Electrochemical Quartz Crystal Microbalance Studies of Adsorption and Desorption of Self-Assembled Monolayers of Alkyl Thiols on Gold

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Abstract: The adsorption and desorption behavior of several long chain alkyl thiols on gold electrodes were studied using the electrochemical quartz crystal microbalance (EQCM). The rate of adsorption of the self-assembled monolayer (SAM) from various nonaqueous solutions was determined by using the EQCM to monitor the mass change at the electrode surface caused by the formation of the SAM. The EQCM method also allowed for monitoring the mass change due to reductive desorption of the SAM. Significantly different behavior was observed for the SAM formation in acetonitrile (ACN) and dimethylformamide (DMF). For example, exposure of a bare gold electrode to alkyl thiol in ACN leads to multilayer formation which slowly evolves to a stable SAM, while in DMF no initial multilayer formation is observed. Also, the time scale for deposition of submonolayer amounts of alkyl thiols was much shorter in DMF (ca. seconds at millimolar concentrations) than in ACN (ca. minutes at millimolar concentrations). Detailed comparisons of charge consumption and mass change during the reductive desorption, along with some model calculations for the amount of double layer charge passed during the desorption event, suggest that a considerable fraction of the charge harvested during reductive desorption could originate from charging the double layer.

Introduction

A large body of literature has been published on the behavior of various types of self-assembled monolayers on various types of surfaces.[1] The great interest in these systems (especially the alkyl thiol monolayers on coinage metals) stems, at least in part, from the recognition that they have highly ordered structures. This high degree of order has allowed detailed structure–function relationships to be developed for various types of interfacial processes, such as wetting,[2] electron transfer,[3-6] and lubrication.[7]

While much has been learned about the static structures of these SAMs,[1] relatively less is known about the kinetics of their formation. Bain et al.[8] studied the kinetics of formation of alkyl thiol SAMs on Au using ellipsometric thickness and contact angle measurements. They found that at concentrations of ca. 1 mM alkyl thiol in ethanol, the formation exhibited biphasic kinetics. Within a few minutes, the contact angles and thicknesses had reached ca. 80–90% of their final values. Then, in a slower process which lasted several hours, these two parameters reached their final values. They also found that the adsorption kinetics were faster for alkyl thiols bearing longer chains than for those with shorter chains. Due to the requirement for removal of the substrate from the adsorption solution for the contact angle or ellipsometric measurement, they were unable to quantitatively determine kinetics for times shorter than a few tens of seconds. Bard and co-workers have also studied certain aspects of the formation of SAMs from solution.[9] In particular, they used ex situ STM and QCM measurements to monitor the deposition of monolayers and multilayers of octadecanethiol from 1 mM, air saturated absolute ethanol solutions. They found that, while short (ca. 4–5 h) exposures of a Au surface to this solution led to spontaneous adsorption of only a single monolayer of the organothiol, prolonged (>24 h) exposures led to formation of multilayer deposits comprised of up to four monolayers of the organothiol. As will be seen below, their results are in general agreement with those which are reported here.

Recently Porter and co-workers[10,11] have discovered that these alkyl thiol SAMs can be electrochemically desorbed from Au and other surfaces via either reductive desorption (RD) or oxidative desorption. They have studied in detail the chemistries associated with these electrochemical processes[10,11] as well as their kinetics and thermodynamics.[10-12] Their work provides the basis for new methods of formation of SAMs,[12] and also for studies of the kinetics of their formation. The advantage of using electrochemically induced desorption to study formation kinetics is that the electrode potential can be used to control the time at which the kinetic experiment starts, by scanning or stepping the electrode potential from a value at which monolayer formation is not possible to one at which it is. In this report we describe such experiments in which the EQCM is used to monitor SAM adsorption and desorption in acetonitrile (ACN) and dimethylformamide (DMF).

Experimental Section

The EQCM apparatus and its application to measurements of monolayer mass changes have been previously discussed.[5,6,13] For the purposes of the present discussion, we reiterate the essential features of the experiment. The EQCM allows simultaneous measurement of electrochemical parameters (i.e., current, charge, etc.) and mass changes at electrode surfaces by virtue of changes in the resonant frequency of the quartz crystal which are caused by these mass changes. Thus, decreases in mass correspond to increases in frequency and vice versa. The frequency

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and mass changes are related by a simple, linear equation, as shown below:

$$\Delta f = -C_f \Delta m \qquad (1)$$

where Δf (Hz) is the frequency change, Δm (μg cm^{-2}) is the mass change, and C_f (= 56.6 Hz cm^2 μg^{-1}) is the proportionality constant for the 5 MHz, overtone polished crystals used in this study. This equation is called the Sauerbrey equation, and its applicability to measurement of monolayer mass changes has been detailed before.[5,6,13] A discussion of the various effects which can influence the interpretation of these frequency changes is presented below.

