

Formation of a Self-Assembled Monolayer via the Electrospreeding of Physisorbed Micelles of Thiolates

Martin Byloos, Hassan Al-Maznai, and Mario Morin*

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Canada, K1N 6N5

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We present a spectroelectrochemical study of the reductive desorption/oxidative redeposition of a monolayer of hexadecanethiols observed in an aqueous alkaline electrolyte solution. We found that the solvent/thiol interactions play an important role in the electrodeposition of self-assembled monolayers of insoluble thiols such as hexadecanethiols. Ex situ vibrational spectroscopy shows that the same monolayer can go from a chemisorbed state to a physisorbed state and back to a chemisorbed state without noticeable change in the orientation of the alkane chains. In situ spectroelectrochemical measurements reveal that the reductive desorption and the oxidative redeposition proceed through the same two-step mechanism. The first step of the reductive desorption is assigned to the reduction of the chemisorbed thiols. The thiolates formed in this step remain physisorbed, and only a small change in the orientation of the alkane chains is observed. The second step of the reduction occurs at more negative potentials and is assigned to the formation of physisorbed micelles of thiolates. This gives rise to a capacitive current and an important reorientation of the thiolates. The physisorbed micelles of thiolates are oxidatively redeposited on the positive-going potential scan of a cyclic voltammogram by the same two steps but in the reverse order.

Introduction

The electrochemical deposition of self-assembled monolayers of thiols is a simple, low-cost alternative to the commonly used adsorption of thiols from a solution.^{1,2} The electrodeposition of thiols is generally done by immersing a metallic substrate in an alkaline aqueous solution containing thiolates.^{3–6} A potential sufficiently positive to cause a rapid (in a few seconds) oxidative deposition of a monolayer of thiolates is then applied to the substrate. The electrodeposited monolayers of thiols were found to have the same surface coverage, structure, and electrochemical properties as those of the monolayers obtained from the incubation of a substrate in a solution of thiolates. The rapidity of the electrodeposition method contrasts with the longer time (hours to days) needed to form an ordered monolayer via the spontaneous adsorption of thiols.^{1,2,7,8} The electrochemical approach also has the practical advantage of allowing the in situ cleaning of the substrate prior to the deposition of the monolayer. The cleaning of the substrate is important since it has been shown to influence the quality and stability of the monolayer.⁹ Finally, it is possible to obtain a submonolayer coverage of thiols by making a proper selection of the value and duration of the potential applied to the electrode.

The oxidative adsorption of thiolates on Au³, Ag,^{4,5} and Hg⁶ from alkaline aqueous solutions has been reported. The electrodeposition of ethanethiolates on silver and mercury was studied in the most detail. It was found that ethanethiolates are oxidatively adsorbed on annealed Ag(111) film and on Hg via a two-step process.^{4–6} The first step is the formation of a low-coverage phase via a Langmuir process. This is followed by the formation of a higher coverage phase via a nucleation and growth process. On Ag, Raman spectroscopy showed the presence of gauche defects in the alkane chains when the low-

coverage phase is formed. These gauche defects disappeared when the high-coverage phase was formed. A thermodynamic analysis of their electrochemical data yielded an electrosorption valency of one for the oxidative adsorption of ethanethiolates on Ag. The electrodeposition of thiolates on the most commonly used substrate, Au(111), is less understood. The oxidative deposition of dodecanethiolates and hexanethiolates occurs in *one* step³ on gold since one symmetrically shaped oxidative current peak is observed for the deposition of the thiolates and one symmetrically shaped reductive current is observed for the desorption of the chemisorbed thiols. The small difference of 5 mV between the potentials of the reductive and the oxidative current peaks for ethanethiolates was taken as an indication of a fast and reversible electron transfer. The origin of the different mechanisms of oxidative deposition of ethanethiolates on gold and on silver and mercury is not clear.

The electrodeposition of thiols is a complex process which depends not only on the substrate but also on the electrolyte solution and the interactions among thiols and between the thiols and the solvent molecules. The solubility of the adsorbates plays a role in the electrodeposition of thiolates. Lower surface coverages are observed when the electrodeposition is carried out in nonpolar solvents where the solubility of thiolates is high.¹⁰ In aqueous electrolyte solutions, the increase of the length of the alkane chain decreases the solubility of the thiols and causes changes in the voltammogram of their reductive removal from a gold substrate. On ordered Au(111) substrates, two current peaks are observed in the voltammogram of the reduction of chemisorbed thiols with more than 12 carbons¹¹ compared to a single current peak observed for thiols with shorter alkane chains.^{11–13} Two models were suggested to explain the multiple-step reduction of insoluble thiols chemisorbed on Au(111).^{11,12} The first model consists of the formation of two domains of slightly different packing densities. The different ionic permeabilities of the domains would lead to different potentials of

* Corresponding author. E-mail: mgmorin@science.uottawa.ca.

reduction for the thiols in each domain. In the other model, the two reductive current peaks are assigned to the reduction of thiols from two adsorption sites. The presence of a second adsorption site for the longer chain thiols was explained by an increase of the interadsorbate interactions. However, there is no direct evidence favoring either of these models. Monolayers of insoluble thiols display a particular electrochemical characteristic. Insoluble thiols such as hexadecanethiols remain physisorbed at the gold surface after their reduction, probably forming micelles.^{11,12} They can be quantitatively redeposited by doing a positive-going potential scan after the reduction of the chemisorbed thiols. Thus, the same molecules go from a chemisorbed state to a physisorbed state and back to a chemisorbed state. Furthermore, the chemisorbed thiols remain well-ordered after this treatment. The study of the mechanism of the oxidative electrodeposition/reductive removal of insoluble chemisorbed thiols should provide useful information for the development of an electrochemical method of forming self-assembled monolayers. We present here the results of a spectroelectrochemical study of the oxidation and the reduction of hexadecanethiols chemisorbed on Au(111). Our results show that the decrease of the solubility of the alkanethiols causes the reductive desorption and the oxidative redeposition to proceed through two steps. These data allowed us to develop a new model for the electrodeposition of insoluble thiols which consists of the electrospreading of physisorbed micelles of thiolates.

