit. With 1-octanol there was an initial mass decrease, extending over a very short potential interval at 0.1 V s^{-1} , but over 0.4 V at 0.02 V s^{-1} . In previous work [2] we reported that this mass decrease at the beginning of the scan increased with the chain length of the alcohol and its concentration, since both would increase physisorption of the alcohol, which displaces water molecules from the interface.

At 0.1 V s^{-1} , during most of the positive scan, the mass of the aged electrode in 1-octanol was lower than that in its absence (Fig. 3(c)), indicating that physisorbed 1-octanol remaining on the surface decreased the adsorption of water and/or anions, as was the case with

a fresh electrode (Fig. 2(b)). In the negative scan, at potentials lower than 0.5 V , the mass in 1-octanol was considerably higher than that in 0.5 M HClO_4 , which could be due to a viscosity increase of the aqueous surface layer, perhaps involving adsorbed residues. The $\Delta m_{\text{O}}F/Q_{\text{O}}$ ratio in base electrolyte was 6.3 , nearer the theoretical value of 8.0 for anhydrous Pt oxide than the value of 4.4 obtained with a fresh Pt electrode deposit (Table 1). The $\Delta m_{\text{O}}F/Q_{\text{O}}$ ratio was much higher, 11.5 , in 1-octanol, due both to the higher mass increase and the lower charge, in the oxide region.

At a scan rate of 0.02 V s^{-1} , the final mass after one potential cycle of the aged Pt/Au/Q electrode was higher than the initial one even in base electrolyte, which is characteristic of aged electrodes, owing to a higher adsorption and/or absorption of water in the negative scan. In the positive scan the initial mass decrease produced by 1-octanol (Fig. 3(d)) was much smaller than that observed at 0.1 V s^{-1} (Fig. 3(c)), and the same occurred for the global mass increase between the positive and negative sweep limits. We cannot offer a reasonable explanation for this marked influence of the scan rate. In the negative scan, at potentials lower than 0.5 V the mass in 1-octanol was considerably higher than that in 0.5 M HClO_4 , as was also the case at 0.1 V s^{-1} . The $m_{\text{O}}F/Q_{\text{O}}$ ratio was 6.9 in base electrolyte, only 14% lower than the theoretical value for anhydrous Pt oxide, and about the same in 1-octanol. As with the mass curves, the influence of the scan rate on the value of the $\Delta m_{\text{O}}F/Q_{\text{O}}$ ratio in 1-octanol is hard to explain.

3.2.3. Second positive scans of aged Pt/Au/Q electrodes in solutions 2 mM in 1-octanol (added at open circuit) and with several concentrations of β -CD (added at open circuit)

The current (Fig. 4(a)) and the simultaneous mass change (Fig. 4(b)) of an aged Pt/Au/Q electrode in the second positive scan (this procedure increased the reproducibility of the mass curves) at 0.02 V s^{-1} in $0.5 \text{ M HClO}_4 + 2 \text{ mM}$ 1-octanol (added at open circuit) + different concentrations ($0, 0.7, 1.5, 2$ and 5 mM) of β -CD (added successively to the 1-octanol solution, each measurement being carried out after 30 min) show that, in the presence of 1-octanol, β -CD produced a large decrease of the current in the Pt oxide formation range (Fig. 4(a)) and, correspondingly, a much lower mass increase of Pt oxide formation (Fig. 4(b)). The positive linear correlation between the anodic charge between 0.3 V and the positive potential limit and the mass at this potential limit had a regression coefficient of 0.89 .

The total mass increase in the positive scan, $(\Delta(\Delta m) = \Delta m_{\text{pos. lim.}} - \Delta m_{\text{start}})$, is plotted in Fig. 4(c) vs. the concentration of β -CD. It can be seen that β -CD hindered the mass increase, which rapidly reached a plateau, indicating that, the higher the concentration of