The 250–300 nm, thin film Au electrodes on the EQCM quartz crystals are deposited by thermal evaporation using an Edwards 306A oil diffusion-pumped vacuum system at a base pressure of 3 × 10^{-7} Torr at a deposition rate of 0.1 nm per s onto an adhesion layer of $(CH_3O)_3SiCH_2CH_2CH_2$-SH, which provides for strong bonding between the Au film and the underlying quartz surface.[14] The keyhole pattern of the Au thin film electrode provides an electrochemically active (geometrical) area of 0.34 cm^2 and a piezoelectrically active (geometrical) area of 0.28 cm^2. The surface roughness of these electrodes is 1.2 ± 0.1, as determined from the charge required for formation of a monolayer of gold oxide. The procedure used in these determinations is that of Janata and co-workers.[15] This value for surface roughness is in good agreement with the values reported by Porter and co-workers based on either STM (1.11 ± 0.03) or iodine oxidative desorption measurements (1.3 ± 0.3) for Au thin film electrodes deposited by thermal evaporation on glass,[16] and the value of 1.2 reported by Majda and co-workers.[14b] The value of 1.2 ± 0.1 for the chemically etched, optically flat quartz crystals used here is consistent with expectations for surfaces of this type. Except where indicated, all calculations and discussions of surface coverage given below take this surface roughness into account. Observations of the double layer charging currents for these electrodes after both short and long term exposures to the solutions of the alkyl thiols (see below) indicated that there were no detectable changes in the surface roughness due to possible corrosion processes induced by the presence of the alkyl thiols. This may be due to the fact that the electrode potential was controlled at a value of –0.4 V throughout the assembly process.

In the sections below, the electrochemical charge associated with reductive desorption of an alkyl thiol monolayer will be compared with the mass change observed (via the EQCM) for the desorption process. It is important to understand the relationship between these measurements and how it depends on surface roughness. If either the charge or the mass change per unit area is used independently to calculate a surface coverage (or a change in surface coverage), the surface roughness discussed above enters directly into the calculation (i.e., the apparent surface coverage is divided by the surface roughness to calculate the true surface coverage per unit area). However, when charge and mass are compared directly (for example to determine the charge consumed per molecule in a desorption process), the surface roughness does *not* influence the comparison, because both quantities are affected in precisely the same way by surface roughness. This point will be important in the discussion of electrosorption valency presented below. Further, it should be noted that both the piezoelectrically and electrochemically active areas are confined essentially completely to the Au film; mass changes due to adsorption or desorption processes at the quartz surface surrounding the Au electrode contribute negligibly to the observed frequency changes.[13]

Salts for the supporting electrolyte solutions were recrystallized to purity (usually three times). Solvents were dried either by distillation from CaH_2 or P_2O_5 or exposure to molecular sieves (3 Å for ACN and 4 Å for DMF). Special attention was paid to removal of as much dimethylamine as possible from the DMF due to its possible action as a competitive adsorber against the thiols. The alkyl thiols were purified by passage through a small column of chromatographic grade alumina. Solutions were purged with Ar and kept under positive pressure to prevent the solvents from becoming wet with atmospheric water. All chemicals were of reagent grade or better. All potentials are referenced to a Pt quasireference, which was used to minimize contamination of the supporting electrolyte solutions with water or other reagents usually present in more standard reference electrodes. The potential of this Pt quasireference with respect to a saturated calomel electrode is ca. –0.2 V.

Prior to use, the Au electrodes were chemically cleaned with a 50/50 solution of 30% H_2O_2/concentrated H_2SO_4 for a few seconds and then rinsed copiously with deionized water. (**Note:** This cleaning solution reacts very violently with organics and should be used with extreme caution!) For cases in which monolayers were formed on the EQCM Au electrodes prior to the electrochemical experiments, the monolayers were produced by immersing the Au electrodes into a solution of the alkyl thiol in air-saturated ethanol for periods of time ranging from a few hours to several days. Then, the electrode was rinsed repeatedly with ethanol and placed into an electrochemical cell which contained only pure, degassed supporting electrolyte (i.e., no alkyl thiol). For cases in which the monolayers were formed in the electrochemical cell, the alkyl thiol was added directly to the previously degassed supporting electrolyte solution. We refer to these two types of monolayers as "preformed" or "in situ", respectively.

Results and Discussion

In Situ SAMs. Several attempts were made to examine the adsorption and reductive desorption of monolayers of alkyl thiols in aqueous and/or ethanolic solutions containing various concentrations of hydroxide ion, so as to duplicate as nearly as possible the experimental conditions used previously.[10–12] However, the Au thin film electrodes were not stable under the high pH conditions necessary to move the solvent window sufficiently negative to observe the RD process. This was presumably due to attack of the quartz surface by the hydroxide ion and consequent delamination of the Au film. Thus, the experiments described below were conducted in nonaqueous supporting electrolytes because these offer sufficiently negative potential limits (ca. –2.0 V) so that the RD process can be observed without interference from solvent decomposition.

Behavior in DMF. Figure 1 shows the results of a RD experiment in a DMF solution of 0.1 M tetrapropylammonium perchlorate (TPAP) containing 4 mM dodecyl thiol (C12SH) at a scan rate of 100 mV s^{-1}; these data are typical of a large number of experiments done under similar conditions. The data were obtained by placing the electrode into the degassed solution, leaving it there for 10 h, and then scanning. The electrode was not exposed to air at any time, nor was it removed from the solution or rinsed prior to the scan. The electrode potential was maintained at a value of –0.4 V throughout the assembly process. Curve A is the cyclic voltammogram (CV) and curve B is the EQCM frequency change. By analogy to the observations of Porter and co-workers,[10–12] the large peak at –1.6 V is attributed to reductive desorption of the C12SH SAM, according to the following reaction:

$$AuS(CH_2)_{11}CH_3 + \gamma e^- \rightarrow Au(0) + {}^-S(CH_2)_{11}CH_3 \qquad (2)$$

where γ is the number of electrons involved in the process (we return to a discussion of this quantity later). The frequency increase seen in curve B is a clear indication of mass loss during the RD process, and it can be seen that the electrode mass changes smoothly from one plateau value to another during the RD. The frequency is seen to decrease during the return (positive) scan to nearly reattain its initial value, indicative of a mass gain which we attribute to fairly rapid reformation of the monolayer at potentials where its formation is favorable.[12] In contrast to the well-defined peak for the RD process, the anodic charge for the readsorption process during the return scan is ill-defined because it is distributed over a large fraction of the potential axis, a feature which has been previously observed.[11] In addition, it should be noted that some fraction of the material involved in reformation of the monolayer could be alkyl thiol from solution which had not been previously adsorbed. For this case, it may be possible that readsorption occurs with zero current flow. (There is still uncertainty as to the exact mechanism by which these SAM's are formed.[1]) Both the shape and the time scale of the frequency change during the return scan suggest that the reassembly process is diffusion controlled, an observation which is in accordance with the reports of Porter and co-workers.[10–12]

