Electrochemical characterization of gold electrodes modified with 1-hexadecanethiol in different ratios of water/ethanol

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Abstract

Gold disc electrodes were fabricated using gold wires of 1mm and 60 μm diameter. Scanning electron microscopy (SEM) was used to determine the surface real shape, and to obtaine information about the quality of the seal at the electrode material-insulator material interface. These electrodes were modified with 1-hexadecanethiol in different ratios of water/ethanol solutions. The adsorption of 1-hexadecanethiol on gold electrodes from different ratios of water/ethanol was studied by differential capacitance measurements and heterogeneous electron transfer measurements. These studies showed that low defect density monolayers of 1-hexadecanethiol can be deposited on gold electrodes in a short time of exposure of the electrode in a solution prepared of this thiol in water/ethanol (1:1).

Key words: Adporption of organic compounds; gold modified electrodes.

Caracterización electroquímica de electrodos de oro modificados con 1-hexadecanethiol en diferentes relaciones de agua/etanol

Resumen

Electrodos de oro en forma de disco fueron construidos utilizando alambres de oro de 1 mm y 60 μm de diámetro. La Técnica de Microscopía de barrido electrónico fue utilizada para determinar la forma real de la superficie de los electrodos y observar la calidad del sello entre la interfase electrodo-material aislante. Estos electrodos fueron modificados con 1-hexadeca-nethiol utilizando diferentes relaciones de agua/etanol. La adsorción de este compuesto orgánico sobre la superficie del electrodo de oro fue investigada por mediciones de capacitancia y mediciones de transferencia electrónica. Estos estudios mostraron que películas de 1-hexade-canethiol con baja densidad de defectos pueden ser depositadas sobre electrodos de oro en un tiempo corto de exposición del electrodo en una mezcla de este tiol más agua/etanol 1/1.

Palabras clave: adsorptición de compuestos orgánicos; electrodos de oro modificados.

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Introduction

Interest in the properties of thin film organic materials, especially regarding organized mono assemblies (1), has grown enormously in recent years. Application of highly organized organic monolayers constitutes a promising approach to electrode modification. The formation of oriented monolayer films on a surface by the spontaneous adsorption of molecules from solution has become known as self assembly (2-5). Long chain alkanethiols have been known to form well-ordered and insulating monolayer assemblies on gold surface which is caused by the spontaneous adsorption of thiol unit (6-8). The formation of self assembled monolayers (SAMs), by the immersion of a clean gold substrate in a dilute solution of alkythiols have been studied and reported as model interfacial structure by a variety of techniques (9-11). High quality films are formed by the adsorption of these compounds on gold from ethanolic solution (12-14) and it seems that this is due to the fact that thiols chemisorb as thiolates at gold (15,16):

$$Au + HS(CH_2)_n X \rightarrow Au - S(CH_2)_n X \qquad [1]$$

However effects of solvent incorporation into the monolayer can hinder its full packing. The ability of the solvent to be incorporated in the monolayer has been investigated by Bain et. al (4), using ellipsometry and contact angle to explore the influence of organic solvents on the character of the monolayers formed by adsorption of alkanethiols on gold. Other authors as Wang et. al (17), have suggested that the compatibility of the monolayer with the solvent play a role important in the electron transfer properties. Until now the modification of gold electrodes with thiols compounds have been carried out by adsorption of these compounds from alcoholic solutions of them (12-14), or from solutions of organic compounds in which the thiols are soluble (18). The electrodes are leaved in these solutions during hours period for obtaining a very good insulating barrier. If the electron transfer properties are affected by the type of interactions between the solvent and the monolayer, it is also possible consider that the nature of the solution from with the thiols are adsorbed can in some way affect the process of adsorption of the monolayer. Less or more insulating monolayer can be formed.

In the present study the dynamics of the process of adsorption of self assembled monolayers of 1-hexadecanethiol from different ratios of water/ethanol used as solvent on gold electrodes was investigated by differential capacitance measurements. Studies of capacitance and relative coverage vs. time were made and analyzed assuming the two parallel capacitor model proposed by Frumkin and Damaskin (19). The quality of the 1-hexadecanethiol film was analyzed by cyclic voltammetry and capacitance measurements using the system $Fe(CN)_6^{-4}$. These studies point out that ratio between water and ethanol in the solutions where the electrode is modified, plays a role important during of process of self assembly of the monolayer.

Experimental

Reagent grade concentrated 70% $HClO_4$, KF and 1-hexadecanethiol were obtained from Fluka; All these chemicals were used as received. Supporting electrolyte solutions of $HClO_4$ and KF were treated with purified active charcoal for gas adsorption (particle size 0.85-1.70 mm) from BDH to eliminate organic impurities, which can be adsorbed on the electrode surface. Gaseous N_2 was passed through the solution in the cell for 15 min before measurements were made.