Experimental Section

Two Au(111) single-crystal electrodes were aligned within 0.5° of the (111) plane. They were then mechanically and electrochemically polished.¹³ The geometrical area of the two Au(111) electrodes used in the experiments were 0.71 and 0.65 cm². A three-electrode potentiostat and a computer were used for the electrochemical measurements. The working electrode was the Au(111) single crystal. The counter electrode was a platinum foil, and the reference electrode was a saturated calomel electrode (SCE). All the potentials given in this paper are relative to a SCE. The potential scan rate used to record the cyclic voltammograms was 20 mV s⁻¹. All measurements were done in a 0.1 M KOH (Aldrich, semiconductor grade) solution made with deionized distilled water (Milli-Q, Millipore). The solutions were degassed with argon or nitrogen prior to the measurements. The cyclic voltammograms were measured after lifting up the Au(111) above the surface of the solution in order to form a hanging meniscus such that only the (111) surface is in contact with the electrolyte solution. The charge densities were obtained from the numerical integration of the current measured in the voltammograms. The hexadecanethiols were purchased from Aldrich and used as received. The monolayers were obtained by annealing the Au(111) electrode in a natural gas flame and then incubating it in a 10 mM ethanolic solution of hexadecanethiols for 1 h.

The ex situ infrared differential reflectance spectra were recorded with an IR beam polarized in a plane perpendicular to the gold surface. The angle of incidence of the IR beam was 80° relative to the surface normal. The setup for the SNIPTIRS measurements was described previously.¹⁴ The spectra were recorded at a resolution of 2 cm⁻¹. The intensity of the spectra is expressed in units of differential reflectance $\Delta R/R$. This is done by subtracting a sample spectrum and a reference spectrum to get ΔR . ΔR is then divided by the reference spectrum, R . The choice of sample and reference spectra vary between experiments.

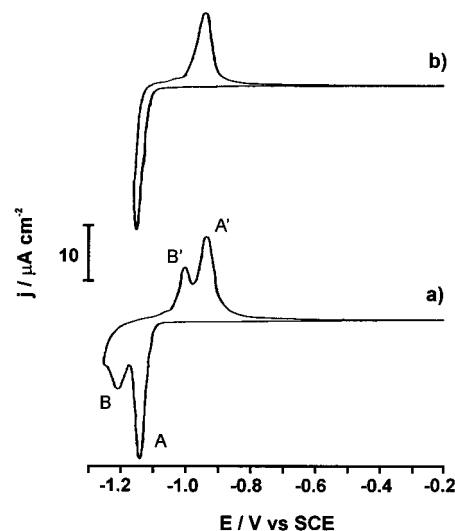


Figure 1. Cyclic voltammograms of a Au(111) electrode covered with a monolayer of chemisorbed hexadecanethiols in 0.1 M KOH recorded at a potential scan rate of 20 mV s⁻¹: (a) between -0.20 and -1.25 V; (b) between -0.20 and -1.16 V.

Results and Discussion

The cyclic voltammogram in Figure 1a shows that the reductive desorption and the oxidative redeposition of the hexadecanethiols occur in two steps. This voltammogram is obtained by immersing a Au(111) covered with a monolayer of hexadecanethiols in the electrolyte solution while holding the potential at -0.30 V. Then, three cyclic voltammograms between -0.30 and -1.25 V were recorded. A typical third voltammogram is shown in Figure 1a. Two reductive current peaks, A at -1.13 ± 0.01 V and B at -1.20 ± 0.01 V, are observed on the negative-going potential scan. They are assigned to the reduction of the chemisorbed thiols.^{11,12,15} After the reduction, a monolayer of physisorbed thiolates is formed. On the subsequent positive-going potential scan, two oxidative current peaks, B' at -0.99 ± 0.01 V and A' at -0.93 ± 0.01 V, are observed. These current peaks are assigned to the oxidative redeposition of the physisorbed thiolates. The absolute values of the integrated oxidative and reductive charges measured after three voltammograms are both equal to $85 \pm 5 \mu\text{C cm}^{-2}$. This charge density is 10–15% lower than the one recorded on the first voltammogram, indicating a loss of adsorbates. The peaks A and A' and B and B' have been shown to be related.¹¹ This is illustrated in Figure 1b where the negative limit of the potential scan was set at -1.16 V just before the reductive current peak B. The potential was scanned from -1.16 to -0.30 V. Only the oxidative current peak A' is observed on this positive-going potential scan. We note that the current peak A' has a symmetrical shape, and its full width at half the maximum current is 60 mV. These characteristics are compatible with a one-electron oxidation of adsorbed molecules.¹⁶

The overlap of the oxidative current peaks A' and B' prevents an accurate determination of the charge of each of the current peaks. However, an estimate of the charge due to the peak B' can be obtained by measuring the oxidative charge redeposited when the peak B' disappears from the positive-going scan recorded after holding the potential at -1.01 V for 3 min. The oxidative charge measured in this way corresponds to $36 \pm 7\%$ of the total charge. We thus assign 1/3 of the total oxidative charge ($25\text{--}30 \mu\text{C cm}^{-2}$) to the current peak B'. The remaining 2/3 of the oxidative charge ($55\text{--}60 \mu\text{C cm}^{-2}$) is assigned to the peak A'. Although these values are estimates, the charge