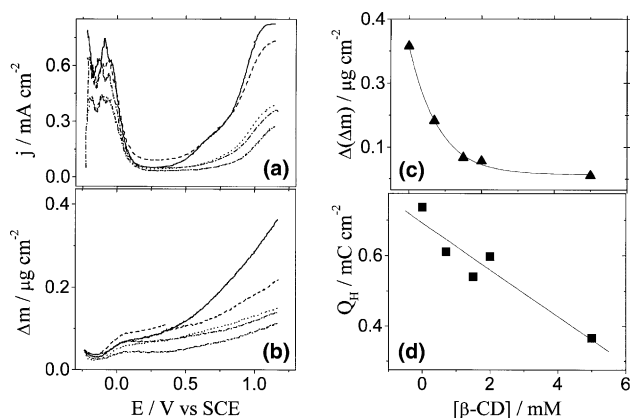


Fig. 4. Current and mass curves obtained in the second positive potential scan at 0.02 V s^{-1} with an aged Pt/Au/Q electrode in $0.5 \text{ M HClO}_4 + 2 \text{ mM 1-octanol} + 0\text{--}5 \text{ mM } \beta\text{-CD}$, both added at open circuit. 30 min were allowed for equilibration after each successive $\beta\text{-CD}$ addition. (a) Current density. (b) Mass change. (c) Mass difference between the final and the initial potential as a function of $\beta\text{-CD}$ concentration. (d) Hydrogen desorption charge as a function of $\beta\text{-CD}$ concentration. In (a) and (b) the concentration of $\beta\text{-CD}$ was 0 (solid line), 0.7 (dashed line), 1.5 (dotted line), 2 (dashed-dotted line) and 5 (dashed-double-dotted line) mM. $R_F = 19.1$.

the $\beta\text{-CD}$ -1-octanol inclusion complex, the greater is the inhibition of the electrooxidation of Pt. Therefore, adsorption of this complex should be mainly responsible for the inhibition of the electrooxidation of Pt. As for the hydrogen desorption charge, it decreased in a roughly linear relationship with increasing $\beta\text{-CD}$ concentration (Fig. 4(d)), which suggests that $\beta\text{-CD}$ itself, and not its inclusion complex, was responsible for this decrease.

The values in base electrolyte of $Q_{\text{O}}/Q_{\text{H}}$ and $\Delta m_{\text{O}}F/Q_{\text{O}}$ of this electrode, 2.9 and 4.0, respectively, were similar to those of a fresh electrode, 2.3 and 4.4, respectively, although the roughness factor of this electrode was 50% higher.

3.2.4. Mass changes at a constant potential of -0.22 V of an aged Pt/Au/Q electrode produced by the addition of 1-octanol and/or $\beta\text{-CD}$, and current and mass curves in a subsequent positive potential scan

In Fig. 5, the evolution with time at a constant potential of -0.22 V of the mass of an aged Pt/Au/Q electrode after addition of 2 mM 1-octanol and/or 1 mM $\beta\text{-CD}$, followed by a positive potential scan, was recorded. After stabilization for 50 s, 1-octanol and/or $\beta\text{-CD}$ was admitted (arrow 1), the solution was stirred by nitrogen bubbling up to 200 s in order to homogenize the electrolyte, and at 240 s (arrow 2) a positive potential scan was started. The initial mass curves in the background electrolyte were made to coincide. The sharp downward spikes in the mass curves are artifacts due to electromagnetic interference.

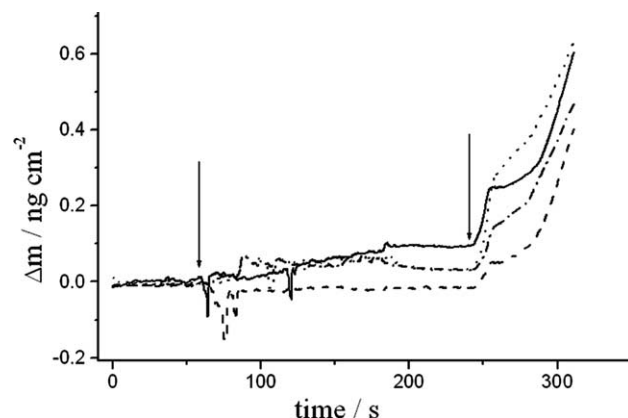


Fig. 5. Mass change as a function of time of an aged Pt/Au/Q electrode. The potential was held at -0.22 V , 2 mM 1-octanol (dashed line), 1 mM $\beta\text{-CD}$ (dotted line), or both (solid line), were added at 50 s, stirring by N_2 bubbling was effected between 50 and 200 s, at which time stirring was stopped, and at 240 s a positive potential scan at 0.02 V s^{-1} , during which current and mass curves were recorded, was started. The mass change in the background electrolyte, 0.5 M HClO_4 , is also included (dashed-dotted line).

3.2.5. Mass changes of an aged Pt/Au/Q electrode at a constant potential of -0.22 V

It should be noted that, even in the 0.5 M HClO_4 base electrolyte, N_2 stirring produced an apparent mass increase of the electrode, which disappeared, but only partially, upon cessation of stirring (dashed-dotted line in Fig. 5). The behaviour of the mass upon addition of $\beta\text{-CD}$ (dotted line in Fig. 5) was basically the same as in base electrolyte, indicating that $\beta\text{-CD}$ did not adsorb or interact with aged Pt at -0.22 V . With 1-octanol the mass was slightly lower than in 0.5 M HClO_4 , which should be due to some physisorption with displacement of water molecules (dashed line in Fig. 5). On the contrary, with 1-octanol + $\beta\text{-CD}$, the mass increased linearly with time during the whole stirring period, from 90 to 200 s, and did not decrease when the stirring was stopped at 200 s (solid line in Fig. 5). Probably this mass increase was due to the adsorption of the $\beta\text{-CD}$ -1-octanol inclusion complex, perhaps through the OH group of 1-octanol.