Gold disc electrodes were fabricated by sealing gold wires of 1 mm and 60 μm diameter, 99.99% (Goodfellow Metal) in soda glass and in a composite of araldite CY1301 and Hardener HY 1300 from Ciba-Geigy Plastics. The gold wires were cleaned chemically with

1:1 concentrated H_2SO_4/H_2O. This solution reacts violently with most organic materials and must be handled with extreme care. The wires were rinsed with ultrapure water and dried in an oven for 30 min.

Each gold wire was then soldered to a nickel wire and threaded through a glass pipette until the gold projected out of the pipette tip by at least 2 mm. After sealing with softy glass or epoxy, the gold disc electrodes were cut flat to obtain the discs and cleaned by polishing with finer grades of aluminum oxide sheet (lapping film, 3M, 30, 3 and 0.3 μm), rinsing with ultra pure water and sonification. Several attempts were made using different types of glass and epoxy to obtain a good seal between the gold and the insulator material. The main difficulty for reproducing a good seal stems from the relatively large difference between the thermal expansion coefficients of the gold and glass, which produces a large gap at the gold-glass interface. A mix of soft glasses was employed to obtain a material with a thermal expansion coefficient near to the metal ($14.2x10^{-6}$ m/mºC. It was found that using a composite of Araldite™ CY1301 + Hardener HY 1300 from Ciba-Geigy Plastic, very good seals between the gold and the composite could be obtained.

All, the gold electrodes fabricated were treated electrochemically by cycling between 0 and 1.45 V vs. SCE in 0.2 mol/L $HClO_4$ for obtaining a clean surface before carrying out the modification of the electrode surface with 1-hexadecanethiol.

The process of adsorption of 1-hexadecanethiol on electrode surfaces was made by dipping the electrode surface into solutions which have different ratios of water/ethanol 9/1, 3/1 and 1/1 as solvent plus a constant concentration of 1-hexadecanethiol $2.5x10^{-4}$ mol/L during 15 min. After modification the electrodes were rinsed first with ethanol and then with water. This procedure was carried out three times.

Electrochemical experiments were carried out using a single compartment cell with a three electrodes configuration. The cell was cleaned by using a solution of H_2O/H_2SO_4 (1/1), and rinsing with ultra pure water to remove residual organic. A saturated Calomel electrode (SCE), model K4040 from Radiometer Electrodes was used as reference electrodes in different experiments and a platinum wire was used as counter-electrode.

Cyclic voltammetry experiments were carried out using a waveform generator PPR1 and a potentiostat (sensitivity 10μA/V) coupled to a XYT recorder.

Capacitance measurements were carried out using gold microelectrodes (60 μm diameter) and gold electrodes (1 mm diameter), sealed in glass or epoxy resin. These measurements were made after calibration using an equivalent circuit of a resistor and a capacitor in series. The differential capacity curves (C-E) were recorded, by the application of a slow potential sweep (5 mV/s) to the working microelectrode plus a sinusoidal ac component of low amplitude (6 mV p/p) at 15 Hz. A two-phase lock in amplifier (Bentham) was coupled to a sine-square wave oscillator (Farnell-LFM4). Potentiostatic control was achieved using a home built potentiostat (sensitivity 1 μA/V) and a potentiostat (sensitivity 10 μA/V) coupled to a XYT recorder a waveform generator (Hitek Instruments).

