

Phase Transitions of Alkanethiol Self-Assembled Monolayers at an Electrified Gold Surface

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Received: August 24, 2000; In Final Form: February 21, 2001

We report an in situ vibrational study of the reductive desorption and the oxidative adsorption of an alkanethiol monolayer on Au(111) in an alkaline solution between 5 and 37 °C. Cyclic voltammograms show that the reduction of a hexadecanethiol monolayer gives rise to two current peaks at low temperature. These two peaks slowly merge into a single peak as the temperature increases. The oxidative chemisorption displays a similar behavior. Three oxidative current peaks are observed at low temperature and only one at higher temperature. In situ vibrational spectroscopy shows that these electrochemical changes are related to a sharp phase transition. A sudden increase of the wavenumber of the methylene asymmetric CH stretching ν^- band from 2918 cm^{-1} below 12 °C to 2927 cm^{-1} above 12 °C indicates an abrupt disordering of the monolayer. A sharp transition at the same temperature of 12 °C is observed for the intensity of the differential reflectance CH stretching bands. This shows that changes in orientation of the alkane chains occur simultaneously with the disordering of the monolayer. We suggest that the phase transition from an ordered phase to a disordered phase is related to a sudden increase of ion permeation into the hexadecanethiol monolayer above 12 °C.

Introduction

Organic surfaces can form a variety of phases¹. For example, Langmuir–Blodgett (LB) monolayers of organic molecules at the air/liquid interface undergo a series of phase transitions as a function of applied pressure, solvent, electrolyte, and temperature¹. Strongly chemisorbed thiols on gold also form ordered phases.^{1–3} In contrast to LB monolayers, monolayers of alkanethiols do not undergo a discrete phase transition at temperatures close to the melting temperature of the bulk alkanethiols when under ambient or UHV conditions. Instead a gradual disordering of the monolayer is observed.^{4–6} It thus seems that strong chemisorption and dense packing prevent sharp phase transitions in which the area per molecule varies significantly. This thermal stability of self-assembled monolayer (SAM) of thiols makes them good candidates for the development of organic devices in photonics, sensing, and membrane technologies.

When thiol monolayers are in contact with solvent or electrolyte solutions, ions and solvent molecules can permeate into the alkanethiols monolayer.^{7–11} Important variations of ion permeation with temperature have been reported.^{7,9} In one case, increases of the reduction current of ferricyanide have been observed.⁹ The variations of the current were assigned to phase transitions of adsorbed alkanethiols on gold. These transitions cause the variations of ion permeation across the monolayer. A correlation with phase transitions of LB films was also found. However, for hydroxyl-terminated alkanethiols, the current of redox molecules is found to be independent of the temperature.¹² Hence, in this case, the electron transfer would occur via tunneling across the organic monolayer instead of the redox molecules permeating across the monolayer to the metal surface.

These electrochemical results^{7–11} do not probe directly the structure formed by the alkanethiols. They could be (partly) related to the presence of defects in the organic layer or to

interactions of the terminal groups with the electrolyte solution. STM and spectroscopic measurements would provide more direct evidence of the effect of the temperature on the structure of alkanethiol monolayers under electrochemical conditions. Such measurements are important to the development of electrodeposition methods for organic films and, for biosensors. The effect of the electrode potential on alkanethiol monolayers at room temperature has been studied with vibrational spectroscopy,^{13–15} Raman spectroscopy,¹⁶ and STM.¹⁷ No strong effect of the potential on the chemisorbed alkanethiols was observed.

We examine in this paper the effect of temperature on the vibrational spectrum and electrochemical properties of a monolayer of hexadecanethiol adsorbed on Au(111) in an alkaline aqueous solution. Vibrational reflectance spectroscopy can follow the average orientation of adsorbed molecules and give qualitative information on their environment.⁴ Hence, the study reported here provides more direct results on the organic phase(s) formed in a range of temperature where SAM could be used as electrochemical sensors.