3.2.6. Cyclic voltammograms and mass curves of an aged Pt/Au/Q electrode recorded after the potential hold at -0.22 V

In Fig. 6, the same mass curves of the positive potential scan of Fig. 5, together with the corresponding current curves, are plotted as a function of the potential. The CV of the aged Pt/Au/Q electrode in 0.5 M HClO_4 was similar to that of a polycrystalline Pt electrode, with a $Q_{\text{ox}}/Q_{\text{H}}$ ratio of 1.8.

The mass in 1-octanol (dashed line in Fig. 6(b)) was lower than that in 0.5 M HClO_4 (dashed-dotted line in same figure) over the whole potential range, as was also the case with a fresh Pt/Au/Q electrode (Fig. 2), and over

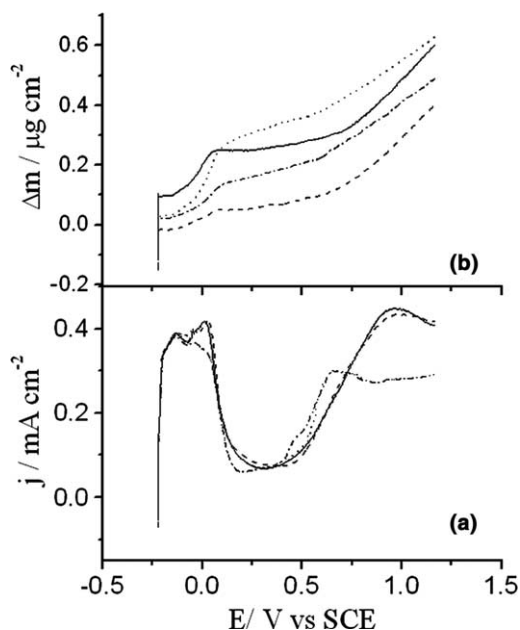


Fig. 6. Current and mass curves recorded in the positive potential scan at 0.02 V s^{-1} of Fig. 5 of an aged Pt/Au/Q electrode in 0.5 M HClO_4 (dashed-dotted line), in $0.5 \text{ M HClO}_4 + 1 \text{ mM } \beta\text{-CD}$ (dotted line), in $0.5 \text{ M HClO}_4 + 2 \text{ mM } 1\text{-octanol}$ (dashed line) and in $0.5 \text{ M HClO}_4 + 2 \text{ mM } 1\text{-octanol} + 1 \text{ mM } \beta\text{-CD}$ (solid line). The admission potential was -0.22 V in all cases. $R_F = 28.1$.

a limited potential range with an aged Pt/Au/Q electrode (Fig. 3(c) and (d)), in these two last cases with 1-octanol addition at open circuit. Visual inspection of the dashed and dashed-dotted lines shows that most of the mass decrease produced by 1-octanol occurs upon completion of the H desorption, indicating that the mass decrease should be due to *physisorbed* 1-octanol, since any eventual dissociative chemisorption of 1-octanol would necessitate higher potentials. The influence of the very small coverage of chemisorbed CO produced in the anodic peak at 0.0 V was negligible, contrary to the behaviour of a fresh Pt/Au/Q electrode (Fig. 2).

The anodic current in 0.5 M HClO_4 was practically unaffected by the addition of $\beta\text{-CD}$ at a controlled potential of -0.22 V (dashed-dotted and dotted lines in Fig. 6(a), respectively). In spite of this, the mass in $\beta\text{-CD}$ (dotted line in Fig. 6(b)) was higher than that in 0.5 M HClO_4 (dashed-dotted line in same figure) over nearly the whole potential range, which should be due to adsorption of $\beta\text{-CD}$, this in turn promoting the adsorption of water and/or ions. Visual inspection of the dotted and dashed-dotted lines readily shows that the adsorption of $\beta\text{-CD}$ takes place mainly, if not exclusively, in the H desorption range, which indicates that $\beta\text{-CD}$ occupies the Pt sites left free by the H atoms. This mass increase produced by $\beta\text{-CD}$ is just the opposite of the mass decrease produced by 1-octanol, this clear-cut discrimination between hydrophilic and hydrophobic adsorbates being made possible by the EQCM.