Discussion

The quality of the seals between the electrode materials and the insulating materials depend on the difference of thermal expansion coefficient between them, this difference must be small or zero, so that the electrode material does not shrink away from the insulating material as the assembly cools. Scanning electron microscopy (SEM) was employed for the characterization of the quality, shape and size of the electrodes fabricated. Figures 1a and 1b, show the SEM
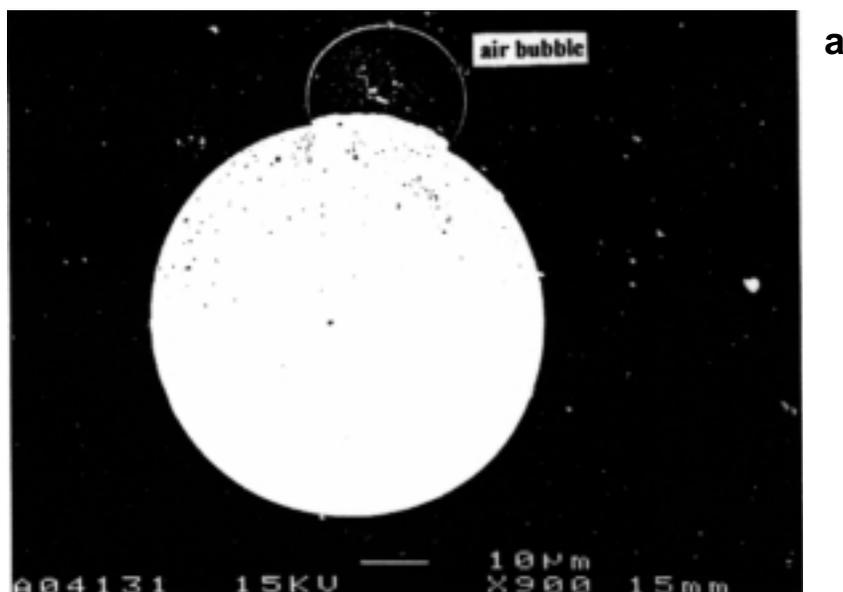
Figura 1a. SEM photograph of a gold microelectrode fabricated with gold wire (60 µm diameter) sealed in soft glass, showing bubble formation.
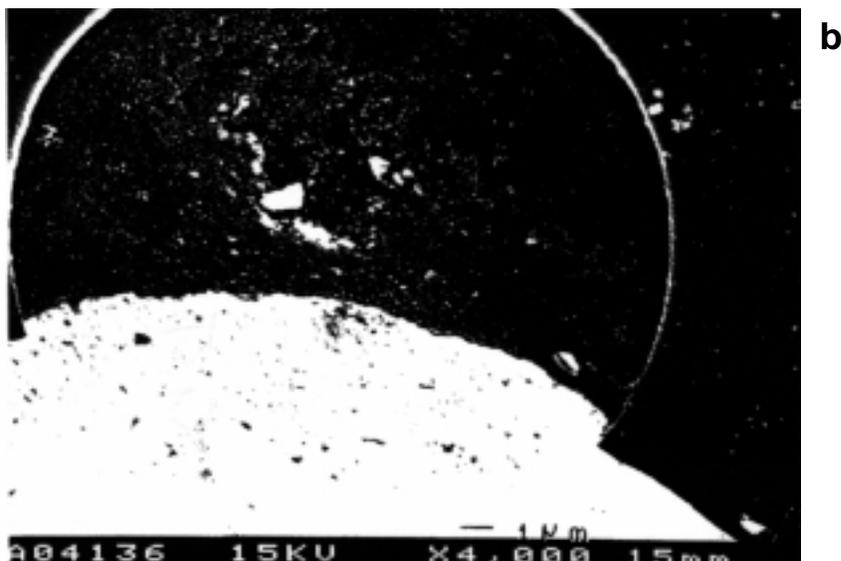

Figura 1b Gold-glass interface of a gold microelectrode fabricated with gold wire (60 µm diameter), showing bubble formation.

photographs for a gold microelectrode (60 µm diameter) sealed in glass which exhibited an anomalously high capacitance value. The SEM photographs showed that the high capacitance arises from leakage due to an air bubble trapped at the gold-glass inter-face, which produces a gap at the interface. For that reason, the process of sealing was generally carried out under vacuum when glass materials are used as insulators.

Cyclic voltammetry and capacitance measurements were used before doing the

modification of the gold electrodes with 1-hexadecanethiol to test the cleanness of the electrode surface and to establish if the electrode was not leaking or not.

Characterization of the gold electrodes fabricated

a) Voltammetric measurements

Figure 2 shows the voltammograms obtained using the gold electrodes fabricated in 0.2 mol/L $HCLO_4$ as electrolyte. Two peaks were observed in the region of oxide formation and one peak on the cathodic side. The potential scan includes the double layer region (0.1 to 1 V vs. SCE), as well as the region of oxide formation (1 to 1.4 V). In the region of oxide formation, replacement of the adsorbed anions by OH^- occurs and two peaks are observed. The first peak at 1.25 V is attributed to formation of the first sublattice of OH^- deposited in between adsorbed anions (20).

$$\lfloor M_x A^- \rfloor M + H_2O \rightarrow \lfloor M_x A^- \rfloor MOH + H^+ + e^- \quad [2]$$

The second peak at 1.35 V has been attributed to the deposition of OH^- accompanied by desorption of the anions (21):

$$M_x A^- + H_2O \xleftrightarrow[\Leftrightarrow]{} M_{x-1} + MOH + A^- + H^+ + e^- \quad [3]$$
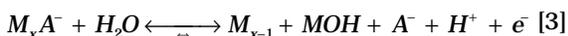
A peak is observed on the cathodic side of the voltammogram between 0.85 to 0.9 V vs SCE, which corresponds to the reduction of adsorbed oxygen (oxide stripping).

