

Electrochemical Response of a Vitreous Carbon Electrode Modified by a Thiomacrocyclic Compound Film

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Abstract

A Langmuir-Schaefer (LS) film of a thiomacrocyclic (ThM) compound was deposited on the surface of a glassy carbon electrode (GCE) rod, from a subphase containing Cu(II) ions. The voltammetric response of this modified GCE when the ThM was bonded to Cu^{2+} , showed that the LS film moved the oxidation peaks of copper to more positive values. On the other hand, a LS film of the ThM compound was deposited on the surface of a GCE rod from a subphase of pure water. When the voltammetric response of the GCE-ThM electrode was studied in a Cu^{2+} - SO_4^{2-} solution, it was found that the modified electrode increases its sensitivity respect to Cu^{2+} at low bulk Cu^{2+} concentrations in solution, and a surface-complexation reaction is proposed to explain the effect of the LS film on the GCE surface.

Keywords: modified electrodes, Langmuir-Schaefer films, cyclic voltammetry, surface-complexation reaction.

Introduction

Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) film formation are techniques used to deposit organized thin films on surfaces [1, 2]. The LB technique can create monolayer and multilayer structures with large-scale order and this technique has been used to fabricate modified electrodes at the nanometric scale [3], with potential applications in sensors and optical and electronic devices. The LB technique can also provide new insight into electron transfer reactions at interfaces [4-9]. The LS technique, i.e. horizontal deposition, has also been employed for transferring monolayers onto substrates [10].

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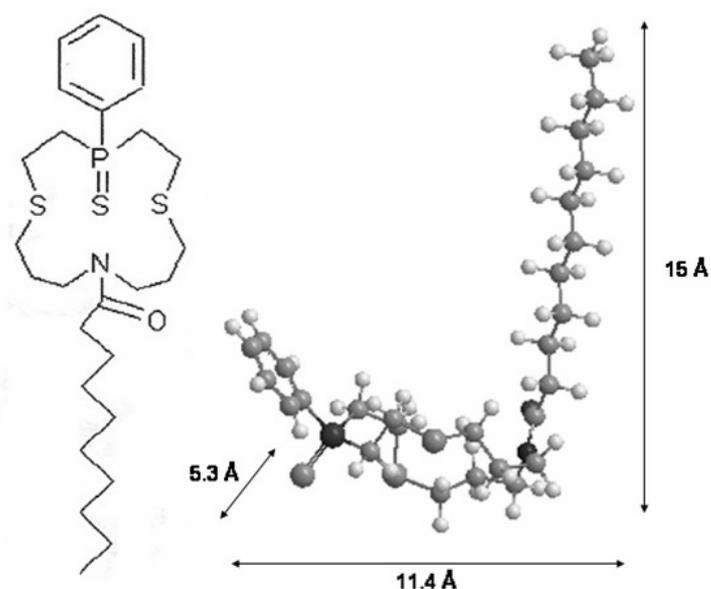


Figure 1. Thiomacrocycle (ThM) 4-phenil-4-sulfide-11-(1-oxodecyl)-1,7-dithia-11-aza-4-phosphacictetradecane.

In this work we used the LS technique to modify the surface of vitreous carbon electrodes with films of this new thiomacrocylic compound bonded or not to Cu(II) ions. The aim of this paper is to characterize these modified electrodes studying their voltammetric response to Cu(II) ions in a sulphate medium and to compare this electrochemical response with that obtained for a bare vitreous carbon electrode (GCE). This electrochemical response is also compared to that obtained when a thicker coating is deposited on the GCE surface. The application of a GCE modified with a LS film of the thiomacrocycle as amperometric sensor of Cu(II) ions is also tested.