Experimental Section

The preparation of the Au(111) single-crystal electrode has been described elsewhere.¹⁸ The hexadecanethiol monolayer was prepared by immersing a flame-annealed Au(111) electrode in a 1 mM solution of hexadecanethiols (Aldrich) in ethanol (OmniSolv, BDH) for 1 h. It was then transferred to a water-cooled, three-electrode spectro-electrochemical cell containing a 0.1 M KOH solution where the electrochemical and vibrational measurements were done. The electrolyte solution was made with KOH (semiconductor grade, Aldrich) and deionized and distilled water. All potentials cited in this paper are relative to a Saturated Calomel Electrode (SCE). The SNIFTIRS setup was described previously.¹³ A SNIFTIRS spectrum consists of the difference between a reference and a sample reflectance spectrum taken at two different potentials. This difference spectrum is then divided by the reference spectrum to give a normalized

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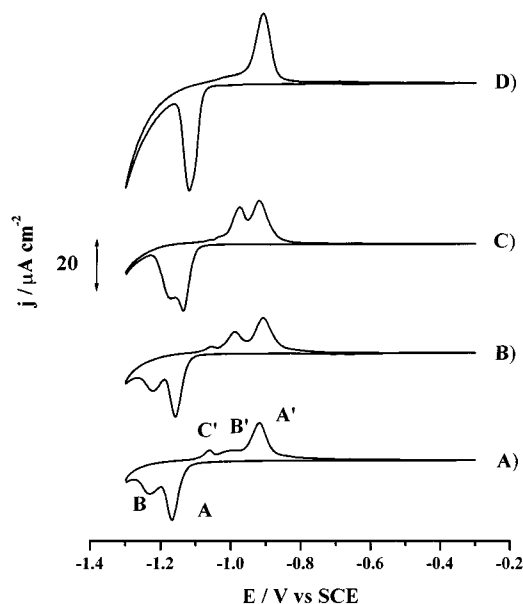


Figure 1. Cyclic voltammograms of a hexadecanethiol monolayer on Au(111) in 0.1 M KOH recorded at (A) 5.5, (B) 12, (C) 22, and (D) 36.5 °C. Potential scan rate: 20 mV s⁻¹.

differential reflectance spectrum called SNIFTIRS spectrum. For the oxidative deposition of alkanethiolates, the reference spectrum is taken at -1.20 V, and the sample spectrum is taken at -0.30 V. The reference spectrum is taken at -0.30 V, and the sample spectrum is taken at -1.20 V for the reductive desorption of alkanethiols. A positive differential reflectance band indicates a smaller intensity in the sample spectrum than in that the reference spectrum, whereas a negative differential reflectance band corresponds to a larger intensity in the sample spectrum. The temperatures cited in the text were measured at the position of the Au(111) electrode with a thermocouple. The electrode was kept at a given temperature for 10 min before measurements were taken. The uncertainty on the temperature is estimated to be ± 0.2 °C.

Results

In Figure 1, we see that the cyclic voltammograms of the reductive desorption and the oxidative adsorption of hexadecanethiolates immobilized on Au(111) undergo significant modifications between 5 and 37 °C. At low temperatures, multiple current peaks are observed for the reduction and oxidation processes, whereas at higher temperatures, a single current peak is observed for each process.

Before describing the voltammograms in Figure 1 in more details, we will briefly describe the voltammogram at 22 °C (Figure 1C) since it was studied previously.^{17,19–22} Because of their low solubility, the hexadecanethiols remain physisorbed after their reduction. This allows the same molecules to be oxidatively redeposited on the anodic (positive going) potential scan. Repetitive desorption/adsorption is thus possible.^{17,19–22} Two different interpretations of this cyclic voltammogram have been given.^{17–21} The first interpretation,^{17–19,21} which we will use in this paper, assigns the two peaks for the reduction (oxidation) to a faradaic peak A (A') and a capacitive peak B (B') related to the formation (electrospreading) of micelles of physisorbed thiolates. Porter et al.²⁰ proposed that the reductive current peaks were related to different domains having different ionic permeabilities.