The shape of the voltammogram is similar to that reported for polycrystalline gold (22). The effective area of the gold electrode was calculated taking into account that the cathodic charge in aqueous solutions of $HClO_4$ increases almost linearly with the applied potential above 1.2 V vs. SCE and that this charge is independent of pH (23). The charge value (Q_B) used was taken from the curve cathodic charge vs. anodization potential reported by Brummer
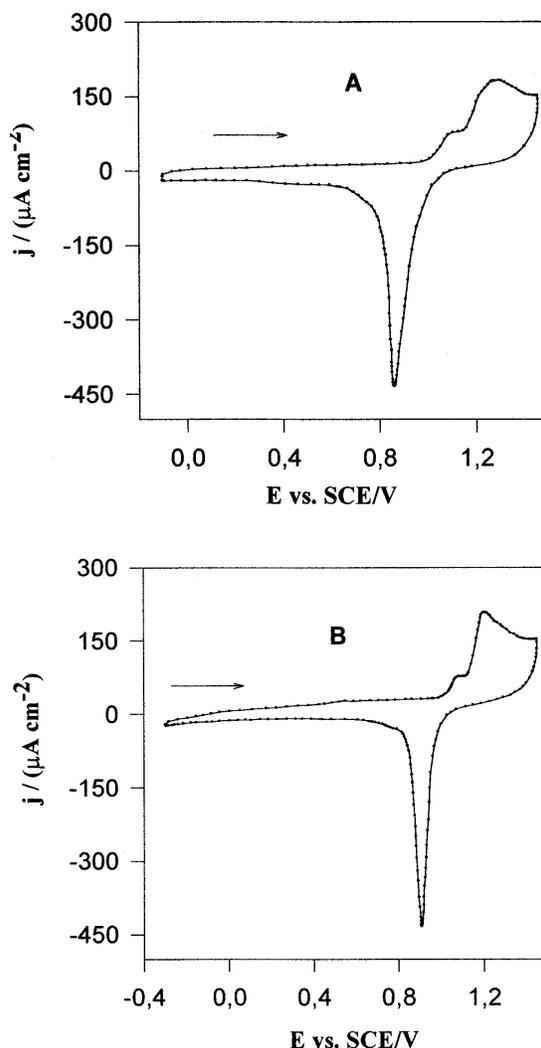

Figure 2. Cyclic voltammograms at: A) a gold electrode sealed in epoxy composite); B) a gold electrode sealed in glass in 0.2 mol dm^{-3} $HClO_4$; v = 60 mV/s.

et.al. (23). This value and the charge obtained experimentally by integration of the oxide-stripping peak were used to calculate the real area of the disc electrode from the radio:

$$A_{real} = \frac{Q_{exp}}{Q_B} \quad [4]$$

The apparent radius was calculated by assuming that the area of the electrode is an ideal disk:

$$r = \sqrt{\frac{A_{real}}{\pi}} \qquad [5]$$

For a series of experiments carried out at 60 mV/s, using gold wires of 60 μm diameter, the values of apparent radius obtained was 29.90 ± 0.13 mm. This value corresponds closely to the nominal value of 30 μm

b) Capacitance measurements

Capacitance experiments were carried out using a gold microelectrode (60 μm diameter) sealed in glass. Measurements of capacitance vs. potential for different concentrations of supporting electrolyte (Figure 3) showed a high capacity maximum in the vicinity of 0.3 V vs. SCE. A poorly defined minimum was observed between -0.1 V to -0.05 V vs. SCE, which could be attributed to the potential of zero charge (p.z.c.). The maximum in the vicinity of + 0.3 V vs. SCE increased and shifted to more negative potential when the concentration of the elec-trolyte KF was increased from $1x10^{-5}$ to $1x10^{-2}$ mol/L. This maximum may be attributed to the adsorption of F^- anions. However, this behavior may be masked by the presence of a small amount of oxide on the electrode as the experiments were made between 0.8 V to -0.3 V vs. SCE. The p.z.c. cannot be assigned more accurately as the minimum of capacitance is not well defined. This behavior is attributed to complications such as an adsorbed film of oxygen atoms or heterogeneity of the microelectrode surface.

Study of the dynamics of the process of adsorption of self assembled monolayers of 1-hexadecanethiol in different ratios of water/ethanol used as solvent on gold electrodes

Figure 4 shows a differential capacitance vs. potential curve recorded during the process of adsorption of 1-hexadecanethiol onto the surface of a gold disc sealed in epoxy. It was observed that the capacitance decreases when the electrode is introduced and cycled between –0.4 to 0.8 V vs. SCE in a solution water/ethanol (9/1) + 0.2 mol/L $HCLO_4$ + $2.5x10^{-4}$ mol/L 1-hexadecanethiol.
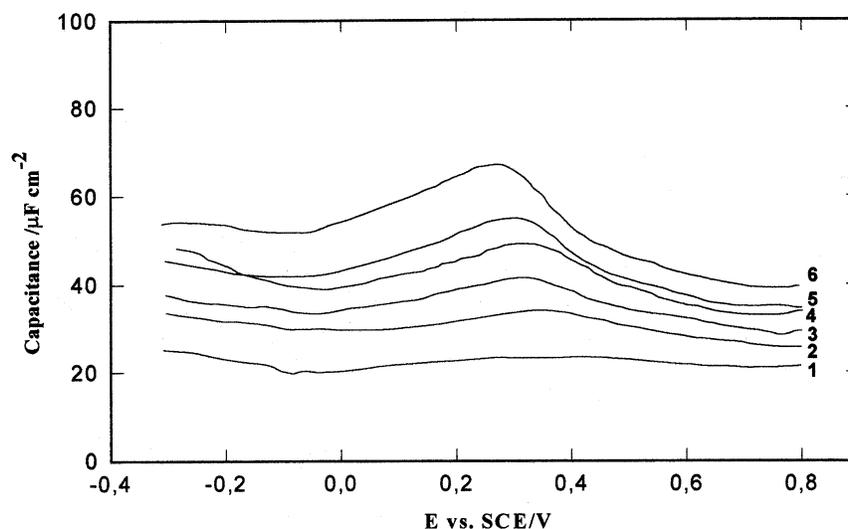