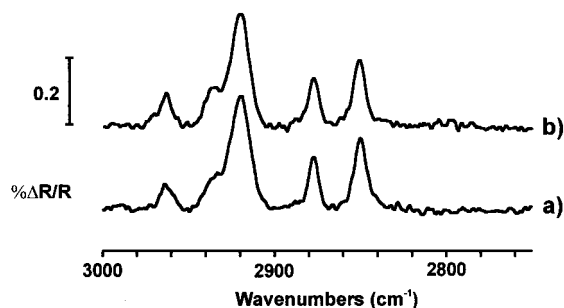


Figure 2. Differential reflectance spectra of (a) a chemically deposited monolayer of hexadecanethiols on Au(111); (b) the same monolayer after it went through two cyclic voltammograms between -0.20 and -1.30 V in 0.1 M KOH (scan rate = 20 mV s^{-1}).

assigned to B' is too small to be due to the oxidative redeposition of all the thiolates since a one electron per thiolate oxidative redeposition would give rise to a charge density of $73 \mu\text{C cm}^{-2}$. However, the charge assigned to A' can account for the oxidative deposition of 80–85% of a monolayer. A similar distribution of charge between the reductive current peaks A (2/3) and B (1/3) was obtained from a cyclic voltammogram recorded at a slow potential scan rate of 0.5 mV s^{-1} (data not shown) which allowed a better separation of these peaks. These results provide more evidence that the current peaks A– A' and B– B' are related.

A qualitative comparison of the orientation of the aliphatic chains of the electrodeposited and the chemically deposited hexadecanethiols was done by recording the vibrational spectra of the CH stretching region shown in Figure 2. The vibrational spectrum of the chemically deposited monolayer of hexadecanethiols in Figure 2a displays five C–H stretching bands and is identical to previously published spectra.^{1,17} The bands at 2964 , 2937 , and 2878 cm^{-1} are assigned to the methyl group. They are, respectively, the asymmetric out-of-plane, and the symmetric mode split by a Fermi resonance with a bending mode into the two other bands.¹⁸ The bands at 2919 and 2851 cm^{-1} are the asymmetric and symmetric modes of the methylene groups. The wavenumbers of the methylene C–H stretching bands are typical of all-trans aliphatic chains forming an ordered monolayer.^{1,17} Once the IR spectrum has been recorded, the electrode covered with a monolayer of hexadecanethiols was immersed in a 0.1 M KOH solution at a potential of -0.30 V. Thereafter, two cyclic voltammograms between -0.30 and -1.30 V were done. After the second cycle, the electrode was removed from the electrochemical cell while holding the potential at -0.30 V. The electrode was rinsed with Milli-Q water and transferred into the FTIR spectrometer. The vibrational spectrum in Figure 2b was then recorded. The same five C–H stretching bands are present in the spectrum of the electrodeposited monolayer. Their relative intensities and wavenumbers are identical to those of a chemically deposited monolayer (see above). We note that the 10–15% decrease of the reductive charge observed after the first cyclic voltammogram did not lead to a decrease of the intensity of the CH stretching bands. This may be an indication that the loss of the reductive charge after the first cycle is due to thiols adsorbed at the edge of the crystal which do not contribute to the IR spectrum. The spectra in Figure 2 show that the electrodeposited and the chemically deposited monolayers of thiols have the same average orientation of their aliphatic chains. Hence, one monolayer of chemisorbed hexadecanethiols can be reductively desorbed and it can then form a monolayer of physisorbed thiolates which can be oxidatively redeposited without changing the initial orientation of the aliphatic chains.

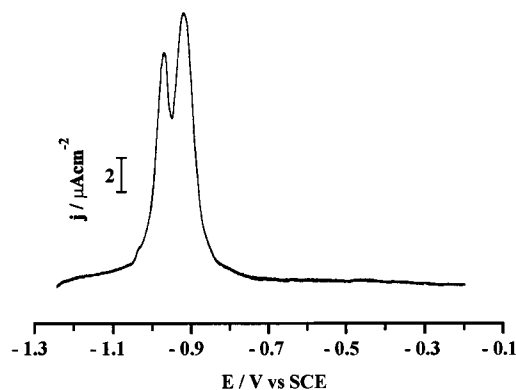


Figure 3. Voltammogram recorded after scanning the potential of a Au(111) coated with a monolayer of hexadecanethiols from -0.30 to -1.25 V and holding the potential at -1.25 V for 3 min and then scanning the potential to -0.3 V in 0.1 M KOH. The scan rate was 20 mV s^{-1} .

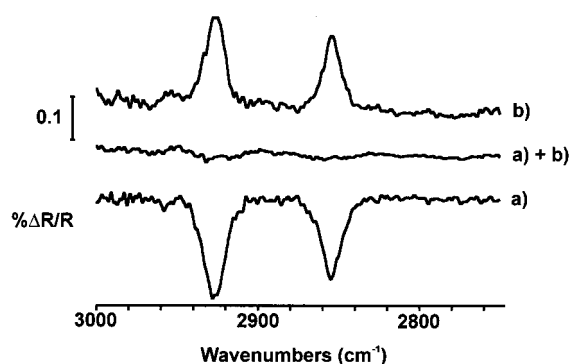


Figure 4. SNIFTIRS spectra of a monolayer of hexadecanethiols chemisorbed on Au(111) after (a) a potential step from -0.30 to -1.20 V and (b) a potential step from -1.20 to -0.30 V; (a + b) is the sum of the two spectra a and b. Each spectrum is an average of five different sets of 200 spectra recorded at a resolution of 2 cm^{-1} .