Since the system has only been characterized at 22 °C, we will describe the voltammetric changes relative to the cyclic

voltammogram recorded at this temperature. When the temperature increases from 22 °C (Figure 1D), there is a slow merging of peaks B and B' with peaks A and A', respectively. The potentials of peak A move by 30 mV to -1.10 V, and peak A' remains at -0.91 V when the temperature is increased to 37 °C. Peaks B and B' are both shifted to more positive potentials. This behavior agrees with the previous assignment of peaks A and A' to faradaic processes and peaks B and B' to capacitive processes. It is not expected that the reductive destruction (A) and the oxidative formation (A') of the S–Au bond be influenced by a 15 °C increase. The capacitive peaks B and B' are likely to show a stronger dependence on the temperature. The displacements of peaks B and B' to more positive potentials when the temperature is increased suggest that the formation of physisorbed micelles occurs immediately after the reduction of the chemisorbed thiols. Then in the reverse process, the micelles directly form a chemisorbed monolayer during the oxidative adsorption.

Lowering the temperature below 22 °C (Figure 1A,B) also causes substantial changes in the voltammograms. Once again, peak B shows a more important temperature dependence than peak A. The reductive current peaks A and B become more separated mostly because peak B moves to more negative potentials. This gives further support to our assignment of peak B to a capacitive process. The changes are more complex for the oxidative deposition of the physisorbed thiolates. The faradaic peak A' retains its shape and intensity and remains at the same potential. There is a gradual decrease of peak B', and a small-current peak C' at -1.06 V develops as the temperature decreases. The appearance of the current peak C' is difficult to explain. We do not know if this current peak is capacitive and/or faradaic. More detailed studies would be required to identify the process related to peak C'. However, this observation does not change our overall conclusions on the two most important oxidative current peaks (A' and B'). At 5.5 °C, the oxidative deposition of the physisorbed thiolates occurs over a larger range of potentials. The change of the early (capacitive) stages of oxidative deposition suggests that the physisorbed state at low temperature is different than that at room temperature.

The cyclic voltammograms in Figure 1 show that the faradaic peaks A and A' shift only by 50 and 15 mV, whereas the capacitive peaks B and B' undergo larger and more complex intensities and potential shifts between 5 and 37 °C. We investigated the voltammetric results shown in Figure 1 with in situ infrared spectroscopy (SNIFTIRS) to see if the voltammetric changes are related to structural changes of the hexadecanethiol monolayer. In these experiments, the region of the CH stretching bands was measured for a potential step between -0.3 V and -1.20 V at various temperatures between 5 and 37 °C. These bands were chosen because their intensities and wavenumbers have been shown to depend on the orientation and packing structure of the adsorbed alkanethiols.^{4,23}

The SNIFTIRS spectrum underwent substantial modifications between 5 and 37 °C. Three regions of temperature giving rise to different reflectance spectra have been identified. Typical spectra corresponding to each region are displayed in Figure 2. Starting from the lowest-temperature region between 5 and 10 °C, two unipolar positive reflectance bands are observed at 2850 and 2918 cm⁻¹ for the reductive potential step from -0.30 to -1.20 V (Figure 2D). These bands are the methylene symmetric d⁺ and asymmetric d⁻ CH stretching modes, respectively. The wavenumbers of these bands are typical of crystalline alkanes.^{4,23} Thus, the interactions of the methylene groups with solvent and ions are small. Identical but negative reflectance bands are

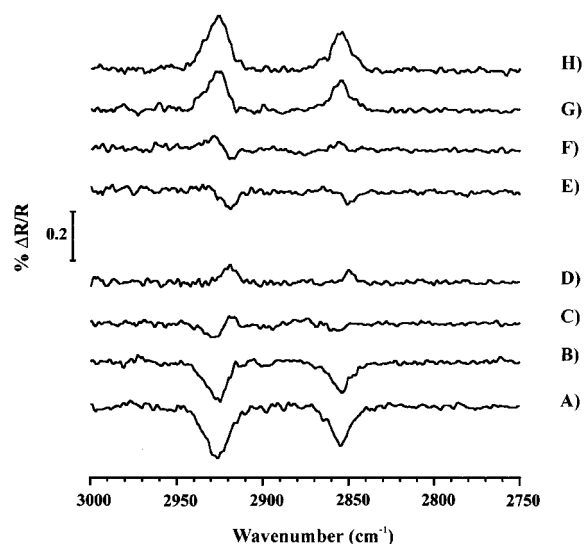


Figure 2. SNIFTIRS spectra for a potential step from -0.30 to -1.20 V, which causes the reduction of hexadecanethiols chemisorbed on Au(111) recorded at (A) 36.5 , (B) 22.0 , (C) 12.0 , and (D) 5.5 °C. SNIFTIRS spectra for a potential step from -1.20 to -0.30 V, which causes the oxidative adsorption of physisorbed hexadecanethiols onto Au(111) recorded at (E) 5.5 , (F) 12.0 , (G) 22.0 , and (H) 36.5 °C. Each spectrum is an average of 200 scans.

