

Cyclic voltammetry and XPS studies of monolayers deposited on gold and platinum electrodes displaced by mercaptopyrindines.

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Abstract

We present studies, by cyclic voltammetry and X-ray photoelectron spectroscopy (XPS), of the under and overpotential deposition of copper on polycrystalline platinum and gold electrodes in aqueous 0.50 M sulfuric acid solution in the presence and absence of adsorbed layers of 2- and 4-mercaptopyridine (2-MP, 4-MP). In general we find that the presence of adsorbed layers of either 2-MP or 4-MP gives rise to an inhibition of the electrodeposition processes consistent with very strong interaction of the adsorbates with both Pt and Au surfaces. 2-MP gave rise to a higher degree of inhibition which we ascribe to a stronger degree of interaction likely due to a formation of a surface chelate via bonding through both N and S atoms. We have also investigated the reaction of 2-MP and 4-MP in solution with polycrystalline platinum and gold electrodes in aqueous 0.50 M sulfuric acid solution and which were either bare or covered by electrodeposited oxide or copper monolayers. Our studies reveal that the electrodeposited copper monolayer is displaced (oxidized), partially or completely, depending on the electrode material (Pt vs. Au), by 2-MP and 4-MP. On the other hand, the platinum and gold oxide monolayers are completely displaced by both adsorbates. The reactions of the oxide and copper monolayers with 2-MP and 4-MP gave rise to adsorbed intermediates and we present possible mechanistic pathways for these processes. © 1997 Elsevier Science S.A.

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1. Introduction

Among their previous uses, 2- and 4-mercaptopyridine (2-MP, 4-MP) have been studied in order to assess their ability to promote the direct electrochemistry of cytochrome c at modified gold electrodes [1,2]. Strong adsorption of mercaptans, primarily through the sulfur atom, to platinum and gold is now well established [3,4]. Surface enhanced Raman scattering (SERS) studies have demonstrated that 4-MP adsorbs on gold through the sulfur atom in a normal orientation, forming a dimer at high potentials [5]. Surface Raman spectra have been obtained from monolayer films of 4-MP adsorbed on polycrystalline Pt, Ag and Au surfaces, although a partial photodecomposition of the monolayer was observed [6].

Adsorption of 4-MP on Ag(111) has been studied by Gui et al. [7] using electron energy loss spectroscopy

(EELS), low energy electron diffraction (LEED), Auger spectroscopy and electrochemistry. They proposed that 4-MP forms an ordered layer on the Ag(111) surface, bonding through the S atom upon breakage of the S–H bond and formation of the Pt–S bond. This behavior is consistent with the behavior generally accepted for both aliphatic and aromatic thiol compounds on commonly employed transition metal surfaces such as Au, Ag and Pt [8].

Platinum electrodes pretreated with mercaptopyrindines in water or 0.50 M sulfuric acid not only inhibit copper [9] and silver [10] underpotential deposition (upd), but also delay the onset of bulk deposition. These results suggest that adsorption of 4-MP and 2-MP is through the sulfur atom. Studies of silver deposition onto Pt(111) in the presence of a 2-MP adlayer suggest that its adsorption is through a surface chelate [11].

In the present study, the strong affinity of Pt and Au for mercaptans and its comparatively weak affinity for aro-

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matic carbon and nitrogen have been employed to form adsorbed layers containing pendant pyridine rings in which the ring nitrogen atom is either close to or distant from the electrode surface. The influence of electrode potential and pH during the adsorption process on packing density and mode of surface bonding of 2-MP and 4-MP has been explored by voltammetric methods. Equally, we present electrochemical and X-ray photoelectron spectroscopy (XPS) studies of the effects of 2- and 4-mercaptopyridine on copper electrodeposition at under- and overpotentials. We also present studies of the interaction of these adsorbates with platinum and gold electrodes which were either bare or covered with electrodeposited oxide or copper monolayers and suggest possible mechanisms for these reactions.

2. Experimental

Polycrystalline gold and platinum were employed as working electrodes. Potentials are referenced to a SHE. A platinum foil and a gold coil were used as counter-electrodes when employing platinum and gold as working electrodes, respectively. Pretreatment of the platinum electrodes consisted in polishing with 1 μm diamond paste (Buehler) and rinsing with water, followed by electrochemical activation in 0.50 M H_2SO_4 by means of cyclic voltammetry between +1.55 and 0.0 V vs. SHE at a scan rate of 100 mV/s. For experiments involving a bare, oxide-free Pt surface, the cycle was stopped at +0.45 V vs. SHE (double-layer region) on the positive sweep. Conversely, the sweep was stopped at +1.20 V on the negative scan, prior to oxide reduction, for those studies involving an oxidized surface.

Evaluation of the electrochemical area (0.10 cm^2) of the Pt electrode was carried out through integration of the voltammetric peaks for hydrogen adsorption in 0.50 M H_2SO_4 using a conversion factor of 210 $\mu\text{C cm}^{-2}$.

Before each experiment, the gold electrode (99.999% Johnson Mathey) was cleaned by flaming and quenching with Milli-Q water. The electrochemical activation of gold electrodes was carried out between +1.74 V and 0.0 V vs. SHE. In experiments involving a bare gold surface, the cycle was arrested at +0.70 V on the positive sweep. On the contrary, the sweep was stopped at +1.60 V on the negative scan for those studies involving an oxidized surface.

The electrode area (0.20 cm^2) was measured in 0.50 M H_2SO_4 by integration of the charge required for reduction of an oxidized gold surface produced in a previous positive scan up to +1.74 V vs. SHE. A conversion factor of 400 $\mu\text{C cm}^{-2}$ (two electrons per gold surface atom) were used in the calculations [12].

A three-compartment cell (separated by medium-porosity sintered glass disks) and with the provision for addition and withdrawal of solutions was employed. All joints were

standard taper so that all compartments could be hermetically sealed with teflon adapters. In addition, the cell could be under a positive pressure of prepurified nitrogen at all times. Rinsing of the electrode and/or solution exchange was carried out in a flow-through fashion inside the cell without exposing the electrode to the environment. This was particularly important in experiments where a pre-electrodeposited copper monolayer was subsequently exposed to 2-mercaptopyridine and 4-mercaptopyridine.

Cyclic voltammetry was carried out using a Brucker Model 310 potentiostat and a PAR model 175 universal programmer. Data were recorded on a Hewlett-Packard model 7047A X-Y recorder.

All solutions were prepared using water purified with a Millipore Milli-Q system. 4-MP was purified by sublimation. All other reagents were of high purity (Merck, Janssen Chimica, Aldrich) and were used as received.

XPS spectra were recorded under ultrahigh vacuum (UHV) conditions with a commercial VG-CLAM hemispherical electron energy analyser. The excitation energy was Mg K- α . The base pressure in the UHV chamber during measurements was better than 10^{-9} mbar. During transport from the electrochemical cell to the UHV chamber the samples were briefly (≈ 5 – 10 s) exposed to air. Nevertheless, a direct interaction between sample and air was avoided by allowing a small drop of solution to remain on the sample surface during transport. This remaining solution was pumped away inside the UHV chamber.

3. Results

3.1. Electrochemical behavior of 4-MP and 2-MP on polycrystalline platinum electrodes

Both 2- and 4-mercaptopyridine can be oxidized in acid medium on polycrystalline platinum electrodes. A cyclic voltammogram carried out between the water oxidation and reduction limits at 10 mV s^{-1} in a 1×10^{-3} M 4-mercaptopyridine solution in 0.50 M H_2SO_4 exhibits irreversible behavior and significant hysteresis with oxidation currents in scans in both directions (Fig. 1). For 2-mercaptopyridine, the oxidation starts at +0.55 V, 100 mV prior to the oxidation of 4-mercaptopyridine and the voltammogram shows a current 'plateau' in both scans.

After adsorption of 4-mercaptopyridine from a 0.50 M H_2SO_4 solution at open circuit during 3 min, the initial positive scan (Fig. 2a) of a cyclic voltammogram starting at +0.50 V, shows no evidence of the wave corresponding to Pt oxide formation. Instead, a rising current is observed. During the subsequent negative scan, a Pt oxide reduction peak occurs at +0.80 V with a peak height that is considerably less than that resulting from a bare Pt electrode under identical conditions. During the second and subsequent cycles, the current at +1.40 V decreases and

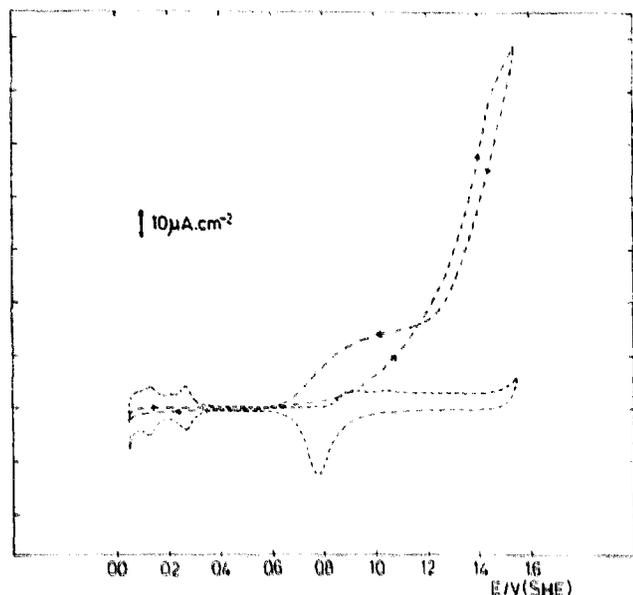


Fig. 1. Cyclic voltammogram at 10 mV s^{-1} for a platinum electrode in $0.50 \text{ M H}_2\text{SO}_4$ in the absence (---) and presence of 1×10^{-3} solution of 4-MP in $0.50 \text{ M H}_2\text{SO}_4$ (- · -).

the peak current due to Pt oxide reduction shows a concomitant increase (Fig. 2A).