In situ vibrational spectroscopy (SNIFTIRS) was used to monitor the change in orientation of the aliphatic chains after the reductive desorption and after the oxidative redeposition. We verified the stability of the monolayer of physisorbed thiolates during the time required to record an in situ vibrational spectrum (3 min). This is necessary since the vibrational spectra and the voltammograms are recorded under different conditions. A SNIFTIRS spectrum is the difference between two spectra measured at fixed potentials (i.e., under equilibrium conditions), whereas the voltammograms are recorded under conditions further from equilibrium since the potential is scanned at a rate of 20 mV s^{-1} . This measurement was done by scanning the potential from -0.30 to -1.25 V to reduce the chemisorbed thiols and then holding the potential at -1.25 V for 3 min. The potential was then scanned to -0.30 V to oxidatively redeposit the physisorbed thiolates. The voltammogram recorded on this positive-going potential scan is shown in Figure 3. We see that the voltammogram is similar to the one obtained by continuous cycling shown in Figure 1. The peak B' is smaller than the peak A' , and the peaks remain at -0.99 and -0.93 V, respectively. This gives us confidence that the SNIFTIRS spectra shown below are related to the current peaks observed on the cyclic voltammogram displayed in Figure 1.

The SNIFTIRS spectra of the CH stretching region for these processes are shown in Figure 4. The SNIFTIRS spectrum in Figure 4a corresponds to the reduction of adsorbed hexadecanethiols after a potential step from -0.30 to -1.20 V. The reference spectrum is measured at -0.30 V (where there is a

monolayer of chemisorbed thiols). Two negative peaks are observed at 2926 and 2855 cm^{-1} . The wavenumbers of these methylene's CH stretching bands are higher than those observed in the spectrum taken in air (see Figure 2). This indicates that the monolayer becomes disordered when immersed in an aqueous solution.^{19–21} However, this disorder is believed to be localized at the liquid/thiol interface.^{19,20} This disorder could explain the absence of intensity change of the methyl CH stretching bands. Disordered methyl groups would have weak and broad CH stretching bands in both the chemisorbed and physisorbed states. Thus, no (or very small) change of the intensity of these bands would occur for the transition between the chemisorbed and physisorbed states. The negative reflectance peaks correspond to an increase of the intensity of the methylene's CH stretching bands once the thiols have been reduced. The infrared surface selection rule²² indicates that the infrared transition dipoles (TD) of the CH stretching bands become more perpendicular to the Au(111) surface after the reduction of the chemisorbed hexadecanethiols. The reorientation of the TDs can be related to the orientation of the aliphatic chains since the TDs of the methylene CH stretching modes are perpendicular to the molecular axis of an all-trans aliphatic chain. However, we must make the assumption that the alkane chains remain in an all-trans configuration after their reduction. The observation that the electrodeposited thiols have their alkane chains in an all-trans configuration suggests that the reduction of the hexadecanethiols does not create a significant number of gauche defects. On the basis of this result, we believe that the assumption that the alkane chains remain mostly in an all-trans configuration after their reduction is appropriate. We thus assign the increase of the intensity of the methylene CH stretching bands to an orientation of the all-trans aliphatic chains of the physisorbed thiols that is *more parallel* to the surface than that of chemisorbed thiols.

The spectrum in Figure 4b corresponds to the oxidative redeposition of the same monolayer following a potential step from -1.20 to -0.30 V. The reference spectrum in this case is a spectrum recorded at -1.20 V (where there are physisorbed thiols). There is an increase of the reflectance at 2926 and 2855 cm^{-1} . These reflectance peaks are assigned to a decrease of the intensity of the methylene's CH stretching bands after the oxidative adsorption of the thiols. The analysis of this decrease in intensity is also done by using the surface selection rule and by making the assumption that the aliphatic chains are in an all-trans configuration. This interpretation indicates that the aliphatic chains become *more perpendicular* to the surface after the oxidative reposition of the physisorbed thiols.

The addition of the two spectra, shown as a+b in Figure 4, unequivocally shows that the changes in the orientation of the aliphatic chains observed during one reduction/oxidation cycle are *reversible*. The SNIFTIRS spectra of the reductive desorption and of the oxidative redeposition are almost equal in magnitude but of different signs. This *in situ* result also agrees with the observation that the electrodeposited hexadecanethiols have the same orientation as the chemically deposited thiols (see Figure 2b). We repeated these measurements using s-polarized (polarized perpendicular to the plane of incidence) IR light and observed no peaks in the SNIFTIRS spectra. This result shows that the thiols are physisorbed at the surface.

The repulsion between the thiols probably causes the reorientation of the molecules during the reductive desorption. At a monolayer coverage,²³ the chemisorbed thiols are only separated by 5 Å. After the reduction, the repulsion between the negatively charged thiols becomes important at this short

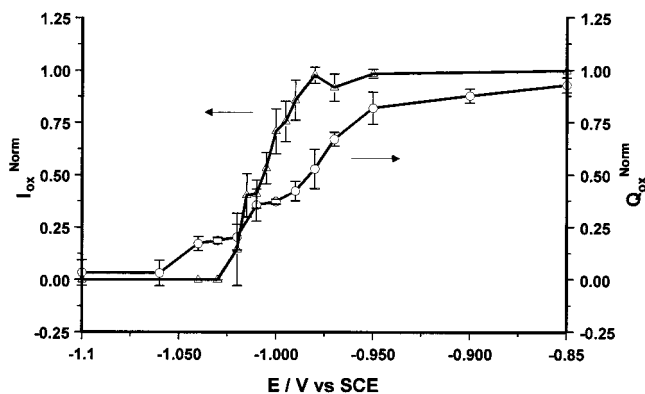


Figure 5. Normalized intensities of the band at 2926 cm^{-1} , $I_{\text{norm}}^{\text{ox}}$, and the normalized oxidative charge, $Q_{\text{norm}}^{\text{ox}}$, measured after potential steps from -1.20 V to potentials between -1.10 and -0.85 V. Each data point is an average of three measurements. Each measurement is an average of 200 spectra recorded at a resolution of 2 cm^{-1} . The error bars represented one standard deviation. See text for more details.

distance and the separation between the thiols should increase. It is likely that the increased attraction of the thiols toward the gold surface when the potential is scanned in the positive direction causes the reorientation of the physisorbed thiols and their chemisorption. The low solubility of the hexadecanethiols in the aqueous electrolyte also plays a role in the reorientation of the alkane chains (see below).

