

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231672550>

A Kinetic Model for the Reductive Desorption of Self-Assembled Thiol Monolayers

ARTICLE *in* LANGMUIR · MAY 2001

Impact Factor: 4.46 · DOI: 10.1021/la001283b

CITATIONS

32

READS

17

3 AUTHORS:



Willem Mulder

The University of the West Indies at Mona

49 PUBLICATIONS 613 CITATIONS

SEE PROFILE



Juan Jose Calvente

Universidad de Sevilla

68 PUBLICATIONS 837 CITATIONS

SEE PROFILE



Rafael Andreu

Universidad de Sevilla

75 PUBLICATIONS 960 CITATIONS

SEE PROFILE

A Kinetic Model for the Reductive Desorption of Self-Assembled Thiol Monolayers

Willem H. Mulder,[†] Juan José Calvente,[‡] and Rafael Andreu^{*,‡}

Department of Chemistry, University of the West Indies, Mona Campus, Kingston 7, Jamaica,
and Departamento de Química Física, University of Sevilla, 41012 Sevilla, Spain

Received September 7, 2000. In Final Form: February 26, 2001

A kinetic model for the reductive desorption of self-assembled monolayers of short-chain alkanethiols has been developed. The monolayer is described as a set of close-packed thiol domains, which for mathematical convenience are modeled as circular and equal in size. Desorption is assumed to occur via two parallel paths, a first route involving the removal of the thiol molecules at the edge of the adsorbate domains, and a second route involving the desorption of the thiol molecules inside the patches through a nucleation and growth mechanism. Analytical expressions for the chronoamperometric current resulting from reductive desorption of the monolayer are also derived and compared with experimental results. Theoretical predictions were found to account satisfactorily for the dependence of the chronoamperometric shape with the desorption potential for butanethiol and nonanethiol monolayers. Thus, the observed chronoamperometric broadening, and the simultaneous increase of the initial current, could be explained as a consequence of the greater importance of the edge desorption route when the overpotential is made more negative.

Introduction

Adsorptive oxidation of thiols on metallic substrates leads to the spontaneous formation of well-ordered interfacial structures known as self-assembled monolayers (SAMs).^{1–5} These adlayers have been extensively characterized^{6–12} in view of their intrinsic scientific interest and technological importance. However, much less is known about the mechanistic aspects that determine their formation and desorption. It is generally accepted that the monolayer formation is initiated by a fast one-electron oxidation step that results in the covalent attachment of the sulfur head to the metallic surface.^{13–16} Then, the hydrophobic interactions between adjacent organic chains drive a slow surface rearrangement process to yield the final structure,^{17–20} which consists of densely packed thiol domains with different molecular orientations.^{21–23}

Formation of a thiol self-assembled monolayer may occur either under open circuit conditions, i.e., by immersing a clean metal in a dilute solution of thiols,²⁴ or under potentiostatic control, i.e., by applying a sufficiently positive potential to the metallic substrate in contact with a thiol solution.²⁵ Identical monolayers can be obtained in both cases, though the electrochemical route provides a more complete control of the deposition conditions. These adlayers are stable over a wide potential range (~1 V for alkanethiols deposited on gold), thus opening the possibility to exploit the electrochemical properties of modified electrodes that incorporate specific group functionalities.^{26–28}

Reductive desorption of a thiol self-assembled monolayer can be prompted by the external application of a sufficiently negative potential.^{25,29,30} Current transients, associated with the removal of thiol molecules, are expected to provide valuable information on the mechanistic aspects that govern the kinetic stability of the monolayer. Particularly, chronoamperometric transients^{31–33}

* Corresponding author. Phone: 34-954557177. Fax: 34-954557174. E-mail: fondacab@cica.es.

[†] University of the West Indies.

[‡] University of Sevilla.

(1) Bain, D. C.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506.

(2) Dubois, L.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(3) Finklea, H. O. In *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, p 110.

(4) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

(5) Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117.

(6) Camillone, N.; Chidsey, C. E. D.; Liu, G. Y.; Scoles, G. *J. Chem. Phys.* **1993**, *98*, 3503.

(7) Fenter, P.; Eisenberger, P.; Liang, K. S. *Phys. Rev. Lett.* **1993**, *70*, 2447.

(8) Poirier, G. E.; Tarlov, M. J.; Rushmeier, H. E. *Langmuir* **1994**, *10*, 3383.

(9) Liu, G. Y.; Salmeron, M. B. *Langmuir* **1994**, *10*, 367.

(10) Alves, C. A.; Smith, E. L.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 1222.

(11) McDermott, C. A.; McDermott, M. T.; Green, J. B.; Porter, M. D. *J. Phys. Chem.* **1995**, *99*, 13257.

(12) Schonenberger, C.; Sondag-Huethorst, J. A. M.; Jorritsma, J.; Fokink, L. G. *J. Langmuir* **1994**, *10*, 611.