Figure 3.   Capacitances vs. potential plots at a gold electrode (60 μm diameter) sealed in soda glass for different concentrations of HF as supporting electrolyte: 1) $1x10^4$; 2) $5x10^{-4}$; 3) $1x10^{-3}$; 4) $5x10^{-3}$; 5) $1x10^{-2}$; 6) $1x10^{-1}$ mol dm^{-3}; ν = 10 mV/s; 15 Hz; 6 mV p/p.
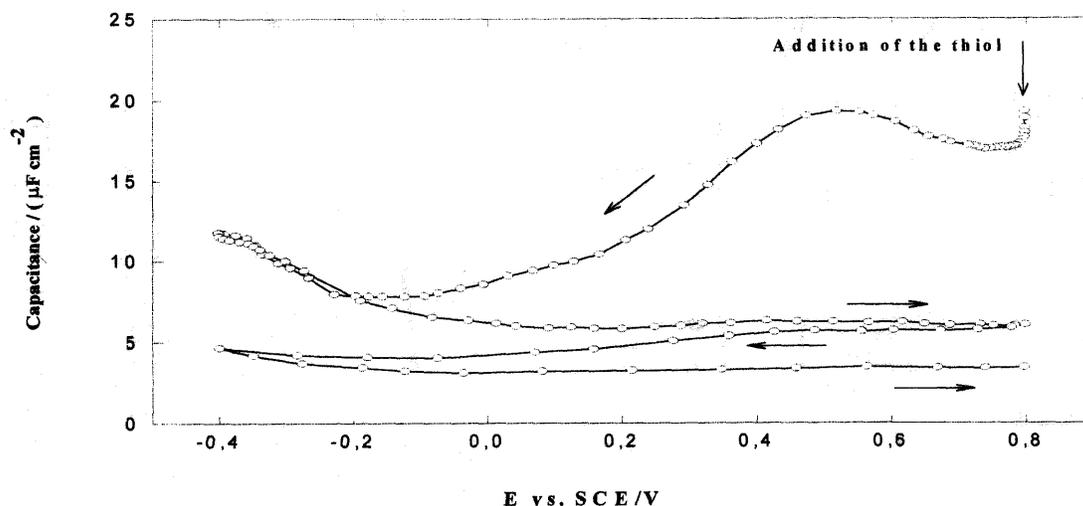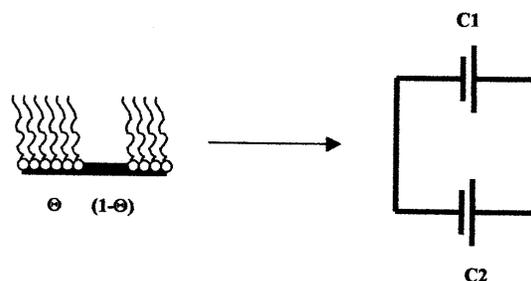
Figure 4.   Capacitances vs. potential plots at a gold electrode sealed in epoxy during the adition of 1-hexadecanethiol from a solution water/ethanol (9/1); supporting electrolyte: 0.2 mol dm^{-3} HClO$_4$; v = 10 mV /s; 15 Hz; 6 mV p/p.

Figure 5a and 5b shows a family of capacitance vs. potential curve obtained when gold electrodes were used without modification, modificated with 1-hexadecanethiol and after cycling in the potential range where the formation of gold oxide and its reduction occur. It was observed that the capacitance is decreased significantly after modification and that the ratio water/ethanol present in the solution where the gold electrode is modified affect the quality of the film. When these electrodes modified in different ratios of water/ethanol plus 1-hexadecanethiol are cycling between –0.3 to 1.4 V vs. SCE, the capacitance of these electrodes increase and they are completely different. This behavior can be attributed to defects on the monolayer films, which produce damage of the film in the potential range where the gold surface is oxidized.