This suggests that the presence of adsorbed 4-MP gives rise to an inhibition of the platinum oxide formation so that the anodic charge is likely to represent the sum of the oxidation of the adsorbed 4-MP ($180 \mu\text{C cm}^{-2}$; Table 1) along with platinum oxide formation. The inhibition of platinum oxide formation and reduction in subsequent cycles is likely to be due to the presence of residual 4-MP and/or the presence of adsorbed products resulting from the oxidation of the adsorbed 4-MP.

If the initial scan is in the negative direction, the adsorption of hydrogen is completely suppressed. However, upon scan reversal, a broad oxidation peak appears with an E_p value of $+1.20 \text{ V}$ (Fig. 2C). This peak appears only when the lower limit is sufficiently negative. In this case, the difference between anodic and cathodic charges is ca. $337 \mu\text{C cm}^{-2}$. It is interesting to note that this peak is similar to that appearing in the second scan of Fig. 2B suggesting that the oxidation product of adsorbed 4-MP remains on the surface.

When 4-MP is adsorbed from water onto a polycrystalline platinum electrode, the behavior is qualitatively similar to that described above with the exception that the oxidation charge is larger.

When adsorbed onto a platinum surface, 2-MP ($1 \times 10^{-3} \text{ M}$ solution in $0.50 \text{ M H}_2\text{SO}_4$ or water) is extremely resistant to oxidation. The onset of oxidation is gradual and becomes clearly detectable only at potentials above $+1.30 \text{ V}$ (Fig. 3A). The charge due to oxidation of adsorbed 2-MP is about $130 \mu\text{C cm}^{-2}$. In a manner analogous to 4-MP, the positive sweep obtained following the initial negative one shows an oxidation peak at $+1.20$

V (Fig. 3B) which is similar to the second scan in Fig. 3A. The coulometric charges are presented in Table 1.

In summary, the oxidation charge of 4-MP is greater than that of 2-MP in both media, such charge being greater in neutral than in acid medium for each adsorbate. This fact is more evident on Pt(111) electrodes [13]. In the 2-MP molecule, the sulfur and nitrogen atoms are positioned in a manner that may allow both to be bonded to the electrode surface. However the 4-MP binds to the electrode surface through the sulfur atom in a vertical orientation. In this case the packing density is greater than that for 2-MP giving rise to a larger oxidation charge.

At $\text{pH} = 0$ the pyridine nitrogen is protonated in both molecules. Such protonation would (by inductive effects) cause a weakening of the sulfur-platinum bond besides diminish the possibility to adsorb on the electrode surface, giving rise to less oxidation charge.

3.2. Displacement of electrodeposited copper monolayers on platinum by mercaptopyridines

When a copper monolayer is electrodeposited at underpotentials on a platinum electrode and subsequently exposed at open circuit to a solution of 2-MP (in $0.50 \text{ M H}_2\text{SO}_4$ or water), the copper monolayer is displaced, as is observed in the first positive scan (Fig. 4A) where there is no evidence of copper stripping. At more positive potentials ($+1.0 \text{ V}$), an increase in current is observed, partly due to the oxidation of the platinum surface, although in a smaller proportion, relative to a bare platinum surface, as well as to the oxidation of adsorbed 2-MP (see XPS results in Section 3.8). These last processes involve a charge of $420 \mu\text{C cm}^{-2}$.

Contrary to 2-MP if a platinum electrode with an electrodeposited monolayer of copper is immersed in a $1 \times 10^{-3} \text{ M}$ 4-MP solution (in $0.50 \text{ M H}_2\text{SO}_4$ or water), the positive scan exhibits the stripping of strongly adsorbed copper in addition to the processes described before (Fig. 4B). It is clear that in this case the adsorbate does not displace the copper monolayer completely.

3.3. Displacement of platinum oxide monolayers by mercaptopyridines

If a platinum electrode covered by a platinum oxide monolayer is exposed to a $1 \times 10^{-3} \text{ M}$ solution of 4-MP in $0.50 \text{ M H}_2\text{SO}_4$ or water for 3 min at open circuit, the initial negative scan starting at $+1.20 \text{ V}$ shows a complete absence of the platinum oxide reduction peak, as well as an inhibition of hydrogen electroadsorption. On the positive scan, the hydrogen desorption peaks are again completely suppressed and the surface is only partially oxidized, as shown by the subsequent negative scan. The difference between the anodic and cathodic charges can be attributed to adsorbate oxidation (Fig. 5A). The subsequent

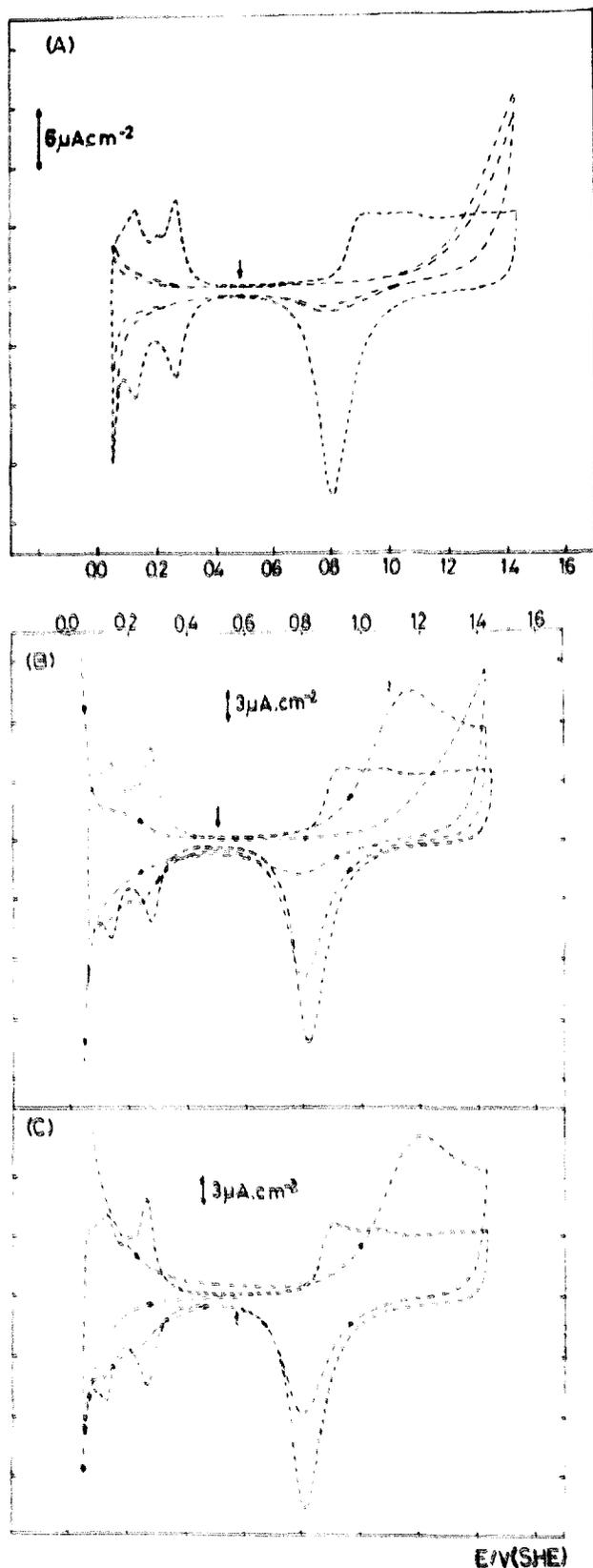


Fig. 2. Cyclic voltammogram for a platinum electrode in 0.50 M H_2SO_4 (---). Cyclic voltammogram for a platinum electrode pretreated with a 1×10^{-3} M solution of 4-MP in 0.50 M H_2SO_4 (- - -). (A) Initial positive potential scan at 0.5 V (- · -); second scan (- · -); lower limit potential +0.05 V. (B) Initial positive potential scan at 0.5 V; lower limit potential 0.0 V. (C) Initial negative potential scan at 0.6 V; lower limit potential 0.0 V.

Table 1
Oxidation charge for adsorbed mercaptopyridines on platinum

Adsorbate	Solvent	Scan	Q_{AD} ($\mu\text{C cm}^{-2}$)
4MP	H_2SO_4	positive	180
4MP	H_2SO_4	negative	337
4MP	H_2O	positive	199
4MP	H_2O	negative	365
2MP	H_2SO_4	positive	128
2MP	H_2SO_4	negative	265
2MP	H_2O	positive	131
2MP	H_2O	negative	231

scans are practically identical to the first one except when the lower limit goes into the hydrogen evolution region, in which case a peak at +1.20 V is obtained on the positive sweep (Fig. 5B) in a way similar to that shown in Fig. 2B.