Experimental

Langmuir-Schaefer film formation

The thiomacrocylic compound was synthesized as described previously [11]. This compound forms stable Langmuir and Langmuir-Blodgett films [11]. Langmuir films were obtained in a NIMA 1232D1D2 trough placed on an isolation platform. Pure water, Millipore MilliQ grade (resistivity of 18 MΩ cm), and solutions of copper(II) nitrate (from analytical reagent Cu(NO₃)₂ and MilliQ water) were used as subphases. A volume of 50 μL of a solution of the compound in chloroform, at a concentration of 1 mg/mL (1.9 mM), was spread over the corresponding subphase, and there was a 15 min lag before measurements in order to permit evaporation of the solvent. The compression speed was of 50 cm² min⁻¹, that is 2.5 cm min⁻¹, that is 8.5 Å² molecule⁻¹ min⁻¹. The surface pressure was measured using the Wilhelmy method incorporated to the NIMA trough and a paper sheet. The Langmuir-Schaefer (LS) films (see scheme 1) were transferred at constant pressure onto a clean vitreous carbon rod, of 0.0314 cm² area, for electrochemical measurements. The transfer was done

surface after their modification by a thiomacrocyclic film, it was polished with SiC paper and alumina of different grades.

The chemicals used were $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and Na_2SO_4 , all of analytical grade. All solutions were freshly prepared with water that had been distilled and then treated with a Millipore Milli Q system. In the experiments with the vitreous carbon rod electrode modified with a LS film of thiomacrocyclic bonded to Cu^{2+} (Cu^{2+} -ThM), the electrochemical cell contained 0.1 M Na_2SO_4 at the pH of the salt (4.95). In the other experiments the electrochemical cell contained 0.1 M Na_2SO_4 as the supporting electrolyte and aliquots of CuSO_4 were pipetted into the cell from a 0.5 M CuSO_4 solution. The total Cu^{2+} ion bulk concentration in solution, c_{Cu} , was varied from 0.01 mM to 10 mM. The measured pH of the cell oscillated between 5-5.5. Before the experiments, and after each new CuSO_4 addition, the solutions were de-aerated with argon. The Cu^{2+} ion was soluble in solution in the interval of concentrations studied.

Results

Langmuir films formation and surface pressure-area isotherms

Fig. 2 shows the surface pressure-area isotherms for the Langmuir films of the studied ThM compound, in both a water subphase and a 0.05 M copper(II) aqueous solution subphase. The isotherms show the influence of copper(II) ions on the ThM film. The deposition surface pressures for the LS films, which are 12 mNm^{-1} for the pure water subphase and 22 mNm^{-1} for the copper(II) aqueous solution subphase, are also indicated with arrows in Fig. 2.

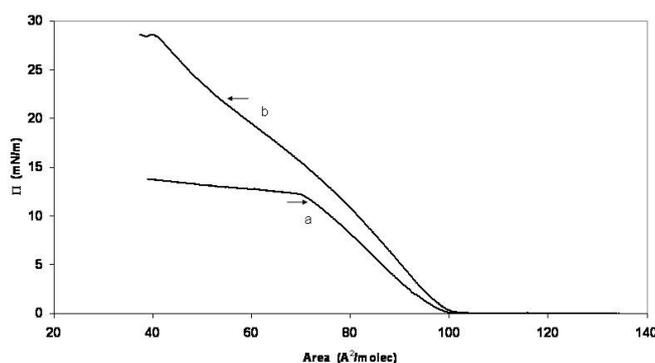


Figure 2. Surface pressure – area per molecule isotherms at different subphases: a) pure water; b) 0.05 M copper(II) aqueous solution. Arrows indicate deposition surface pressures for LS films: a) 12 mNm^{-1} ; b) 22 mNm^{-1} .

Voltammetric experiments*Vitreous carbon electrode rod modified with LS films of Cu²⁺-ThM*

Fig. 3 shows the electrochemical response, in a 0.1 M Na₂SO₄ electrolyte solution, of the vitreous carbon rod electrode without modification (curve a) and modified with a LS film of the ThM transferred from a 0.05 M subphase of Cu²⁺ ions at a surface pressure $\pi = 22$ mNm⁻¹ (curve c). A weak electrochemical reduction wave and a double oxidation wave, peaks I_{r} and I'_{o} , are obtained with a peak potential of $E_p(I'_{o}) = 150$ mV. This response does not change with repeated cycling. Curve b shows the behavior of the vitreous carbon electrode rod immersed in the same solution subphase, but without the Langmuir film of the ThM. This procedure has been used to test if Cu²⁺ ions can be adsorbed on the vitreous carbon electrode surface. After the extraction, the electrode surface is cleaned by immersion in purified water three times, and immersed in the electrolyte solution. Curve b shows that despite cleaning the electrode surface, some Cu²⁺ ions remain adsorbed on the electrode giving a reduction peak, I_r , at a potential of $E_p(I_r) = -100$ mV and an oxidation wave with an oxidation peak, labeled as $I_o+I'_o$, at a potential of $E_p(I_o+I'_o) = -40$ mV. This response does not change with repeated cycling. From the charge calculated below the oxidation peak $I_o+I'_o$, an electrode surface coverage of 0.3 % can be calculated. The same calculus below the oxidation peak I'_{o} , taking into account the projected geometrical area of the thyomacrocycle molecule, 40 Å² [11], gives 14% coverage of Cu²⁺ on the surface of the modified GCER. This result implies a ratio of 0.14 Cu²⁺ ions per ThM molecule in the LS film.

