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Effects of Mercaptopyridines on the Underpotential and Overpotential Deposition of Copper on Pt(111)

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We present cyclic voltammetry studies of the under- and overpotential deposition of copper on a Pt(111) electrode in aqueous 0.50 M sulfuric acid solution in the presence and in the absence of adsorbed layers of 2- and 4-mercaptopyridine (2-MP, 4-MP). In general, the presence of adsorbed layers has been found to inhibit electrodeposition processes, suggesting very strong interactions between the adsorbates and the Pt(111) surface. 2-MP originates a higher degree of inhibition, which is ascribed to a stronger interaction probably due to the formation of a surface chelate via bonding through both N and S atoms. Studies have also been made of the reaction of 2-MP and 4-MP in solution with a Pt(111) electrode covered by an electrodeposited copper monolayer. The latter is shown to be partially or completely displaced (oxidized), depending on the electrode potential, by 2-MP and 4-MP. The reaction of the copper monolayer with 2-MP and 4-MP gives rise to an adsorbed intermediate, and a possible mechanistic pathway for this process is proposed.

1. Introduction

Thiols chemisorbed on metallic surfaces form films that are suitable for application on electrochemical sensors.¹ Although this is their best known application, these films can also be used as corrosion inhibitors² or for the construction of nanostructure-based devices³ among other uses. Aromatic thiols have been studied on Ag(111),⁴ Pt(111),^{5,6} and Au^{7,8} by surface-enhanced Raman scattering (SERS),^{9,10} electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), Auger spectroscopy, and electrochemical methods.^{4,5} The behavior generally accepted for both aliphatic and aromatic thiol compounds on these metals is that they form an ordered layer on the metallic surface, in which the molecules are bound through the S atom upon breakage of the S–H bond and formation of the metal–S bond.

Platinum,¹¹ gold,¹² and silver⁴ electrodes pretreated with organic adsorbates, e.g., mercaptans and aromatic carbon

and nitrogen, not only inhibit copper^{12,13} and silver^{6,14} underpotential deposition (upd) but also delay the onset of bulk deposition. In fact compounds such as mercaptopyridines are able to displace copper and silver monolayers^{8,14} deposited on these electrodes.

In this paper the influence of the electrode potential and the electrolyte on the adsorption process and mode of surface bonding of 2-mercaptopyridine (2-MP) and 4-mercaptopyridine (4-MP) on Pt(111) has been explored by cyclic voltammetry and X-ray photoelectron spectroscopy (XPS) methods. Also, we present electrochemical studies of the effects of Pt(111) electrode pretreated with 2-MP and 4-MP on copper electrodeposition at under- and overpotentials. Additionally we also present studies of the interaction of these adsorbates with Pt(111) covered with copper monolayer and suggest a possible mechanism for this reaction.

2. Experimental Section

The working electrode was a 10 mm diameter Pt single-crystal disk (oriented to $\pm 0.5^\circ$) supplied by Goodfellow Cambridge Limited. The crystal was supported by two 0.5 mm Pt wires spot-welded to its sides in such a way as to allow only one face of the crystal to be in contact with the solution. Prior to the experiments the crystal was immersed in hot ($\sim 80^\circ\text{C}$) nitric acid for 10 min.

The electrode pretreatment consisted of heating the crystal to ca. 1000°C in a gas/oxygen flame for 3 min and then allowing it to cool for 60 s in the vapor of deaerated supporting electrolyte before quenching in the same solution. Surface cleanliness was determined by cyclic voltammetry in 0.5 M H_2SO_4 , showing the characteristic “butterfly” shape first described by Clavilier.¹⁵

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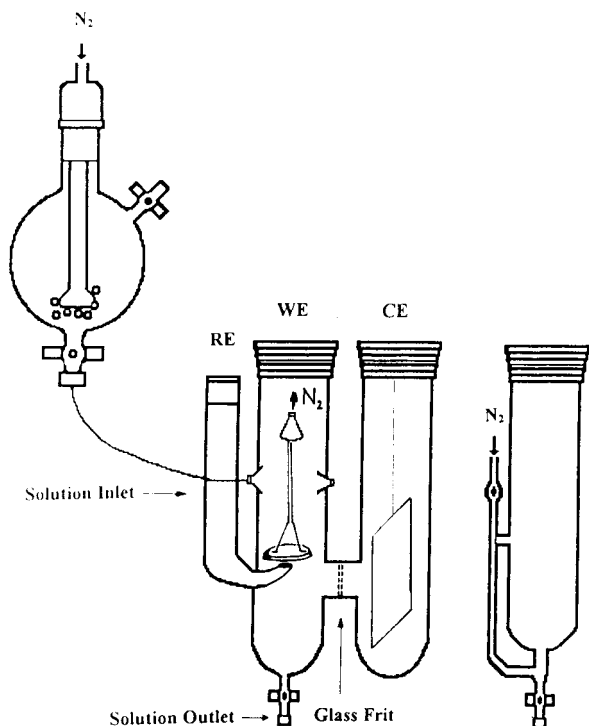


Figure 1. Schematic of the electrochemical cell employed.

Electrochemical area evaluation was carried out following the method described by Clavilier.¹⁶

The annealed crystal was held at open circuit or constant potential for 3 min in contact with a solution of the adsorbate in either water or 0.5 M H_2SO_4 and was then put into contact with 0.5 M H_2SO_4 , for recording the background current, or with 1.0 mM copper ion solution (in 0.5 M H_2SO_4). The potential was scanned in the negative direction at $1.0 \text{ mV}\cdot\text{s}^{-1}$ from a starting potential of +0.80 V.

The solutions were 1 mM in the adsorbate of interest. The experimental setup consisted of a three-compartment cell (separated by medium-porosity sintered glass disk) with provision for the addition and withdrawal of solutions (Figure 1). All joints were standard taper so that all the compartments could be hermetically sealed with Teflon adapters. The cell was 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-MP and 4-MP.

Cyclic voltammetry was carried out with a Brucker model 310 potentiostat and a PAR model 175 universal programmer. Data were recorded on a Hewlett-Packard model 7047A X-Y recorder. The reference electrode was $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ M } \text{H}_2\text{SO}_4$, but potentials were quoted against the normal hydrogen electrode (NHE). A platinum foil was used as counter electrode.