(13) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.

(14) Weisshaar, D. E.; Walczak, M. M.; Porter, M. D. *Langmuir* **1993**, *9*, 323.

(15) Yang, D. F.; Wilde, C. P.; Morin, M. *Langmuir* **1996**, *12*, 6570.

(16) Calvente, J. J.; Gil, M. L.; Andreu, R.; Roldán, E.; Dominguez, M. *Langmuir* **1999**, *15*, 1842.

(17) Hahner, G.; Wöll, Ch.; Buck, M.; Grunze, M. *Langmuir* **1993**, *9*, 1955.

(18) Poirier, G. E.; Pylant, E. D. *Science* **1996**, *272*, 1145.

(19) Himmel, H. J.; Wöll, Ch.; Gerlach, R.; Polanski, G.; Rubahn, H.-G. *Langmuir* **1997**, *13*, 602.

(20) Xu, S.; Cruchon-Dupeyrat, S. J. N.; Garno, J. C.; Liu, G.; Jennings, G. K.; Yong, T.; Laibinis, P. E. *J. Chem. Phys.* **1998**, *108*, 5002.

(21) Schonenberger, C.; Jorritsma, J.; Sondag-Huethorst, J. A. M.; Fokink, L. G. *J. Phys. Chem.* **1995**, *99*, 3259.

(22) Poirier, G. E.; Tarlov, M. *Langmuir* **1994**, *10*, 2853.

(23) Delamarche, E.; Michel, B.; Gerber, C.; Anselmetti, D.; Guntherodt, H. J.; Wolf, H.; Ringsdorf, H. *Langmuir* **1994**, *10*, 2869.

(24) Huzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.

(25) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860.

(26) Steinberg, S.; Tor, Y.; Sabatini, E.; Rubinstein, I. *J. Am. Chem. Soc.* **1991**, *113*, 5176.

(27) Malem, F.; Mandler, D. *Anal. Chem.* **1993**, *65*, 37.

(28) Creager, S. E.; Olsen, K. G. *Anal. Chim. Acta* **1995**, *307*, 277.

(29) Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391.

(30) Bunding-Lee, K. A.; Mowry, R.; McLennan, S.; Finklea, H. O. *J. Electroanal. Chem.* **1988**, *246*, 217.

(31) Calvente, J. J.; Kovocova, Z.; Sanchez, M. D.; Andreu, R.; Fawcett, W. R. *Langmuir* **1996**, *12*, 5696.

(32) Yang, D. F.; Morin, M. *J. Electroanal. Chem.* **1997**, *429*, 1.

(33) Yang, D. F.; Morin, M. *J. Electroanal. Chem.* **1998**, *441*, 173.

are characterized by the presence of a current maximum, whose height and time of appearance depend on the desorption potential. Initial attempts^{31–33} to explain this chronoamperometric behavior were based on classical nucleation and growth theory,³⁴ but they failed to account for a progressive transient broadening, together with the development of higher initial currents, observed as the desorption potential was made more negative. Recently, Vinokurov et al.³⁵ have proposed an explanation of the chronoamperometric broadening observed during the desorption of nonanethiol monolayers in terms of diffusion control over the rate of removal of the reduced thiol molecules.

The observation of initial desorption currents in a chronoamperometric experiment, overlapping with the double layer charging transient, suggests the existence of a desorption route to produce a finite rate of adsorbate removal as soon as the potential perturbation has been applied. Cationic permeation, and therefore thiol desorption, is expected to be facilitated along the less ordered contact lines between adjacent thiol domains. Starting from these line defects, a desorption of the partially exposed thiol molecules at the edge of the domains would follow, leading thus to a progressive shrinkage of the thiol patches. This type of mechanism has been proposed before to describe electrochemically triggered surface phase transitions in the absence of point defects.^{36,37}

The aim of the present work is to develop a simple kinetic model to account for the main qualitative features observed in the chronoamperometric desorption of thiol self-assembled monolayers. The model incorporates two desorption routes, which are assumed to occur simultaneously in a given experimental situation, the shrinkage of the thiol domains and the nucleation and growth of holes inside these shrinking domains. To simplify the mathematical analysis, thiol domains are modeled as circular and of uniform size, though a straightforward extension to the case of a size distribution is also considered. Under these assumptions, analytical expressions for the chronoamperometric current are derived, and the theoretical predictions are compared with the results reported by Yang and Morin^{32,33} on the desorptive reduction of butanethiol and nonanethiol monolayers deposited on Au(111).

Theory

(a) The Model. In agreement with microscopic evidence,^{21–23} we will assume that the thiol monolayer consists of a large number of ordered domains, reflecting the substrate microcrystallinity and/or the limits attained by neighboring growing centers during the process of self-assembly. These domains can be viewed as compact hydrophobic patches with a thickness close to the thiol molecular length (typically ~ 1 nm) and a relative permittivity $\epsilon_m \sim 3$ similar to that of pure hydrocarbons.