observed for the oxidative deposition potential step from -1.20 to -0.30 V (Figure 2E). This observation is taken as an indication that the reduction/oxidation of hexadecanethiols is a reversible process at these temperatures. The unipolar reflectance bands indicate that the wavenumbers are the same for the physisorbed and chemisorbed thiols. The decrease of the intensity of the CH stretching bands during the reductive desorption and their increase during the oxidative deposition indicate that the transition dipoles of the vibrational modes are more parallel to the metallic surface when they are physisorbed. If we assume an all-trans alkane chain, the molecular axis of the alkane chains would be more vertical relative to the surface for the physisorbed thiols than for the chemisorbed thiols.

In a small region, between 10 and 12 °C, bipolar bands are visible (Figures 2C and 2F). The bands are, again, the same for the reductive (Figure 2C) and oxidative (Figure 2F) potential steps except that they are inverted. Bipolar bands show that the wavenumbers of the bands differ in the physisorbed and chemisorbed states. There is an increase of the intensity of a d^- band at 2927 cm^{-1} and a decrease of a d^- band at 2919 cm^{-1} during the reductive potential step. The reverse effect is observed for the oxidative potential step. This observation is assigned to a physisorbed state more disordered (higher wavenumbers) than the chemisorbed state (lower wavenumbers).

Above 12 °C, unipolar and negative bands at 2927 (d^-) and 2856 cm^{-1} (d^+) are observed for the reduction (Figure 2A,B). Positive bands at the same wavenumbers are observed for the oxidation (Figure 2G,H). This inversion of direction of the bands relative to the lowest-temperature region (5 – 10 °C) shows that above 12 °C, there is an increase in the intensity of the bands for the physisorbed thiols and a decrease for the chemisorbed thiols. The unipolar bands indicate that above 12 °C, the wavenumbers are the same for the physisorbed and chemisorbed molecules. Between 13.5 and 37 °C, the vibrational bands increase in intensity but remain at the same wavenumbers. The larger intensity of the vibrational bands of the physisorbed thiols was previously assigned to the formation of physisorbed micelles of thiols.¹⁹ In this configuration, the alkane chains are, on average, more parallel to the surface, and thus,

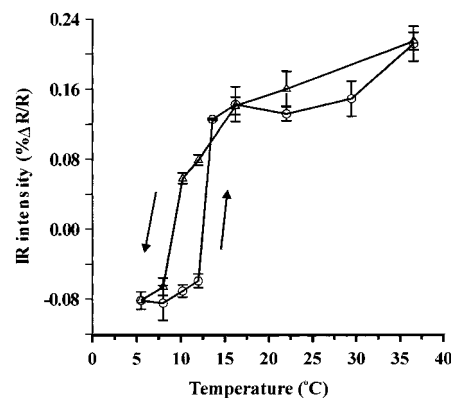


Figure 3. Intensity of the d^- band from 5.5 °C to 36.5 °C (circles) and from 36.5 °C to 5.5 °C (triangles) for potential steps from -1.20 V to -0.30 V. Each data point is an average of a minimum of 6 sets of 200 scans.

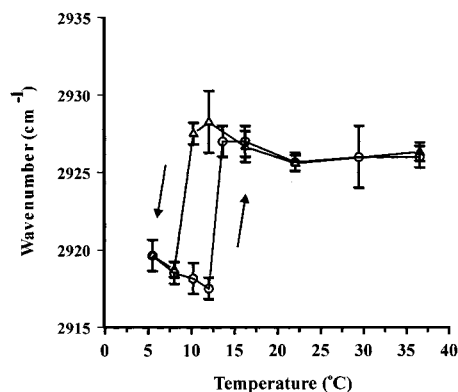


Figure 4. Wavenumber of the d^- band from 5.5 to 36.5 °C (circles) and from 36.5 to 5.5 °C (triangles) for potential steps from -1.20 to -0.30 V. Each data point is an average of a minimum of 6 sets of 200 scans.

the CH stretching bands are more intense in the physisorbed state.