Furthermore, there is no oxide reduction peak for platinum oxide surfaces treated with a 1×10^{-3} M solution of 4-MP in water. The PtO_2 layer is thus displaced by 4-MP, suggesting that the S–Pt bond is stronger than the Pt–O bond and that the kinetics of displacement are rapid. For platinum surfaces covered by an oxide monolayer and immersed in a solution of 2-MP (in 0.5 M H_2SO_4 or

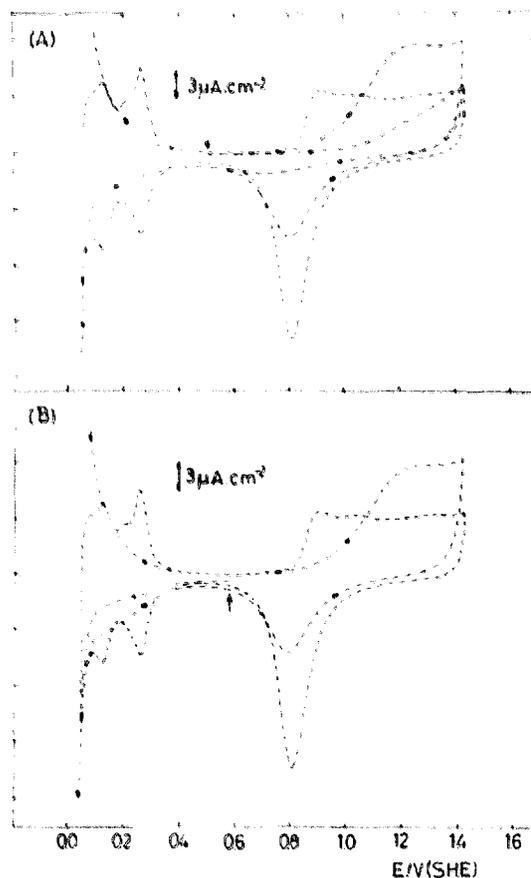


Fig. 3. Cyclic voltammogram for a platinum electrode in 0.50 M H_2SO_4 (---). Cyclic voltammogram for a platinum electrode pretreated with a 1×10^{-3} M solution of 2-MP in water. (A) Initial positive potential scan at 0.5 V; lower limit potential was 0.0 V. (B) Initial negative potential scan at 0.6 V; lower limit potential was 0.0 V.

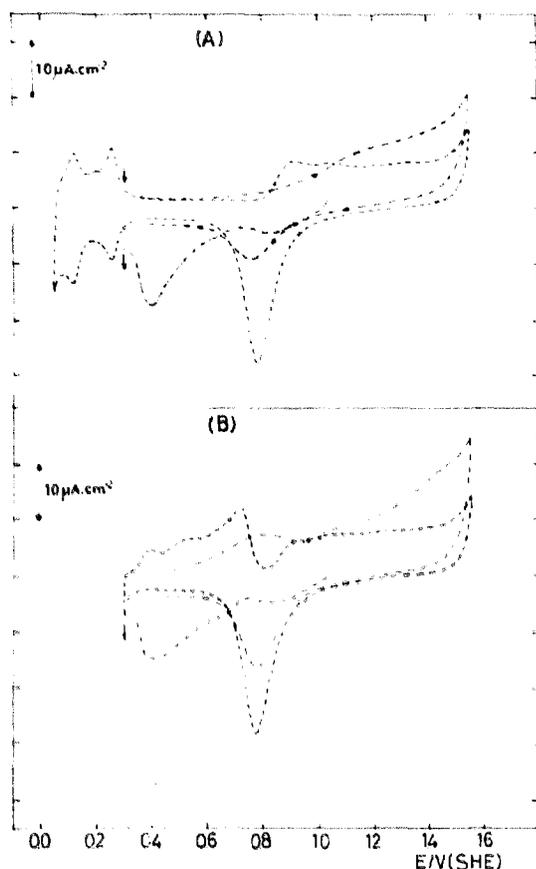


Fig. 4. (A) Cyclic voltammogram for a platinum electrode in 0.50 M H_2SO_4 (---). Deposition of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a bare platinum electrode (- - -). The electrode was rinsed with 0.50 M H_2SO_4 before introducing in a 1×10^{-3} M solution of 2-MP in water for 3 min at open circuit. The electrode was then rinsed with 0.50 M H_2SO_4 and an anodic sweep was initiated at 0.25 V (- - -). (B) Deposition of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a bare platinum electrode (- - -). The electrode was rinsed with 0.50 M H_2SO_4 before introducing in a 1×10^{-3} M solution of 4-MP in water for 3 min at open circuit. The electrode was then rinsed with 0.50 M H_2SO_4 and an anodic sweep was initiated at 0.25 V (- - -). Stripping (- - -) of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a bare platinum electrode.

water) for 3 min, the voltammetric response shows similar features to those described in Section 3.1. However, in this case there is virtually no platinum oxide formed in the following positive scan, as is ascertained from the lack of an oxide reduction peak in a subsequent negative scan. In addition, the current density obtained for the adsorbate oxidation is smaller. Again, this voltammogram resembles that for the oxidation of adsorbed 2-MP shown in Fig. 3a.

For a Pt surface initially covered with an oxide monolayer and subsequently treated with 2-MP or 4-MP in water or sulfuric acid, there is complete inhibition of the Cu upd processes (Fig. 6). This indicates that the platinum oxide has been reduced by the 4-MP, which is itself adsorbed onto the electrode surface. The oxidation of the adsorbed 4-MP can be seen in the subsequent positive scan. A qualitatively similar behavior is observed for 2-MP.

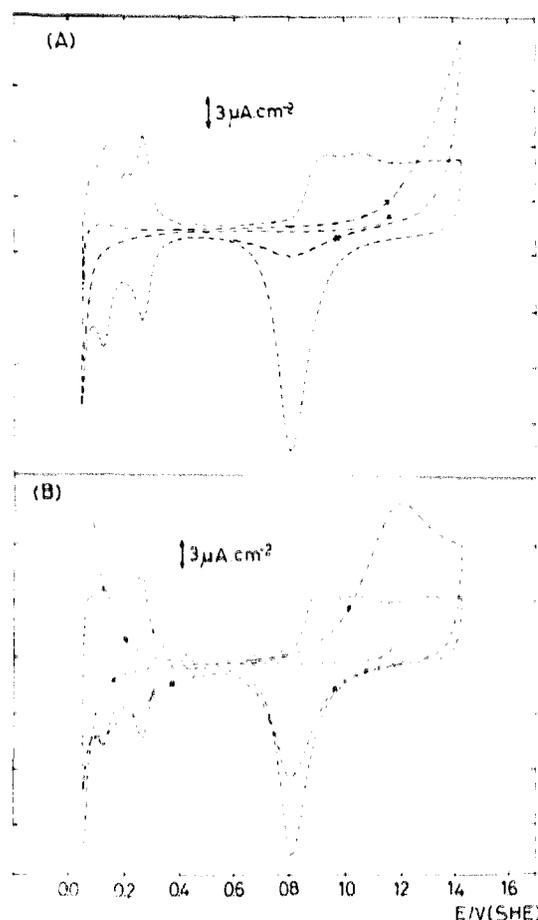


Fig. 5. Cyclic voltammogram for a platinum electrode in 0.50 M H_2SO_4 (---). PtO_2 electrode pretreated with 4-MP in 0.50 M H_2SO_4 for 3 min at open circuit. The electrode was then rinsed with 0.50 M H_2SO_4 and a negative sweep was initiated at 1.15 V (- - -). (A) Lower limit potential was +0.05 V. (B) Lower limit potential was 0.0 V.

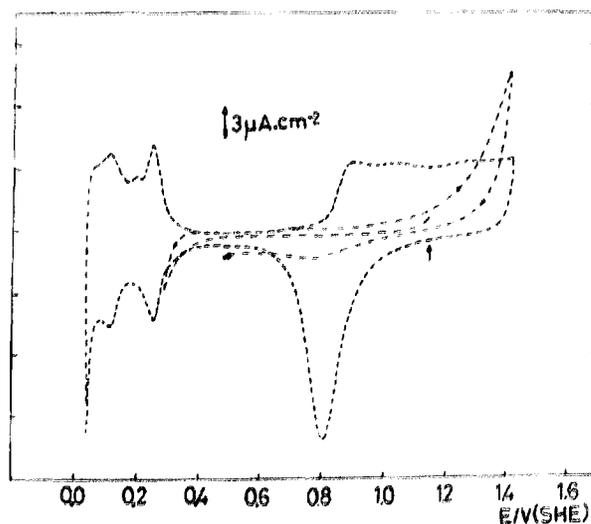


Fig. 6. Cyclic voltammogram for a platinum electrode in 0.50 M H_2SO_4 (---). PtO_2 electrode pretreated with 4-MP in 0.50 M H_2SO_4 for 3 min at open circuit. The electrode was then rinsed with 0.50 M H_2SO_4 and a negative sweep was initiated at 1.15 V in presence of 1×10^{-3} M CuSO_4 (- - -).

3.4. Behavior of mercaptopyridines on polycrystalline gold electrodes

Fig. 7 shows the voltammetric response over the potential range between 0.0 V and +1.75 V for a 1×10^{-3} M solution of 4-MP in 0.50 M H_2SO_4 on a gold electrode. Oxidation starts at ca. +1.0 V and reaches two current maxima, at +1.32 V and at +1.53 V, respectively. In the following negative scan, the reduction peak (ascribed to oxide reduction) is relatively small, probably due to the direct reduction of the gold oxide layer by the 4-MP at potentials positive of those corresponding to gold oxide reduction.