Knowing that adsorption of the 1-hexadecanethiol gives rise to a marked change in the electrode capacitance, this behavior was utilized to study the dynamics of the process of adsorption on gold. Studies of capacitance and relative coverage vs. time were made and analyzed assuming the two parallel capacitor model proposed by Frumkin and Damaskin (19):

where:

$$C1 = C_{film} x \Theta \quad and \quad C2 = C_w x (1-\Theta) \qquad [6]$$

The values of capacitance obtained vs. time were related with values of relative coverage through the follow relation:
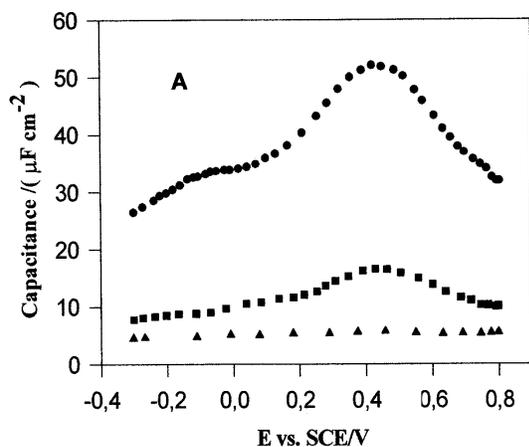
$$C_{exp} = C_{film} x \Theta + C_w x (1-\Theta) \qquad [7]$$

Figura 5a. Capacitances vs. potential plots at a gold electrode (1 mm diameter) sealed in soda glass; supporting electrolyte: 0.2 mol dm^{-3} HClO$_4$; ν = 10 mV/s; 15 Hz; 6 mV p/p; • before modification; ▲ after modification in water/ethanol (9/1) + 2.5x10^{-4} mol dm^{-3} 1-hexadecanethiol during 40 min; ■ after modification in water/ethanol (9/1) + 2.5x10^{-4} mol dm^{-3} 1-hexadecanethiol during 40 min and cycling between –0.3 to 1.4 V.

where:

$$\Theta = C_w - \frac{C_{exp}}{C_w - C_{film}} \qquad [8]$$

C_{exp} = value of capacitance obtained experimentally

C_{film} = value of capacitance with the film

C_w = value of capacitance without film

Θ = relative coverage

Figure 6a shows the family of capacitance vs. time curves obtained by modifying the gold electrode in different ratios of water/ethanol + 1-hexadecanethiol, 2.3 x10^{-4} mol/L. It was observed that the capacitance decreases more rapidly when the electrode is modified in water/ethanol (1/1). This behavior is attributed to a decrease of the in-
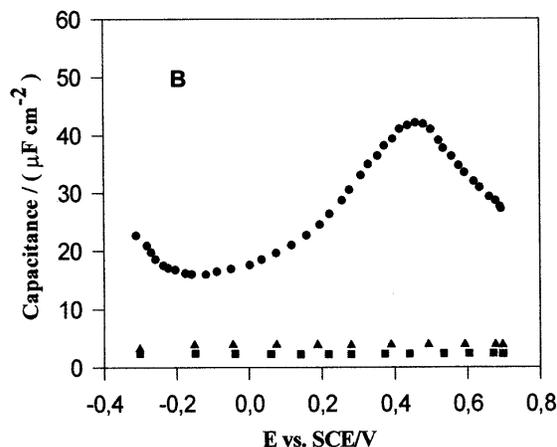

Figure 5b. Capacitances vs. potential plots at a gold electrode (1 mm diameter) sealed in epoxy; supporting electrolyte: 0.2 mol dm^{-3} HClO$_4$; ν =10 mV/s; 15 Hz; 6 mV p/p; • before modification; ▲ after modification in water/ethanol (1/1) + 2.5x10^{-4} mol dm^{-3} 1-hexadecanethiol during 30 min; ■ after modification in water/ethanol (1/1) + 2.5x10^{-4} mol dm^{-3} 1-hexadecanethiol during 30 min and cycling between –0.3 to 1.4 V.

terfacial tension in this system, which enhance the process of adsorption. When a solution prepared with water/ethanol (9/1) + 2.5x10^{-4} mol/L 1-hexadecanethiol was used to modify the electrodes, some changes in the slop of the curve capacitance vs. time were observed (Figure 6a). These changes can be related to continuous ordering of the chains of some molecules of the thiol adhering to the surface of the electrode during the process of adsorption of others molecules.