The absence of methyl bands in the spectra shown in Figure 2 might be surprising since these bands are intense in spectra measured in air.^{3,6,14,15,19} However, in the in situ measurements reported here, the spectra subtracted both have CH stretching bands. This differs from the ex situ (in air) spectrum, which corresponds to a subtraction between a thiol-covered and a clean gold surface. Hence, the absence of the methyl bands in the spectra shown in Figure 2 indicates that the methyl bands do not change intensities and wavenumbers for these potential steps.

We further studied the thermal behavior of the hexadecanethiol monolayer by subjecting it to a heating cycle and a cooling cycle. SNIFTIRS spectra were recorded at different temperatures along the two cycles for an oxidative deposition potential jump from -1.20 to -0.30 V. The intensity and the wavenumber of the asymmetric CH stretching d^- band from these spectra are compiled in Figures 3 and 4. The data in these Figures are the average of a minimum of 6 sets of 200 scans recorded on three different monolayers. A complete heating and cooling cycle was done on each monolayer.

Figure 3 displays the intensity of the d^- band during the heating/cooling cycle. The circles represent the data recorded during the heating cycle. We see that up to 12 °C, negative differential reflectance intensities of -0.08% are measured for the d^- band. A very sharp increase of the intensity of the differential reflectance peak is seen between 12 and 13.5 °C. It goes from -0.06% to 0.12% . After this transition, the intensity increases smoothly and reaches a value of 0.21% at 36.5 °C.

The data (triangle) of the cooling cycle reveal that the intensity decreases slowly from 36.5 to 16.5 °C, where it has a value of 0.14%. The rate of decrease of the intensity then becomes faster down to 10 °C. A sudden inversion of the peak intensity occurs between 10 (0.08%) and 8 °C (−0.06%). Cooling down to 5.5 °C does not change the intensity significantly.

Figure 4 shows that the variation of the wavenumbers of the d^- band during the heating (circle)/cooling (triangle) cycle follows that observed for its intensity. From 5.5 to 12 °C, the band remains at an average wavenumber of 2918 cm^{-1} . Then the band suddenly shifts to 2927 cm^{-1} at 13.5 °C. It remains at this value ($\pm 1 \text{ cm}^{-1}$) up to 36.5 °C. On the cooling cycle, the wavenumber remains between 2926 and 2928 cm^{-1} down to 10 °C. Another sudden jump back to 2918 cm^{-1} occurs at 8 °C. No change is observed upon further cooling to 5.5 °C.

Although not shown, the data for the reduction of the chemisorbed hexadecanethiols exactly match the data shown in Figures 3 and 4, except that the sign of the intensity is inverted.

Discussion

The smooth changes in the cyclic voltammograms shown in Figure 1 contrast with the sharp changes in the vibrational spectra shown in Figures 2–4. Hence, the cyclic voltammetry measurements do show strong evidences of the phase transition suggested by the vibrational data. This is not surprising since cyclic voltammetry lacks the chemical specificity of vibrational spectroscopy. The relationship between the oxidative deposition or reductive desorption current peaks and the organization of the physisorbed or chemisorbed alkanethiols is complex. Ion permeation influences the potential of oxidation and reduction.^{18,20} It is thus difficult to relate ion permeation to the organization of a physisorbed or chemisorbed monolayers.

Cyclic voltammetry provides qualitative information on the type of processes giving rise to the current peaks. The temperature dependence of the current peaks A and A' and of B and B' are very different. The first set of peaks (A and A') shows a small change with temperature, whereas the second set of peaks (B and B') undergoes significant changes with temperature. As we mentioned above, this behavior is compatible with peaks B and B' being related to nonfaradaic (i.e., capacitive) processes. A recent study by Porter et al.²⁴ provides further evidence of the complexity of the processes giving rise to the structure of the voltammograms. They found that the separation of the faradaic (A and A') and capacitive (B and B') currents is related to the presence of large flat terraces on Au(111).