The anodic current in the presence of 1-octanol was almost the same as that in 1-octanol + $\beta\text{-CD}$ (dashed and solid lines in Fig. 6(a), respectively), both solutions having been added at the controlled potential of -0.22 V . Therefore, with this condition it is clear that the inclusion complex affects neither the hydrogen desorption nor the electrooxidation of Pt and 1-octanol. Interestingly, this behaviour is different from that observed when the solutions were added at open circuit, in which case, with increasing $\beta\text{-CD}$ concentration both the anodic current in the Pt oxide region and the hydrogen desorption current decreased markedly (Fig. 4(a)). This crucial effect of the admission potential is remarkable. Probably it involves the formation of adsorbed residues of 1-octanol upon its addition at open circuit, these residues being absent when the addition is carried out at -0.22 V .

The behaviour of the mass in 1-octanol + $\beta\text{-CD}$ is interesting. As above said, at the beginning of the scan the mass was higher in 1-octanol + $\beta\text{-CD}$ than in $\beta\text{-CD}$ alone (solid and dotted lines in Fig. 6(b), respectively), probably owing to adsorption of the $\beta\text{-CD}$ -1-octanol inclusion complex and/or to a higher adsorption of water in the former case. However, the mass increase in the H desorption region was higher in $\beta\text{-CD}$ alone than in 1-octanol + $\beta\text{-CD}$, the two curves crossing at 0.09 V owing to the larger mass increase in $\beta\text{-CD}$ alone, after which the mass in $\beta\text{-CD}$ alone was higher than that in 1-octanol + $\beta\text{-CD}$. In the double layer and Pt oxide regions, the trend in 1-octanol + $\beta\text{-CD}$ (solid line in Fig. 6(b)) is similar to that in 1-octanol (dashed line in same figure), in perfect agreement with the coincidence of the corresponding anodic currents (solid and dashed lines, respectively, in Fig. 6(a)).

The values of Q_O/Q_H and $\Delta m_O F / Q_O$ of this electrode in base electrolyte, 1.7 and 3.0, respectively, are the lowest of all those in Table 1. It must be concluded that the holding period at -0.22 V inhibited the oxidation of Pt, and, to an even higher extent, the mass increase in the oxide region.

3.2.7. Cyclic voltammetry of a Pt wire electrode in the presence of 1-octanol and/or $\beta\text{-CD}$

As above said, the activity of electrodeposited Pt in Pt/Au/Q electrodes, as measured by the hydrogen and oxygen charges, changes quickly upon potential cycling in the presence of 1-octanol. For this reason, in order to obtain more reproducible results, CVs of 1-octanol electrooxidation were carried out with a Pt wire electrode (sold by Elchema as an auxiliary electrode), initial R_F 5.5, with 1-octanol admissions at -0.22 V and at open circuit. As was indeed to be expected, the results were very similar to those already reported for primary alcohols with 4–8 carbon atoms on smooth Pt [2], a peak near 0.0 V appearing when 1-octanol is admitted at -0.22 V , whereas a decrease

in current in the H region, due to the residues of the dissociative chemisorption of 1-octanol, is observed when it is added at open circuit. The currents in the double layer and Pt oxide regions were unaffected by the admission potential.

The electrooxidation of 1-octanol seemed to be controlled by diffusion, since a plot of j_p (after subtraction of the current density in base electrolyte) vs. the square root of the scan rate is linear, and, furthermore, the slope is $1.0 \times 10^{-3} \text{ A V}^{0.5} \text{ s}^{-0.5}$, somewhat lower than the value of $1.31 \times 10^{-3} \text{ A V}^{0.5} \text{ s}^{-0.5}$ calculated for an irreversible four-electron charge transfer (corresponding to the formation of the carboxylic acid) with a Tafel slope of 0.12 V dec^{-1} (evaluated from the slope, near 60 mV dec^{-1} , of the E_p vs. \log vs. plot) and a diffusion coefficient $D = 0.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (evaluated by extrapolation from a plot of D vs. number of carbon atoms for alcohols with 1–4 carbons).

The CVs of the Pt wire electrode in the presence of β -CD and 1-octanol + β -CD (although not in 1-octanol added at open circuit) were also very similar to those described above for Pt/Au/Q electrodes. Therefore, the impedance measurements reported below were carried out with the Pt wire electrode, which ensured a higher reproducibility.