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

As a complement to the electrochemical measurements, XPS spectra of 2-MP and 4-MP adsorbed on Pt(111) were recorded using a commercial VG-CLAM hemispherical electron energy analyzer and a twin-cathode X-ray source, set to $\text{Al K}\alpha$ excitation (1486.7 eV). The base pressure in the ultrahigh vacuum (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

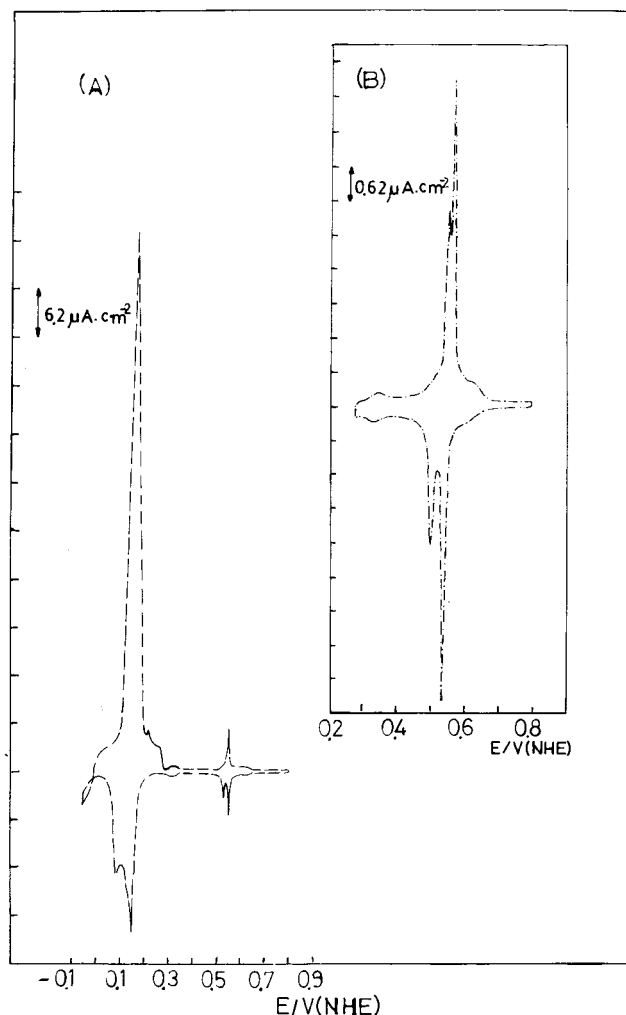


Figure 2. (A) Deposition (updown and opdown) of copper from a $1 \times 10^{-3} \text{ M}$ copper solution in 0.50 M H_2SO_4 onto a Pt(111) electrode ($v = 1 \text{ mV}\cdot\text{s}^{-1}$). The potential range from +0.80 to +0.28 V (updown region) ($v = 1 \text{ mV}\cdot\text{s}^{-1}$).

sample surface during transport. This remaining solution was subsequently pumped inside the UHV chamber.

3. Results

3.1. Deposition of Copper on a Pt(111) Electrode.

Figure 2A shows the cyclic voltammogram at $v = 1 \text{ mV}\cdot\text{s}^{-1}$ for copper deposition on a Pt(111) electrode from a 1 mM CuSO_4 solution in both underpotential deposition (upd) and overpotential copper deposition (opdown) regions. Figure 2B shows an expanded view of the upd regime.

On the initial cathodic scan, two peaks at +0.535 and +0.505 V, corresponding to copper upd, and one peak at +0.15 V, corresponding to opdown, are observed. In the stripping of the electrodeposited copper during the subsequent positive scan, two features are observed: a sharp stripping peak at a potential of +0.17 V, corresponding to the removal of bulk copper, and the stripping of upd copper. In this last region two peaks at +0.560 and +0.575 V are distinguished. The copper deposition charge is $396 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$. According to the literature^{17–19} the processes that takes place during the copper upd in a sulfuric acid solution are as follows: Prior to copper upd, bisulfate

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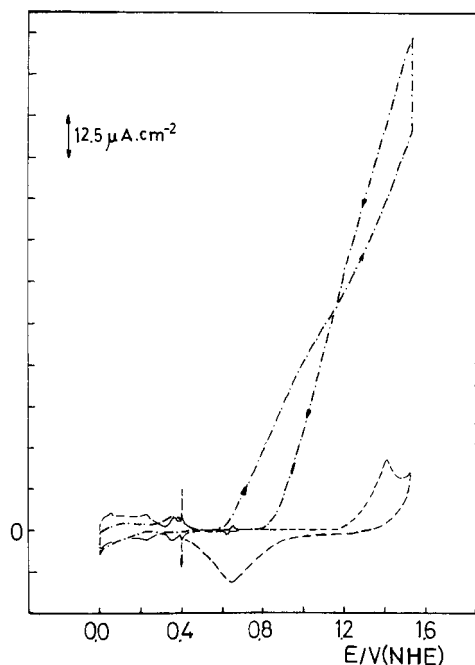


Figure 3. Cyclic voltammogram at $10 \text{ mV}\cdot\text{s}^{-1}$ for a Pt(111) electrode in $0.50 \text{ M H}_2\text{SO}_4$ in the absence (—) and presence of $1 \times 10^{-3} \text{ M}$ solution of 4-MP in $0.50 \text{ M H}_2\text{SO}_4$ (---).

anions are adsorbed forming a $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ$ structure on Pt(111). At the first upd peak, surface bisulfate changes into sulfate, while the copper is continuously adsorbed onto the surface to form a uniform coadsorption structure $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ$ of $\text{Cu}^{\delta+}$ and SO_4^{2-} . At the second upd peak, copper adsorption proceeds through the replacement with sulfate ions on Pt(111). After the second upd peak, the monolayer deposition of copper on Pt(111) is completed, and the sulfate ions are adsorbed on the (1×1) copper layer. Accordingly, the theoretically expected value for $\theta = 1$ is $480 \mu\text{C}\cdot\text{cm}^{-2}$. However for $\theta = 1$ the value for $Q_{\text{measured}}/Q_{\text{theoretic}} < 1$. This fact can be explained by the partially charged nature of the Cu monolayer.^{20–23}

3.2. Electrochemical Behavior of 4-MP and 2-MP on Pt(111) Electrodes. Both 2-MP and 4-MP can be oxidized in an acid medium on Pt(111) electrodes. A cyclic voltammogram carried out between the water oxidation and reduction limits at $10 \text{ mV}\cdot\text{s}^{-1}$ in a 1 mM 4-MP solution in $0.50 \text{ M H}_2\text{SO}_4$ exhibits irreversible behavior and significant hysteresis with oxidation currents in both the anodic and cathodic scans (Figure 3). The behavior followed by 2-MP is similar to that of 4-MP, showing a current plateau in the voltammogram in the scans in both directions.