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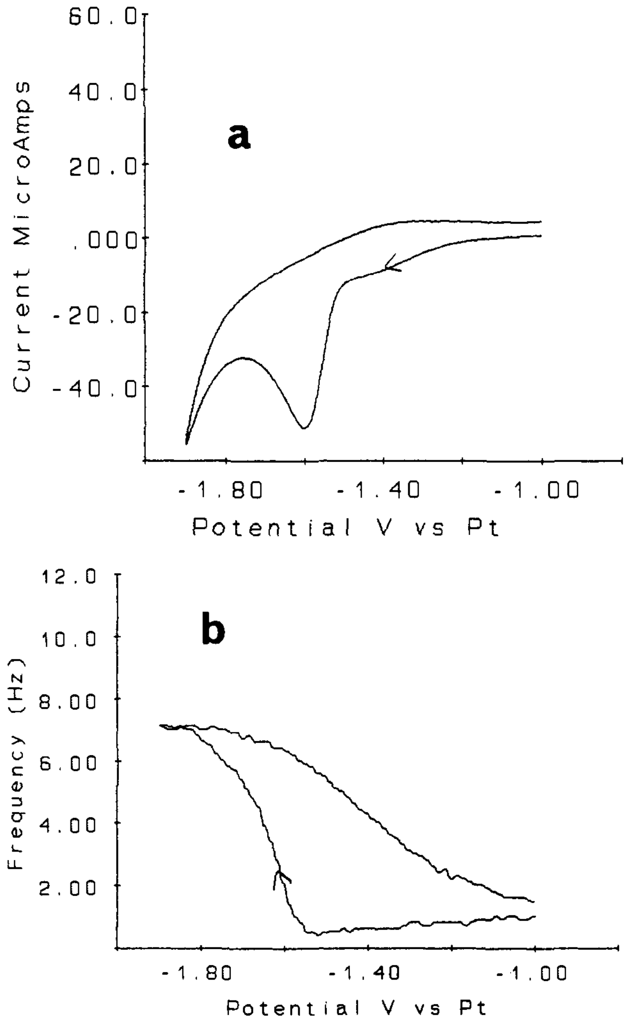

Figure 1. EQCM scan after 10 h solution exposure for 4 mM C12SH in 0.1 M TPAP in DMF, scan rate = 100 mV s^{-1}: curve A, CV; curve B, EQCM frequency change.

The fact that both the current peak and the frequency increase shown in Figure 1 are distinct and easily discernible allows one to calculate both the charge consumed and the mass lost during the RD process. These values are 117 $\mu C\ cm^{-2}$ and 0.12 $\mu g\ cm^{-2}$, respectively. Correcting for the surface roughness of 1.2 and assuming (for the moment) a value for γ of 1 in eq 2, one can use these values to calculate a change in surface coverage based on both the charge and mass change of 1.0×10^{-9} and 4.8×10^{-10} mol cm^{-2}, respectively. Assuming that the RD process shown in Figure 1 leads to desorption of the entire SAM, these values may be compared to the saturation surface coverage predicted from geometrical considerations for these monolayers which (corrected for our surface roughness) is 9.1×10^{-10} mol cm^{-2}.[1,10,11] This geometrically derived value is comparable to the surface coverage calculated from the charge and nearly a factor of 2 larger than that from the mass change. Similar results have been obtained for at least five monolayers, with the discrepancy between the two values ranging from a factor of 1.7–2.3. Key questions are as follows: which of these two values accurately reflects the change in surface coverage caused by the RD process, and why are the charge- and mass-based values different?

Before proceeding further, it is worth pointing out a few features of the data shown in Figure 1. First, there is a marked similarity of the general shape of the EQCM frequency response for the experiment shown in Figure 1 and those which we have previously obtained for another system. In three previous reports, we described the use of EQCM to monitor the electrochemically induced adsorption/desorption of a redox surfactant with a ferrocene group pendant from the hydrophilic head group.[6,17,18] This compound is strongly adsorbed in its reduced (ferrocene) state and desorbs when oxidized to the ferrocenium state (interaction of the surfactant with the electrode surface is strictly physical in nature; no bonds are made or broken, in contrast to the alkyl thiol Au case at hand). Reformation of the adsorbed layer after rereduction appears to be diffusion controlled, and the EQCM frequency change very closely mimicks that shown in Figure 1, with a comparable shape at similar scan rates and concentrations. Further, the mass changes derived from the frequency changes in these previous studies were in excellent agreement with those predicted based on the number of electrons consumed during oxidation of the redox surfactant in the monolayer and a model for desorption in which each oxidation event led to desorption of a single surfactant molecule. These measurements give considerable confidence that the EQCM is capable of direct measurement of monolayer, and even submonolayer, mass changes at electrode surfaces[5,6,17,18] and that such data can be reliably used to make the type of mass/charge comparison described above. These considerations suggest that of the two calculated values for surface coverage presented above, the one derived from the EQCM frequency change is likely to be the correct one. In fact, we now present arguments which suggest that the electrochemical RD charge should be **significantly** affected by the simultaneous passage of double layer charging current during the RD event, a phenomenon which complicates the interpretation of the RD charge.