Knowing that emulsions have a large interfacial area (24), a decrease of the size of the droplets at the emulsion can be related with a reduction in the interfacial tension. This behavior produces a decreasing of the turbidity of the system. It was observed that the turbidity of the system decreases when the ratio water/ethanol is decreased from 9
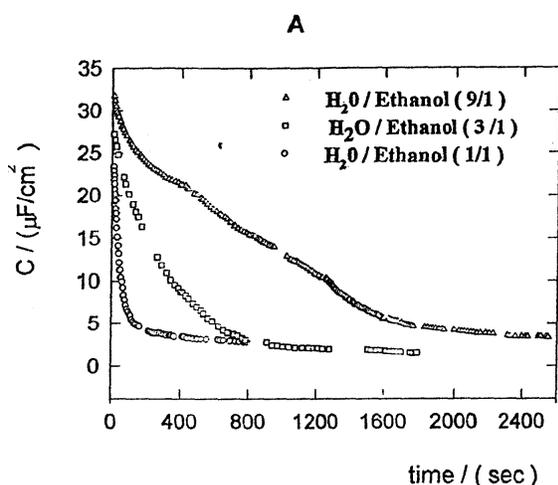
A

Figure 6a. Capacitances vs. time plots at a gold electrode (1 mm diameter) sealed in soda glass; supporting electrolyte: 0.2 mol dm^{-3} HClO$_4$; n = 10 mV/s; 15 Hz; 6 mV p/p; During the process of modification in different ratios of water/ethanol + a constant concentration of 1-hexadecanethiol (2. 5x10^{-4} mol dm^{-3}).

to 1. The decreasing of the turbidity in the solutions used to modify the gold electrodes when the ratio water/ethanol is decreased from 9 to 1 enhances the process of adsorption of the 1-hexadecanethiol, producing monolayer films with an exceptional degree of perfection.

Figure 6b shows the curves of coverage relative vs. time obtained from the data in figure 6a using equation [8]. The experimental time dependence of the double layer capacity was described theoretically using the model of adsorption control formulated by Delahay (25). According to this model the temporal change of the degree of coverage can be related through the equation:

$$\Theta = 1 - \exp(-K_{ad}xt) \qquad [9]$$

Where: K$_{ad}$ is the adsorption rate constant. In this study a value of 0.01 s^{-1} was assumed of K$_{ad}$. Figures 7a and 7b show the
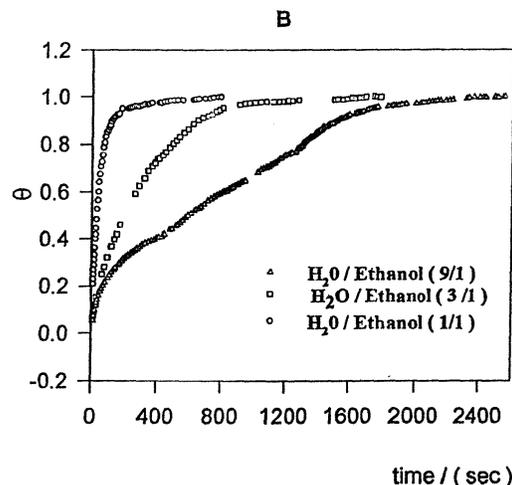
B

Figura 6b. Relative coverage vs. time plots at a gold electrode. Data from figure 6a.

experimental behavior and the theoretical behavior for the system water/ethanol (1/1) + 2.3 x10-4 mol/L 1-hexadecanethiol. A very good fit was observed at the beginning of the adsorption process (Figure 7b). The decrease observed at relative coverage obtained experimentally with respect to theoretical relative coverage in this range of time, can be attributed to processes of salvation and that molecules of water or alcohol adsorbed on the surface can hinder the process of adsorption of the thiol.

Cyclic voltammetric experiments using gold electrodes sealed in soda glass and derivatized by 1-hexadecanethiol using different ration of water/ethanol, were performed in order to determine the effect of the adsorbed layer on faradic processes occurring at these derivatized electrodes. Figure 8 shows the family of voltammograms obtained for the oxidation of Fe(CN)$_6$$^{-4}$ in 0.2 mol/L HClO$_4$ using these derivatized electrodes. In this Figure 8, the electrodes modified with 1-hexadecanethiol in systems water/ethanol (1/1) act as insulating barriers better than the electrodes modified with 1-hexadecanethiol in systems with water/ethanol (9/1) and (3/1) and ethanolic solutions. It seems that in the electrodes modified with 1-hexadecanethiol in systems
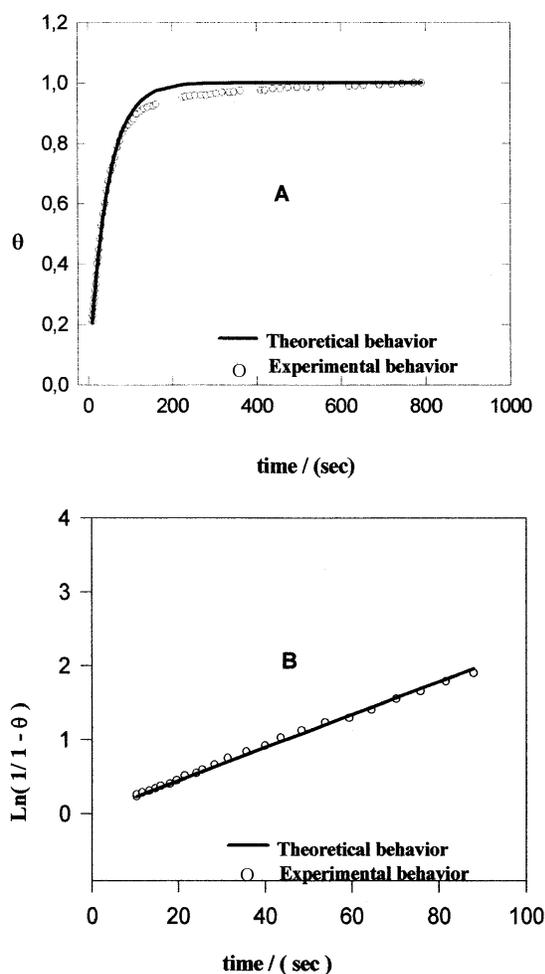
Figura 7. Relative coverage vs. time plot at a gold electrode(1 mm diameter) sealed in soda glass; supporting electrolyte: 0.2 mol dm^{-3} HClO$_4$; v = 10 mV/s; 15 Hz; 6 mV p/p; After modification in water/ethanol (1/1) + 2.5x10^{-4} mol dm^{-3} 1-hexadecanethiol; — Theoretical behavior; μ Experimental behavior.