When 2-MP (in $0.50 \text{ M H}_2\text{SO}_4$) is adsorbed onto Pt(111) at a constant potential of $+0.20 \text{ V}$ for 3 min, the initial positive scan (Figure 4A) of a cyclic voltammogram starting at $+0.10 \text{ V}$ shows a rising current due to two processes that are the oxidation of surface platinum and the oxidation of 2-MP. During the subsequent negative scan a Pt oxide reduction peak occurs at $+0.68 \text{ V}$, with a peak height that is considerably less than that resulting from a Pt(111) electrode under identical conditions. This suggests that the presence of adsorbed 2-MP gives rise to

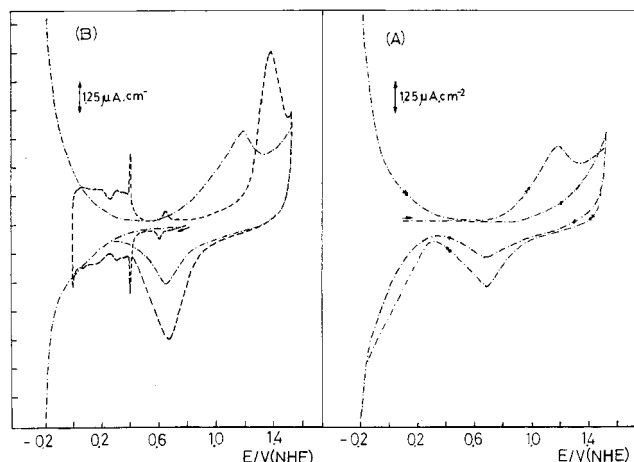


Figure 4. Cyclic voltammogram for a Pt(111) electrode in $0.50 \text{ M H}_2\text{SO}_4$ (—). Cyclic voltammogram for a platinum electrode pretreated with a $1 \times 10^{-3} \text{ M}$ solution of 2-MP in $0.50 \text{ M H}_2\text{SO}_4$, $v = 10 \text{ mV}\cdot\text{s}^{-1}$: (A) initial positive potential scan at 0.10 V (---), lower limit potential -0.20 V ; (B) initial negative potential scan at 0.80 V (---), lower limit potential -0.20 V .

Table 1. Oxidation Charge for Adsorbed Mercaptopyridines on Platinum

adsorbate	solvent	scan	$Q_{\text{ADS}}/\mu\text{C}\cdot\text{cm}^{-2}$
2MP	H_2SO_4	positive	121
2MP	H_2SO_4	negative	242
2MP	H_2O	positive	140
2MP	H_2O	negative	280
4MP	H_2SO_4	positive	196
4MP	H_2SO_4	negative	340
4MP	H_2O	positive	230
4MP	H_2O	negative	390

the diminution of platinum oxide formation and that the main process taking place is adsorbate oxidation ($121 \mu\text{C}\cdot\text{cm}^{-2}$; Table 1).

If the initial scan is in the negative direction, the adsorption of hydrogen is inhibited. However, upon scan reversal, a broad oxidation peak appears with an E_p value of $+1.19 \text{ V}$ (Figure 4B). This peak only appears when the lower limit is sufficiently negative (-0.10 V). In this case the difference between the anodic and cathodic charges is ca. $242 \mu\text{C}\cdot\text{cm}^{-2}$. It is interesting to notice that this peak is similar to that appearing in the second scan of Figure 4A, suggesting that the oxidation product of adsorbed 2-MP remains on the surface.

When 2-MP (in water) is adsorbed onto a Pt(111) electrode at $+0.20 \text{ V}$ for 3 min, the voltammogram recorded in $0.5 \text{ M H}_2\text{SO}_4$ shows a qualitatively similar behavior to that described for 2-MP adsorbed from an acid medium, with the exception that the oxidation charge is greater (Table 1). In this case it is necessary to set a more negative potential (-0.20 V) in order to obtain the oxidation peak at $+1.19 \text{ V}$, probably because the adsorbate is more strongly bonded to the surface. In the 2-MP molecule, sulfur and nitrogen atoms are positioned in a manner that may allow both to be bonded to the electrode surface, resulting in a chelate structure.

When 4-MP (1 mM solution in $0.50 \text{ M H}_2\text{SO}_4$ or H_2O) is adsorbed onto a Pt(111) electrode at $E = +0.20 \text{ V}$ for 3 min, it gives rise to a lesser inhibition of platinum oxide formation and a smaller overpotential for adsorbate oxidation. The charge due to oxidation of adsorbed 4-MP is $196 \mu\text{C}\cdot\text{cm}^{-2}$ in acid medium and $230 \mu\text{C}\cdot\text{cm}^{-2}$ in a neutral medium. In summary, the oxidation charge of 4-MP is higher than that of 2-MP in both media and the charge is higher in the neutral than in the acid medium

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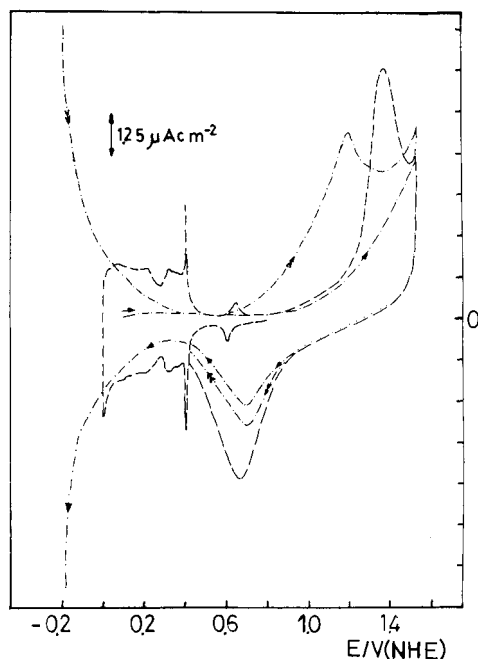


Figure 5. Cyclic voltammogram for a Pt(111) electrode in 0.50 M H_2SO_4 (—) and for a Pt(111) electrode pretreated with a 1×10^{-3} M solution of 4-MP in 0.50 M H_2SO_4 : initial positive potential scan at 0.10 V (---); second scan (— · —); lower limit potential -0.20 V.

for both adsorbates. This behavior is similar to that described for polycrystalline platinum.⁸ 4-MP binds to the electrode surface through the sulfur atom in almost vertical orientation. In this case the packing density is larger than that for 2-MP, giving rise to a higher oxidation charge.

