

## THE EFFECTS OF MERCAPTOPYRIDINES ON MONOLAYERS DEPOSITED ON GOLD AND PLATINUM ELECTRODES.

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The present work is a voltammetric study on the behavior followed by gold and platinum electrodes covered by copper or oxide monolayers, in aqueous 0.5 M sulphuric acid solution, and in the presence of organic adsorbates containing a sulphur heteroatom. The adsorbates employed were 2-Mercaptopyridine (2-MP) and 4-Mercaptopyridine (4-MP). All experiments were made with both electrodes.

### Introduction:

The use of electrochemical techniques such as cyclic voltammetry allows the characterization of the processes taking place in the electrodeposition of metals, both in the presence and absence of coadsorbed species, reflecting the interactions existing between the co-adsorbates, the electrode surface and the metal overlayer.

Strong adsorption of mercaptans to polycrystalline platinum and gold electrodes takes place through the sulfur atom [1,2]. Reductive elimination of alkyl and aryl groups from adsorbed mercaptans on platinum yields a layer of adsorbed sulfide [1].

Hubbard et al. have studied the adsorption of 4-MP and 2-MP on Ag (111) surfaces and concluded that it is potential dependent, with the adsorbed molecule forming a dimer at higher potentials [3]. The adsorbate binds to the electrode surface through the sulfur atom in a normal orientation rather than through the nitrogen site as would be anticipated.

When a Pt electrode was pretreated with a solution of 4-MP in water or H<sub>2</sub>SO<sub>4</sub> 0.5M, the UPD processes of copper [4] or silver [5] were inhibited and the onset of bulk deposition was shifted. These results suggested that the 4-MP or 2-MP adsorption is through the sulfur atom. Studies of silver deposition onto Pt (111) in the presence of a 2-MP adlayer reveal further evidence for a chelate adsorption model [6].

Studies of Surface Enhanced Raman Scattering (SERS) have demonstrated that 4-MP adsorbs on gold through the sulfur atom in a normal orientation [7], forming a dimer at high potentials, as observed on platinum.

Results obtained in this work indicate a strong dependence of the voltammetric response on the nature of the adsorbate that is consistent with the strength of adsorption on the platinum and gold surfaces.

**Experimental Section:**

Polycrystalline platinum and gold were employed as working electrodes:

**-Platinum:**

It consisted of a polycrystalline platinum disk of ca. 0.01 cm<sup>2</sup> that was sealed in glass. Evaluation of the electrochemical area was done through the integration of the voltammetric peaks for hydrogen adsorption in 0.5 M H<sub>2</sub>SO<sub>4</sub> and using a conversion factor of 210 μC/cm<sup>2</sup>. The electrode pretreatment consisted of polishing with 1 μm diamond paste ( Buehler ) and rinsing it with water, prior to electrochemical activation in 0.5 M H<sub>2</sub>SO<sub>4</sub> by means of cyclic voltammetry between 1.55 and 0.0 V vs NHE. The counterelectrode was a large area Pt foil.

**-Gold:**

It consisted of a polycrystalline gold wire of ca. 0.2 cm<sup>2</sup>. The area of the electrode was measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> by integration of the charge required for the reduction of the gold surface previously oxidized by an anodic scan until the potential limit of 1.74 V vs NHE, using a charge of 400 μC/cm<sup>2</sup> and 2 e<sup>-</sup> per gold surface atom. Before each experiment, the gold electrode ( 99.999% Johnson Mathey) was cleaned by flaming and quenched with Milli-Q water. The counterelectrode consisted of a large area rolled up gold wire.

In those experiments involving a bare, oxide-free surface, the cycle was arrested at 0.45 V vs NHE for platinum electrodes and at 0.7 V vs NHE for gold electrodes (double-layer region) on the anodic sweep. Conversely, the sweep was stopped at 1.15V for platinum and 1.6 V for gold on the cathodic scan, prior to oxide reduction, for those studies involving an oxidized surface, which will be referred to in the text as PtO and AuO.