Since thiols can only desorb in their reduced form, the low permittivity of the monolayer would require a very negative external potential to trigger its electrochemical desorption. However, no incommensurate order is found in real monolayers, so that some degree of solvent and ion permeation is facilitated in those areas where local order is absent, i.e., at point defects within the domains and at

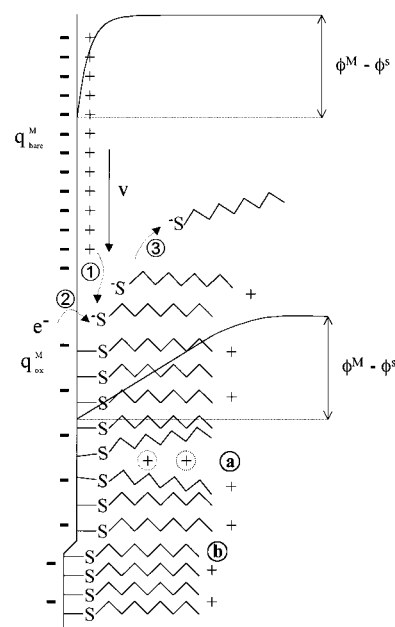


Figure 1. Schematic representation of the reductive desorption of a thiol monolayer at a fixed potential drop $\phi^M - \phi^S$. The upper potential profile corresponds to the bare surface and the lower to a surface patch where oxidized thiols remain attached to the electrode. The desorption potential has been assumed to be negative with respect to the potentials of zero charge of both the modified and unmodified electrodes. Desorption from the film edge is assumed to consist of three elementary steps: (1) surface redistribution of electrolyte ions, (2) electron transfer, and (3) detachment of the reduced thiol molecules. Active sites for nucleation may be identified with (a) local conformational disorder of the hydrocarbon chains and (b) metal surface defects.

the contact lines between contiguous patches. Such permeation causes a local increase of the negative surface charge on the metal adjacent to the oxidized sulfur heads, thus facilitating the reduction of the sulfur (see Figure 1).

On the basis of the above ideas, we will model the monolayer as consisting of a set of circular thiol islands. Molecules at the edge of an island experience a much stronger electric field than those in the interior, so that they are far more likely to become reduced and subsequently detached from the metal. This leads to shrinking of the islands at a certain constant radial rate v , which most likely will depend on the applied potential.

On the other hand, thiols will also be reductively desorbed from the interior of the circular domains at a rate which is governed by nucleation and growth processes. One could imagine small pinholes of a certain critical size appearing randomly at some predetermined active sites, of which there are initially N_0 per unit area. The rate v_N at which these critical holes form on unit area at some time t will be proportional to the number of active sites left at time t , leading to the following rate expression for nucleation:³⁸

$$v_N = \frac{dN}{dt} = k_N(N_0 - N(t)) \quad (1)$$

where k_N is the nucleation rate constant.

With the initial condition $N(0) = 0$, eq 1 is readily solved to give

(34) Harrison, J. A.; Thirsk, H. R. In *Electroanalytical Chemistry*; Bard, A. J. Ed.; Marcel Dekker: New York, 1971; Vol. 5, p 67.

(35) Vinokurov, I. A.; Morin, M.; Kankare, J. *J. Phys. Chem. B* **2000**, *104*, 5790.

(36) Mulder, W. H. *J. Electroanal. Chem.* **1994**, *366*, 287.

(37) Poelman, M.; Buess-Herman, C.; Badiali, J. P. *Langmuir* **1999**, *15*, 2194.

(38) Sluyters-Rehbach, M.; Wijenberg, J. H. O. J.; Bosco, E.; Sluyters, J. H. *J. Electroanal. Chem.* **1987**, *236*, 1.

$$v_N(t) = k_N N_0 e^{-k_N t} \quad (2)$$

which has two important limiting forms:

(1) When $k_N \rightarrow \infty$

$$v_N(t) = N_0 \delta(t) \quad (3)$$

instantaneous nucleation, where $\delta(t)$ is the Dirac delta function.

(2) When $k_N \rightarrow 0$ and $N_0 \rightarrow \infty$

$$v_N(t) = k_N N_0 \quad (4)$$

progressive nucleation.

Once a hole of critical size has formed, it will continue to grow at a radial speed v as a result of the same mechanism that is responsible for the shrinking of islands (Figure 2). For simplicity it will henceforth be assumed that all islands are circular and have identical radii R (isodisperse islands model), though we will consider in the Appendix the consequences of an island size distribution.