In 0.5 M H_2SO_4 (pH = 0) pyridine nitrogen is protonated in both molecules (pK_a 2-MP = 1.07). Such protonation would (by inductive effects) cause a weakening of the sulfur–platinum bond, besides diminishing the possibility of adsorption onto the electrode surface (see XPS measurements), and consequently give rise to a lower oxidation charge than when the adsorbates are dissolved in water.

As with 2-MP, the positive sweep obtained following the initial negative one shows an oxidation peak at $+1.20$ V, which is similar to the second scan in Figure 5 and corresponds to the sulfide/sulfur oxidation process (see discussion). The coulometric charges are gathered in Table 1.

3.3. Copper Deposition on a Pt(111) Electrode Pretreated with 2-MP. Figure 6A shows the cyclic voltammogram for copper deposition in the upd region onto a Pt(111) electrode pretreated with a 1 mM solution of 2-MP in 0.50 M H_2SO_4 for 3 min at open circuit ($+0.71$ V). The charge for copper deposition is $162 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$. In these conditions the upd copper process on polycrystalline platinum was completely inhibited. It seems that copper displaces 2-MP easier when it is adsorbed on Pt(111) than on polycrystalline platinum.

Another possibility is that in the presence of 2-MP full coverage is not achieved and copper ions are deposited on free sites. Copper deposition usually implies the presence of sulfate since the coadsorption of Cu and sulfate is mutually enhancing.²³ In this case the upd copper in the presence of adsorbed 2-MP takes place over a wide potential range (not through two sharp peaks). This is due to the existence of lateral interactions with their neighbors (adsorbate molecules or copper adatoms) as well as to heterogeneity induced by them. To ensure complete

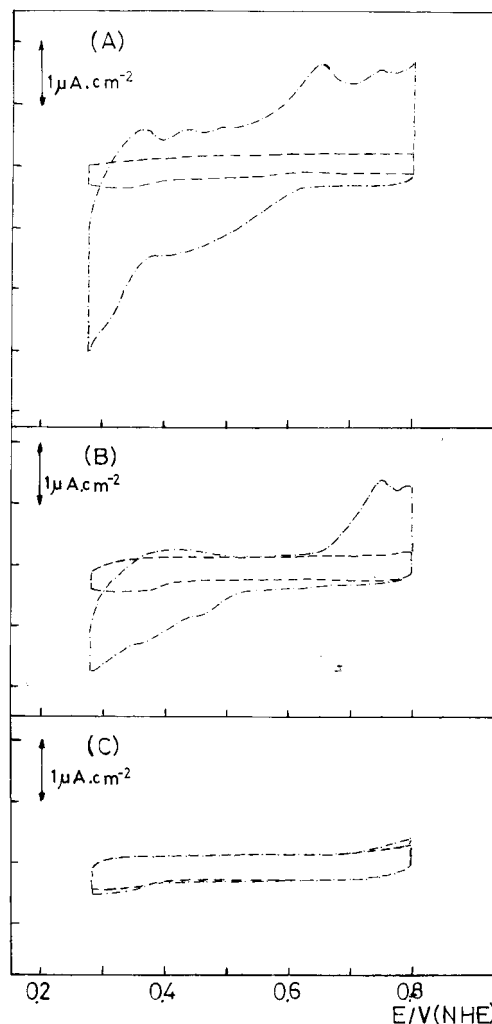


Figure 6. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a Pt(111) electrode pretreated with 1×10^{-3} M 2-MP in 0.50 M H_2SO_4 (— · —). Pt(111) electrode pretreated with 1×10^{-3} M 2-MP in 0.50 M H_2SO_4 (—). $v = 1 \text{ mV}\cdot\text{s}^{-1}$. For 3 min at open circuit. (B) For 15 min at open circuit. (C) For 3 min at $+0.20$ V.

coverage of the electrode by the adsorbate, the Pt(111) electrode was pretreated with 2-MP in 0.50 M H_2SO_4 at open circuit for 15 min (Figure 6B). The charge for copper deposition decreased to $80 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$. Finally for an adsorption potential $E = +0.20$ V for 3 min (Figure 6C) copper upd was practically inhibited, giving very strong evidence that the surface of the electrode was completely covered by the adsorbate. In these conditions bulk copper deposition (opd) takes place at a potential of $+0.15$ V, the same as in the absence of adsorbate. However the Tafel slope ($\partial E / \partial \log i$) is higher in this latter case, which means that the process is more impeded. In the anodic scan a hysteresis loop appears followed by the bulk copper stripping peak ($+0.46$ V) (Figure 7A). This shift (i.e., 290 mV more positive than in the absence of adsorbate) probably reflects the overpotential required to displace 2-MP adsorbed on the bulk copper deposit. Due to the fact that copper monolayer has been formed at potentials more cathodic (opd region) than in absence of 2-MP, its stripping takes place at more positive potentials, over a wide potential range, instead of by two peaks as in the absence of adsorbate (Table 3).