Consider the following rough calculation. The double layer capacitance (C_{dl}) for these SAMs is typically in the range of 1 $\mu F\ cm^{-2}$ for a C12SH monolayer in aqueous solution,[14b,19] with the exact value depending on the thickness and defectiveness of the monolayer. If the potential of zero charge (pzc) on these surfaces is ca. 0.0 V vs Pt (i.e., ca. −0.2 V vs SCE[20]), then between the pzc and the reductive desorption potential of −1.6 V (in DMF), about 1.6 $\mu C\ cm^{-2}$ of double layer charge will be passed. Several values of C_{dl} on bare gold have been reported or can be calculated from literature data. These range from 20–40 $\mu F\ cm^{-2}$ in acidic aqueous electrolytes[21] to ca. 70 $\mu F\ cm^{-2}$ in 0.1 M tetramethylammonium tetrafluoroborate in DMF.[22] Our own measurements from the double layer charging current during a cyclic voltammetric experiment at bare Au in 0.1 M tetraethylammonium perchlorate (TEAP) in DMF also give a value of ca. 70 $\mu F\ cm^{-2}$.[23] Using this value of 70 $\mu F\ cm^{-2}$ in DMF, one can calculate that **at a bare Au surface** over the range of the scan prior to the RD potential, 112 $\mu C\ cm^{-2}$ of double layer charge should be passed. Thus, when the reductive desorption process occurs and the surface is transformed from a low capacitance surface to a high capacitance surface, a little more than 100 $\mu C\ cm^{-2}$ of double layer charge should be passed under the peak. (The exact amount of charge passed will depend on the exact values of the pzc and C_{dl} for the SAM-covered electrode; however, the major factors in determining this charge are the (very well-known) values of pzc and C_{dl} for the bare electrode, because its capacitance is by far the larger of the two surfaces.) Further, this charge should be captured as the SAM is desorbed (i.e., under the peak for the RD process), thereby making it virtually impossible to distinguish from the faradaic charge associated with the RD process, which is also ca. 100 $\mu C\ cm^{-2}$ for a fully formed SAM **if one electron is required to desorb each thiol**. This calculation suggests that the charge passed to charge the double layer should be comparable

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to the faradaic RD charge (assuming 1e$^-$ is required to desorb each thiol, but see below). For the in situ DMF SAMs described here, the defectiveness of the monolayer will surely lead to a considerable increase of C_{dl} for the monolayer,[19] which will decrease the amount of double layer charge passed under the RD peak. Nevertheless, these considerations make it clear that the considerable double layer charge expected to be passed at the RD potential is the most likely cause of the consistent discrepancy between the amount of material lost during the RD process as calculated from the charge (assuming $\gamma = 1$) and the mass change. In the specific case of the experiment in Figure 1, these arguments suggest that a fairly large fraction of the charge passed must be due to double layer charging. This model also predicts that much shorter or longer alkyl thiol monolayers should give considerably different double layer charges. However, since we have focused on the behavior of decyl and dodecyl thiol, which would be only slightly different, the present set of measurements does not allow this hypothesis to be reliably tested.

These arguments suggest that the double layer charge is significant in comparison to the expected faradaic charge for a 1e$^-$ reductive desorption process even if C_{dl} for the bare Au surface in DMF is as low as 20–40 μF cm^{-2} and that these two charges are comparable for C_{dl} values on the order of 70 μF cm^{-2}. A caveat to this line of thinking relates to the actual number of electrons require to do the faradaic electrochemistry associated with the desorption. Electrochemists think of these issues in terms of the electrosorption valency, γ, which, for a surface redox reaction of a chemisorbed species (such as thiols studied here), is analogous to the *n* value (in the Nernst equation) for a bulk redox process. However, there are some very important distinctions between *n* and γ, which we shall return to below. γ is defined by the following equation (which is actually an approximation that is applicable at nondilute supporting electrolyte concentrations[24])

$$(\partial q_{\mathrm{m}}/\partial \Gamma_{\mathrm{ad}})_E = -\gamma F \qquad (3)$$

where q_{m} is the charge on the electrode, Γ_{ad} is the quantity of the adsorbate, E is the electrode potential, and F is the Faraday constant. Thus, in the present case γ represents a measure of the differential charge consumed to change the adsorbate surface coverage by the RD process. A key difference between γ and *n* is that γ need not be an integer. Rather, its value depends on the nature of the bonding interactions between the surface and the adsorbate, the amount of double layer charge passed as the surface coverage of the adsorbate is changed, and a variety of other factors as well.[24] An important point of clarification is that γ actually contains the double layer charging which was referred to above. In other words, the faradaic charge discussed above is only a part of γ, and the double layer charge is another part. In a great many cases, γ spans a large range from less than 0 to greater than *n*,[24,25] depending on the signs and magnitudes of the faradaic and double layer charges passed during the process. The point to be made here is that, because the interaction of the thiol S atom with the Au surface atoms is clearly a bonding interaction[26] characteristic of chemisorption rather than physisorption, and because significant double layer charge should be passed during the RD process, there is no reason for γ to have an integer value. In fact, recent measurements by Majda and co-workers[27] of the so-called "partial charge number" (which can be interpreted as the faradiac component of γ) suggest that its value ranges between 0.25 and 0.4e$^-$ per thiol in the potential range –0.3 to +0.8 V (vs SCE), a finding entirely consistent with the arguments above.