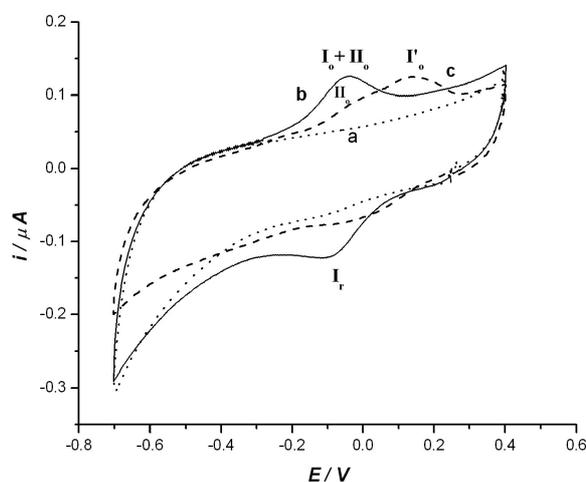


Figure 3. Cyclic voltammograms at 50 mV s⁻¹ in a 0.1 M Na₂SO₄ solution on: a) GCE rod (dotted line); b) GCE rod with adsorbed Cu²⁺ (solid line), and c) GCE rod modified with a LS film of Cu²⁺-ThM (dashed line).

Vitreous carbon electrode rod modified with LS films of ThM (GCER-ThM)

The curves a and b in Fig. 4-7 compare the voltammetric response of the bare GCER and GCER-ThM when aliquots of CuSO₄ are added into the electrolyte cell solution. The LS film of the ThM was transferred from a subphase of pure water at a surface pressure $\pi = 12$ mNm⁻¹. The electrochemical reduction wave of Cu²⁺

ions on the bare GCeR at the lowest concentration studied (Fig. 4, curve a) presents one reduction peak, I_r and two oxidation peaks, II_o and I_o (see Table 1 for the peak potential values). When the total bulk concentration of Cu^{2+} increases (Fig. 5 and 6, curves a), a second reduction peak, II_r , appears and in the anodic scan peak II_o becomes more important than peak I_o . The study of the i_p dependency vs. the scan rate at $c_{\text{Cu}} = 0.01 \text{ mM}$ showed a linear dependency for $i_p(I_r)$ and $v < 100 \text{ mVs}^{-1}$. Cyclic voltammetric experiments made at different potential limits in the forward scan, for c_{Cu} in solution between 0.1-10 mM, have shown that only the second reduction peak II_r corresponds to an electrodeposition process, giving the typical nucleation loop of current intensity [14].

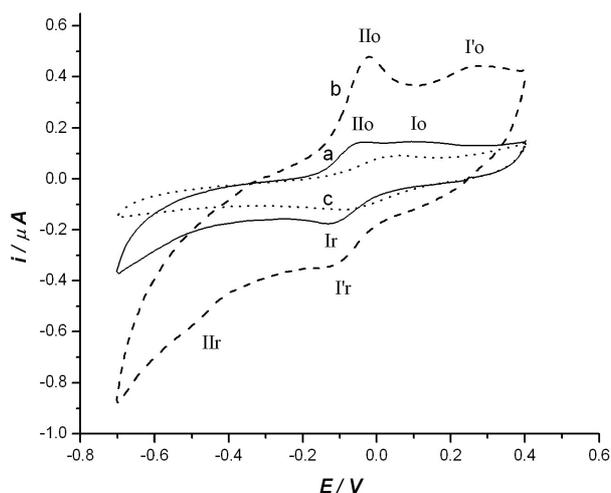


Figure 4. Cyclic voltammograms at 50 mV s^{-1} in a $0.1 \text{ M Na}_2\text{SO}_4 + 0.01 \text{ mM CuSO}_4$ solution of a : a) GCE rod (solid line); b) GCE rod modified with a LS film of ThM (dashed line); c) GCE rod modified with a coating of ThM (dotted line).