The adsorbate concentration was typically 1×10<sup>-3</sup> M. All solutions were prepared using water purified with a Millipore Milli-Q system. High purity reagents ( Merck, Aldrich ) were used as received.

Cyclic voltammetry was carried out using a Bruker Model 310 potentiostat, and a PAR model 175 Universal Programmer. Data were recorded on a Hewlett-Packard model 7047 X-Y recorder.

A three-compartment electrochemical cell with provision for degassing and solution exchange was used. A Normal Hydrogen Electrode (NHE) was used as reference electrode.

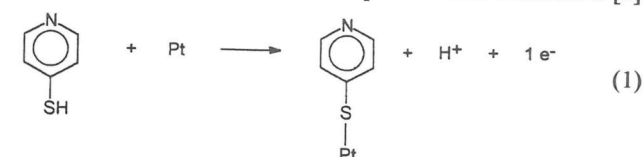
**Results and Discussion:**

**Behavior followed by mercaptopiridines on polycrystalline platinum electrodes:**

Both 2-MP and 4-MP are electrochemically active both in solution and when adsorbed on the electrode.

The voltammogram recorded in H<sub>2</sub>SO<sub>4</sub> 0.5 M for a platinum electrode pretreated with a 4-MP acid solution does not show any distinct wave corresponding to the Pt oxide formation. During the first scan, the oxidation of the Pt surface is minimum due to the presence of the 4-MP layer, taking place mainly the oxidation of adsorbate with a charge of 180 μC/cm<sup>2</sup> ( fig 1 ).

The adsorption reaction of 4-MP on Pt reported in the literature is [3] :



If, on the other hand, the initial scan is in the cathodic direction, the adsorption of hydrogen is suppressed and an oxidation peak appears at 1.2 V ( Q = 330 μC/cm<sup>2</sup> ) in the ensuing positive scan. This peak only appears when the cathodic limit is significantly negative. This behavior is similar to that observed for other carbon compounds containing sulfur in low oxidation states. For comparison, adsorbed 4-MP is reduced in the hydrogen region as depicted below ( Equation 2 ). A subsequent anodic scan shows the peak corresponding to the oxidation of chemisorbed H<sub>2</sub>S to sulfur [1].

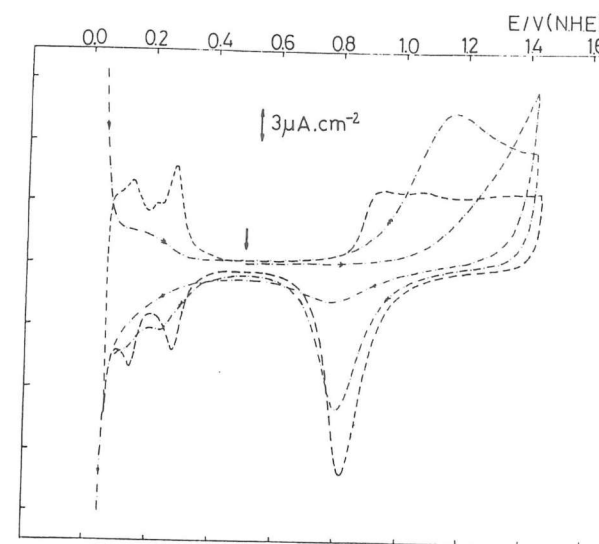
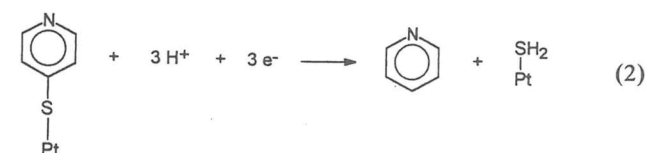


Fig.1  
Cyclic voltammogram of adsorbed 4-MP at Pt.  
C4-MP = 10<sup>-3</sup> M in H<sub>2</sub>SO<sub>4</sub> 0.5 M; v = 10 mV/s.