The data in Figures 3 and 4 reveal that the variations of intensities and wavenumbers of the d^- band are related. The intensity of the vibrational band is related to the (average) orientation of its transition dipole moment, and its wavenumber is sensitive to the (average) environment in which the alkanes are. Our data show that changes in the environment and orientation are related. We also note that the two regions where the vibrational spectra are relatively constant are separated by a sharp transition from one state to the other. This transition is almost reversible since only a small hysteresis of 4 °C is observed.

The alkane chains in the low-temperature region between 5.5 and 12 °C form a relatively crystalline phase in both the physisorbed and chemisorbed states. This suggests that the alkane chains form a phase where ion and solvent molecules are (mostly) absent. Thus, the interadsorbate interactions are strong enough to prevent the insertion of ions and solvent

molecules into the alkanethiol monolayer. Furthermore, the negative reflectance peaks and the wavenumbers of the d^- and d^+ bands for the oxidative adsorption below 12 °C are compatible with the physisorbed monolayer forming an ordered lamellar structure.²³ Also, the all-trans alkane chains of the physisorbed molecules must be more perpendicular to the surface than the all-trans alkane chains of the chemisorbed molecules.

We can rule out that the physisorbed thiulates form micelles below 12 °C. Two observations support this statement: The decrease of the intensity and the low wavenumbers of the methylene CH stretching bands of the physisorbed thiulates. Micelles are disordered; thus, higher wavenumbers and larger intensities should have been observed.¹⁹

At temperatures higher than 12 °C, the increase of intensity of the differential reflectance bands for the physisorbed thiulates is assigned to the formation of micelles. Their high wavenumbers are indicative of disorder. We believe that this is caused by the insertion of ions and solvent molecules between alkane chains in both the physisorbed and chemisorbed phases. The shift of peak B' to positive potentials suggests an increase of the energy required to the electrosorption of the micelles. It is possible that physisorbed thiulates, which form aggregates of approximately 10 nm at room temperature,¹⁷ merge into larger aggregates when the temperature is increased. These larger aggregates should be more difficult to chemisorb.

The sharp change observed in the SNIPTIRS spectra at 12 °C is indicative of a phase transition. The intensity and wavenumbers of vibrational bands of the alkanes chains are related to the entropy (order/disorder) of the monolayer. We also have a system where the number of molecules is constant. We thus believe that our spectro-electrochemical results are indicative of a phase transition. The sharp variation of the vibrational spectra is interpreted as an almost discontinuous increase in the entropy of the physisorbed and chemisorbed hexadecanethiol monolayer as the temperature increases. Such a discontinuity is characteristic of a first-order phase transition. The transition of the physisorbed thiulates corresponds to an ordered lamellar-disordered micellar phase transition. The transition for the chemisorbed thiols is from an ordered lamellar phase to a disordered lamellar phase. The dipolar vibrational bands suggest that disorder appears first in the physisorbed layer.

The phase transition that we observed could be related to a sudden insertion of solvent and ions between the hexadecanethiols. It has been reported that solvent molecules are inserted into the organic monolayer during the adsorption of alkylthiols from an ethanol solution.^{25–27} The solvent molecules are then slowly expelled from the organic layer.

Limited solvent and ion insertion has been observed for an octadecanethiol monolayer formed in an ethanol solution and transferred to an aqueous electrolyte solution at room temperature.^{13–16} The broad d^- band at 2918 cm^{-1} observed in these IR studies^{14,15} is identical to the one measured in air or under UHV.^{4,6} The broadening of the vibrational bands under electrochemical conditions^{13–15} is suggested to be related to disordering localized near the electrolyte/organic interface.¹⁵ Similar conclusions were drawn by Pemberton et al.¹⁶ on the basis of SERS measurements of low-energy vibrational modes of alkanethiols chemisorbed on gold.

Numerous electrochemical studies^{7–11} found that ions and solvent diffuse into alkanethiol monolayers. Two of these studies examined the temperature dependence of the electron-transfer rate of ferricyanide⁹ and the differential capacitance⁷ of alkanethiol monolayers on gold. The differential capacitance of

alkanethiols coated gold electrodes was found to increase when the electrolyte temperature increases. This variation was assigned to an increase of ion permeation with temperature.⁷ Lennox et al.⁹ observed two separate increases with maximum currents at 35 and 39 °C for ferricyanide measured with a hexadecanethiol-covered gold electrode. They assigned these variations to phase transitions. They saw no evidence of the transition observed in our vibrational data at 12 °C. They⁹ also found that the transitions are irreversible. This contrasts with the reversibility of the electrodeposition/electrodesorption processes reported here. This difference could be related to the fact that we oxidatively deposit a monolayer at each temperature whereas they used the same chemisorbed monolayer. Their irreversibility could also be related to thermal annealing of the defects of the chemisorbed monolayer.