3.3. Impedance measurements with a Pt wire electrode

Impedance measurements with a Pt wire electrode were performed at $-0.22, 0.0, 0.22, 0.44, 0.66, 0.88$ and 1.1 V in the following electrolytes: 0.5 M HClO_4 ; $0.5 \text{ M HClO}_4 + 2 \text{ mM 1-octanol}$ admitted both at -0.22 V (squares) and at open circuit (circles); and $0.5 \text{ M HClO}_4 + 2 \text{ mM } \beta\text{-CD} + 2 \text{ mM 1-octanol}$ (triangles), the latter two being added in this order. At these concentrations, 40% of 1-octanol is present as its inclusion complex. The complex impedance plane plots obtained with these systems are shown in Fig. 7(a)–(g). The solid line corresponds to the results in 0.5 M HClO_4 .

At -0.22 V , the four curves overlap at high frequencies only. The curves resemble flattened semicircles, the height of which (related with the charge-transfer resistance) increases in the order (1-octanol added at -0.22 V) < (1-octanol added at open circuit) < (base electrolyte) \cong (1-octanol + β -CD). The exceedingly low values of the impedance should correspond to the hydrogen evolution reaction, owing to its very high exchange rate on Pt.

The impedance, and especially its imaginary component, increases very much when increasing the potential

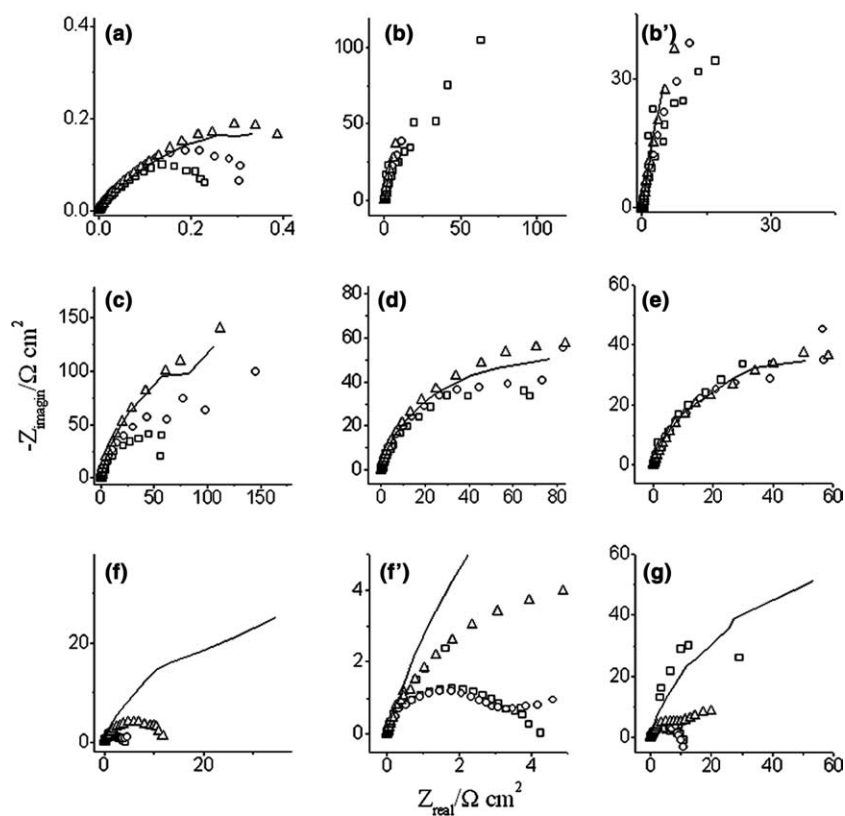


Fig. 7. Complex impedance plane plots of a Pt wire electrode in 0.5 M HClO_4 (solid line), in the presence of 2 mM 1-octanol added at -0.22 V (squares) and at open circuit (circles), and in $0.5 \text{ M HClO}_4 + 2 \text{ mM } \beta\text{-CD} + 2 \text{ mM 1-octanol}$ added at open circuit and left for 1 h (triangles). The impedance curves were obtained at the following potentials: (a) -0.22 V ; (b) and (b') 0.0 V ; (c) 0.22 V ; (d) 0.44 V ; (e) 0.66 V ; (f) and (f') 0.88 V ; and (g) 1.1 V .

to 0.0 V, at which hydrogen evolution is not possible (Fig. 7(b) and (b')). The large scatter at low frequencies in the presence of 1-octanol added at -0.22 V (Fig. 7(b)) should be related to the voltammetric peak of physisorbed alcohol electrooxidation yielding chemisorbed CO, which, with smooth Pt, appears only with alcohol admission at -0.22 V. At higher frequencies the four impedance plots practically coincide (Fig. 7(b')).