When an electrode is pretreated with a 1 mM solution of 2-MP in water at open circuit for 3 min ($+0.80$ V) the copper upd charge is $37 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$, indicating that the

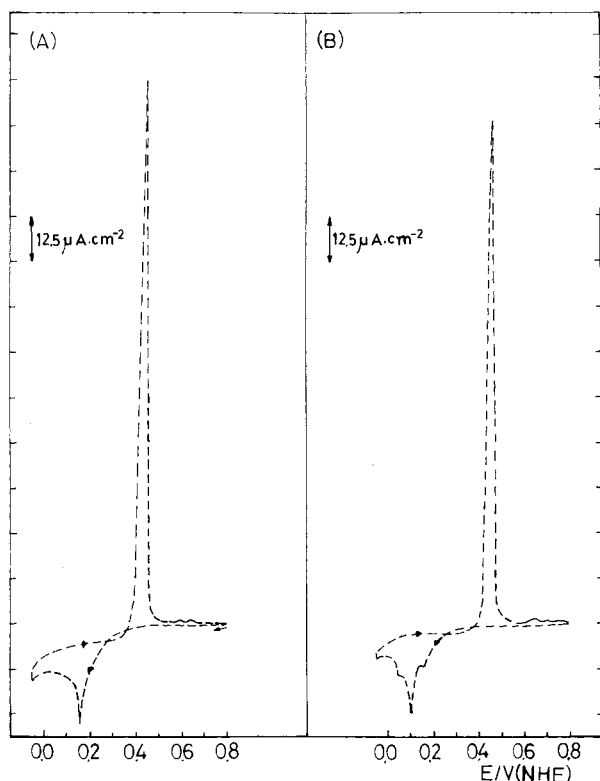


Figure 7. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a Pt(111) electrode pretreated with 1×10^{-3} M 2-MP (A) in 0.50 M H_2SO_4 and (B) in water (upd and opd regions). $\nu = 1 \text{ mV}\cdot\text{s}^{-1}$.

Table 2. Copper Deposition (upd) on a Pt(III) Electrode Pretreated with Mercaptopyridines

adsorbate	$t_{\text{ADS}}/\text{min}$	E/V	$Q_{\text{upd}}/\mu\text{C}\cdot\text{cm}^{-2}$
copper			396
2-MP/ H^+	3	c.a.	162
2-MP/ H^+	15	c.a.	80
2-MP/ H^+	3	+0.20	0
2-MP/ H_2O	3	c.a.	37
2-MP/ H_2O	3	+0.20	0
4-MP/ H^+	3	c.a.	205
4-MP/ H^+	3	+0.20	70
4-MP/ H_2O	3	c.a.	165
4-MP/ H_2O	3	+0.20	63

surface covered by adsorbate is greater than that pretreated in an acid medium (Table 2). This can be due to the higher molecular footprint of 2-MP adsorbed on Pt(111) in a neutral medium. For an adsorption potential $E = +0.20 \text{ V}$ for 3 min the copper upd was completely inhibited, indicating a full coverage by the adsorbate. In these conditions if the cathodic limit is extended into the opd region (Figure 7B), it is possible to observe a peak at +0.10 V, involving an overpotential of 50 mV, although a shoulder appears at +0.16 V. As already mentioned, 2-MP probably adsorbs forming a chelate structure with Pt(111), thus giving rise to a more strongly chemisorbed layer (see XPS measurements). In the anodic scan, a stripping peak at +0.47 V appears after a hysteresis loop. In this case the shift in bulk copper stripping potential is 300 mV relative

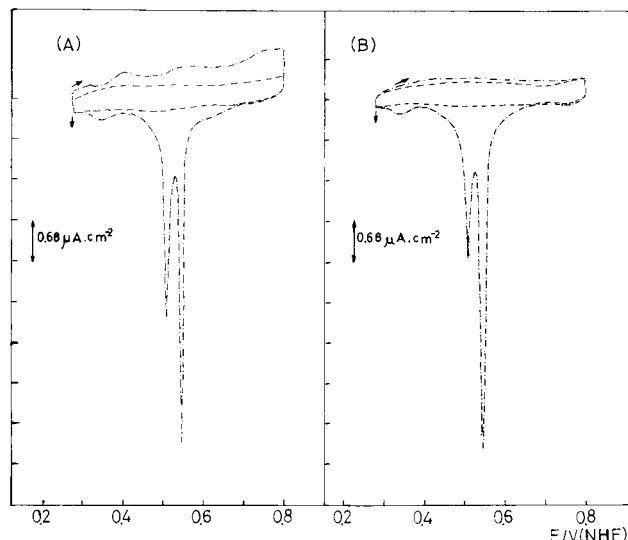


Figure 8. Deposition of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a Pt(111) electrode. At open circuit, the electrode was put into contact with 1×10^{-3} M 2-MP (A) in 0.50 M H_2SO_4 and (B) in water, for 3 min. The electrode was rinsed with 0.50 M H_2SO_4 and an anodic sweep was initiated (---). Pt(111) electrode pretreated with 1×10^{-3} M 2-MP in (A) 0.50 M H_2SO_4 (B) in water (---). $\nu = 1 \text{ mV}\cdot\text{s}^{-1}$

to that in the absence of adsorbate. The reason for this behavior is probably the same as that mentioned above. In the upd region copper stripping takes place at +0.64 and +0.69 V, slightly more anodic than copper stripping in acid medium.

When these results, both in acid and neutral media, are compared with those obtained for polycrystalline platinum,¹³ it can be noted that copper monolayer stripping is only observed in the present case. Therefore, it has not previously been displaced, at least completely, by 2-MP. The reason for this is probably that the adsorption potential for reaching full coverage on Pt(111) is +0.20 V and at this potential copper opd takes place (Figure 7). On polycrystalline platinum the full coverage is reached at open circuit ($E = 0.72 \text{ V}$). This potential is close to those at which stripping copper monolayer takes place.

3.4. Displacement of Electrodeposited Copper Monolayers on Platinum by 2-Mercaptopyridine.

When a copper monolayer is electrodeposited at underpotentials (upd) on a Pt(111) electrode and subsequently exposed at open circuit for 3 min to a solution of 2-MP (in 0.50 M H_2SO_4), the copper monolayer is partially stripped, as can be observed in the first anodic scan (Figure 8A). The copper stripping charge was $158 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$. However when the contact time was about 1 h, there was no evidence of copper stripping. The same result is obtained for $E = +0.20 \text{ V}$ and $t = 3 \text{ min}$. In these conditions 2-MP reaches the maximum coverage. This suggests that the strength of interaction between the sulfur atom and the platinum surface is greater than that between the deposited copper and the surface.