The rate at which the electrode surface is being exposed due to nucleation and growth inside the domains will now be investigated, while initially ignoring the effect of the receding edge, i.e., we will first consider the $R \rightarrow \infty$ limit corresponding to a uniform monolayer and denote the fraction of bare surface by $S(t)$. The Avrami theorem accounts for hole growth, overlap, and exposure of active sites according to the formula³⁹

$$S(t) = 1 - \exp(-S_x(t)) \quad (5)$$

where the extended surface coverage $S_x(t)$, i.e., the coverage as obtained without correction for overlap between growing centers, is given by

$$S_x(t) = \pi v^2 \int_0^t (t - \tau)^2 v_N(\tau) d\tau \quad (6)$$

Returning next to the electrode surface which is covered by the island film, it should be noted that the Avrami theorem can be directly transposed to describe the variation of $S(t)$ due to nucleation and growth within a given island. The reason is that any finite size (edge) effect will be automatically eliminated due to the fact that the outer rim of any island recedes at the same radial speed v at which the holes grow. In particular, if we regard the shrinking domain alternatively as a circular patch of an "infinite", initially uniform film and continuously "zoom in" on it at the proper rate, we would not be able to tell the difference since no expanding (real or phantom) nuclei that appear outside the edge will ever enter our field of vision.

If the number of domains per unit of geometrical surface area is denoted by N_d , the above argument permits us to write for the fraction of the electrode surface which is still occupied by thiol molecules at time t

$$1 - S(t) = N_d \pi (R - vt)^2 \exp(-S_x(t)) \quad (7)$$

where the pre-exponential factor represents the thiol surface coverage in the absence of nucleation and growth processes, while the exponential is the Avrami factor for a uniform monolayer.

Substitution of eq 2 into eq 6 yields for the extended coverage

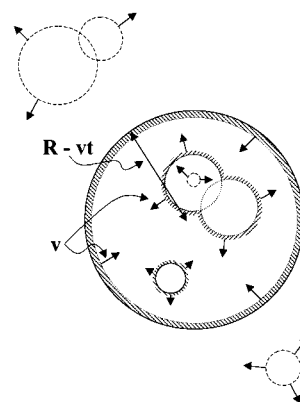


Figure 2. Schematic representation of the thiol desorption from a circular domain of the SAM. Note the simultaneous occurrence of the radial shrinking of the domain at a rate v and the development of internal holes by a nucleation and growth mechanism. The dotted-line circles represent the expansion of external nuclei (real or phantom) at a radial rate v .

$$S_x(t) = \alpha [(k_N t)^2 + 2(1 - k_N t - \exp(-k_N t))] \quad (8)$$

with

$$\alpha = N_0 \pi \left(\frac{v}{k_N} \right)^2 \quad (9)$$

(b) Chronoamperometric Response. In a typical chronoamperometric experiment,^{32,33} a potential step is applied from an initial potential E_{init} , where the monolayer is stable, to a more negative potential E_{fin} , where the monolayer desorption takes place. First, a fast capacitive transient is recorded, and then the desorption transient is usually observed on a much broader time scale. The desorption current I consists of a faradaic and a non-faradaic component, according to

$$I = d(Q^M + nFN_{\text{ox}})/dt \quad (10)$$

where Q^M is the charge on the metal and N_{ox} the number of moles of oxidized thiol molecules attached to the electrode surface.

According to the parallel condensers model,⁴⁰ in the presence of patches of bare and thiol-covered surface, the charge on the metal may be formulated as

$$Q^M = q_{\text{bare}}^M A S(t) + q_{\text{ox}}^M A (1 - S(t)) \quad (11)$$

where q_{bare}^M and q_{ox}^M are the surface charge densities of bare and thiol-modified surfaces at E_{fin} , respectively, and A is the electrode area.

On the other hand, N_{ox} can be expressed as

$$N_{\text{ox}} = \Gamma_{\text{ox}} A (1 - S(t)) \quad (12)$$

where Γ_{ox} is the surface concentration of thiol within the compact domains (i.e., typically $\Gamma_{\text{ox}} \sim 8 \times 10^{-10} \text{ mol cm}^{-2}$).

By combining eqs 10–12, the current density i due to the thiol desorption can be written as

$$i = \frac{I}{A} = (q_{\text{bare}}^M - q_{\text{ox}}^M - nF\Gamma_{\text{ox}}) \frac{dS}{dt} \quad (13)$$

The time dependence of i is contained in the dS/dt factor which can be evaluated, after substitution of eq 8 into eq 7, to obtain

(39) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103; **1940**, *8*, 212; **1941**, *9*, 177.