If 4-MP is adsorbed for 3 min from a 0.50 M H_2SO_4 solution at open circuit, the subsequent positive scan starting at +1.10 V shows a delay of the gold oxide formation, as well as an increase in the peak current density due to oxidation of the adsorbed 4-MP as well as a displacement of the peak potential, E_p , to +1.53 V (Fig. 8). This value is coincident with that of the second current maximum in the oxidation of 4-MP in solution. In the subsequent negative scan, the gold oxide reduction charge is practically the same as that in the absence of adsorbate ($Q_{Au} = 520 \mu C cm^{-2}$). The difference between the anodic and cathodic charges of $315 \mu C cm^{-2}$, is ascribed to oxidation of adsorbed 4-MP.

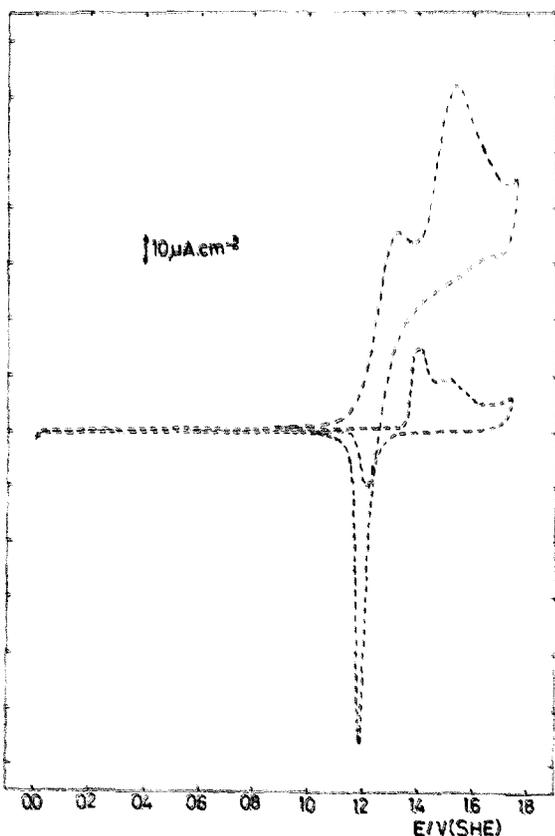


Fig. 7. Cyclic voltammogram for a gold electrode in 0.50 M H_2SO_4 (---), Cyclic voltammogram at a gold electrode in a 1×10^{-3} M 4-MP solution in 0.50 M H_2SO_4 (- · -).

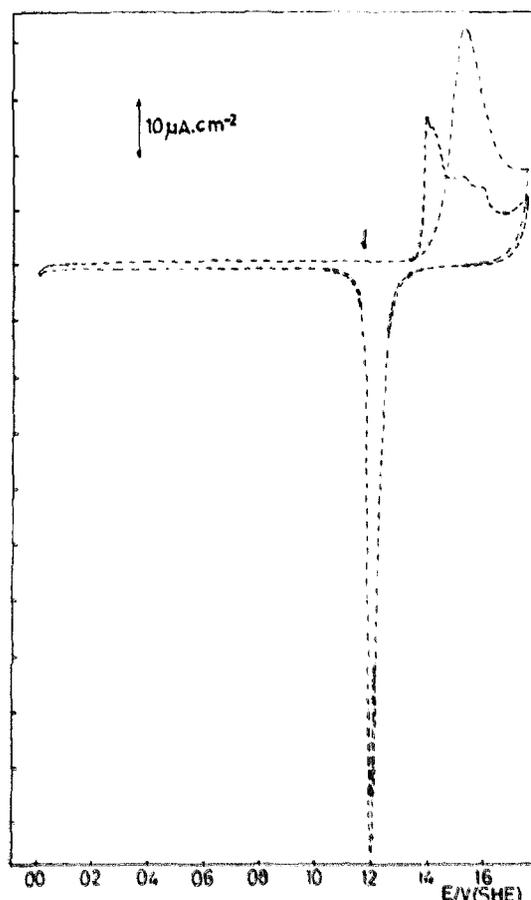


Fig. 8. Cyclic voltammogram for a gold electrode in 0.50 M H_2SO_4 (---), Cyclic voltammogram for a gold electrode pretreated with a 1×10^{-3} M 4-MP solution in 0.50 M H_2SO_4 (- · -).

If during the positive scan the solution is stirred, the voltammogram is not affected, indicating that the oxidation products remain adsorbed. On the other hand, desorption takes place in the negative scan, since the following scan is virtually identical to the voltammogram for gold in acid solution.

With the intent of studying the reduction of adsorbed 4-MP on gold at open circuit, a potential scan into the hydrogen evolution region was carried out, and an overpotential deposition (opd) for such reaction was observed as well as a peak prior to the hydrogen evolution reaction which could be due to the reduction of 4-MP adsorbed to yield 4-MP in solution. However, most of the adsorbed 4-MP remains on the electrode surface and is oxidized in the following positive scan ($Q = 250 \mu C cm^{-2}$).

When 4-MP is adsorbed from water, the behavior is similar to that described above, although its oxidation charge is higher (Table 2) in a way analogous to the behavior described in Section 3.1 for platinum surfaces.

As for 4-MP, a 1×10^{-3} solution of 2-MP in 0.50 M H_2SO_4 also shows two current maxima, at +1.15 V and +1.65 V, respectively.

After 2-MP is adsorbed for 3 min from a 0.50 M H_2SO_4 solution at open circuit, a positive scan starting at +0.60 V shows that its oxidation is at more positive

potentials relative to 4-MP (+1.40 V), and the current maximum is reached at +1.65 V. In Table 2, we present the oxidation and reduction charges for the two scans.

In the case of 2-MP, both in 0.50 M H_2SO_4 and in water, the gold oxide reduction charge (Q_{RED}) is smaller than that corresponding to one monolayer. In addition, the anodic charge (Q_{OX}) corresponding to the gold oxide formation and the adsorbate oxidation is also smaller than that of 4-MP. Besides, the difference between Q_{RED} and Q_{OX} (Q_{AD}) is smaller than that for 4-MP, in a way analogous to the behavior described for platinum surfaces. In addition, the oxidation charge is always higher in the positive than in the negative scan, probably due to desorption in the hydrogen region.

3.5. Copper underpotential deposition on gold electrodes pretreated with mercaptopyridines

Fig. 9 shows the cyclic voltammogram for copper deposition on a gold electrode pretreated with a 1×10^{-3} M solution of 2-MP in 0.50 M H_2SO_4 . In the presence of this adsorbate, upd as well as opd processes are inhibited. Only at considerably more positive potentials is it possible to observe the adsorbate oxidation with a charge of $274 \mu C cm^{-2}$. If the 2-MP is dissolved in water, the behavior is similar and its oxidation charge is $279 \mu C cm^{-2}$ which is very close to the value in the absence of copper (Table 2).

The cyclic voltammetric response for copper deposition onto a gold electrode pretreated with a 1×10^{-3} M solution of 4-MP in 0.5 M H_2SO_4 at open circuit for 3 min shows a small upd wave with a peak potential of +0.43 V and with a significant diminution in charge ($78 \mu C cm^{-2}$) relative to deposition onto a bare gold electrode ($306 \mu C cm^{-2}$). The copper stripping occurs as a somewhat broad peak in the positive scan (Fig. 10). On the other hand, the adsorbed 4-MP is oxidized at more positive potentials, with a charge of $317 \mu C cm^{-2}$. If the 4-MP is dissolved in water, the copper upd charge is $120 \mu C cm^{-2}$ and its oxidation charge is $332 \mu C cm^{-2}$.

These results indicate that in the presence of 2-MP at open circuit, the gold surface is completely covered by 2-MP, while in the presence of 4-MP full coverage is not reached.

Table 2
Oxidation charge for adsorbed mercaptopyridines on gold

Adsorbate	Solvent	Scan	Q_{OX} ($\mu C cm^{-2}$)	Q_{RED} ($\mu C cm^{-2}$)	Q_{AD} ($\mu C cm^{-2}$)
4MP	H_2SO_4	positive	832	517	315
4MP	H_2SO_4	negative	785	535	250
4MP	H_2O	positive	853	517	336
4MP	H_2O	negative	783	518	265
2MP	H_2SO_4	positive	747	467	280
2MP	H_2SO_4	negative	724	464	260
2MP	H_2O	positive	743	467	276
2MP	H_2O	negative	734	482	252

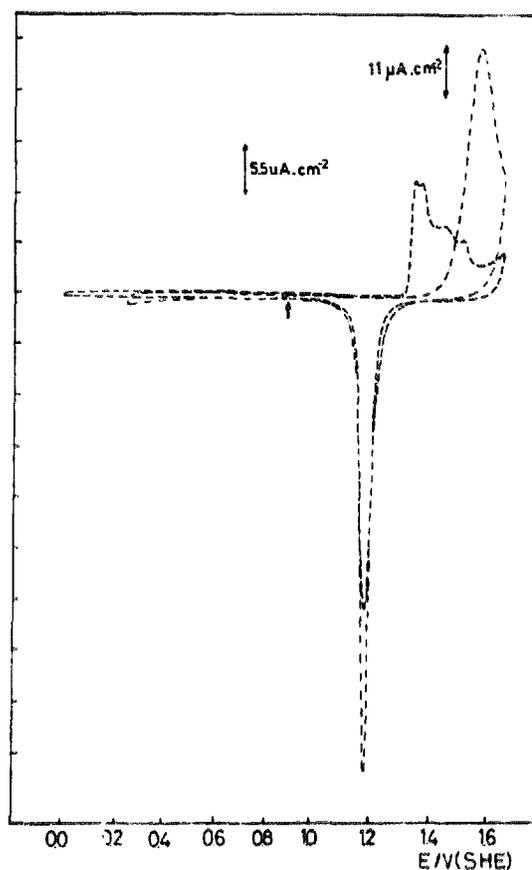
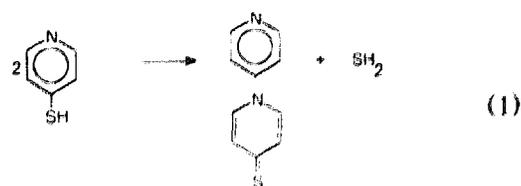


Fig. 9. Cyclic voltammogram for a gold electrode in 0.50 M H_2SO_4 (---). Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a gold electrode pretreated with 1×10^{-3} M 2-MP in 0.50 M H_2SO_4 (- · -).