If 2-MP is dissolved in water and put into contact at open circuit for 3 min with a copper monolayer deposited on Pt(111), the copper stripping charge is only 20 ± 6

Table 3. Copper Deposition on a Pt(III) Electrode Pretreated with Mercaptopyridines

adsorbate	solvent	E_{upd}/V	E_{ups}/V	E_{opd}/V	E_{ops}/V
copper	H_2SO_4	0.34, 0.50, 0.53	0.56, 0.57	0.15	0.17
2MP	H_2SO_4		0.59, 0.64	0.15	0.46
2MP	H_2O		0.64, 0.69	0.16–0.10	0.47
4MP	H_2SO_4	0.36, 0.52	0.65, 0.70	0.15	0.42
4MP	H_2O	0.36, 0.51	0.71, 0.74, 0.77	0.15–0.07	0.48

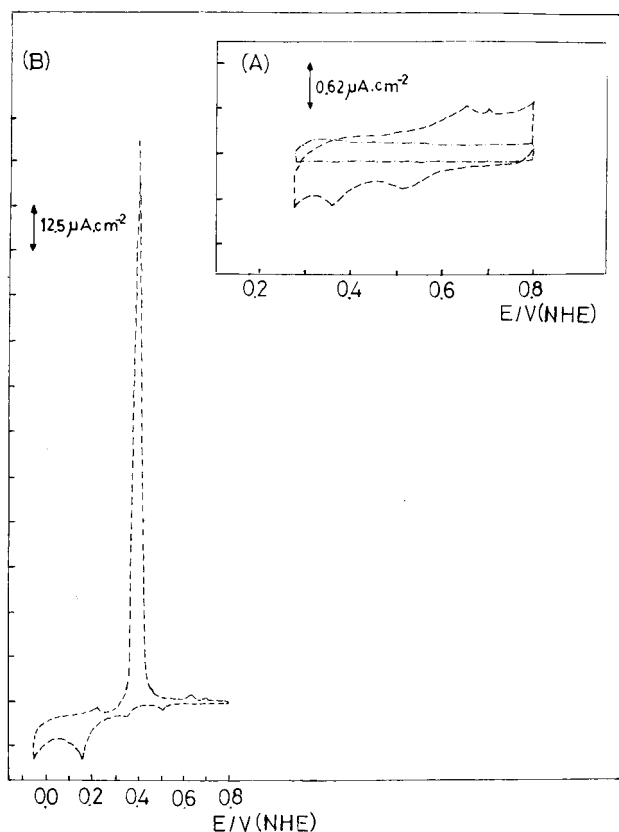


Figure 9. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a Pt(111) electrode pretreated with 1×10^{-3} M 4-MP in 0.50 M H_2SO_4 (A) upd region and (B) opd region. $\nu = 1 \text{ mV}\cdot\text{s}^{-1}$.

$\mu\text{C}\cdot\text{cm}^{-2}$ (Figure 8B). In this case the pyridine nitrogen of 2-MP is not protonated, resulting in an increase in the strength of interaction between the adsorbed layer and the electrode so that 2-MP is rendered able to displace more electrodeposited copper. For $E = +0.20 \text{ V}$ and $t = 3 \text{ min}$ the copper stripping charge was zero. The copper monolayer is only completely displaced by 2-MP (in 0.5 M H_2SO_4 or water) at the potential at which 2-MP reaches full coverage.

3.5. Copper Deposition on a Pt(111) Electrode Pretreated with 4-Mercaptopyridine. If a Pt(111) electrode is pretreated with 1 mM solution of 4-MP in 0.50 M H_2SO_4 at open circuit (+0.72 V) for 3 min, the copper deposition charge is $205 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$. For a similar potential the adsorption of 4-MP is smaller than that of 2-MP. To reach full coverage by 4-MP, this was adsorbed at $E = +0.20 \text{ V}$ for 3 min and a copper deposition charge of $70 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$ was obtained. The same charge results even if the adsorption time is 60 min (Figure 9A). In these conditions two peaks are obtained in the upd region (0.36–0.52 V) corresponding to copper deposition on sites free of adsorbate. The opd copper deposition takes place at a potential of +0.15 V with a Tafel slope higher than that obtained in the absence of adsorbate, implying that the process is less favored. In the anodic scan a small peak at +0.23 V and a large peak at +0.42 V are observed. They correspond to the stripping of bulk copper that was deposited at different potentials. The presence of adsorbed 4-MP inhibits the stripping of the deposited copper, delaying it 250 mV to a more positive potential (Figure 9B). The upd copper stripping potentials are 0.65 and 0.70 V. These potentials are the same if the cathodic limit is set in the upd region (Figure 9A). Therefore these peaks

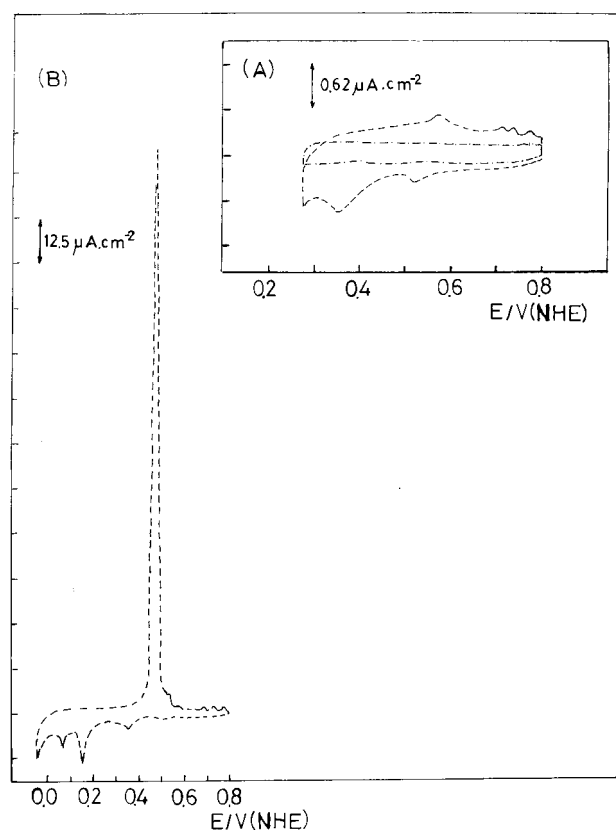


Figure 10. Deposition and stripping of copper from a 1×10^{-3} M copper solution in 0.50 M H_2SO_4 onto a Pt(111) electrode pretreated with 1×10^{-3} M 4-MP in water (A) upd region and (B) opd region. $\nu = 1 \text{ mV}\cdot\text{s}^{-1}$.

correspond to the stripping of copper deposited on sites free of 4-MP.