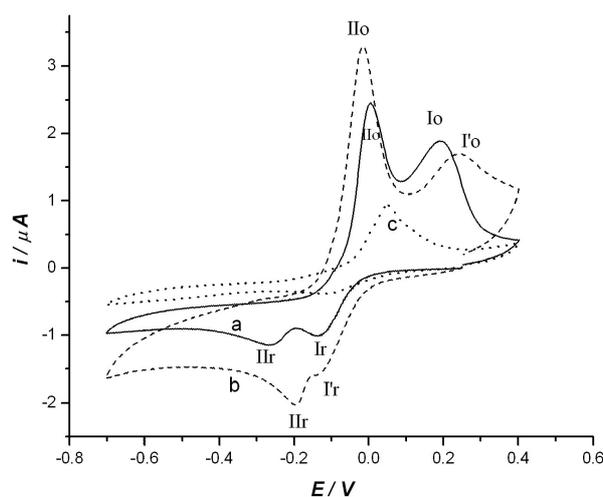


Figure 5. Cyclic voltammograms at 50 mV s^{-1} in a $0.1 \text{ M Na}_2\text{SO}_4 + 0.1 \text{ mM CuSO}_4$ solution of a : a) GCE rod (solid line); b) GCE rod modified with a LS film of ThM (dashed line); c) GCE rod modified with a coating of ThM (dotted line).

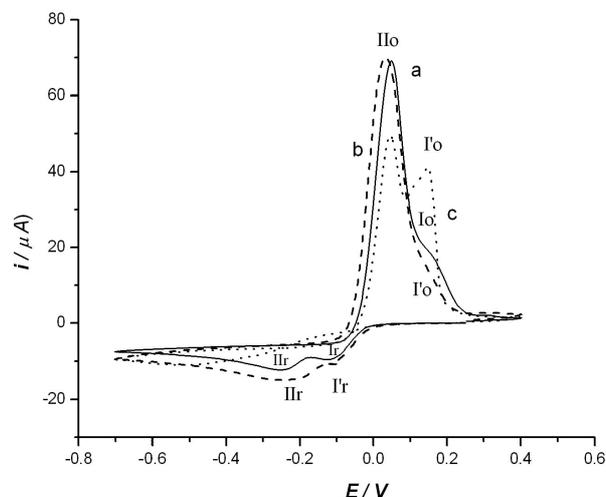


Figure 6. Cyclic voltammograms at 50 mV s^{-1} in a $0.1 \text{ M Na}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$ solution of a: a) GCE rod (solid line); b) GCE rod modified with a LS film of ThM (dashed line); c) GCE rod modified with a coating of ThM (dotted line).

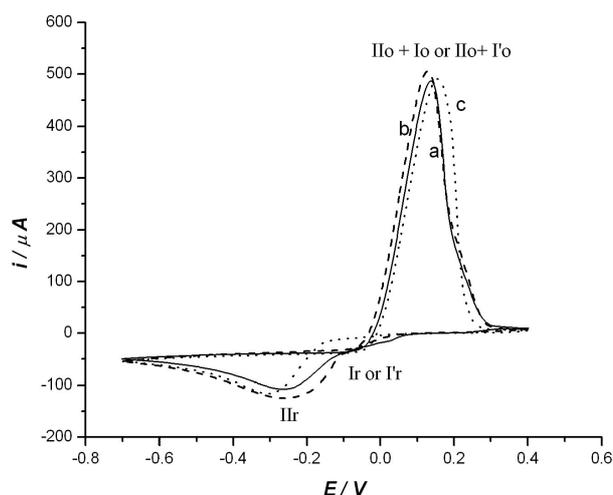


Figure 7. Cyclic voltammograms at 50 mV s^{-1} in a $0.1 \text{ M Na}_2\text{SO}_4 + 10 \text{ mM CuSO}_4$ solution of a: a) GCE rod (solid line); b) GCE rod modified with a LS film of ThM (dashed line); c) GCE rod modified with a coating of ThM (dotted line).