At 0.22 and 0.44 V (Fig. 7(c) and (d), respectively), although the impedances are more than two orders of magnitude higher than at -0.22 V (Fig. 7(a)), the sequence is the same: the highest charge-transfer resistance corresponds to 0.5 M HClO₄ and 1-octanol + β -CD, followed by 1-octanol added at open circuit, and finally by octanol added at -0.22 V, indicating that 1-octanol is involved in the charge transfer, and that this is inactivated by β -CD.

At 0.66 V, the potential of the peak of Pt oxide formation, the four impedance curves nearly overlap (Fig. 7(e)), indicating that at this potential, neither 1-octanol, nor 1-octanol + β -CD, affect the Pt wire electrode as far as its impedance is concerned.

Contrary to the behaviour at potentials ≤ 0.66 V, at 0.88 V, near the potential of the peak of alcohol elect-

rooxidation, the flattened semicircle in background electrolyte lies much higher than that in 1-octanol + β -CD, and this one lies above the two curves in 1-octanol (Fig. 7(f)). The fact that, in 1-octanol + β -CD (triangles), a larger semicircle is observed indicates that, as at 0.22 and 0.44 V, β -CD inactivates the charge transfer, but to a much lower extent.

The influence of the dosing potential of 1-octanol on the impedance at low frequencies at 0.88 V (Fig. 7(f')) is remarkable: while a linear segment appears with 1-octanol addition at open circuit, there is no such segment in the plot of 1-octanol added at -0.22 V, although the impedances at higher frequencies are not significantly affected by the admission potential, indicating that the value of the charge-transfer resistance is much the same. It should be noted that the linear segment in Fig. 7(f') has a slope of 0.21, far too low to correspond to Warburg behaviour [20].

At 1.1 V, a potential slightly past the peak of alcohol electrooxidation, negative values of the imaginary component at low frequencies, which could be due to a layer of adsorbed products [21] associated with the chemical reaction between the alcohol and the surface platinum oxide, are observed for 1-octanol, irrespective

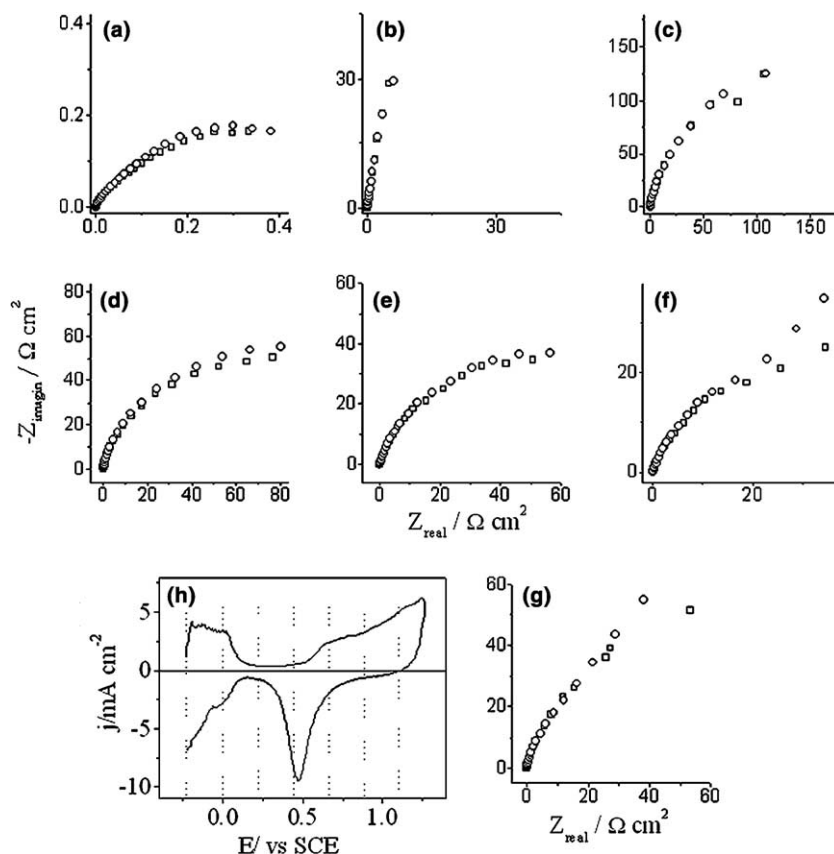


Fig. 8. Complex impedance plane plots of a Pt wire electrode in 0.5 M HClO₄ (\square) and in 0.5 M HClO₄ + 2 mM β -CD (\circ). The impedance curves were obtained at the same potentials as in Fig. 7. (h) CV at 0.1 V s⁻¹ of the Pt wire electrode in 0.5 M HClO₄. The dotted lines indicate the potentials at which the impedance curves were obtained.

of the admission potential (Fig. 7(g)). Again, as at 0.88 V the admission potential of 1-octanol affected the impedance at low frequencies, so much so that with 1-octanol admitted at -0.22 V (squares) the system did not reach stability at the lowest frequencies, as indicated by the overload light, and consequently no measurements could be carried out.