If 4-MP is adsorbed at open circuit for 3 min in aqueous solution, the copper deposition charge diminishes to $165 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$ (Table 2). In this case the pyridine nitrogen is not protonated, like in an acid medium, and there is some probability of N–Pt interaction, which would involve deviations of the adsorption geometry with respect to normal geometry, as has been determined by XPS.²⁴ When adsorption takes place at $E = +0.20 \text{ V}$ the deposition charge is $63 \pm 6 \mu\text{C}\cdot\text{cm}^{-2}$ (Figure 10A). However, as has been mentioned above, full coverage is not reached for longer adsorption times. In these conditions two peaks are obtained in the upd region (+0.51, +0.36 V) for copper deposition. The opd copper appears in two steps (+0.15, +0.07 V) (Figure 10B). Assuming that 4-MP is able to adsorb either in normal geometry (by S atom) or out of normal geometry (N–Pt interaction) on the copper monolayer, the potential for bulk copper deposition will be different depending on the adsorbate orientation.

The assumption of two different adsorption geometries for 4-MP is corroborated by previous results on polycrystalline Pt²⁴ and also by the XPS S-2p spectra of 2-MP and 4-MP adsorbed on Pt(111) shown in Figure 11. The solid line through the data points is the result of a least-squares fitting procedure consisting of Lorentz functions convoluted with a Gaussian to account for the experimental resolution ($\delta(E) \approx 0.6 \text{ eV}$) and a Shirley function to simulate the intensity of inelastically scattered photoelectrons (not shown).²⁵ A small difference in the binding

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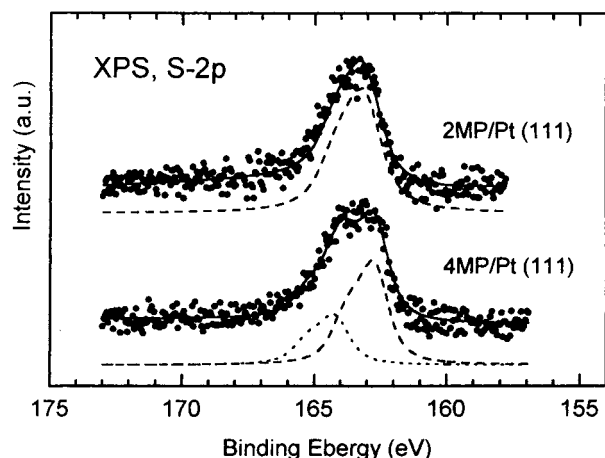


Figure 11. S-2p photoelectron spectra of (a) 2-MP adsorbed on Pt(111) and (b) 4-MP adsorbed on Pt(111). The solid line through the data points, as well as the subspectra, are the results of a least-squares fitting procedure (see text).

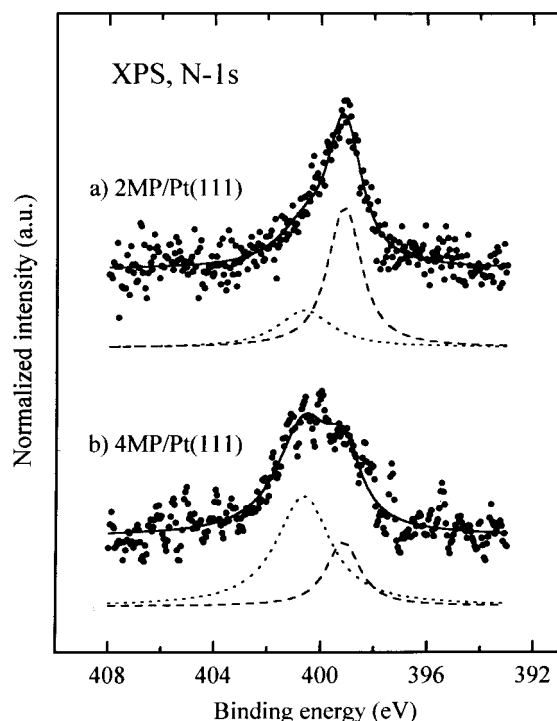
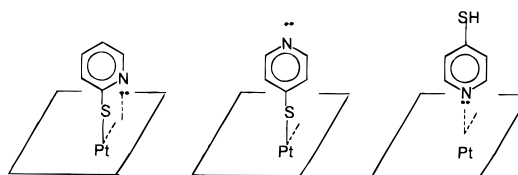


Figure 12. N-1s photoelectron spectra of (a) 2-MP adsorbed on Pt(111) and (b) 4-MP adsorbed on Pt(111). The solid lines through the data points, as well as the subspectra, are the results of a least-squares fitting procedure (see text).

energy (BE) position is observed between the 2-MP and the 4-MP samples, 163.1 eV for 2-MP and 162.7 eV for 4-MP. These peaks are assigned to S–Pt bonds,²⁶ and the different position observed between 2-MP and 4-MP must be related to the different electronic environment around the S atom in both molecules. In 2-MP, the N atom is close to the S atom, allowing the formation of chelate structures of type S–Pt–N, whereas in 4-MP the N atom is located in the “para” position and the S atom only interacts with Pt.

XPS experiments show an additional S-2p subspectrum at ≈ 164.2 eV appearing in the case of the 4-MP/Pt sample, which is absent for the 2-MP/Pt sample. The presence of this subspectrum could be related to the possibility of 4-MP

to form dimers, bound by the S atom whose electronic environment is different from that of the S atoms in 4-MP alone. This result is in concordance with that obtained for aldrithiol onto polycrystalline platinum.²⁴ The similarity between these spectra suggests that the dotted component can be associated with the formation of dimers. The absence of this component in the spectrum of 2-MP is due probably to the presence of a chelate structure hindering the dimer formation. The interpretation of the N-1s data is consistent with the results obtained at the S-2p core level (Figure 12). Two was the minimum number of Lorentz components needed to correctly fit the N-1s experimental data. According to previous results,^{24,27,28} the component at higher binding energy (dotted subspectrum) can be assigned to N in the pyridine ring, whereas the component at lower binding energy (dashed subspectrum) originates from N–Pt interaction. In the case of 2-MP/Pt(111), the N–Pt component predominates, since a chelate structure is the most probable. On the other hand, for 4-MP the dotted subspectrum predominates, since the N atom is in “para” position in this case, but the intensity of the N–Pt component is not zero, indicating the existence of a second, out of normal, adsorption geometry.