A comparison with the vibrational studies^{4,6} of the thermal stability of chemisorbed alkanethiols on gold under ambient air and UHV conditions reveals the very different behavior observed under electrochemical conditions. In these studies, the alkanethiol monolayers are found to progressively disorder as the temperature is increased between 0 and 100 °C. An IR study⁴ shows a small increase of 3 cm⁻¹ of the antisymmetric CH₂ stretch d⁻ band of hexadecanethiols on gold when the temperature goes from 80 (2916 cm⁻¹) to 380 K (2919 cm⁻¹). This contrasts with the sudden 9 cm⁻¹ shift of the d⁻ band of hexadecanethiols in a temperature range of 2 °C. This comparison gives strong support to our assignment of the wavenumber shift to an increased disorder caused by the permeation of the electrolyte solution into the organic monolayer above 12 °C.

In contrast to the strongly adsorbed thiols self-assembled monolayers, sharp phase transitions of organic monolayer at the air/water interface have been observed.^{1,28,29} These transitions have been assigned to a melting of the organic monolayer. They are observed at temperatures higher (by 3–11 °C) than that of the bulk alkane. This suggests a stronger cohesive energy for the surface layer. In our case, the transition is observed at a temperature 6 °C lower than the melting temperature of hexadecanethiols. This can be explained by the fact that this transition is caused by the potential-driven permeation (expulsion) of solvent and ions and not only by interadsorbate interactions.

Our spectro-electrochemical data give a macroscopic description of the hexadecanethiol monolayer. Complementary microscopic (i.e., STM and AFM) data would be required to obtain a more detailed molecular mechanism for the phase transitions reported here. Such molecularly resolved phase transitions of organic monolayers adsorbed on metal electrode induced by potential and temperature have been reported recently.^{30–32} A very sharp reversible transition from an ordered to a disordered phase was observed at 33 °C in the case of 2,2'-bipyridine on a Au(111) electrode.³⁰ An applied potential also induced transitions of organic monolayers.^{30–32} A reversible transition from an hemimicellar structure to a lamellar structure has been reported for dodecyl sulfate adsorbed on Au(111).³² These authors also suggested that adsorbed water molecules stabilize the hemimicelles. A comparison of our study with these previous^{30–32} studies reveals common features of organic monolayers that are not very strongly adsorbed. Temperature and potential can induce reversible transitions between ordered and disordered phases. Physisorbed insoluble molecules can form aggregates such as micelles and hemimicelles. However, for the strongly chemisorbed thiols on Au(111), we observed only a temperature-induced transition. The effect of the potential on a chemisorbed monolayer of hexadecanethiols is not

important.^{13–15,19–22} Furthermore, our spectroscopic results suggest that ion permeation is involved in these transitions.

A recent STM study of Porter et al.²⁴ clearly showed that the separation of the faradaic and capacitive current peaks that we observed is related to the size of the terrace on the gold surface. This raises questions on the dependence of phase transitions on the size of domains of alkylthiols. The phase transition that we observed on Au(111) might not occur on less homogeneous gold substrates. Also, different phase transitions could occur depending on the substrate used.⁹ Again, in situ STM/AFM measurements would be required to answer the question of which is important to the development of self-assembled monolayers as chemical sensors.

Summary

The results presented here show that the properties of self-assembled monolayers of alkanethiols in contact with electrolyte solutions change with temperature. A monolayer of hexadecanethiols on Au(111) immersed in an alkaline electrolyte solution is found to undergo a sharp transition at 12 °C. We suggest that this pseudo-first-order transition is related to the expulsion of solvent and ions from the monolayer at temperature lower than 12 °C. We also suggest that ions and solvent insertion into the monolayer cause the formation of micelles of physisorbed thiolates above 12 °C.

Acknowledgment. M. B. thanks the Government of Ontario for a scholarship. The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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