The current intensity of the electrochemical response of Cu^{2+} ions on the GCeR-ThM electrode shows an important increase at the lowest c_{Cu} studied (Fig. 4, curve b) and two reduction waves are obtained, I'_r and II_r . In the reverse scan two oxidation peaks, II_o and I'_o , are obtained as for the bare electrode, but the second one presents an oxidation peak potential, $E_p(I'_o)$, more positive than for the bare electrode (see Table 1). When the total bulk concentration of Cu^{2+} ions in solution increases, (Fig. 5-7, curves b), $E_p(II_r)$ moves to more positive potentials and the wave II_r becomes more important than the wave I'_r . In the reverse scan, two oxidation peaks, II_o and I'_o , are obtained at the potentials shown in Table 1

with $E_p(II_o)$ moving to more positive values when c_{Cu} increases. The current intensity of the electrochemical response of Cu(II) ions on the modified electrode is higher than on the bare electrode at the lowest c_{Cu} , but tends to be equal at $c_{Cu} \geq 1$ mM.

Table 1. Peak potentials.

[Cu ²⁺]	Electrode	E(I _r)	E(I' _r)	E(II _r)	E(II _o)	E(I _o)	E(I' _o)
1×10 ⁻⁵ M	GCEr	-120 mV			-45 mV	108 mV	
	GCEr+ThM		-126 mV	-430 mV	-16 mV		280 mV
1×10 ⁻⁴ M	GCEr	-130 mV		-262 mV	10 mV	196 mV	
	GCEr+ThM		-140 mV	-200 mV	-11 mV		245 mV
1×10 ⁻³ M	GCEr	-120 mV		-250 mV	52 mV	150 mV	
	GCEr+ThM		-120 mV	-238 mV	37 mV		152 mV

Vitreous carbon electrode rod modified with a coating of ThM

The curves c in Fig. 4-7 show the voltammograms obtained at increasing c_{Cu} in solution, when a thicker thiomacrocyclic coating was deposited on a GCEr following the coating technique described in the experimental section, "coating technique". From the volume deposited, we can calculate that the coating has around 20 layers of the ThM compound, and therefore it has around 20 nm of thickness [11]. At 0.01 mM and 0.1 mM Cu²⁺ total bulk concentration (Fig. 4 and 5, curves c) a weak reduction wave is obtained in the forward scan and a wide oxidation wave in the reverse scan. The current intensity is very low compared with that of the bare electrode. When the $c_{Cu} = 1$ mM (Fig. 6, curve c), a more marked reduction peak, labeled as II_r, is obtained, and two oxidation peaks, II_o and I'_o, appear. At $c_{Cu} = 10$ mM (Fig. 7, curve c), a clear electrodeposition wave II_r is obtained in the forward scan and a wide oxidation peak II_o+ I'_o appears. In this last case the current intensity of the voltammetric response is close to that of the bare electrode.

Chronoamperometric experiments

The previous voltammetric results showed in Fig. 4-6 let us design chronoamperometric experiments to compare the response of the bare GCEr and the modified GCEr-ThM electrodes. Series of chronoamperometric experiments were made, measuring the current intensity response when a potential step was applied on the working electrode from an initial potential of 250 mV, where faradaic reaction does not take place, to a final potential of -200 mV. Fig. 8 shows the plots of the faradaic current intensity measured after 5 s of the applied final potential, vs the c_{Cu} in solution, for the bare GCEr and the modified GCEr-ThM electrodes. The linearity of both plots is good in the concentration range

between 0.01-1 mM. The least-squares approximation gives a slope of 0.0025 mA/mM ($R^2=0.99$) for the bare electrode, and a slope of 0.0045 mA/mM ($R^2=0.98$) for the modified electrode.