The relationship between the current peaks and the changes in the SNIFTIRS spectra was examined in more detail. We discuss first the results of the oxidative adsorption of the physisorbed thiols. The experiment consisted of recording the SNIFTIRS spectra for a series of potential steps from -1.20 V to potentials between -1.10 and -0.85 V. The reference spectrum for this set of SNIFTIRS spectra was measured at -1.20 V (where there are physisorbed hexadecanethiols). The intensity of the band at 2926 cm^{-1} was measured in each spectrum. These intensities were normalized by dividing them with the intensity of the same band in a SNIFTIRS spectrum of a potential step from -1.20 to -0.30 V (where complete redeposition of the thiols occurs). The normalized infrared intensities, $I_{\text{norm}}^{\text{ox}}$, shown in Figure 5 are averages of three measurements done on different monolayers. The measurements of the oxidative charges consisted of holding the potential for 3 min at a potential, $E_{\text{hold}}^{\text{ox}}$. The potential was then scanned from $E_{\text{hold}}^{\text{ox}}$ to -0.30 V. The resulting oxidative current between $E_{\text{hold}}^{\text{ox}}$ and -0.30 V was integrated to obtain the oxidative charge, Q^{ox} . The total oxidative charge, $Q_{\text{total}}^{\text{ox}}$, is obtained by recording a cyclic voltammogram between -0.30 and -1.30 V immediately after the measurement of Q^{ox} and integrating the oxidative current between -1.30 V and -0.30 V. We then calculate $Q_{\text{norm}}^{\text{ox}} = (Q_{\text{total}}^{\text{ox}} - Q^{\text{ox}})/Q_{\text{total}}^{\text{ox}}$. $Q_{\text{norm}}^{\text{ox}}$ corresponds to the fraction of the oxidative charge deposited during the recording of a SNIFTIRS spectrum at $E_{\text{hold}}^{\text{ox}}$. The $Q_{\text{norm}}^{\text{ox}}$ values shown in Figure 5 are averages of three measurements done on different monolayers.

The most striking result in Figure 5 is the contrasting rates of variation of $I_{\text{norm}}^{\text{ox}}$ and $Q_{\text{norm}}^{\text{ox}}$. $I_{\text{norm}}^{\text{ox}}$ increases from 0% to 100% over 50 mV (from -1.03 and -0.98 V), whereas it takes 260 mV (from -1.06 to -0.80 V) for $Q_{\text{norm}}^{\text{ox}}$ to go from 0% to 100%. We also note that $Q_{\text{norm}}^{\text{ox}}$ does not increase smoothly. Two plateaus are observed. The first plateau occurs between -1.04 and -1.02 V where $Q_{\text{norm}}^{\text{ox}}$ is constant at $20 \pm 2\%$. The second plateau is between -1.01 and -0.99 V where $Q_{\text{norm}}^{\text{ox}}$ has a value of $40 \pm 4\%$. After these two plateaus, $Q_{\text{norm}}^{\text{ox}}$

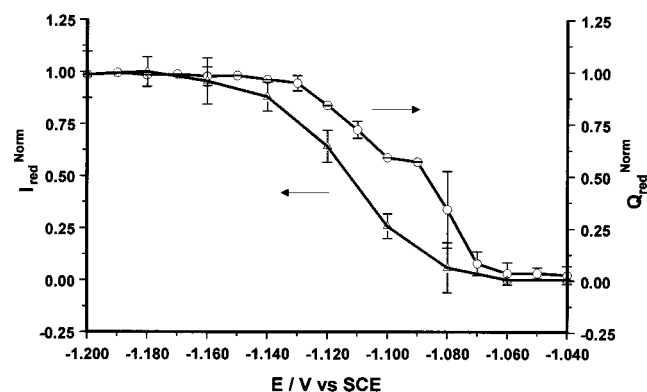


Figure 6. Normalized intensities of the band at 2926 cm^{-1} , $I_{\text{norm}}^{\text{red}}$, and the normalized reductive charge, $Q_{\text{norm}}^{\text{red}}$, measured after potential steps from -0.30 V to potentials between -1.04 and -1.20 V . Each data point is an average of three measurements. Each measurement is an average of 200 spectra recorded at a resolution of 2 cm^{-1} . The error bars represented one standard deviation. See text for more details.

increases smoothly. We observed the disappearance of the current peak B' from the positive-going potential scan from $E_{\text{hold}}^{\text{ox}}$ to -0.3 V when $E_{\text{hold}}^{\text{ox}}$ is more positive than -1.02 V . We thus assign most of the charge corresponding to the second plateau to the current peak B'. This observation allows us to establish the relationship between the current peak B' and the changes in the SNIPTIRS spectra. The results in Figure 5 show that most of the variation of $I_{\text{norm}}^{\text{ox}}$ occurs over the second plateau (from -1.01 to -0.99 V). Thus, most of the increase of the IR reflectance can be assigned to the disappearance of the oxidative current peak B'.