(40) Frumkin, A. N. *Z. Phys.* **1926**, *35*, 792.

$$i = \Omega_1(\gamma - k_N t)[1 + \alpha(\gamma - k_N t)(k_N t - 1 + e^{-k_N t})] \exp(-\alpha[(k_N t)^2 + 2(1 - k_N t - e^{-k_N t})]) \quad (14)$$

$$0 \leq t \leq \frac{R}{v}$$

where

$$\gamma = k_N R/v \quad (15)$$

$$\Omega_1 = (q_{\text{bare}}^M - q_{\text{ox}}^M - nF\Gamma_{\text{ox}})\phi_{\text{init}} \frac{2k_N}{\gamma^2} = \Delta \frac{2k_N}{\gamma^2} \quad (16)$$

$\phi_{\text{init}} = N_d \pi R^2$ is the initial thiol coverage and Δ is the charge density corresponding to the full desorption transient.

For a uniform film, desorption only takes place through a nucleation and growth route, and $S(t)$ is obtained directly from eq 5. The following expression for the current density can be derived by combining eqs 5 and 13

$$i = \Omega_2 e^{-S_x(t)} (k_N t - 1 + e^{-k_N t}) \quad (17)$$

where

$$\Omega_2 = (q_{\text{bare}}^M - q_{\text{ox}}^M - nF\Gamma_{\text{ox}})2\alpha k_N \quad (18)$$

Note that for the isodisperse islands model (eqs 14–16), $i \rightarrow 2\Delta v/R$ when $t \rightarrow 0$, whereas for the uniform film model (eq 17), $i \rightarrow 0$ when $t \rightarrow 0$.

Results and Discussion

(a) Chronoamperometric Shapes. Chronoamperometric transients can be computed from eq 14 for fixed values of the Ω_1 , γ , α , and k_N parameters. However, Ω_1 and k_N are just scaling factors for current and time coordinates, respectively, and the shapes of chronoamperograms can be discussed in terms of the γ and α values only. To facilitate the interpretation of the results, it is convenient to define a new parameter:

$$\sigma = \alpha \gamma^2 = N_d \pi R^2 \quad (19)$$

which represents the average number of active sites per domain, and it is related to the physical and structural properties of the monolayer, whereas γ accounts for the relative kinetic contributions of the nucleation and radial desorption processes (see eq 15).

The values of the four model parameters that fit a given chronoamperogram can be obtained in two steps. First, we note that normalized chronoamperograms (to be displayed as I/I_{max} vs t/t_{max} plots, where I_{max} and t_{max} stand for the current and time at the chronoamperometric maximum), are independent of the specific choice of the k_N and Ω_1 values and can be compared with the theoretical predictions of eq 14, written as a scaled current $i\Omega_1^{-1}$ as a function of the scaled time parameter $k_N t$, to determine the values of σ and γ . Once the normalized chronoamperometric shape has been reproduced satisfactorily, then the ratio between the dimensionless time corresponding to the appearance of the maximum $(k_N t_{\text{max}})_{\text{theo}}$ and the observed time $(t_{\text{max}})_{\text{exp}}$ gives the value of k_N . Likewise, the ratio $(i_{\text{max}})_{\text{exp}}/(i_{\text{max}}\Omega_1^{-1})_{\text{theo}}$ yields the value of Ω_1 .

A comparison between normalized chronoamperograms derived from our isodisperse islands model and from the classical progressive and instantaneous nucleation mod-

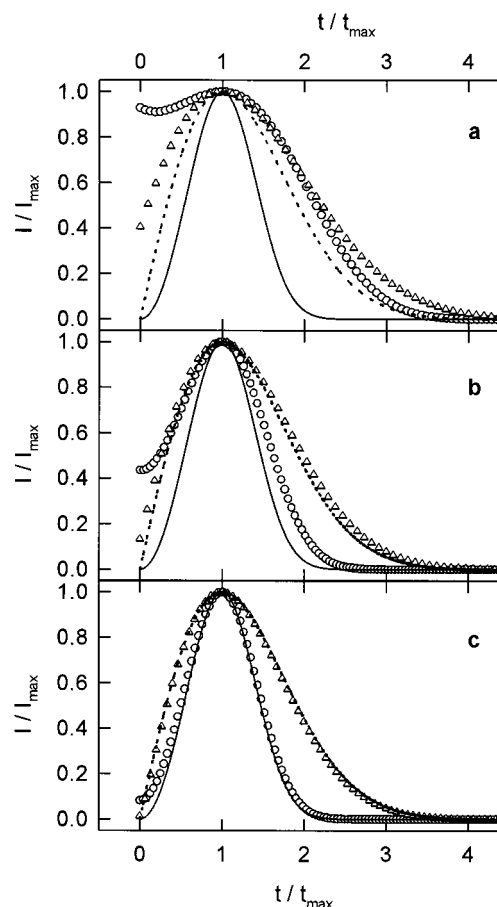


Figure 3. Theoretical chronoamperometric shapes: (a) $\sigma = 30$, (b) $\sigma = 300$, (c) $\sigma = 30\,000$; (○) $\gamma = 1$, (△) $\gamma = 10\,000$. Solid lines represent the classical progressive nucleation limit. Dotted lines represent the classical instantaneous nucleation limit.