A consequence of (a) the potential passage of considerable double layer charge during RD and (b) the possibility of γ values considerably different than one is that the charge measured during RD cannot be simply interpreted as resulting from extraction of one electron per alkyl thiol. Thus, it is likely that previous reports[10,11] of good agreement between experimental RD charges and expectations based on the geometrically calculated saturation surface coverage for such a monolayer were due to fortuitous summation of the double layer charge and the faradaic charge passed during RD. This suggests that the charge for the RD process is probably not a reliable measure of surface coverage, because the double layer charging component will be sensitive to the defectiveness of the monolayer in a way which is likely to be quite unpredictable.

Another possible source of discrepancies between surface coverages derived from charge and mass is related to the degree of interfacial acoustic coupling between the EQCM electrode and the solution. This effect has been previously discussed[28,29] and is related to the degree of slippage between the surface and the solution (i.e., the efficacy with which the shear displacement at the electrode surface is made to appear in the adjacent solution). Changes in this interfacial coupling have been predicted[29] to potentially lead to very large frequency changes (100's to 1000's of Hz). However, neither the present work nor previous experiments on monolayer mass changes due to electrochemically induced adsorption/desorption processes[5,6,17,18,28] have revealed any experimental evidence for such large effects. In the face of this negative evidence, it seems unlikely that dramatic changes in interfacial coupling are influencing the present measurements.

Behavior in ACN. The following data serve to summarize observations of monolayer formation and desorption in ACN. Several concentrations were used, spanning a range from 10 μM to 10 mM. Both C10SH and C12SH were examined; qualitatively similar results were obtained for these two alkyl thiols.

Figure 2 shows the results of a RD experiment for 10 μM decyl thiol (C10SH) in ACN containing 0.1 M TEAP. For this experiment, the electrode was placed in the above solution, left there for 10 h, and then scanned in the same solution. The electrode was not exposed to air at any time, nor was it removed from solution or rinsed prior to the scan. Note also that the electrode potential was maintained at a value of –0.4 V throughout exposure of the Au electrode to the solution. The CV (curve A) shows the desorption current peaking slightly negative of –1.8 V. The reduction process exhibits considerable fine structure (i.e., multiple peaks) which may be due to the presence of several crystal faces on our vapor deposited electrodes and slightly different energetics for desorption from these various crystal faces.

In contrast to the case for DMF, the reductive desorption in ACN occurs very near to the negative edge of the solvent window, which precludes direct comparison of mass changes with electrochemical charges. The frequency change shown in curve B reveals mass loss coincident with the cathodic current. The frequency nearly reaches a plateau value toward the end of the negative scan, suggesting that most of the monolayer has been desorbed by that point. The magnitude of the frequency change during desorption corresponds to a loss of 1.4 × 10^{-9} mol cm^{-2}. This is considerably larger than the expected value for a saturated SAM of C10SH (see above), indicative of *multilayer* formation in ACN solutions. Another, very important point to be made about the EQCM data in Figure 2 is that the readsorption during the positive scan is *very slow*. While this is undoubtedly due in part to the low concentration, similarly slow readsorption is also seen at much higher concentrations (see below).

Figure 3 reinforces the notion that multilayer adsorption can occur in ACN. It shows the frequency change for a RD experiment done 20 min after the experiment in Figure 2 (i.e.,

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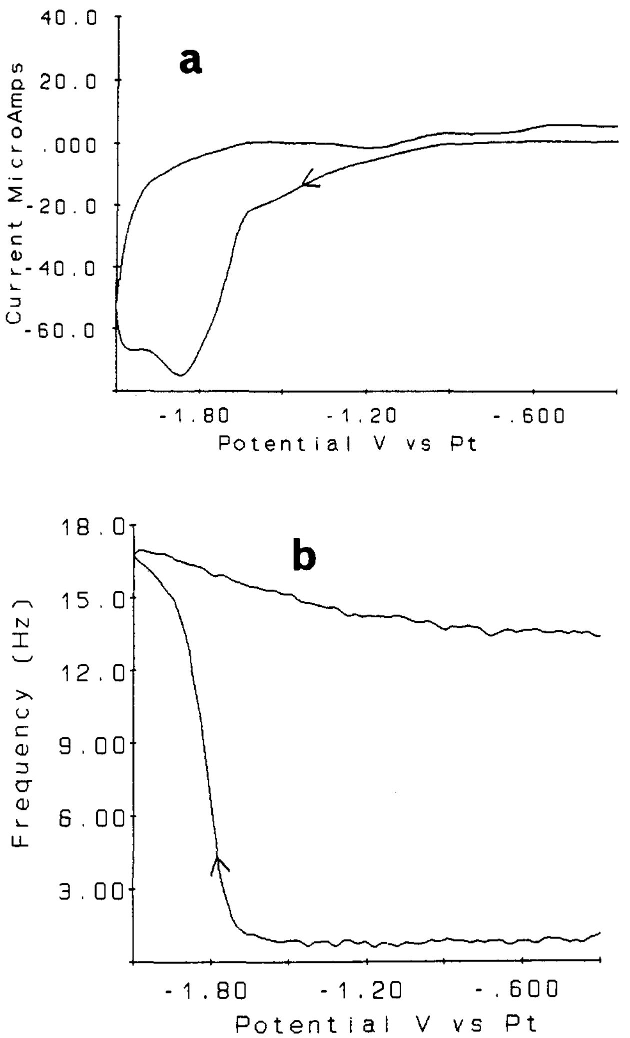

Figure 2. EQCM scan after 10 h solution exposure for 10 μM C10SH in 0.1 M TEAP in ACN, scan rate = 100 mV s^{-1}: curve A, CV; curve B, EQCM frequency change.