The results for the reductive desorption of the chemisorbed thiolates are shown in Figure 6. The SNIPTIRS spectra for the reductive desorption were recorded for potential steps from -0.30 V to potentials between -1.04 and -1.20 V . $I_{\text{norm}}^{\text{red}}$, the intensity of the band at 2926 cm^{-1} divided by the intensity of the same band obtained from SNIPTIRS spectrum of a potential step from -0.30 to -1.20 V (This potential step causes the complete reduction of the monolayer.) is taken as a measure of the IR changes. The reference spectrum for this set of SNIPTIRS spectra is that of a Au(111) covered with a monolayer of chemisorbed hexadecanethiols measured at -0.30 V . The reductive charge deposited during the recording of a SNIPTIRS spectrum was measured as follow. The potential was scanned from -0.30 V to a more negative final value of $E_{\text{hold}}^{\text{red}}$ (between -1.04 and -1.20 V) where it was held for 3 min. The potential was then scanned from $E_{\text{hold}}^{\text{red}}$ back to -0.30 V . The resulting oxidative current was integrated to obtain the charge. The negative value of this charge was taken to be equal to the amount of reductive charge Q^{red} deposited while the SNIPTIRS spectrum is recorded at $E_{\text{hold}}^{\text{red}}$. This assumption is based on the equality between the $Q_{\text{hold}}^{\text{red}}$ and $Q_{\text{total}}^{\text{ox}}$. After the measurement of Q^{red} , a cyclic voltammogram from -0.30 to -1.30 V was recorded. The total reductive charge, $Q_{\text{total}}^{\text{red}}$, is obtained from the integrated current between -0.3 and -1.30 V . From these two charges we calculate the normalized reductive charge, $Q_{\text{norm}}^{\text{red}} = Q^{\text{red}}/Q_{\text{total}}^{\text{red}}$. $Q_{\text{norm}}^{\text{red}}$ represents the fraction of the total reductive charge deposited during the time required to record a SNIPTIRS spectrum at $E_{\text{hold}}^{\text{red}}$.

The variations of $I_{\text{norm}}^{\text{red}}$ and $Q_{\text{norm}}^{\text{red}}$ in the range of potentials of the reduction of the chemisorbed hexadecanethiols are shown in Figure 6. $I_{\text{norm}}^{\text{red}}$ and $Q_{\text{norm}}^{\text{red}}$ are averages of three measurements done on different monolayers. $Q_{\text{norm}}^{\text{red}}$ goes from 0% at -1.06 V

to 100% at -1.13 V , whereas $I_{\text{norm}}^{\text{red}}$ varies from 0% to 100% between -1.08 and -1.16 V . The range of potentials required for the complete reduction of the monolayer is much smaller than in the case of the oxidative redeposition because of the small separation between the current peaks A and B. We also find that $Q_{\text{norm}}^{\text{red}}$ and $I_{\text{norm}}^{\text{red}}$ vary over the same potential range. This contrasts with what is observed for the oxidative redeposition. However, their detailed variations differ. In the case of $Q_{\text{norm}}^{\text{red}}$, there is a large standard deviation ($\pm 18\%$) of its value at -1.08 V , indicating a variation of the onset of reduction for different monolayers. Between -1.09 and -1.10 V , $Q_{\text{norm}}^{\text{red}}$ is constant at $57(\pm 1)\%$. This short but reproducible plateau coincides with the potential where only the oxidative current peak A' is observed on the positive-going potential scan from -1.10 to -0.30 V . We thus assign the charge of this plateau to the peak A, and the remaining 42% of the charge is assigned mostly to the peak B. After this plateau, $Q_{\text{norm}}^{\text{red}}$ increases smoothly and reaches a value of 100% at -1.13 V . We also observed that the two oxidative current peaks B' and A' are present on positive-going potential scans which start from a potential more negative than -1.10 V . The onset of the increase of $I_{\text{norm}}^{\text{red}}$ is at the same value of -1.08 V as that of $Q_{\text{norm}}^{\text{red}}$. However, at -1.10 V , $I_{\text{norm}}^{\text{red}}$ has a value of $25(\pm 5)\%$, whereas $Q_{\text{norm}}^{\text{red}}$ is $58(\pm 1)\%$. Most of the increase of $I_{\text{norm}}^{\text{red}}$ (75%) occurs for potentials more negative than -1.10 V , where the last 42% of the reductive charge is measured. The largest increase of $I_{\text{norm}}^{\text{red}}$ is observed in the potential range corresponding to the current peak B. This result is similar to that observed for the oxidative deposition where the increase of $I_{\text{norm}}^{\text{ox}}$ was found to occur over only 40% of the total oxidative charge. These two results provide clear evidence that most of the changes in the SNIPTIRS spectra are related to the current peak B and B'.

The results in Figures 5 and 6 strongly suggest that the reduction of chemisorbed hexadecanethiols and the oxidative redeposition of physisorbed hexadecanethiolates proceed via two consecutive steps. The spectroelectrochemical characteristics of these two steps are different. In one of the steps (represented by the peak A (A')), most of the thiols are reduced (oxidized). The reduction (oxidation) of most of the thiols does not cause a noticeable change of the orientation of their alkane chains. The other step, represented by the peak B (B'), involves a smaller charge but a significant change of the orientation of the alkane chains.

The distribution of the total charge between the current peaks A (A') and B (B') observed in this study is similar to that obtained from a model previously used to estimate the surface concentration of thiols from the reductive charge.¹³ In this model, the total reductive charge is divided into two components. There is a capacitive component, which is equal to approximately 30% of the total charge ($29\text{--}31\text{ }\mu\text{C cm}^{-2}$). This capacitive charge is due to the formation of a double layer at the surface of the Au(111) electrode once the thiols have been reductively removed from the surface of the electrode. The remainder of the charge (70% or $69\text{--}71\text{ }\mu\text{C cm}^{-2}$) is the faradaic component. It corresponds to the electron transfer from the electrode to the chemisorbed thiols. This faradaic charge density was converted to a thiol coverage by assuming a one-electron reduction process. A thiol coverage of 7.2×10^{-10} ($\pm 10\%$) mol cm^{-2} was obtained. This value was compatible with a full monolayer coverage of thiols ($7.6 \times 10^{-10}\text{ mol cm}^{-2}$). The absolute values of the reductive and the oxidative charge densities of the peaks A and A' ($55\text{--}60\text{ }\mu\text{C cm}^{-2}$) and that of the estimated faradaic charge for the reduction a monolayer of thiols are quite close. Consequently, the absolute values of the

charge densities of the current peaks B and B' ($25\text{--}30\text{ mC cm}^{-2}$) are also close to the absolute value of the capacitive charge involved in the removal of a monolayer of thiols. These similarities between the distribution of the charges into the two steps suggest that the reduction of the chemisorbed thiols proceeds through a faradaic step (peak A) followed by a capacitive step (peak B). The oxidative redeposition would proceed through the same mechanism but in the reverse order. The capacitive step would occur first (peak B') followed by the faradaic step (peak A').