els³⁴ is displayed in Figure 3. In the $\sigma \rightarrow \infty$ limit (Figure 3c), corresponding to high values of R and/or of the active site density N_d , the uniform film behavior is recovered, including the two limits for instantaneous ($\gamma \rightarrow \infty$) and progressive ($\gamma \rightarrow 0$) nucleation. As σ decreases (parts b and a of Figure 3), normalized transients become broader and are characterized by a higher value of the initial current ratio $(I/I_{\text{max}})_{t=0}$, which is associated with the shrinking of the thiol domains. For a given initial state of the monolayer (i.e., for a fixed σ value), $(I/I_{\text{max}})_{t=0}$ increases upon decreasing γ , which can be attributed to a higher contribution stemming from the radial desorption process due to a large value of the total perimeter length (corresponding to the presence of many islands of small size) and/or a high radial desorption rate v . Moreover, broader normalized transients are always obtained upon approaching the instantaneous nucleation regime at high γ values.

On the other hand, $\log I_{\text{max}}$ and $\log t_{\text{max}}$ both exhibit a linear dependence on $\log \gamma$ with slopes close to 1 (see Figure 4). A detailed analysis of these plots provides the dependence of I_{max} and t_{max} on the model parameters. Thus, for a given initial coverage ϕ_{init} , higher chronoamperometric maxima, showing up at shorter times, are expected for monolayers made up of small islands with a high density of nucleation centers, and high values of k_N and v .

(b) Comparison with Experiment. Chronoamperometric transients corresponding to the reductive desorption of butanethiol, nonanethiol, and hexadecanethiol self-assembled monolayers on Au(111) have been reported by

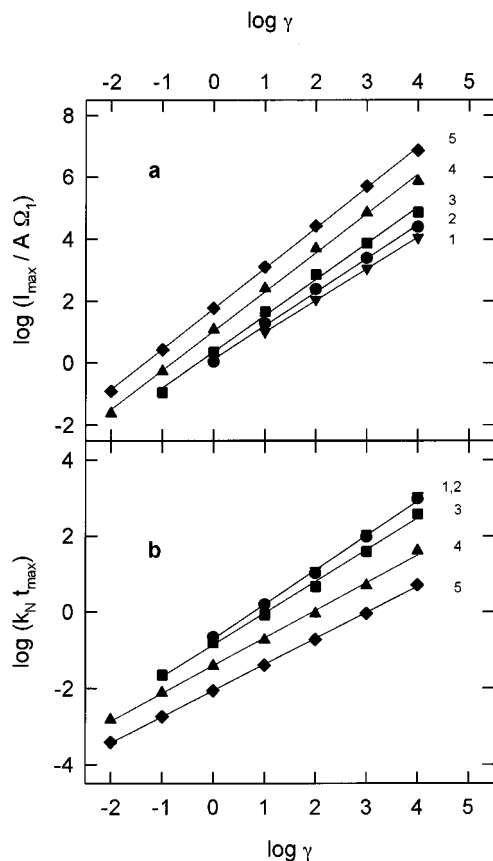


Figure 4. Coordinates of the chronoamperometric maximum as a function of the model parameters: (a) current density I_{\max}/A and (b) time t_{\max} ; $\sigma = 3$ (1), 30 (2), 300 (3), 3×10^4 (4), and 3×10^6 (5).

Yang and Morin.^{32,33} In the cases of butanethiol and nonanethiol, the chronoamperometric shapes show the same qualitative dependence on E_{fin} . Thus, for low $|E_{\text{fin}}|$ values, transients could be described by a classical progressive nucleation mechanism. However, as E_{fin} was made more negative, normalized chronoamperograms approached, and eventually surpassed, the expected width for a classical instantaneous nucleation mechanism. This chronoamperometric broadening was accompanied by a simultaneous increase of the initial desorption current, in qualitative agreement with the theoretical predictions of our present model (see Figure 3). In the case of hexadecanethiol (not shown), chronoamperograms are characterized by an abrupt initial rise and a subsequent exponential decay with time. This type of behavior, which cannot be reproduced by the present model, has been interpreted by Yang and Morin³³ in terms of a homogeneous reduction of the monolayer. It should be noted also that a complete and fast removal of the reduced thiols has been implicitly assumed in our model and that this assumption is likely to break down for long-chain alkanethiols, due to their tendency to remain adsorbed on the electrode surface in their reduced form.^{15,41} Therefore, we will limit our discussion to the analysis of the reductive desorption of butanethiol and nonanethiol monolayers.