Adsorbed 2-MP is less reactive both for oxidation ( Q = 130 μC/cm<sup>2</sup> ) and reduction. Although 2-MP likely adsorbs primarily through the sulfur atom, the presence of the pyridine atom could give rise to the formation of a chelate with the platinum surface, thus originating a more strongly chemisorbed layer .

- Influence of mercaptopyridines on the electrodeposition of copper on Pt:

In the presence of these adsorbates, the Cu UPD process is completely inhibited, and only bulk copper deposition (OPD) takes place at a considerable overpotential with respect to the potential at which it occurs on a clean surface (see Table I).

Figure 2 shows that after the stripping of OPD copper on a platinum electrode pretreated with 2-MP, no stripping peak of UPD copper is observed. This suggests that the strength of the interaction between the sulfur atom and the Pt surface is greater than that between the deposited copper and the surface. This would mean that 2-MP displaces the copper monolayer. Such a displacement can also be observed when an electrode with an initially deposited copper monolayer (fig 3.b) is exposed to a solution of 2-MP. On the initial anodic scan there is no evidence of copper stripping, consistent with the previous argument. The proposed mechanism is that, at open circuit, 2-MP is reduced to sulfide with the concomitant oxidation and displacement of the electrodeposited copper.

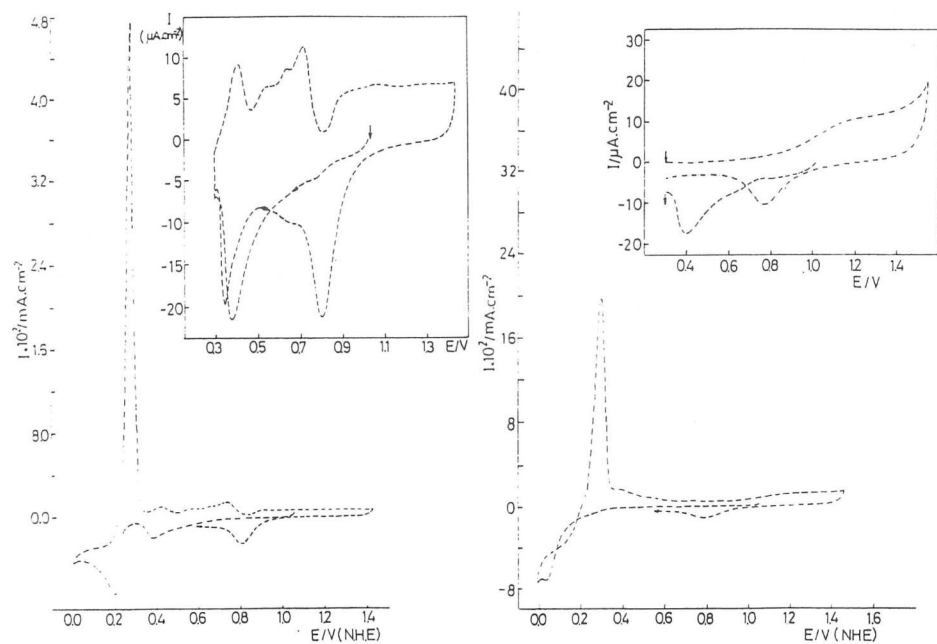


Fig 2  
a) UPD and OPD of copper on Pt.  $C_{CuSO_4} = 10^{-3}$  M in  $H_2SO_4$ , 0.5 M;  $v = 10$  mV/s.  
b) UPD of copper.  $C_{CuSO_4} = 10^{-3}$  M in  $H_2SO_4$ , 0.5 M,  $v = 10$  mV/s.

Fig 3  
a) Deposition of copper on a platinum electrode pretreated with a solution of 2-MP in water.  $C_{2-MP} = 10^{-3}$  M,  $C_{CuSO_4} = 10^{-3}$  M in  $H_2SO_4$ , 0.5 M;  $v = 10$  mV/s.  
b) Displacement of a copper monolayer by 2-MP.  $C_{2-MP} = 10^{-3}$  M;  $v = 10$  mV/s.