The two models previously suggested to explain the presence of two reduction and two oxidation peaks in the voltammogram in Figure 1a are not compatible with our results. We can rule out, based on our results, the model which states that the two reductive peaks are caused by the reductive desorption of thiols from two domains of different packing densities.^{11,12} In this model, the peaks A and A' were assigned to a domain with a lower density of thiols. The peaks B and B' were assigned to a domain with a higher density of thiols. To explain our observations, the reduction of the high-density domain (peak B) would cause a reorientation of the alkane chains, whereas the thiols forming the lower density domain (peak A) would cause only a small change of the orientation of the alkane chains. This is unlikely to occur because the Coulombic repulsions between the thiolates are expected to be important for both domains, since their packing densities cannot differ significantly because of the high surface coverage of the thiols. Thus, in this model, the variations of the intensity of the CH stretching bands should closely follow the variation of the charge, and this is in contradiction with our results. In the other model, the two reduction peaks were assigned to the adsorption of thiols on two different sites. *Ab initio* calculations give some support to this model.²⁴ Two stable adsorption sites, a 3-fold hollow and an on-top site, differing by only 2 kcal mol^{-1} , were predicted. The appearance of a second current peak for alkanethiols with more than 12 carbons was explained by the stabilization of the second adsorption site due to the increased interactions between the chains. The reductive desorption of a thiol from either adsorption site should lead to a change in the vibrational spectrum. Thus, the SNIPTIRS spectrum should change over the whole potential range where a reductive current is measured. This, again, disagrees with our results. Furthermore, there is no evidence of more than one binding site in the XPS measurements done on gold covered with a monolayer of hexadecanethiols.¹¹

Neither model takes into account the effect of the large overpotential needed to reduce chemisorbed thiols with long aliphatic chains. The reduction potential of the chemisorbed hexadecanethiols is 300 mV more negative than that of butanethiol.^{11–13,15} This overpotential is not due to a change in the strength of the gold–sulfur bond¹¹ since there is no change of the energy of the 2p levels of sulfur with the chain length. The negative shift of the potential of the reductive current peaks is caused by the increased screening of the applied electric field by the aliphatic chains.¹⁵ An alternative interpretation assigns the negative shift of the reduction potential to the increase of the energy required to transfer an alkane thiols into water.⁴ These two effects, the increase screening of the electric field and the hydrophobicity, are not easily decoupled. An hydrophobic monolayer will also have a low dielectric constant which results in a screening of the applied electric field. Notwithstanding the origin of an overpotential, it has the effect of making the reduction of the chemisorbed thiols faster.²⁵ Thiols adsorbed on sites with binding energies differing by only 20 meV are

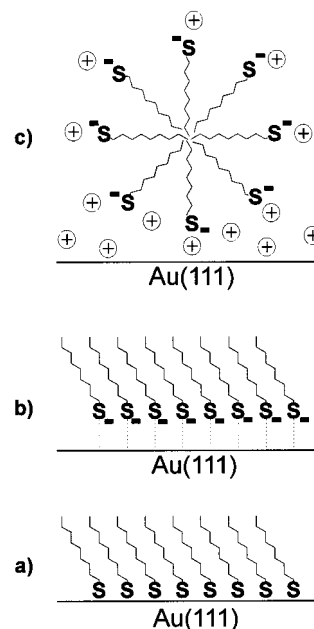


Figure 7. Model for the repetitive reductive desorption/oxidative redeposition of a chemisorbed monolayer of insoluble thiols. The reduction proceeds through the following steps: (a) chemisorbed thiols; (b) the reduction of the chemisorbed thiols created the physisorbed thiolates, which form a lamellar structure; (c) when the potential is made more negative, physisorbed micelles of thiolates are formed. The oxidative redeposition proceeds through the reverse order of steps.

expected to be reduced at similar rates and thus they should not give rise to well-separated current peaks.

In contrast to the previously proposed models, our results suggest that the current peaks are due to two consecutive processes involving all the thiols. We thus propose an alternative mechanism for the repetitive reductive desorption of chemisorbed thiols/oxidative redeposition of physisorbed thiolates. The main elements of our model are the formation and the electrospreading of physisorbed micelles of thiolates. We start the description of the model with a monolayer of chemisorbed thiols on Au(111) at a potential of -0.30 V in a 0.1 M KOH solution shown in Figure 7a. The alkane chains are assumed to be mainly in an all-trans configuration. When the potential is scanned in the negative direction, the electrochemical properties of the monolayer of hexadecanethiols and the orientation of the alkane chains are not influenced by the applied field up to -1.06 V since no faradaic current or change in the vibrational spectrum has been observed in this range of potential (see Figure 5). When the potential reaches a value of -1.09 V , the chemisorbed thiols are reduced via a one-electron process. As mentioned previously, the integrated charge of $55\text{--}60\text{ }\mu\text{C cm}^{-2}$ assigned to this process (the peak A) is compatible with the reduction of an almost complete (80%) monolayer of hexadecanethiols. There is a reorientation of the alkane chain of some of the thiolates over the range of potential corresponding to the current peak A since an increase of as much as 25% of $I_{\text{norm}}^{\text{red}}$ is observed. However, most of the reduced thiols remain in their original orientation as shown in Figure 7b). After the reduction of the chemisorbed thiols, there is a high concentration of insoluble thiolates at the Au(111) surface. When the potential is scanned to potentials more negative than -1.10 V , the interaction between the negatively charged thiolates and the gold surface becomes less favorable. This leads to the formation of micelles of thiolates. Although our data does not allow us to determine the shape of the micelles, we assume that they have a spherical shape. However, our model is also compatible with the