In order to ensure complete coverage of the electrode by adsorbate, the gold electrode was pretreated with 4-MP in 0.50 M H_2SO_4 at $E = +1.1$ V for 3 min. Under these conditions, the copper upd was completely inhibited, providing very strong evidence that the surface of the electrode was completely covered by adsorbate. The same response was obtained if the electrode was pretreated with 4-MP in water at $E = +0.65$ V for 3 min.

Nuclear magnetic resonance (NMR) analysis of a solution of 4-MP, without previous purification, in 0.5 M H_2SO_4 , indicates that there are three different species present, although 4-MP is the predominant one.

One of these is believed to arise from the coupling reaction:



This product was virtually removed by sublimation. The other molecule has been identified as bis-(4-pyridyl)di-

sulfide (aldriethiol). Its presence in 0.5 M sulfuric acid solution is more pronounced at longer times as shown by nuclear magnetic resonance (eventually reaching concentrations similar to 4-MP). A gold electrode pretreated with such an aged solution at open circuit for 3 min exhibited a complete inhibition of copper upd processes.

The adsorption of aldriethiol on gold has been studied by Taniguchi et al. [5] using SERS and by Hinnen and Niki [1] using UV-visible electroreflectance. They propose that aldriethiol can be oxidized only if it has previously been reduced to 4-MP. They also suggest that at potentials more positive than +0.10 V, aldriethiol molecules should remain on the gold surface without any chemical change. However, we found that the voltammogram for a gold electrode pretreated with 1×10^{-3} M aldriethiol solution in 0.50 M H_2SO_4 at open circuit for 3 min, shows the adsorbate (aldriethiol) oxidation at about +1.55 V ($347 \mu C cm^{-2}$) (Fig. 11). The copper upd processes are inhibited at gold electrodes pretreated with aldriethiol in water or 0.5 M sulfuric acid solution. This demonstrates that aldriethiol is capable of adsorbing onto gold electrodes at open circuit reaching full coverage, contrary to 4-MP. In fact, aldriethiol adsorption on gold is strong and irreversible [1,14].

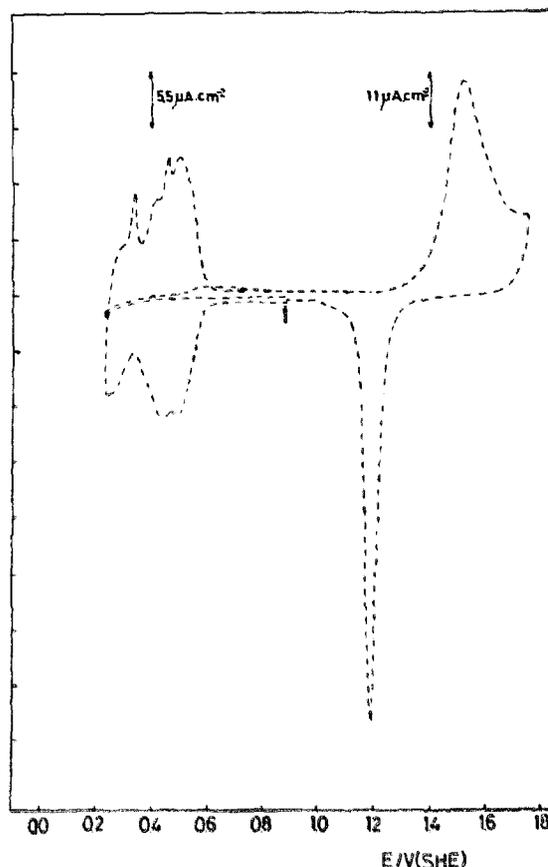


Fig. 11. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a gold electrode pretreated with 1×10^{-3} M aldriethiol in 0.50 M H_2SO_4 first and second scan (---).

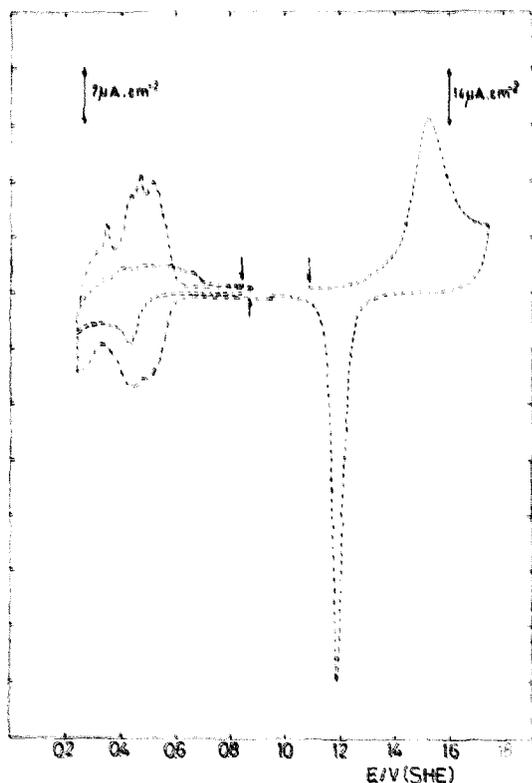


Fig. 10. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a gold electrode pretreated with 1×10^{-3} M 4-MP in 0.50 M H_2SO_4 , first scan (---), second scan (---).

3.6. Displacement of electrodeposited copper monolayers on gold by mercaptopyridines

When, after deposition of a copper monolayer, a gold electrode is immersed in a solution of 4-MP (in 0.50 M H_2SO_4 or water), there is no evidence of stripping of the copper adlayer on a positive sweep. This observation suggests strongly that the monolayer has been displaced by adsorbed 4-MP.

However, in the double-layer region, a peak (1 in Fig. 12) appears at a peak potential value $E_p = +0.88$ V and an associated charge of $150 \mu C cm^{-2}$. It is worth noting that this peak becomes much more symmetric after extensive rinsing with H_2SO_4 , suggesting the elimination of a weakly adsorbed intermediate while a more strongly adsorbed species remains. In this case, the coulometric charge decreased to $116 \mu C cm^{-2}$.

If the scan is reversed after peak 1, there are no current peaks on the negative sweep implying that this oxidation process is irreversible. At more positive potentials, the oxidation of adsorbed 4-MP takes place (Fig. 12, peak 2). The charge associated with this oxidation can be calculated from the difference between the measured anodic and cathodic charges. The cathodic charge corresponds to the reduction of the gold oxide monolayer, this being virtually

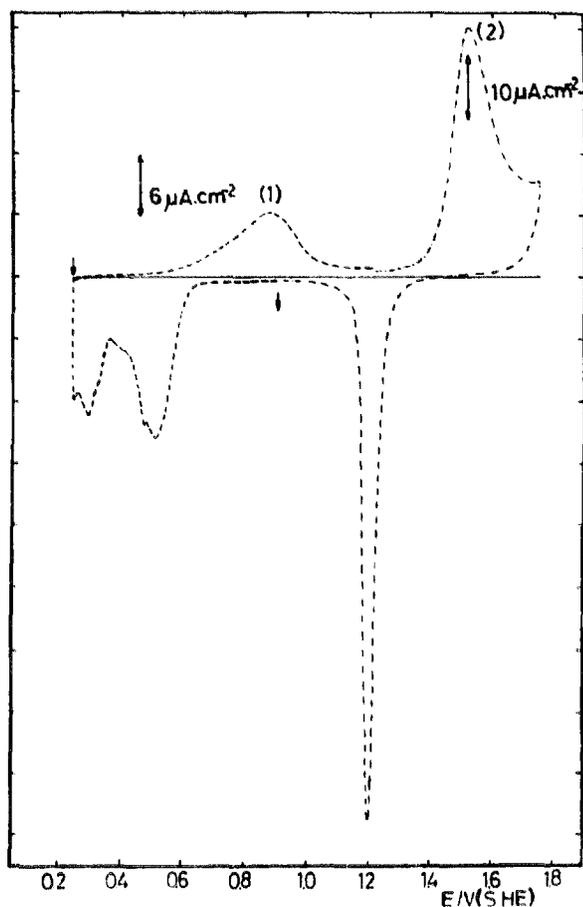


Fig. 12. Deposition of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a bare gold electrode (---). The electrode was then rinsed with 0.50 M H_2SO_4 before introducing it into a solution of 1×10^{-3} M 4-MP in 0.50 M H_2SO_4 for 3 min at open circuit. The electrode was rinsed with 0.50 M H_2SO_4 and a positive sweep was initiated at 0.25 V (---, ---).

the only process taking place since the peak potential is the same as in the absence of adsorbate (+1.20 V). With the exception of the peak obtained in the double-layer region, the voltammogram is similar to that in Fig. 8.