The chronoamperometric responses associated with the reductive desorption of butanethiol and nonanethiol monolayers, for some representative values of E_{fin} , are illustrated in Figures 5 and 6, respectively. Satisfactory fits were obtained at all potentials for nonanethiol

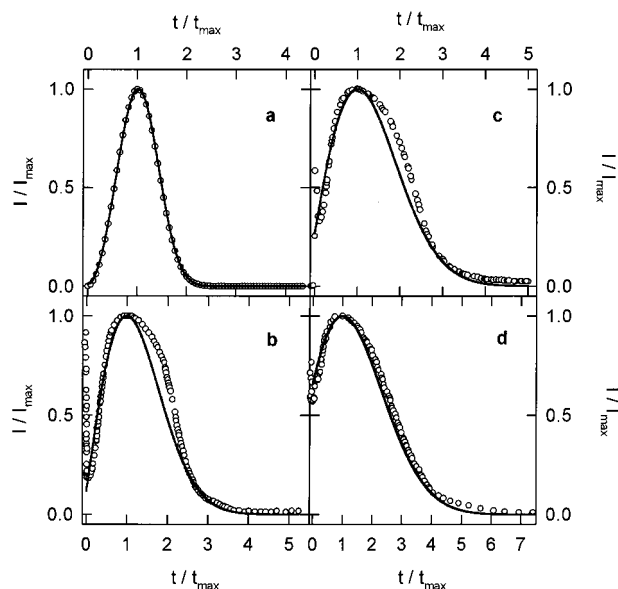


Figure 5. Chronoamperograms obtained from the reductive desorption of butanethiol self-assembled monolayers at $E_{\text{fin}}/V(\text{SCE}) = -0.95$ (a), -1.05 (b), -1.15 (c), and -1.25 (d). Circles are experimental results from refs 32 and 33. Solid lines are theoretical fits.

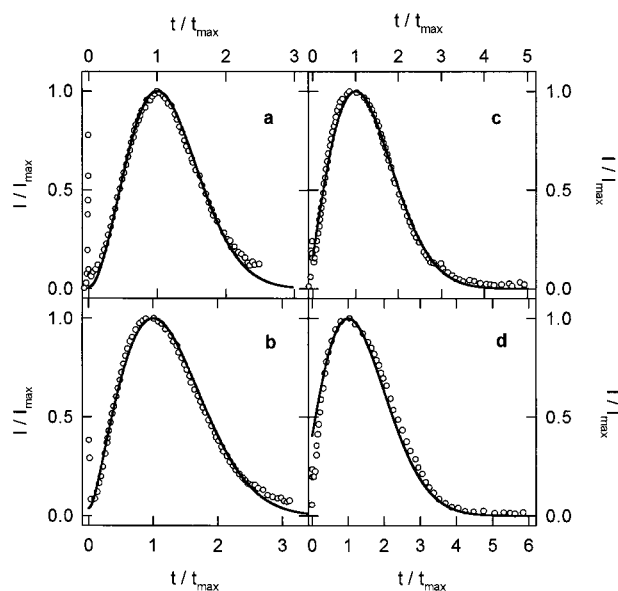


Figure 6. Chronoamperograms obtained from the reductive desorption of nonanethiol self-assembled monolayers at $E_{\text{fin}}/V(\text{SCE}) = -1.09$ (a), -1.14 (b), -1.19 (c), and -1.24 (d). Circles are experimental results from ref 33. Solid lines are theoretical fits.

monolayers and only at low and high overpotentials in the case of butanethiol monolayers (parts a and d of Figure 5). Experimental current densities for butanethiol desorption at intermediate potentials and $t/t_{\max} \sim 2$ (parts b and c of Figure 5) were found to be higher than could be accounted for by the present model. This type of discrepancy is likely to have its origin in an increase in the number of active sites with time, as discussed below.

Values of the fit parameters are collected in Table 1. As the desorption potential is made more negative, higher values of γ and lower values of σ are required to reproduce the chronoamperometric shapes. It is also observed that both the nucleation rate constant and the radial desorption rate increase with overpotential. Good agreement was obtained between the Δ_{exp} values, obtained by numerical

(41) Calvente, J. J.; Andreu, R.; Gil, M. L. A.; González, L.; Alcudia, A.; Domínguez, M. J. *Electroanal. Chem.* **2000**, *482*, 18.