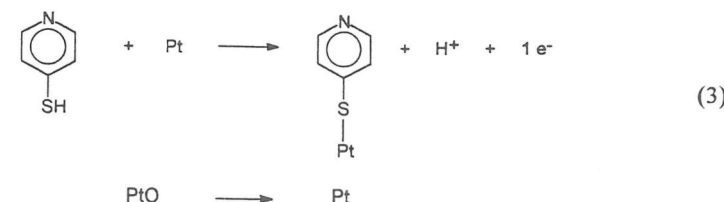
If this assignment is correct, the anodic sweep would correspond to the oxidation of adsorbed sulfide besides to the oxidation of the Pt surface and that of adsorbed 2-MP.

Contrarily to the case of 2-MP, when a platinum electrode with an electrodeposited monolayer of copper is contacted with a 4-MP solution in  $H_2SO_4$  or water, the anodic scan exhibits the stripping of strongly adsorbed copper. The structure of 4-MP precludes the formation of a chelate with the platinum surface, as was the case for 2-MP. Thus, the bond 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 is rendered unable to displace the strongly adsorbed copper.

-Adsorption of mercaptopyridines on a platinum electrode with an oxide monolayer:

The voltammogram for a PtO electrode pretreated with a 4-MP solution in acid medium or water shows no evidence of the reduction peak of the formed platinum oxide. The response is very similar to that obtained for the oxidation of 4-MP adsorbed on a platinum electrode.

The proposed mechanism for the displacement of the platinum oxide is:



4-MP reduces the platinum oxide due to its oxidative adsorption on the surface. Moreover, the resulting electrode completely inhibits the UPD process of copper and on the other hand, if sufficiently negative potentials are applied, the oxidation peak at 1.2 V is obtained in the anodic scan. It can also be concluded that the Pt-S bond is stronger than the Pt-O one.

The voltammetric response for Pt surfaces covered with an oxide monolayer and put in contact with 2-MP shows similar characteristics to those described above. Once more, the voltammogram resembles that obtained for the oxidation of 2-MP adsorbed on Pt.

Behavior followed by mercaptopyridines on polycrystalline gold electrodes:

Both 2-MP and 4-MP are electrochemically active both in solution and when adsorbed on the electrode.

The voltammogram for a gold electrode pretreated with 4-MP shows a delay in the oxide formation, as well as an increase in the current density of the corresponding peak and an anodic displacement of its maximum potential to 1.53 V. The difference between the anodic and cathodic charges corresponding to the reduction of the formed gold oxide gives the oxidation charge for 4-MP adsorbed on gold. This difference is similar for both 4-MP and 2-MP.

-Influence of mercaptopyrindines on the deposition of copper on gold:

Adsorbed 2-MP on gold inhibits completely the UPD of copper. However, this process takes place when the adsorbate is 4-MP, although the deposition charge in this latter case is smaller (ca. 122  $\mu\text{C}/\text{cm}^2$ ) than that achieved in the absence of adsorbate (ca. 300  $\mu\text{C}/\text{cm}^2$ ).

Table II summarizes the deposition and stripping potentials of Cu on gold in the presence of mercaptopyrindines. It can be observed that the OPD of copper in presence of 4-MP occurs at -50 mV, what implies an overpotential of 230 mV; however in presence of 2-MP the OPD proces is not detectable until a potential of -300 mV is reached which demonstrates that the Au-S interaction is stronger than the Au-Cu one.

It can also be deduced that the Au-S bond is stronger than the Pt-S one, due to the high overpotentials required to obtain OPD of copper on both electrodes in the presence of these substances.