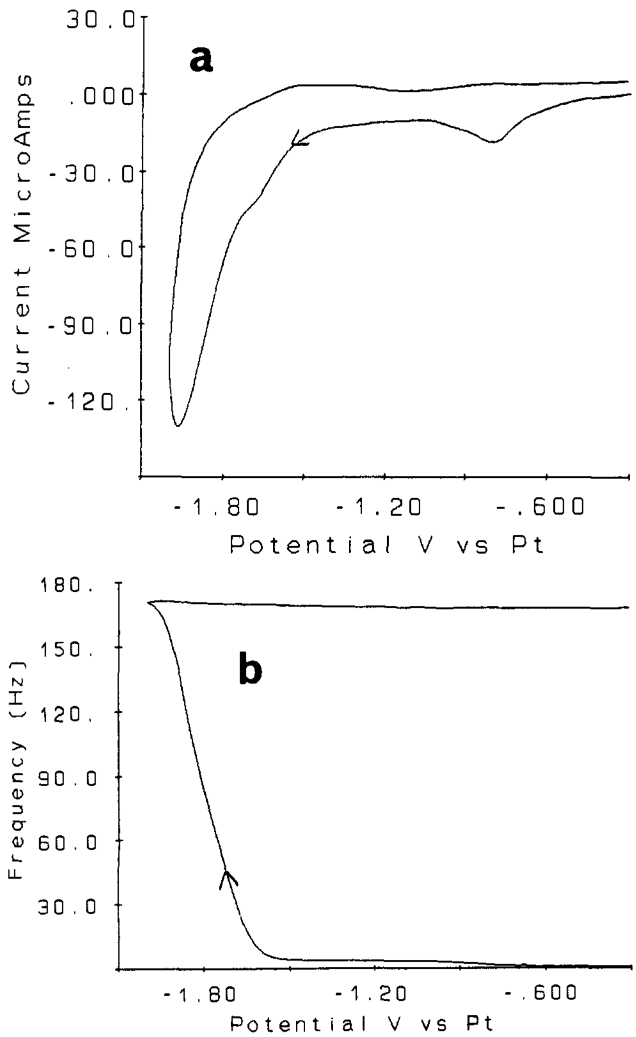

Figure 3. EQCM scan after 20 min solution exposure for 10 μM C10SH in 0.1 M TEAP in ACN, scan rate = 100 mV s^{-1}: curve A, CV; curve B, EQCM frequency change.

a monolayer had been assembled for 10 h, desorbed, allowed to reassemble for 20 min, and then reductively desorbed to give the data in the figure, all of which occurred in a solution containing the alkyl thiol). The frequency increase during the RD experiment is seen to be ca. 160 Hz, which corresponds to loss of ca. 16 monolayers of C10SH. Similar results were observed for a clean, fresh electrode 20 min after its first exposure to the solution (i.e., this behavior is not related to the initial formation and subsequent desorption of the monolayer shown in Figure 2). These results show that if the assembly process is monitored a short time after its initiation, one observes multilayer deposits of alkyl thiol on the surface which can be desorbed in the same way as the monolayer deposit. Clearly, all of the material in the multilayer cannot be chemisorbed to the Au surface; the majority of it must be physically adsorbed onto the partially formed, underlying monolayer of chemisorbed material. This fact is reflected by the similarity of the charges for the reduction processes in Figures 2 and 3. In other words, cathodic charge is only consumed for reduction of the underlying, chemisorbed monolayer, while the mass change sensed is due to the desorption of both the chemisorbed and physisorbed material.

Figure 4 shows the results of a RD experiment in 0.1 M TEAP in ACN containing 50 μM C10SH. Prior to this scan the electrode had been exposed to the solution for ca. 10 h (similar to Figure 2). In this case, we see that the frequency has nearly (but not quite) achieved a plateau value toward the end of the negative scan, indicative of some of the SAM having been left on the surface after scan reversal. The observed frequency change for desorption is very close to the 9.0 Hz expected for a closest packed C10SH SAM. Again a very slow readsorption is observed. As was the case for C10SH at 10 μM, if the monolayer was examined by RD after only short (10's of minutes) periods of exposure of the bare surface to the 50 μM alkyl thiol solution, the mass desorbed during the RD event corresponded to many monolayers of material. These data show that qualitatively similar behavior is observed for both 10 and 50 μM solutions of alkyl thiol.

Figure 5 shows the results of a RD experiment in 0.1 M TEAP in ACN containing 10 mM C12SH after a 10-h exposure to the supporting electrolyte solution containing the alkyl thiol, as before for the lower concentrations. Curve A shows the voltammetry. No peaks are observed during the negative scan, which exhibits only a rising background current (which is not observed in the absence of bulk C12SH in solution), presumably due to the reduction of RSH arriving from solution according to the following reaction:

$$RSH + e^- \rightarrow RS^- + {}^1/_2H_2 \qquad (4)$$

The frequency change, on the other hand, shows a very clearly defined desorption which is coincident with the onset of the cathodic current during the negative scan. The frequency reaches a plateau value at ca. –2.0 V and stays at this value during all of the return (positive) scan. (The small loop at the negative end of the scan may be due to the onset of adsorption of the cation of the supporting electrolyte.) By analogy with the results presented above, this frequency increase is attributed to the desorption of a monolayer of C12SH during the negative scan,