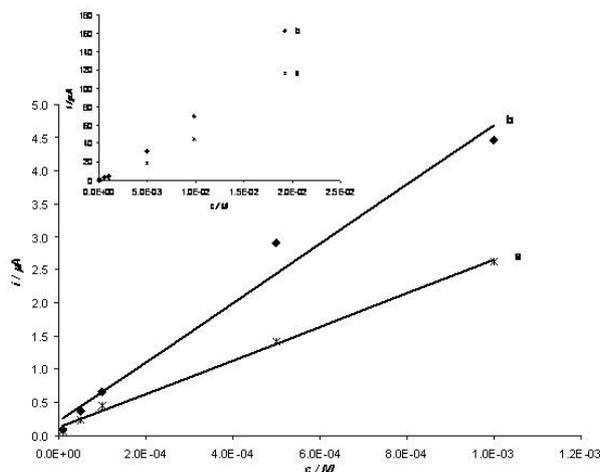


Figure 8. Plot of the faradaic current intensity vs. the total bulk Cu^{2+} concentration in solution of a: a) GCE rod; b) GCE rod modified with a LS film of ThM. The intensity was measured 5 s after having applied a step potential from 250 mV to -200 mV.

Discussion and conclusions

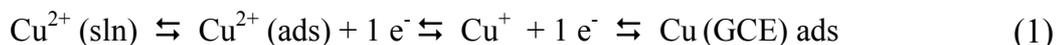
Voltammetric behaviour of the Cu^{2+} - SO_4^{2-} system on a GCE

The electrochemical behaviour of Cu^{2+} ion in a sulphate medium depends on the pH, the complexation equilibria in solution and on the interactions with the electrode surface. The sulphate anion is a ligand of Cu^{2+} ion ($\log K_1 = 2.30$ [15]), but according to the equilibrium diagram of distribution of Cu^{2+} species in solution vs. the pH for the CuSO_4 -water system [16], at $\text{pH} > 4$, the formation of copper hydroxyl sulphate complexes in solution, $\text{Cu}_4(\text{OH})_6\text{SO}_4$, is possible specially at c_{Cu} higher than 1 mM. Also, the formation of the hydroxyl-sulphate complexes will be favoured in the region of positive potentials on the electrode surface, according to the equilibrium $E(\text{Cu}/\text{Cu}^{2+})$ -pH diagram [16]. At pH between 5-5.5, we can expect that Cu^{2+} ion will be present in solution as CuSO_4 and/or $\text{Cu}_4(\text{OH})_6\text{SO}_4$ complexes, with CuSO_4 predominating at low Cu^{2+} ion total bulk concentration.

In this experimental medium, when the total bulk concentration of Cu^{2+} is very low (0.01 mM in Fig. 4, curve a) the reduction of Cu^{2+} ions proceeds via the peak I_r . This peak is the only one obtained in the adsorption test (figure 3, curve b) when only the adsorbed Cu^{2+} on the bare GCE is reduced. When the concentration of $\text{Cu}(\text{II})$ increases (Fig. 5-7, curves a), the ratio $i_p(I_r)/i_p(II_r)$ decreases. As it has been commented in the section “voltammetric experiments”, $i_p(I_r)$ shows a linear dependence vs. ν and only the second reduction peak II_r corresponds to an electrodeposition process. Then, peak I_r has the behaviour of

an adsorption prepeak, i.e, implies the reduction of Cu^{2+} ion via the formation of an adsorbed product [17].

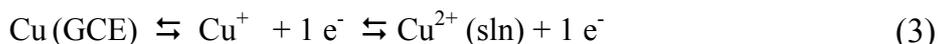
As it has been proposed by different authors [18 and references cited therein, 19, 20], the formation of a metallic Cu layer on the electrode surface implies two consecutive charge transfer steps involving the formation of the intermediate Cu^+ . From our results and in a qualitative way we can represent the reduction of Cu(II) ions in this medium as:



Step (1) corresponds to reduction peak I_r and implies the adsorption of Cu^{2+} ions on the electrode surface and its reduction to form an adsorbed copper layer on the GCE surface that precedes the bulk reduction of Cu(II) ions in solution. As it has been proposed by other authors, the adsorption of Cu^{2+} ions can be favoured by the formation of Cu_xO oxides on the electrode surface [21]. When the concentration of Cu^{2+} ions in solution is very low, step (1) determines the rate of the whole process. In this situation, peak I_r is the main peak obtained in the voltammetric experiments. Then, this first peak is a consequence of the interactions between copper species in solution and the bare electrode surface in the reaction layer, and it is strongly dependent on the pre-treatment of the electrode surface, on the conditioning potential applied on the electrode surface at the beginning of the voltammetric experiment and on the pH in solution.