water/ethanol (1/1), the monolayer film displayed very low defect densities.

In the system 1-hexadecanethiol + ethanol, the molecules of ethanol are more able to solvate the molecule of the thiol and may be incorporated within the monolayer
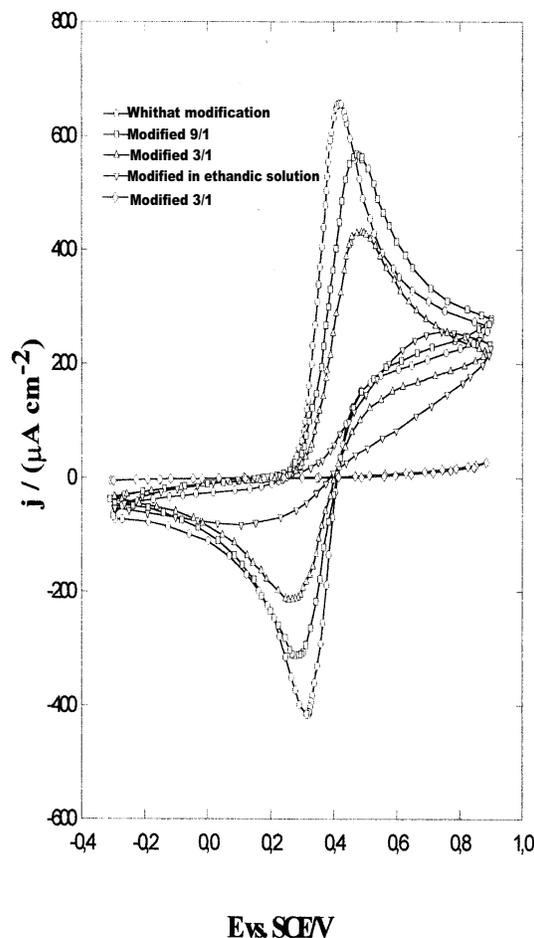

Figure 8. Cycli cvoltammograms at a gold electrode sealed in soda glass in 0.2 mol dm^{-3} HClO$_4$ + 5x10^{-3} mol dm^{-3} Fe(CN)$_6^{4-}$; v = 60 mV/s before and after modification in different ratios of water/ethanol + 2.5x10^{-4} mol dm^{-3} 1-hexadecanethiol.

hindering its full packing. For this reason the electrochemical response of the oxidation of Fe(CN)$_6^{-4}$ is not suppressed completely.

Conclusions

Electrochemical techniques for characterization of the real area, and apparent radius of electrodes must be accompanied with scanning electron microscopy meas-

urement, for determining the real shape of the surface, and for obtaining complete information about the quality of the seal at the electrode material-insulator material interface.

The use water/ethanol (1/1) + 1-hexadecanethiol for modifying gold surfaces produce a low defect density monolayer in short time of exposure of the gold substrate into this solution.

In this study it has been demonstrated that the nature of the solution from which the electrodes are modified play an important role in the process of adsorption as well as in the quality of the monolayer to be deposited on the substrate surface.

The synthesis of films with intentionally formed defect structure could lead the development of devices that can be used for molecular recognition. The behavior observed when different ratios of ethanol/water were used to modify the gold electrodes can be utilized to prepare modified electrodes with intentionally formed defect structure. On the other hands, coadsorption of two or more thiols from solution with different ratios water/ethanol can produce defect structure monolayers with more than one functional group at the surface. The formation of these kinds of monolayers with defect structure could be utilized for the synthesis of monolayers with some characteristics for the selectivity or molecular recognition of certain biological compounds.

The technique of cyclic voltammetry has shown that the measurements of electron transfer at modified electrodes is highly sensitive to film defects.

Acknowledgments

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