The behavior described above can be generalized to electrodeposited copper monolayers treated with 4-MP in water and with 2-MP in both sulfuric acid and water. Similarly the copper monolayer is displaced by aldrithiol in 0.50 M H_2SO_4 , but the peak potential (peak 1) is less positive ($E = +0.70$ V) (Fig. 13).

Table 3 shows the charges (Q_1) associated with peak 1 and adsorbate oxidation (Q_{AD}), as well as the corresponding peak potentials.

3.7. Displacement of gold oxide monolayers by mercaptopyridines

If a gold electrode covered by an oxide monolayer is exposed to a 1×10^{-3} M solution of 2-MP in 0.50 M H_2SO_4 during 3 min at open circuit, the first negative scan from an initial potential of +1.35 V does not show the

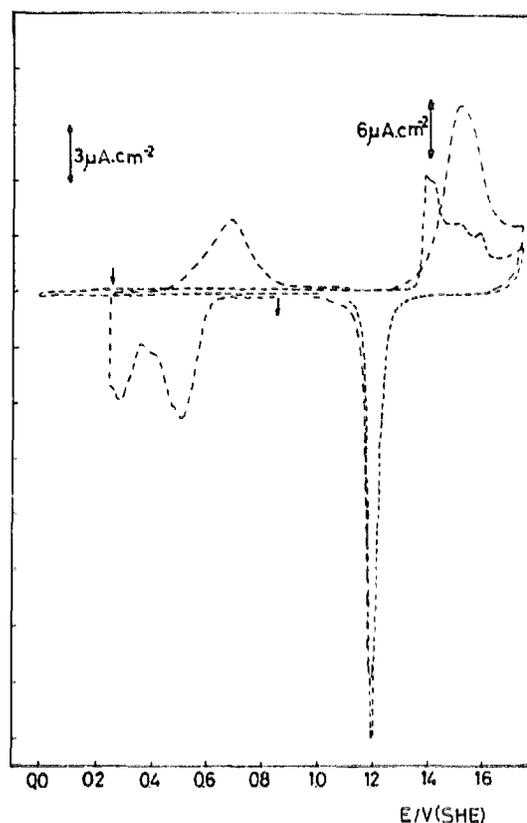


Fig. 13. Cyclic voltammogram for a gold electrode in 0.50 M H_2SO_4 (---). Deposition of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a bare gold electrode (---). The electrode was then rinsed with 0.50 M H_2SO_4 before introducing it into a solution of 1×10^{-3} M aldrithiol in 0.50 M H_2SO_4 for 3 min at open circuit. The electrode was rinsed with 0.50 M H_2SO_4 and a positive sweep was initiated at 0.25 V (---).

gold oxide reduction peak. However, in the subsequent positive scan, the oxidation of adsorbed 2-MP can be observed (Fig. 14). Thus, the gold oxide monolayer has been displaced by the 2-MP. A similar behavior is observed for 2-MP adsorbed from water solution.

If, once the gold oxide monolayer has been displaced by 2-MP, the electrode is immersed in a 1×10^{-3} M CuSO_4 solution and a potential sweep is applied in the negative direction from +1.35 V, both the under- and overpotential depositions of copper are inhibited. This behavior, characteristic of gold electrodes with adsorbed 2-MP, has been observed before [15].

Table 3
Displacement of copper monolayer deposited on gold by mercaptopyridines

Adsorbate	Solvent	Q_{ADS} ($\mu\text{C cm}^{-2}$)	Q_1 ($\mu\text{C cm}^{-2}$)	E_{P1} (V)	E_{P2} (V)
4MP	H_2SO_4	314	116	0.88	1.53
4MP	H_2O	348	102	0.92	1.53
2MP	H_2SO_4	237	105	0.97	1.65
2MP	H_2O	249	107	1.00	1.65

If the adsorbate is 4-MP in 0.50 M H_2SO_4 or water, the gold oxide monolayer is again displaced (Fig. 15). In addition, if a gold electrode, covered by an oxide monolayer, is treated with 4-MP in 0.50 M H_2SO_4 during 3 min at open circuit and then a negative scan is initiated, the copper underpotential deposition is inhibited. On the following positive scan, a peak appears at +0.70 V. At even more positive potentials, the oxidation of the adsorbed product takes place (Fig. 16). In this case the electrode surface appears to be completely covered by reaction products. The oxidation charge is higher than in the case of 4-MP adsorbate oxidation. In fact, it is more similar to that for adsorbed aldrithiol oxidation (Table 4).

3.8. X-ray photoelectron spectroscopy measurements

Fig. 17 shows XPS spectra over a wide binding energy range for: (A) a monolayer of 2-MP on Pt; (B) a ML of 4-MP on Pt; (C) a ML of Cu on Pt displaced by 2-MP; (D) a ML of Cu on Pt displaced by 4-MP; and (E) a PtO_2 ML displaced by 4-MP. In all cases the mercaptopyridines were adsorbed from a water solution. All spectra show similar features, with Pt, C and oxygen peaks. The oxygen

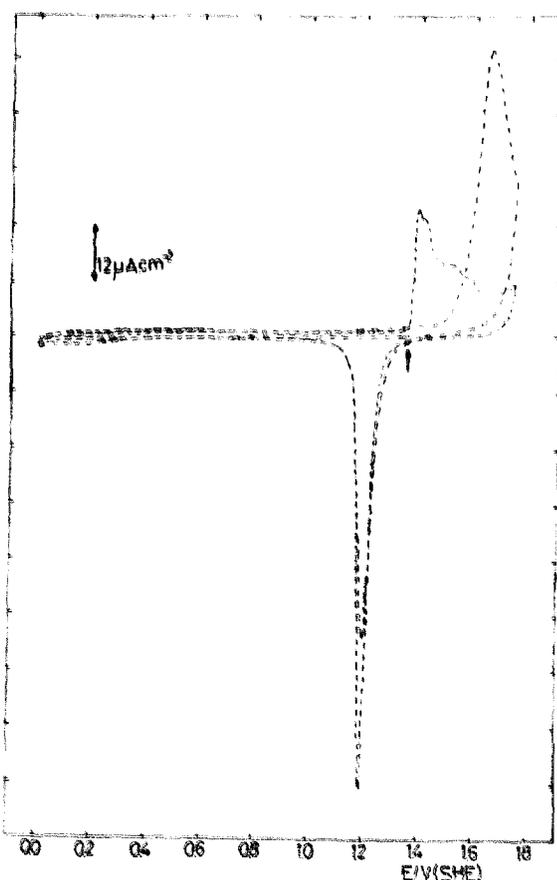


Fig. 14. Cyclic voltammogram for a gold electrode in 0.50 M H_2SO_4 (---). Cyclic voltammogram for a gold electrode covered by an oxide monolayer pretreated with 2-MP in 0.50 M H_2SO_4 for 3 min at open circuit. The electrode was rinsed with 0.50 M H_2SO_4 and a negative sweep was initiated at 1.35 V (- · -).

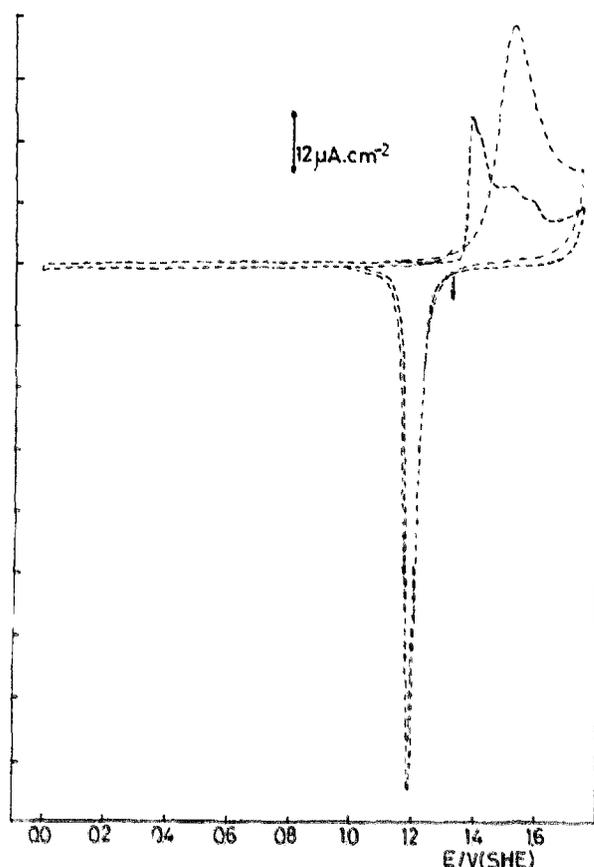


Fig. 15. Cyclic voltammogram for a gold electrode in 0.50 M H_2SO_4 (---). Cyclic voltammogram for a gold electrode covered by an oxide monolayer pretreated with 4-MP in 0.50 M H_2SO_4 for 3 min at open circuit. The electrode was rinsed with 0.50 M H_2SO_4 and a negative sweep was initiated at 1.35 V (- · -).

probably originates from the water excess present at the surface before pumping. This is confirmed by Fig. 18, where XPS spectra of the Pt-4f core level are shown. As can be observed, all spectra correspond to metallic Pt, with no traces of oxides whose peaks are expected to be at 1.5–3 eV higher binding energies with respect to Pt metal.