Step (2) corresponds to the reduction peak II_r and implies the nucleation and growth of the metallic copper deposit on the surface. When the concentration of Cu^{2+} ions in solution increases, step (2) becomes the determinant of the rate of the whole process and then peak II_r becomes the main peak.

In the anodic scan (Fig. 3, curve b, and Fig. 4, curve a), the oxidation of metallic Cu on the GCE proceeds mainly via peak II_o , by the formation of soluble Cu^{2+} species in solution:



But the presence of hydroxyl anions in the reaction layer also permits the Cu oxidation via the formation of oxides or hydroxides, and then peak I_o appears. In this case the formation of Cu_xO species as intermediate oxidation products can be produced [22]. As the final anodic current does not decay to zero, it is possible that some Cu_xO species remain adsorbed on the electrode.

At low total bulk concentration of Cu^{2+} ions in solution, when the reduction proceeds mainly via peak I_r , the oxidation process is more reversible, but when the concentration of Cu^{2+} ions in solution increases, the oxidation process becomes more irreversible (Fig. 5-7 curves a) and $E_p(II_o)$ moves to more positive values and merges with peak I_o .

Voltammetric behaviour of the Cu²⁺-SO₄²⁻ system on a GCE modified with a LS film of the thiomacrocyclic compound (GCEr-ThM)

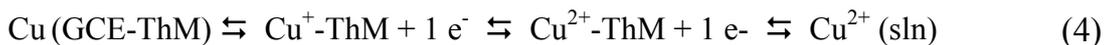
The analysis of Fig. 3-7, for the GCEr modified with a LS film of the thiomacrocyclic compound reveals that the presence of LS film increases the current of the bare electrode for the reduction of Cu²⁺ ions in the range of 0.01 mM-1 mM c_{Cu}. When a thin ThM monolayer (approximately 1 nm thickness [11]) is deposited on the GCEr surface following a Langmuir-Schaefer extraction, the polar heads of ThM molecules (see scheme 1) becomes oriented to the solution. This permits that a surface complexation reaction can take place on the GCEr-ThM electrode between ThM molecules and the Cu²⁺ ions in solution. Then, we propose in this case a step (1') to explain peak I'_r:



That is, the formation of the first copper clusters in the GCE-LS layer, promoted by a surface-complexation reaction in the LS layer-solution interface, between ThM molecules and Cu²⁺ ions. Then, peak I'_r behaves as an adsorption pre-peak and the occurrence of this surface-complexation reaction explains the increase of the current density. This step is followed by the same step (2) defined for the bare electrode. Step (2), i.e., the nucleation and growth of the metallic copper layer takes place only when the complexation equilibrium of Cu²⁺ ions in the LS layer-solution interface is achieved.

When the total bulk concentration of Cu²⁺ in solution is very low, the formation of the first copper clusters is slow and it is controlled by the formation of the Cu²⁺-ThM surface-complex. In these cases the current density of modified GCE is higher than for the bare GCE, but peak II_r appears much separated of peak I'_r (Fig. 4, curve b). When c_{Cu} in solution increases, the surface-complexation reaction is higher and therefore the formation of the first copper clusters is faster, then the control of the process extends more quickly to the solution phase (Fig. 5, curve b), and peak II_r appears closer to peak I'_r. When the c_{Cu} is high enough, the surface-complexation equilibrium is attained before the electrochemical experiment starts (Fig. 6 and 7, curves b), and then the effects of the LS layer become negligible. In this case, the intensity of the modified electrode tends to that of the bare electrode.