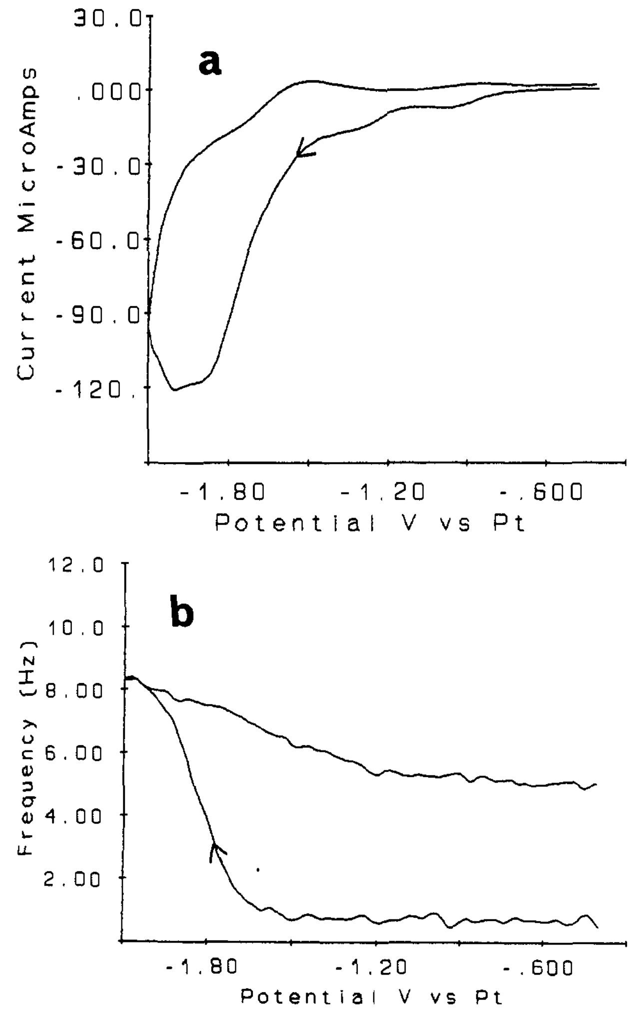

Figure 4. EQCM scan after 10 h solution exposure for 50 μM C10SH in 0.1 M TEAP in ACN, scan rate = 100 mV s^{-1}: curve A, CV; curve B, EQCM frequency change.

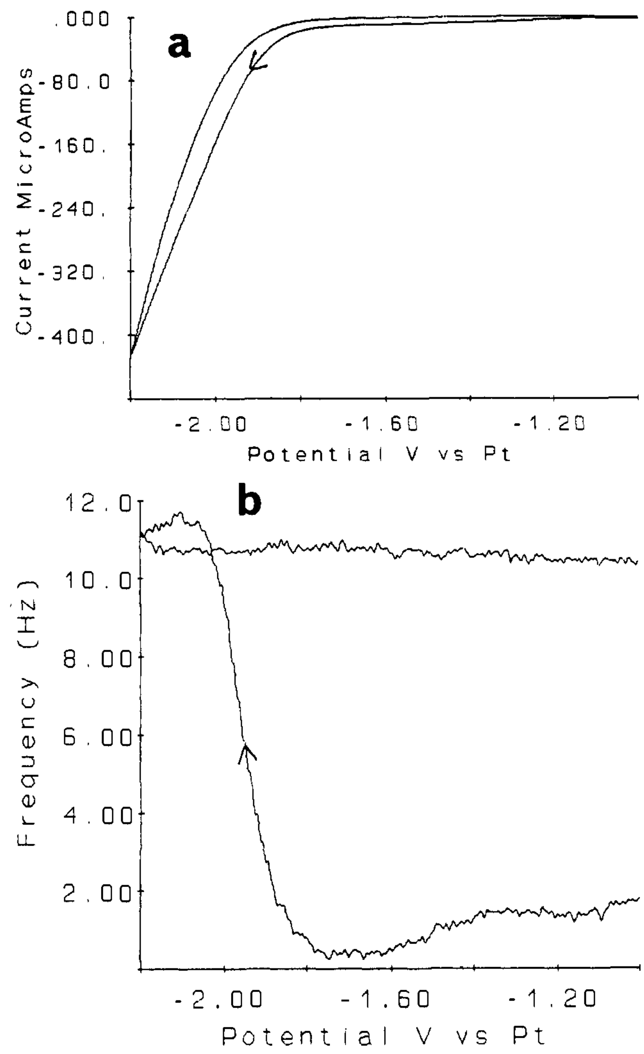

Figure 5. EQCM scan after 10 h solution exposure for 10 mM C12SH in 0.1 M TEAP in ACN, scan rate = 100 mV s^{-1}: curve A, CV; curve B, EQCM frequency change.

with the redox process due to solution-phase alkyl thiol obscuring the RD peak. A salient feature of these data is the apparently very slow rate of readsorption of the C12SH (or C12S$^-$) following reestablishment of a potential at which it should be thermodynamically stable, even though the alkyl thiol concentration in solution is more than adequate to provide sufficient thiol for rapid reformation of the SAM. Thus, SAM formation is very slow at all of the concentrations studied in ACN, in marked contrast to the behavior exhibited by the thiols in DMF where readsorption is rapid even at lower concentrations (see Figure 1). Quantitative analysis of the frequency increase during the RD process reveals that the frequency change is identical to the 10.4 Hz predicted for a closest packed C12SH SAM.