In the anodic scan of Figure 10, bulk copper stripping also appears in two peaks (+0.48, +0.54 V). In the first case the overpotential respect to copper stripping in the absence of adsorbate is 310 mV, similar to that for 2-MP in water, due to the adsorption of 4-MP on bulk copper. However, this displacement is not reflected in upd copper stripping since the potentials are similar to that corresponding to a potential cathodic limit of +0.28 V (Figure 10A). In this case the stripping potential range is larger than that obtained in an acid medium although the deposition potentials are similar (Table 3) due to the different interaction of copper deposited on free sites with 4-MP, depending on adsorbed molecule orientation.

3.6. Displacement of Electrodeposited Copper Monolayers on Platinum by 4-Mercaptopyridine. Contrary to the case of 2-MP, when a Pt(111) electrode with an electrodeposited monolayer of copper is placed in contact with a 4-MP solution in H₂SO₄ or water at $E = +0.20$ V for 3 min, the anodic scan exhibits the stripping of deposited copper ($162 \mu\text{C}\cdot\text{cm}^{-2}$). 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 may result in a diminution of the interaction of the adsorbed layer with the electrode so that 4-MP displaces less copper. This is also found on polycrystalline platinum.⁸ Besides, more copper is displaced by 4-MP/water than by 4-MP/0.5 M H₂SO₄. At pH = 0 the nitrogen atom in 4-MP is protonated. Since the nitrogen site is located “para” to the sulfur, such protonation would (by inductive effects) cause a weakening of the sulfur–platinum bond, diminishing the amount of displaced copper.

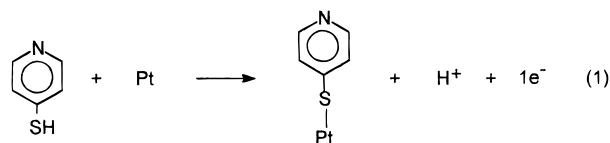
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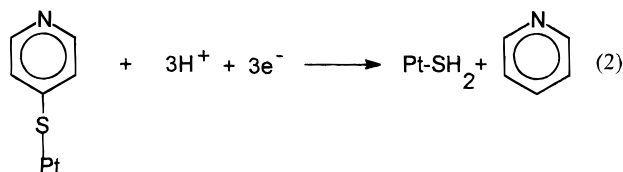
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4. Discussion

It is known that this kind of compound adsorbs on Ag(111)⁴ or Pt(111)⁵ with loss of the mercaptan hydrogen, as can be seen in the following reaction for 4-MP:



When these modified electrodes with thiols are subjected to a positive potential scan, adsorbate oxidation takes place on the surface. The oxidation charge agrees with previous voltammetric studies for aliphatic thiols²⁹ where the oxidation product was sulfinic acid. However, in this case, there is no oxidative removal as occurs with Au(111)³⁰ since the oxidation products are reduced on the subsequent negative potential scan in the region of hydrogen evolution, as depicted in eq 2:



For 2-MP the reduction potential is more negative in a neutral (−0.20 V) than in an acid medium (−0.15 V) due to the bonding of sulfur and nitrogen atoms with the platinum surface, giving rise to a more strongly chemisorbed layer. Reductive removal does not involve the breaking of the platinum–sulfur bond, as can be seen in eq 2 and as is shown by the presence of a large oxidation peak at +1.19 V on the second anodic potential scan corresponding to the sulfide/sulfur oxidation process (Figure 4 and Figure 5). The same behavior has been observed for these compounds on polycrystalline platinum.^{8,31}

The copper monolayer electrodeposited on Pt(111) is displaced by 2-MP at constant potential (+0.20 V). Such displacement implies that the copper is oxidized, and consequently the 2-MP has presumably been reduced to sulfide. This behavior is similar to that observed on polycrystalline platinum although the presence of sulfide has not been determined by X-ray photoelectron spectroscopy (XPS).⁸ The mechanism that takes place is not yet known, but it seems clear that in order to completely displace the copper monolayer from the platinum surface it is necessary to apply a potential corresponding to 2-MP maximum adsorption on Pt(111). However, the surface

free energy of Cu (1.93 J m^{−2}) is lower than that of Pt (2.69 J m^{−2}),³² and therefore the mercaptopyridines could be adsorbed on the copper monolayer. Nevertheless, the reduced mercaptopyridine will remain bonded to Pt since the heat of formation of S–Cu is lower than that of the S–Pt bond.³³ However, the XPS spectra of Pt-4f and Cu-2p core levels do not show the presence of bonded sulfur and the presence of 2-MP or 4-MP adsorbed on Pt(111) surface is given by the spectra at the S-2p and N-1s core levels.^{8,34} These spectra show two possible positions for 2-MP and 4-MP adsorbed on Pt(111) by the S–Pt and the N–Pt interactions.

2-MP completely displaces the copper monolayer at a constant potential of +0.20 V. This is not the case with 4-MP, where it is not possible for a chelate structure to form, diminishing the bond strength with the surface electrode. Besides, at this potential 4-MP does not reach full coverage on Pt(111).

Consequently it is possible to deposit copper on Pt(111) covered by 2-MP at opd potentials only. On the contrary, both upd and opd copper can be obtained on Pt(111) pretreated with 4-MP

5. Conclusions

Thiols adsorb on Pt(111) primarily through the sulfur atom, although in the case of 2-MP its adsorption is believed to be through a chelate structure reaching full coverage at a constant potential of +0.20 V. 2-MP and 4-MP are reduced to sulfide at hydrogen evolution potentials necessary for the large overpotential for 2-MP dissolved in water.

In this study we have seen the effect of 2- and 4-mercaptopyridine on copper monolayer deposited on Pt(111). 2-MP completely displaces the copper monolayer at constant potential while 4-MP does so only partially, due in part to its bonding to the surface through the S atom only and also because it does not reach full coverage at this potential. The mechanism proposed for the displacement of the copper monolayer by mercaptopyridines in water or sulfuric acid solution implies the adsorption of the molecules on the copper monolayer due to its lower surface energy as compared to platinum. However, the reduced mercaptopyridines remain adsorbed on the platinum surface, since the S–Pt bond energy is stronger than that of S–Cu.

By XPS spectra two possible positions for 2-MP and 4-MP adsorbed on Pt(111) have been determined. However, the presence of reduced mercaptopyridines on electrode surface could not be identified.

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