Table I  
Potentials of deposition and stripping(vs. NHE) for the deposition of copper on PLATINUM in the presence of mercaptopyrindines

Adsorbate	Solvent	UPDdep.	UPDstrp.	OPDdep.	OPDstrp.
Cobre	H <sub>2</sub> SO <sub>4</sub>	0.390	0.720	0.200	0.290
2-MP	H <sub>2</sub> O	-	-	0.030	0.290
4-MP	H <sub>2</sub> O	-	-	0.030	0.290
2-MP	H <sub>2</sub> SO <sub>4</sub>	-	-	0.070	0.290
4-MP	H <sub>2</sub> SO <sub>4</sub>	-	-	0.050	0.290

Table II  
Potentials of deposition and stripping ( vs. NHE ) for the deposition of copper on GOLD in the presence of mercaptopyrindines

Adsorbate	Solvent	UPDdep.	UPDstrp.	OPDdep.	OPDstrp.
Cobre	H <sub>2</sub> SO <sub>4</sub>	0.490	0.510	0.180	0.320
2-MP	H <sub>2</sub> O	-	-	-	-
4-MP	H <sub>2</sub> O	0.390	0.690	-0.050	0.360
2-MP	H <sub>2</sub> SO <sub>4</sub>	-	-	-	-
4-MP	H <sub>2</sub> SO <sub>4</sub>	0.430	0.670	-0.050	0.370

When a monolayer of copper is deposited on the gold electrode and then put in contact with a solution of 4-MP in acid medium, the stripping of the monolayer of copper was not observed. It is believed that this is possible because the electrodeposited copper is oxidized and 4-MP is reduced ( fig 5 ).

Nevertheless, a peak appears in the doble layer region at 0.88 V with a charge equals to 116  $\mu\text{C}/\text{cm}^2$ . This peak is believed to correspond to the oxidation of reduced

4-MP or some reaction intermediate. The oxidation of adsorbed 4-MP takes place at more anodic potentials.

It is possible to generalize the described behavior for a copper monolayer treated with 4-MP in water or with 2-MP in both media.

- Adsorption of mercaptopyrindine on gold with a monolayer of oxide:

The recorded voltammogram corresponding to a gold electrode in acid media covered with a monolayer of oxide and treated with 2-MP in water or acid media shows in the first cathodic scan, a total absence of the reduction peak of the formed oxide and, in the anodic scan, the oxidation peak of adsorbed 2-MP.

It is then proposed that the oxide monolayer has been removed by 2-MP due to a reaction similar to that occurring on Pt:

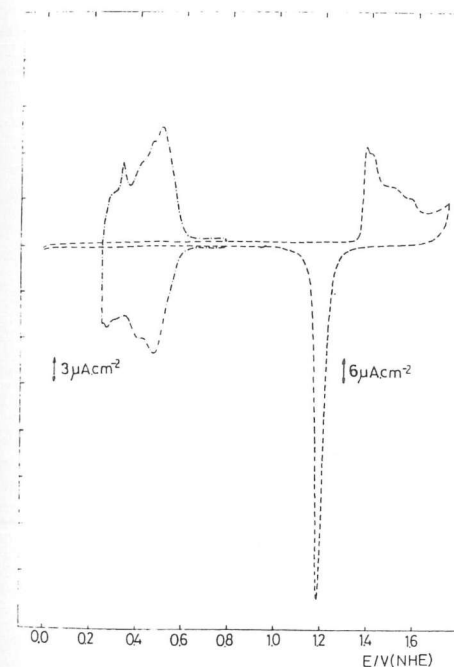
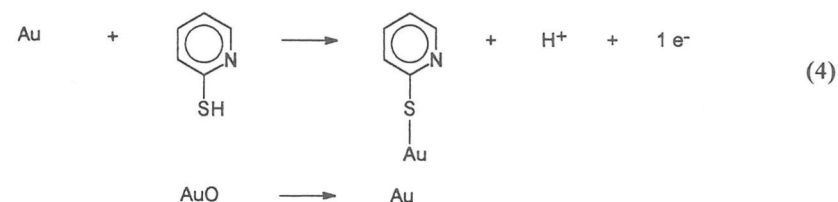


Fig 4  
UPD of copper on gold.  $C_{\text{CuSO}_4} = 10^{-3}$  M in H<sub>2</sub>SO<sub>4</sub> 0.5 M ;  $v = 10$  mV/s.