These data reveal that the formation of these SAMs is quite different in DMF and ACN supporting electrolyte solutions and depends considerably on concentration. In DMF supporting electrolyte solutions, saturated SAMs were never formed, regardless of thiol concentration, but readsorption of the subsaturated SAM is rapid and apparently diffusion controlled. The highest coverages observed were in the range of 50% of saturation. In ACN on the other hand, saturated SAMs can be formed, but the formation kinetics are very slow. Furthermore, thick, multilayer films are formed initially (in the first few minutes), with the total coverage eventually **decreasing** (usually on a time scale of several hours) to give a coverage consistent with a closest packed SAM. As a cause for this behavior, we speculate that initial, slow adsorption from ACN leads to a surface with submonolayer coverage of the thiol which has a high surface energy capable of promoting spontaneous, multilayer physical adsorption of additional thiol from solution. The possible structure of such a high energy surface is unclear, although interdigitation[18] and layer by layer growth[9] are both candidates. As time progresses, the surface coverage of chemisorbed thiol slowly increases, while the coverage of physisorbed thiol decreases (to give a decrease in the total coverage) to finally give a well-formed SAM, which presumably has a low surface energy that does not promote multilayer adsorption.

This model is consistent with inverse correlations of the ease of forming SAMs and the solubility of the thiol in the loading solution described by others;[1,8] both C10SH and C12SH are much more soluble in DMF than in ACN, so better monolayers are formed from ACN than DMF. Knowledge of the contact angles of these SAM surfaces with ACN and DMF would be helpful in interpreting this behavior, but we are aware of no such data.

Preformed SAMs. RD experiments were also conducted in ACN and DMF with preformed SAMs. In these cases, SAMs were assembled for 1 day in air saturated ethanol solutions which were 2 mM in C12SH. The EQCM thin film Au electrodes were then transferred into either DMF or ACN supporting electrolyte solution, purged with Ar, and scanned over the potential range shown. The exposure time to the nonaqueous solution prior to the scan was typically 10–30 min. Under these conditions, the frequency increases observed for the RD process are much smaller (typically ca. 50%) than those predicted for closest packed SAMs (see above). These facts suggest that considerable degradation of the SAM occurs in these nonaqueous solutions. Thus, care must be exercised in the choice of medium for the various applications envisioned for these alkyl thiol SAMs. In no cases were multilayer films observed for SAMs assembled from ethanol and then transferred into either ACN or DMF. This is likely due to relatively rapid dissolution of the physisorbed material in these two solvents.

Conclusions

Several conclusions emerge from this study. First, the comparative behavior in ACN and DMF reveals that the conditions under which the SAM is formed have a great deal to do with the quality of the SAM as well as the rate at which it assembles. The results appear to suggest that poorer solvents for the alkyl thiol may give better SAMs. Second, the EQCM results in ACN clearly point to the formation of multilayer films at intermediate stages of monolayer formation, and saturated, monolayer SAMs after longer exposures. Higher concentrations appeared to lead to relatively more rapid loss of the multilayer deposit in favor of the saturated, monolayer SAM. This behavior is similar to that in a recent report by Bard and co-workers,[9] which described STM identification of formation of up to four monolayers of octadecane thiol on Au after 6 days of immersion of the Au substrate in a 1 mM solution of the thiol in air saturated ethanol. However, in their case, multilayer formation increased over time, while in our case it decreased over time. They speculated that multilayer formation may have been due to air oxidation of the thiol to produce the less soluble disulfide. This seems less likely in our case, both because the multilayer deposits disappear with time, and because the solutions were rigorously degassed for the entire duration of the experiments. Related multilayer formation behavior was also recently reported by Crooks and co-workers,[30] who described multilayer formation of alkyl thiols from the gas phase. Taken in total, these findings clearly reveal that care is needed in choosing the conditions for formation of well-defined monolayers. They also suggest that changes in experimental procedures (e.g., frequent removal and rinsing of the substrate versus prolonged immersion without removal, use of air-saturated versus degassed solvents, degree of wetness of solvents, etc.) in different laboratories may lead to different results, because of the possible influence of these multilayers on the kinetics of formation and ultimate structures of the SAMs.

The origin of the very different formation kinetics in ACN and DMF is uncertain at this time. Two possibilities which are fairly obvious are (1) the influence of any possible protic impurities in the solvents, such as water (in ACN or DMF) or dimethylamine (in DMF), on the chemistry of the self-assembly process,[10] and the likelihood that these two solvents will have different types and quantities of such impurities and (2) that the solvent itself plays a role in determining the formation kinetics. This latter possibility could be due to significantly different strengths of adsorption of the two solvents onto the Au electrode surface. In this context, it has been reported that both long chain amides and nitriles form monolayers on Au,[31] but that they are not stable toward washing with solvent. Thus, it is clear that species bearing the functionalities on these two solvents are capable of interaction with a Au surface, and, therefore, capable of competing with the thiols for surface sites. However, a lack of quantitative information on their relative tendencies for adsorption at Au makes difficult an assessment of their relative abilities to compete with the thiols for surface sites.

Finally, a detailed comparison of the charge consumption and mass change during the RD process, together with arguments based on the double layer capacitances of bare versus SAM-covered surfaces, suggests that a large fraction of the charge passed during the RD event is due to double layer charging. This implies that measurement of RD charges is not likely to be a reliable way to measure surface coverage for alkyl thiols on metal surfaces. On the other hand, these results point to the potential utility of electrochemical measurements of electrosorption valency as an aid in understanding the Au–S bonding in these monolayers.

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