As can be seen in Fig. 8, the complex impedance plots of Pt wire in 0.5 M HClO_4 are barely affected, and that only at low frequencies, by the presence of 2 mM β -CD alone. In agreement with this, the current in the positive sweep of aged Pt/Au/Q in 0.5 M HClO_4 was not affected at all by the presence of 1 mM β -CD added at -0.22 V (dotted and dashed-dotted lines in Fig. 6(a)). However, the mass increase of an aged Pt electrode in the *H desorption region* was twice as high in the presence of β -CD than in its absence (dotted and dashed-dotted lines, respectively, in Fig. 6(b)), showing unequivocally that β -CD adsorbed on Pt, increasing the adsorption on it of water and/or ions, as was to be expected from its hydrophilic character. This adsorption of β -CD should be very weak, since the current in the positive sweep was not affected.

4. Discussion

4.1. Influence of aging on the electrooxidation of 1-octanol on Pt/Au/Q

With a fresh Pt/Au/Q electrode at 0.02 V s^{-1} 1-octanol added at open circuit decreased the Pt oxide reduction charge considerably (Fig. 2(a)). The initial and final masses were the same, i.e., the mass curve in one CV was a closed loop (Fig. 2(b)), both in the absence and presence of 1-octanol. Both in the positive and negative scans, the mass was lower in 1-octanol than in 0.5 M HClO_4 , clearly showing that over the whole potential cycle the hydrophobic chain of adsorbed 1-octanol decreased the adsorption of water and/or ions on a fresh Pt/Au/Q electrode. The anodic charge density in the Pt oxidation region was 23% higher in the presence of 1-octanol than in its absence, indicating that the fresh electrode had some activity for 1-octanol electrooxidation.

Aging of the Pt/Au/Q electrode profoundly affected its behaviour, this change being detected unequivocally by the EQCM. With an aged electrode, both in the absence and presence of 1-octanol added at open circuit, the final mass after one potential cycle was higher than the initial mass (Fig. 3(c) and (d)). This hysteresis cannot possibly be assigned to an incomplete reduction of the Pt oxide, but rather to a potential-induced change in the structure of the aged Pt electrode deposit, which provokes an increase in the amount of water adsorbed after one complete CV, or an increase of the viscosity of the in-

terface. The potential-induced change in aged Pt that is responsible for the hysteresis in the mass curve depends on the scan rate, this hysteresis being far more marked at 0.02 than at 0.1 V s^{-1} , as can be clearly appreciated from a comparison of Fig. 3(d) and (c), respectively.

Another feature in the mass curves that reflects the influence of aging on electrodeposited Pt is that at the beginning of the positive scan, the mass of the aged electrode in 1-octanol decreased initially (very briefly at 0.1 V s^{-1} , but over 0.5 V at 0.02 V s^{-1}) down to a minimum (Fig. 3(c) and (d)), while, with a fresh electrode, the mass increased monotonically during the whole positive scan, both in the absence and presence of 1-octanol (Fig. 2(b)).

Aging also affects the CVs, although less markedly than the mass curves. In the presence of 1-octanol, the anodic current in the Pt oxidation range is about the same (at 0.02 V s^{-1}) or lower (at 0.1 V s^{-1}) than in base electrolyte (see Table 1), and, since a fraction of this anodic charge should be due to the electrooxidation of the alcohol, the cathodic charge in the Pt oxide reduction region is much lower than in base (Fig. 3(a) and (b)). The near absence of cathodic charge in this region at the lower scan rate indicates that in the negative scan the alcohol chemically reduces most of the Pt oxide, since it cannot be envisaged that in the positive sweep the alcohol completely inhibits the electrooxidation of Pt.

4.2. Adsorption of β -CD on aged Pt/Au/Q

When β -CD alone was admitted at -0.22 V, the mass at this potential of an aged Pt/Au/Q electrode was practically the same as in 0.5 M HClO_4 (Fig. 5), in perfect agreement with the fact that at -0.22 V, the impedance curve of a Pt wire electrode was practically the same in the presence and absence of β -CD (Fig. 8(a)). In a subsequent positive scan, the anodic current in β -CD was the same as in 0.5 M HClO_4 (dotted and dashed-dotted lines in Fig. 6(a), respectively), which is again in perfect agreement with the fact that the impedance plots of the Pt wire over the whole potential range -0.22 to 1.10 V were almost unaffected by β -CD (Fig. 8), showing that the adsorbed β -CD did not significantly affect the charge transfer or the interfacial capacitance.