formation of hemi-micelles of thiolates. The micelles remain physisorbed at the surface of the electrode, as shown in Figure 7c. The formation of physisorbed micelles frees a large fraction of the electrode surface. A double layer can then be formed at the unblocked and negatively charged Au(111) surface. This gives rise to a negative capacitive current which we assign to the current peak B. The formation of spherical micelles is also compatible with our vibrational data. The alkane chains of aliphatic compounds in micelles are mainly in an all-trans configuration.²⁶ Thus, the average direction of the vibrational transition dipoles of the methylene's CH stretching modes in micelles is more perpendicular to the surface than in a self-assembled monolayer. This causes an increase of the intensity of the methylene's CH stretching bands.

The physisorbed micelles of thiolates are oxidatively redeposited during the positive-going scan from -1.30 to -0.30 V by the reverse mechanism of the reductive desorption. The first step is the electrospreeding of the physisorbed thiolates. This step corresponds to the transition from part c to part b of Figure 7. It occurs between -1.02 and -0.99 V, where the first oxidative current peak, B', is observed. In this range of potentials, the thiolates reorient and their alkane chains adopt the same orientation as in their chemisorbed state (see Figure 4). The reorientation of the thiols leads to the removal of the electrical double layer. The resulting capacitive current is oxidative since the capacitance will decrease to only a few $\mu\text{F cm}^{-2}$ when the electrode is covered with a monolayer of hexadecanethiolates. The oriented thiolates are then oxidatively chemisorbed when the potential becomes more positive than -1.02 V. This gives rise to the large oxidative current (the peak A') but to small changes in the SNIPTIRS spectra. The oxidative charge density of the current peak A' of $55\text{--}60 \mu\text{C cm}^{-2}$ is compatible with a one-electron deposition of 80% of a monolayer of thiolates. The structure and orientation of the electrodeposited monolayer of hexadecanethiols are the same as those of the initial monolayer shown in Figure 7a.

Our model is supported by many studies that reported the formation of physisorbed micelles of insoluble molecules on metallic substrates.^{27–29} The results most relevant for our model are the in situ STM measurements of the reduction of a monolayer of hexadecanethiols adsorbed on polycrystalline gold.²⁷ Aggregates with diameters ranging from 3 to 12 nm were found to form instantaneously over all the electrode surface at -1.0 V. The size and height of these aggregates increased at a potential of -1.2 V. The aggregates were assigned to the formation of micelles of thiolates. Also, the height of the aggregates formed after the reduction suggests that spherical micelles of hexadecanethiolates are formed. The aggregates disappear upon the oxidative redeposition of the thiolates. These results support our suggestion of a repetitive formation and destruction of physisorbed micelles of thiolates.

Chemisorbed insoluble thiols have electrochemical characteristics similar to those of Langmuir–Blodgett monolayers of insoluble adsorbates. Langmuir–Blodgett monolayers of insoluble aliphatic alcohols and stearic acid have been found to electrochemically desorb and readorb repetitively on a Au(111) electrode.^{28,29} Light-scattering experiments showed that physisorbed micelles of these insoluble adsorbates are formed at potentials negative of the potential of zero charge (pzc) of the Au(111) electrode. These micelles are spread and form a physisorbed monolayer on the surface at potentials positive of the pzc. These results established a clear correlation between the surface charge and the formation of physisorbed micelles of insoluble molecules and give support to our suggestion that

the peaks B and B' correspond to a transition between two physisorbed states (see parts b and c of Figure 7) caused by the applied potential.

In summary, our results provided insights into the mechanism of the electrodeposition of self-assembled monolayers of thiols. In aqueous electrolyte solution, insoluble hexadecanethiols adsorbed on Au(111) go from a chemisorbed state to a physisorbed state after their reduction. The transition from a chemisorbed to a physisorbed state is found to be reversible since the physisorbed thiolates can be oxidatively redeposited. The low solubility of the hexadecanethiols causes their reductive desorption and oxidative redeposition to occur in two steps. Spectroelectrochemical results show that the first step in the reduction of chemisorbed hexadecanethiols is compatible with the reduction of most of the chemisorbed thiols. In situ vibrational measurements indicate there is no substantial reorientation of the alkane chains in this first step. The second step of the reduction occurs at more negative potentials and is assigned to the formation of physisorbed micelles of thiolates. In contrast to the first step, there is a substantial reorientation of the alkane chains in the second step. This observation is compatible with the formation of micelles. The physisorbed thiolates are electrodeposited on the positive-going potential scan from -1.20 to -0.30 V by the reverse mechanism of the reduction. The electrodeposited hexadecanethiols form an ordered monolayer. Finally, the electrochemistry of insoluble thiols chemisorbed on gold was found to display characteristics similar to those of Langmuir–Blodgett monolayers of insoluble adsorbates physisorbed on Au(111). The chemisorbed thiols, like Langmuir–Blodgett monolayers, form physisorbed micelles when the electrode's potential is sufficiently negative to cause their reduction. These common properties of self-assembled and Langmuir–Blodgett monolayers show the important role that the solubility of the adsorbates plays in the electrodeposition of ordered organic monolayers.

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