In the anodic wave, two separated oxidation peaks are obtained when the total bulk concentration of Cu²⁺ in solution is lower than 0.5 mM (Fig. 4 and 5, curves b). We associate the peak II_o with oxidation step (3), i.e., to the formation of soluble Cu²⁺ species in solution and the peak I'_o with oxidation step (4):



that is, the oxidation of metallic copper via the coordination to thiomacrocyclic LS film on the electrode surface. When peak I'_o appears differentiated from peak II_o the surface-complexation equilibrium Cu²⁺(sln) ⇌ Cu²⁺-ThM in the forward scan hasn't been attained before the experiment starts. When total bulk concentration of Cu²⁺ in solution increases (Fig. 6 and 7, curves b), peak II_o merges with peak I'_o. As the surface-complexation equilibrium seems to be a

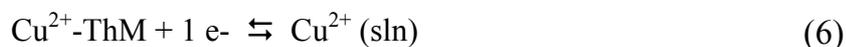
kinetically slow process, it is possible that some of the Cu^{2+} formed in the reverse scan remains bonded to ThM molecules in the LS layer.

Voltammetric behaviour of the vitreous carbon electrode rod modified with a coating of ThM

When a thicker thiomacrocyclic coating was deposited on a GCER, the important decrease of the current at low c_{Cu} (Fig. 4 and 5 curves c) reveals that the coating acts as a blocking layer for the ion transport between the bare electrode and the solution. However, as the current intensity increases (Fig. 6, curve b) and tends (Fig. 7, curve c) to that obtained for the bare electrode when the c_{Cu} increases, we can consider that a membrane model [17, 23] applies to describe the effect of the ThM coating on the electrode surface. In this case permeation equilibrium between ThM coating and solution has to be achieved before the formation of the first copper clusters in the GCE-coating layer can take place. Then, step (1') applies to describe the reduction of Cu^{2+} ions in the forward scan, but now the equilibrium



is controlled by the transport of Cu^{2+} ions across the ThM coating-solution interface (permeation equilibrium). After permeation equilibrium is attained, step (2) can take place, and from our experiments this happens for c_{Cu} higher than 0.1 mM. In the reverse scan steps (3) and (4) also apply to describe the oxidation waves. But now the reaction



implies also the permeation across the ThM coating-solution interface. As the permeation seems to be a kinetically slow process [24], it is possible that some of the Cu^{2+} formed in the reverse scan remains bonded to ThM molecules in the coating layer and permits the permeation equilibrium to be achieved faster when the bulk Cu^{2+} concentration in solution is increased.

Amperometric behaviour of GCER-ThM electrode in the $\text{Cu}^{2+}\text{-SO}_4^{2-}$ system

We can consider the plots shown in Fig. 8 as calibration plots [25, 26] to determine the Cu^{2+} concentration in solution and, as the sensitivity of the GCER-ThM is higher than that of the bare electrode, we could consider that the modified GCER is acting as an amperometric sensor to determine the concentration of Cu^{2+} ions in solution. But this sensing behaviour does not achieve a plateau [24, 25], i.e, a limit of intensity vs. c_{Cu} (see the figure inset inside Fig. 8, which is the same plot but when the bulk Cu^{2+} concentration range is increased until 20 mM). As it was commented in the discussion of the voltammetric behaviour of the GCER-ThM electrode, when the surface complexation equilibrium in the LS layer-solution interface is achieved, the

current intensity of the voltammogram for the GCER-ThM tends to be equal to that of the GCER, and then the current intensity will continue increasing with c_{Cu} .

Final conclusions

The deposition of a Langmuir-Schaefer (LS) film of a thiomacrocyclic compound (ThM), shown in Fig. 1, on the surface of a GCE rod (GCER) changes its voltammetric response vs. Cu^{2+} ions, especially at low total bulk concentrations. An increase of the current intensity and a shift of the oxidation peak I'_o to more positive potentials are obtained when $c_{\text{Cu}} \leq 1$ mM. The increase of the GCER-ThM sensitivity with respect to Cu^{2+} at low bulk Cu^{2+} concentrations in solution is explained by a surface-complexation reaction in the LS layer-solution interface, between ThM molecules and Cu^{2+} ions, which promotes the formation of the first Cu clusters in the GCER-LS layer. This surface-complexation equilibrium also explains the voltammetric behaviour of the vitreous carbon electrode when a thick coating of the thiomacrocyclic compound is deposited on its surface. The amperometric study also shows that the sensitivity of the GCER-ThM is higher than that of a bare electrode. All these results are in agreement with the ionophore character of the thiomacrocyclic compound with respect to Cu(II) ions, previously observed [12, 13].

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