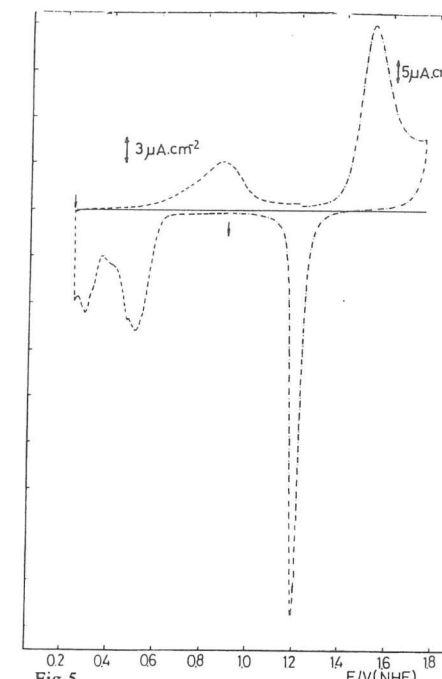


Fig 5  
a) Displacement of a copper monolayer deposited on gold by 4-MP.  $C_{4\text{-MP}} = 10^{-3}$  M in H<sub>2</sub>SO<sub>4</sub> 0.5 M;  $v = 10$  mV/s.

If the adsorbate is 4-MP in water or acid media, the monolayer of gold oxide is removed as well. The resulting electrode inhibits the UPD of copper. The UPD process is more inhibited than when 4-MP is adsorbed on oxide free gold. This is because the potential of the interface AuO-4-MP is more favourable for the 4-MP adsorption than the potential of the interface Au-4-MP.

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#### References:

- 1.- J. L. Stickney, M. P. Soriaga and A.T. Hubbard and S.E. Anderson, *J.Electroanal.Chem.*, **125**, 73 (1981).
- 2.- T. Mebrahtu, G.M. Berry, B.B.G. Bravo, S.L. Michelhaugh and M.P. Soriaga, *Langmuir*, **4**, 1147 (1988).
- 3.- J.Y. Gui, F. Lu, D.A. Stern and A.T. Hubbard, *J.Electroanal.Chem.*, **292**, 245 (1990).
- 4.- C. Alonso, M.J. Pascual and H.D. Abruña. *J.Electrochem.Soc.* (submitted).
- 5.- S.H. Harford, D.L. Taylor and H.D. Abruña. *J. Electrochem.Soc.*, **141**, 9394 (1994).
- 6.- D.L. Taylor and H.D. Abruña, *J.Electrochem.Soc.*, **140**, 3402 (1993).
- 7.- Isao Taniguchi, Masahiro Iseki, Hiroko Yamaguchi and Kazuo Yasukouchi. *J.Electroanal.Chem.*, **193**, 295 (1985).
- 8.- M. P. Soriaga, A.T. Hubbard, *J. Electroanal.Chem.*, **159**, 101 (1983).
- 9.- J.H. White and H.D. Abruña. *J. Electroanal. Chem.*, **125**, 73 (1981).

## ELECTROPOLYMERIZATION IN SOLUTION:

### AN ELECTROCHEMICAL METHOD TO OBTAIN POLYACRYLAMIDE

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#### SUMMARY

The electropolymerization of acrylamide in the presence of NaNO<sub>3</sub> in aqueous solution has been investigated on platinum electrodes. The polymer (polyacrylamide) is obtained in the bosom of the solution. The dependence of yields and molecular weights on parameters such as current density, monomer concentration, electrolyte concentration and temperature was determined.

**Key words:** Electropolymerization, acrylamide

#### INTRODUCTION

The pass of a electric current between two metallic electrodes sumerged in a monomeric solution with a salt can generate, among other products, polymer adhered at the electrode surface<sup>1</sup> or, in other way, in the bosom of the solution<sup>2</sup>. This last type of polymerization has been considered in literature like a homogeneous initiated process<sup>3</sup>. Nevertheless, a few authors proposed the formation of polymer films around the electrode during the initial minutes of current flow<sup>3</sup>. All of this allows us to suppose that the reactions on the electrode are determinant in the electroinitiated polymerizations. The electrode process is a mixed process in which all