Although the adsorption of β -CD on Pt was so weak that it did not affect either the voltammogram or the impedance, the EQCM results showed unequivocally that β -CD did adsorb, although very weakly, on Pt, producing a marked mass increase (owing to the hydrophilic character of β -CD) in the *H desorption region* (dotted line in Fig. 6(b)). The fact that the mass increase occurred in the hydrogen desorption region shows that the adsorption of β -CD takes place only on those Pt sites left free upon hydrogen desorption, in agreement

with the very weak nature of this interaction, which is unable to detach the H atoms from the surface. In this case of a very weak adsorption, the EQCM proved to be more sensitive than the impedance measurements.

4.3. Adsorption in the system 1-octanol- β -CD-aged Pt/Au/Q

When 1-octanol + β -CD was admitted at -0.22 V, an increase in the mass at this potential of an aged Pt/Au/Q electrode was observed (Fig. 5), indicating that a hydrophilic effect predominated over the hydrophobic effect of adsorbed 1-octanol. Since β -CD alone did not affect the mass at -0.22 V, it must be concluded that the inclusion complex does adsorb on the hydrogen-covered Pt surface and that this complex has an overall hydrophilic character, since it produced a mass increase of the aged Pt electrode.

The impedance curve of the Pt wire at -0.22 V in 1-octanol + β -CD admitted at open circuit was slightly above that in 0.5 M HClO_4 , which lay above that in 1-octanol admitted at open circuit, which in turn lay above that in 1-octanol admitted at -0.22 V (Fig. 7(a)). The slight shift to higher real values of the maximum provoked by the inclusion complex, i.e., the slight increase of the resistance of the charge-transfer process, points to a physisorption of the inclusion complex on aged Pt/Au/Q and on the Pt wire. Since the mass in 1-octanol + β -CD remained higher than that in 0.5 M HClO_4 over the whole positive scan, it is inferred that this physisorbed species was not displaced even upon Pt oxidation.

Contrary to the lack of influence of β -CD added at -0.22 V on the current in 1-octanol of aged Pt/Au/Q in a subsequent positive sweep, β -CD added at open circuit did affect the voltammogram of a solution already containing 1-octanol, also added at open circuit. The H desorption and Pt oxidation currents in 1-octanol + β -CD were lower than in 1-octanol alone (Fig. 4(a)), pointing to some interaction between β -CD and/or the (1-octanol- β -CD) inclusion complex and the adsorption residues of the dissociative chemisorption of 1-octanol at open circuit. This interaction was fairly strong, since the adsorbed product inhibited both hydrogen adsorption and Pt oxidation. The mass was also lower than that in 1-octanol over most of the positive scan (Fig. 4(b)), indicating that the result of this interaction was hydrophobic.

The sensitivity of impedance measurements allowed us to establish unequivocally the influence of the potential at which 1-octanol was introduced in the cell on the impedance at low frequencies at 0.88 V, the peak potential of 1-octanol electrooxidation (Fig. 7(f)): a linear segment (although its slope was too low to correspond to Warburg behaviour) appeared when 1-octanol was added at open circuit, while no such linear

segment appeared when 1-octanol was added at -0.22 V, although the charge-transfer resistance was independent of the dosing potential.

5. Conclusions

From the study by cyclic voltammetry, the EQCM and impedance of the 1-octanol- β -CD-aged Pt/Au/Q system, it can be concluded that both 1-octanol and β -CD added at -0.22 V physisorb on Pt in a subsequent positive scan, producing a mass decrease and increase, respectively, as compared with the mass in 0.5 M HClO_4 base electrolyte, owing to the hydrophobic and hydrophilic character of 1-octanol and β -CD, respectively. With a freshly deposited Pt/Au/Q electrode, 1-octanol added at open circuit decreased the mass over the whole potential cycle.

The effect of β -CD on the CV and mass curve of aged Pt/Au/Q in 1-octanol depended on the admission potential of β -CD: if it was added at -0.22 V, β -CD did not affect the CV in 1-octanol, although the mass increased in the H desorption range, indicating that β -CD adsorbed on the Pt sites vacated by the H atoms. On the contrary, if β -CD was added at open circuit to a solution already containing 1-octanol, the H desorption and Pt oxidation currents, as well as the mass, were lower than in 1-octanol, pointing to some interaction between β -CD and the adsorption residues of 1-octanol that would be produced at open circuit, but not upon its addition at -0.22 V.

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