The intensity of the oxygen peak in the spectrum (Fig. 17E) when compared to the nonoxidized samples and the absence of oxides shown in Fig. 18E, indicate that the PtO_2 monolayer has been displaced by the mercaptopyridine. Similarly the Cu monolayer has also been removed by the 2-MP, as can be seen by the negligible intensity of the Cu-2p line (~ 932 eV) in the spectrum (Fig. 17C) (less than 0.5 at.%). In the case of 4-MP, where some Cu content is expected, the Cu-2p peak is also negligible. This can be explained by taking into account that prior to spectroscopic measurements, the electrode was in contact with 4-MP solution for a period of about 2–3 h. We have observed by cyclic voltammetry that for such long exposure times, the 4-MP is able to reduce the Cu monolayer completely.

Spectra of the S-2p core level are shown in Fig. 19. Fig. 19A and B corresponds to 2-MP and 4-MP adsorbed

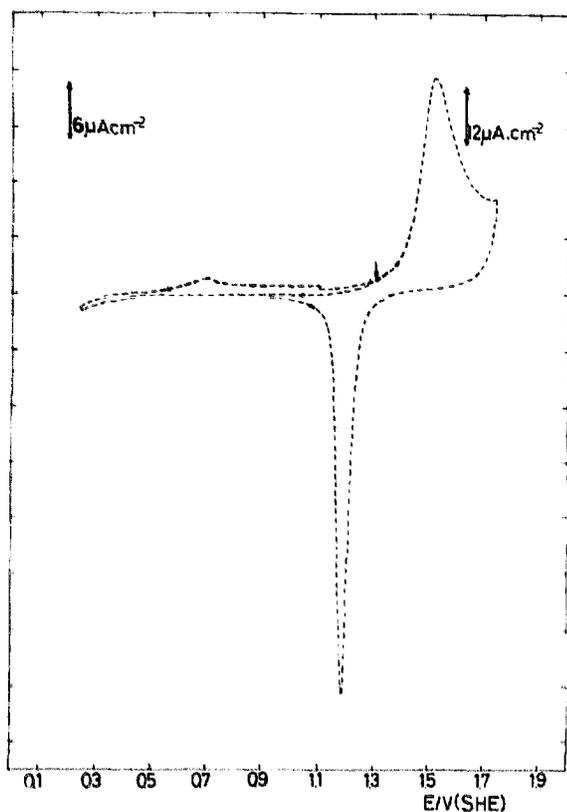


Fig. 16. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a gold electrode covered by an oxide monolayer and pretreated with a 1×10^{-3} M 4-MP solution in 0.50 M H_2SO_4 .

on Pt, respectively. Two bands can be observed at 162.6–163.1 eV and 168 eV. The first band is characteristic of RS species [6,16,17], and is composed of two peaks, at 164.3 eV and 163.1 eV for 2-MP, and at 164.3 eV and 162.6 eV for 4-MP. The peak at lower binding energy is assigned to S–Pt bonds, and the different position observed between 2-MP and 4-MP is probably related to the different interaction of the S atom with Pt when the N atom is in the vicinity (2-MP) as when the N atom is located opposite to the sulfur (4-MP). The second peak, at 164.3 in both cases, can be assigned to S–S bonds, since the same component has been observed in aldrithiol adsorbed on Pt. The second band observed in Fig. 19, at 168 eV, could be due to sulfonate (167.5 eV) and sulfate (168

Table 4
Displacement of gold oxide monolayer by mercaptopyridines

Adsorbate	Solvent	$Q_{\text{ADS}} (\mu\text{C cm}^{-2})$	$Q_{\text{ADS}/\text{Cu}} (\mu\text{C cm}^{-2})$
4MP	H_2SO_4	357	340
4MP	H_2O	387	386
2MP	H_2SO_4	293	317
2MP	H_2O	307	336

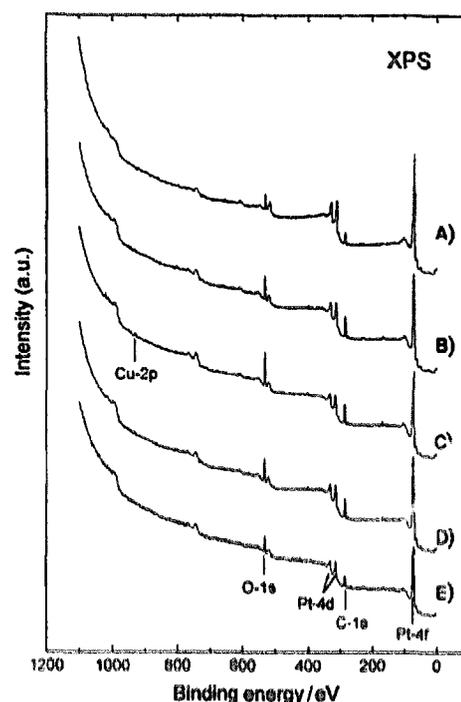


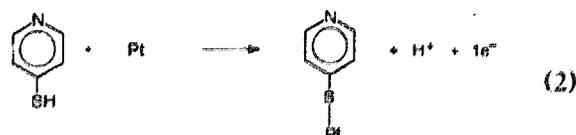
Fig. 17. XPS spectra over a wide binding energy range for: (A) 1 monolayer (ML) of 2-MP adsorbed on Pt; (B) 1 ML of 4-MP adsorbed on Pt; (C) 1 ML of Cu on Pt displaced by 2-MP; (D) 1 ML of Cu on Pt displaced by 4-MP; and (E) PtO_x ML displaced by 4-MP.

eV) species. In these cases, one must consider the possibility of oxidation of the mercaptopyridine molecules, which could occur by diffusion of oxygen through the water drop during sample transport to the UHV chamber [18].

Spectra of Fig. 19C and D corresponds to a Cu monolayer on Pt displaced by 2-MP and 4-MP, respectively. Similar features to those present in Fig. 19A and B are observed. Spectrum of Fig. 19E, which corresponds to a PtO_x monolayer displaced by 4-MP, also shows similar features to those observed in 4-MP adsorbed on Pt.

4. Discussion

Compounds containing sulfur in low oxidation states are strongly adsorbed on Pt. 4-MP is adsorbed through the sulfur atom with loss of the sulfhydryl hydrogen as shown in Eq. (2) below [8]:



The behavior of 4-MP on Ag(111) [7] has been studied by EELS and Auger electron spectroscopy. These studies

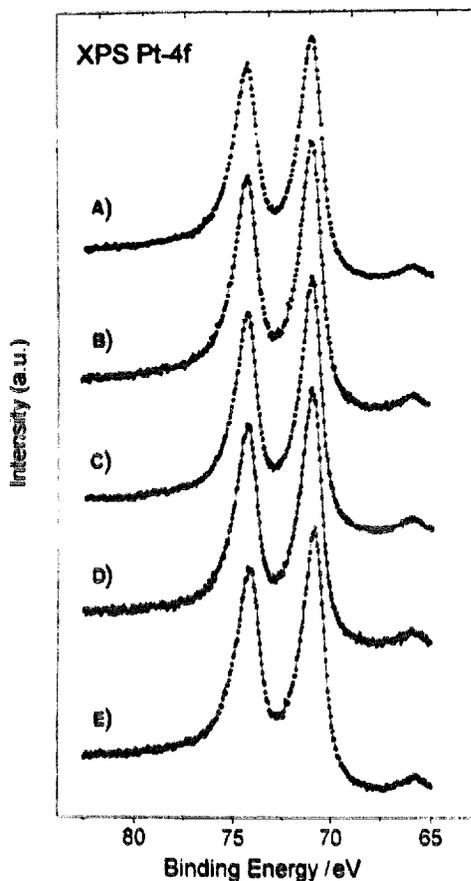
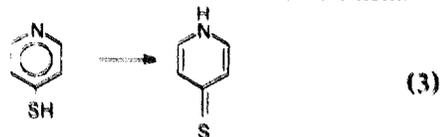
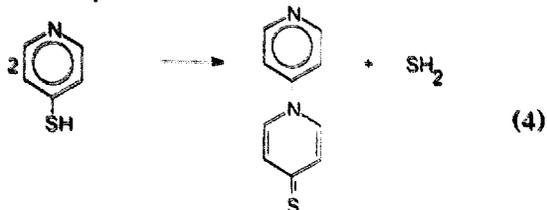


Fig. 18. XPS spectra showing the Pt-4f core level of: (A) 1 ML of 2-MP adsorbed on Pt; (B) 1 ML of 4-MP adsorbed on Pt; (C) 1 ML of Cu on Pt displaced by 2-MP; (D) 1 ML of Cu on Pt displaced by 4-MP; and (E) PtO_x ML displaced by 4-MP.

suggest that the isomerization of the adsorbed 4-MP (as shown in Eq. (3) below) occurs to a measurable extent.



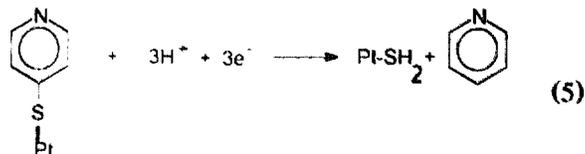
At more positive potentials, a coupling reaction (Eq. (4)) takes place as depicted below:



Although 2-MP probably adsorbs primarily through the sulfur atom, the presence of the pyridine atom could induce the formation of a chelate with the platinum surface giving rise to a more strongly chemisorbed layer [11].

When these modified electrodes are subjected to a positive potential scan, the adsorbate oxidation takes place on the surface.

However the adsorbate (Fig. 2C), as well as the oxidation products, (Fig. 2A,B) appear to remain on the surface until they are reduced at potentials near hydrogen evolution as depicted in Eq. (5):



Reduction does not lead to removal of the sulfur moiety, as shown by the presence of a prominent sulfur/sulfide oxidation peak at +1.20 V in the following positive scan. This behavior is characteristic of compounds containing sulfur in low oxidation states [3].

Although 2-MP is less reactive, it can be made to oxidize and reduce in qualitatively the same way as 4-MP.

The copper monolayer electrodeposited on Pt is displaced by 2-MP (Fig. 4A), suggesting that the strength of interaction between the sulfur atom and the platinum surface is greater than that between the deposited copper and the surface [9]. The copper stripping implies that copper is oxidized as in Eq. (6):



Consequently, the 2-MP has been presumably reduced to sulfide which is subsequently adsorbed. The oxidation current in the positive scan corresponds to oxidation of adsorbed sulfide to sulfur [19], which is consistent with the

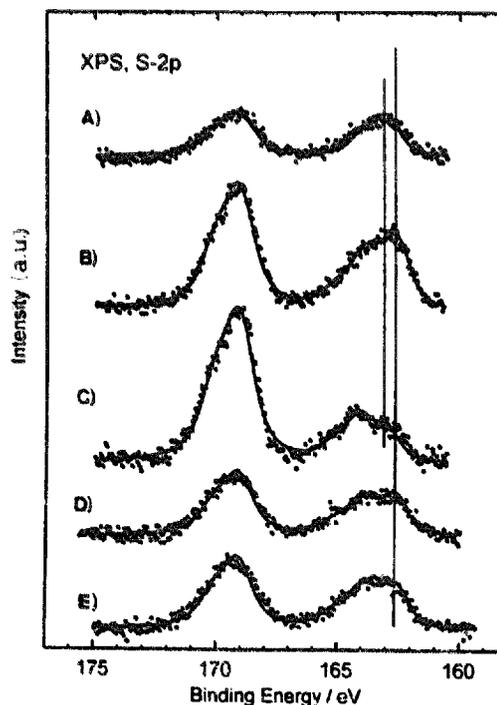
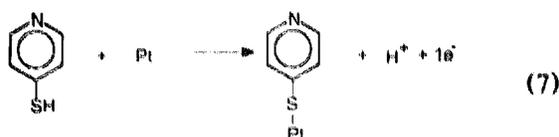


Fig. 19. XPS spectra showing the S-2p core level of: (A) 1 ML of 2-MP adsorbed on Pt; (B) 1 ML of 4-MP adsorbed on Pt; (C) 1 ML of Cu on Pt displaced by 2-MP; (D) 1 ML of Cu on Pt displaced by 4-MP; and (E) PtO_x ML displaced by 4-MP.

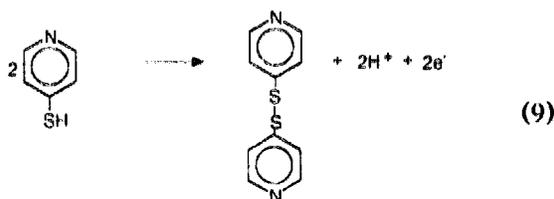
above. Contrary to the case of 2-MP, 4-MP does not displace the strongly adsorbed copper completely. The structure of 4-MP precludes the formation of a chelate with the platinum surface as was the case for 2-MP. Thus, bonding to the surface is solely through the sulfur atom. This results in a diminution of the strength of interaction of the adsorbed layer with the electrode so that 4-MP is rendered unable to displace the strongly adsorbed copper.

If the electrode is covered by an oxide monolayer, 4-MP as well as 2-MP being protonated or not, are capable of displacing the platinum oxide, i.e., the oxide is reduced by the mercaptopyridine molecule. Consequently the electrons necessary for the reduction of the platinum oxide are provided by the oxidative adsorption of the mercaptopyridine on the surface:



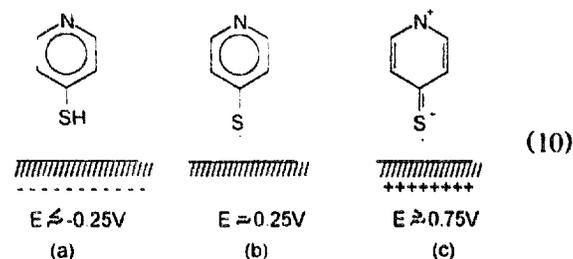
That the platinum surface is covered by adsorbate is evidenced by the fact that in a positive scan, there is a voltammetric peak ascribable to its oxidation (Fig. 5A) and also by the XPS spectra. Moreover, if sufficiently negative potentials are applied, the mercaptopyridine is reduced to sulfide and its subsequent oxidation to sulfur appears at +1.20 V (Fig. 5B). In addition, this modified electrode completely inhibits the Cu upd processes. That is, the adsorbate completely covers the surface, with the Pt–S bond being stronger than the Pt–Cu bond (Fig. 6).

4-MP can be oxidized on a gold electrode in a phosphate buffer solution (pH = 7.0) to form bis(4-pyridil)disulfide [5] (Eq. (9)).



The same reaction takes place when 4-MP is dissolved in water or in 0.5 M H₂SO₄ solution, this being a redox reaction in homogeneous solution. Taniguchi et al. [5] have studied 4-MP adsorption on gold by SERS. At positive potentials (ca. +0.75 V), the aromaticity of the pyridine ring decreases due to a strong interaction between the S atom and the electrode. At potentials negative of –0.250 V, the adsorbed 4-MP would be electroreductively des-

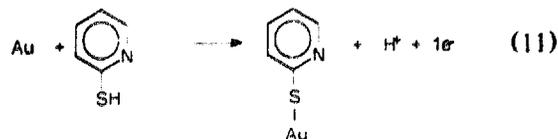
orbed. Possible models of 4-MP adsorbed on a gold electrode as function of potential are depicted below (Eq. (10)):



The open circuit potential is about +0.30 V, consequently the structure of 4-MP adsorbed on the surface is likely to be similar to that depicted in the second configuration of Eq. (10). However at more positive potentials $E = +0.65$ V, the surface concentration increases, since the interaction with the surface is stronger, as shown in the third configuration of Eq. (10). The same reasoning can be applied to 4-MP in acid media.

Contrary to the case of platinum, both 2-MP and 4-MP completely displaced the copper monolayer electrodeposited on the gold electrode. This process implies oxidation of the electrodeposited copper and the concomitant reduction of the mercaptopyridine. In this reaction an intermediate compound is produced. However at positive potentials the oxidation of adsorbed mercaptopyridine appears (Table 3). In the case of 4-MP, its oxidation charge does not differ too much from that obtained at open circuit in which not all surface is covered. On the contrary, for 2MP the oxidation charge is less than that at open circuit where the entire surface is covered by adsorbate. The difference between these suggests that a part of the surface may be covered by an adsorbed intermediate.

For the oxide monolayer on the gold electrode, its removal by 2-MP in acid or neutral medium is proposed to take place in a fashion similar to that occurring on Pt (Eqs. (11) and (12)).



Again the adsorbed 2-MP is oxidized in the positive scan. The oxidation charge is greater than that arising from adsorption of 2-MP at open circuit.

For displacement of the oxide monolayer by 4-MP in 0.50 M H₂SO₄ or water, there are two possibilities. The first is the oxidative adsorption of 4-MP and the concomitant reduction of the gold oxide, resulting in a completely covered surface since there is complete inhibition of copper upd. There is a higher degree of inhibition in this case

than when 4-MP is adsorbed on oxide free gold at open circuit. This could be due to the fact that the potential of the AuO₂/4-MP interface (+1.40 V) is more favourable for the adsorption of 4-MP than the potential of the Au/4-MP interface at open circuit (+0.30 V).

The second possibility is that at these positive potentials, the 4-MP is oxidized to aldrithiol (Eq. (9)) with the concomitant reduction of the oxide monolayer. The adsorbed aldrithiol would inhibit the upd of copper (compare Fig. 11 and Fig. 16). In addition, the oxidation charge (Fig. 16, Table 3) is similar to that for oxidation of adsorbed aldrithiol (347 $\mu\text{C cm}^{-2}$) from acid medium.

5. Conclusions

In this study we have seen the effect of 2- and 4-mercaptopyridine on monolayers deposited on gold and platinum electrodes. These compounds adsorb primarily through the sulfur atom, although in the case of 2-MP its adsorption is believed to be through a surface chelate.

2-MP in water or sulfuric acid solution displaces (via oxidation) the copper monolayer completely, giving rise to sulfide which is subsequently adsorbed. However 4-MP in water or sulfuric acid solution does not displace the strongly adsorbed copper completely. Only after long exposure times is 4-MP able to displace the copper monolayer.

If the copper monolayer is deposited on a gold electrode, it is completely displaced by both 2- and 4-mercaptopyridines, giving rise to an adsorbed intermediate.

When an oxide monolayer of gold or platinum is put in contact with 2-MP or 4-MP in water or 0.5 M sulfuric acid solution, the oxide is completely reduced, and the adsorbate remains on the surface of the electrode. In the case of a gold electrode with an oxide monolayer, reaction with 4-MP appears to give rise to the formation of aldrithiol which is subsequently adsorbed on the surface, and which furthermore appears to inhibit copper upd completely.

Acknowledgements

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