Table 1. Desorption Parameters

Butanethiol						
E_{fin}/V (SCE)	γ	σ	k_N/s^{-1}	$\nu R^{-1}/s^{-1}$	$\Delta_{\text{theo}}/\mu\text{C cm}^{-2}$	$\Delta_{\text{exp}}/\mu\text{C cm}^{-2}$
-0.95	10–30	$(5-15) \times 10^5$	0.4–0.9	$(3-4) \times 10^{-2}$	94–95	94
-1.00	$(3-5) \times 10^2$	$(7-15) \times 10^3$	80–110	0.20–0.26	96–102	96
-1.05	>500	$(2-10) \times 10^2$	> 10^3	1.5–3.2	98–105	100
-1.10	>500	$(1-10) \times 10^2$	> 2×10^3	2–7	91–101	104
-1.15	>500	50–90	> 5×10^3	11–13	98–104	109
-1.20	>500	10–14	> 10^4	32–34	101–108	114
-1.25	>500	8–10	> 2×10^4	44–45	106–112	115
Nonanethiol						
E_{fin}/V (SCE)	γ	σ	k_N/s^{-1}	$\nu R^{-1}/s^{-1}$	$\Delta_{\text{theo}}/\mu\text{C cm}^{-2}$	$\Delta_{\text{exp}}/\mu\text{C cm}^{-2}$
-1.09	$(7-15) \times 10^2$	$(5-20) \times 10^4$	12–23	$(1-2) \times 10^{-2}$	91–100	98
-1.14	$(5-20) \times 10^2$	$(2-8) \times 10^3$	110–400	$(2-3) \times 10^{-1}$	100–111	106
-1.19	>500	$(1-5) \times 10^2$	> 10^3	1.5–3.1	103–110	109
-1.24	>500	20–100	> 4×10^3	6–10	98–118	113

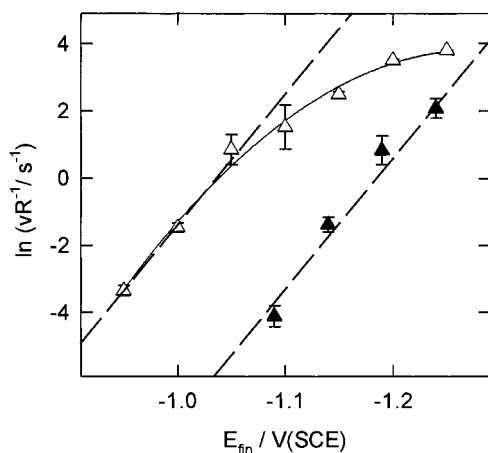


Figure 7. Dependence of the radial desorption rate on the desorption potential. Open and solid triangles correspond to butanethiol and nonanethiol monolayers, respectively. Broken straight lines have been drawn with a slope equal to $-F/RT$. The solid line has been drawn as a guide for the eye.

integration of the transients, and the Δ_{theo} values (see eq 16) derived from the fit procedure.

As shown in Figure 7, the overall radial desorption rate for nonanethiol monolayers varies exponentially with E_{fin} , according to

$$\ln(\nu R^{-1}) = \ln(\nu R^{-1})_{E_{\text{fin}}=0} - \frac{FE_{\text{fin}}}{RT} \quad (20)$$

which also reproduces the low-overvoltage limiting behavior in the case of butanethiol monolayers. This type of potential dependence is expected when the desorption rate is determined by a chemical step that follows a fast electron transfer.⁴² Radial desorption can be imagined to proceed in three steps: electrolyte and solvent redistribution next to thiol molecules in the periphery of oxidized patches, reduction of their sulfur heads under the influence of the stronger electric field corresponding to the unmodified electrode surface, and detachment of the reduced thiol molecules from their neighbors in the monolayer (see Figure 1). Out of these three steps, only the rate of the charge-transfer step is expected to obey a simple exponential dependence on the desorption potential. Though the available information does not allow identification of the nature of the rate-determining chemical step, the above

results are consistent with the hypothesis that the detachment rate of the reduced thiol, to become a free diffusing anion (step 3 in Figure 1), determines the kinetic behavior described by eq 20, since this detachment must follow the charge-transfer step and it is expected to be slower for nonanethiol than for butanethiol molecules, therefore preserving the validity of eq 20 over a wider potential range in the former case. On the other hand, the desorption rate for butanethiol monolayers displays a decreasing slope at higher overpotentials, which indicates that the rate control is being transferred to a preceding step, either to the charge-transfer step itself or to a previous chemical step,⁴² as the desorption potential is made more negative.

The nucleation process can be envisaged as a direct consequence of the cationic permeation of the monolayer, which occurs at preferred sites. Then, active sites would be characterized by the presence of cations (and solvent) in the vicinity of the sulfur heads of oxidized thiols, whereas the nucleation rate constant would be a measure of the probability that such an initial configuration ends up in the formation of a critical hole. From this point of view, both the number of active centers and the nucleation rate constant are expected to depend on the desorption potential. A precise k_N vs E_{fin} dependence could not be established, since theoretical transients become independent of γ (and of k_N) when $\gamma > 500$ and $\gamma > \sigma$, so that k_N values for each monolayer could be determined for the two most positive potentials only (see Table 1). A comparison of these two sets of values indicates a stronger variation of k_N with E_{fin} in the case of butanethiol monolayers, in agreement with the stronger change in the local electric field at the electrode surface to be expected for a thinner organic monolayer.

The number of active sites per domain σ was found to decrease with overpotential (see Figure 8a), indicating that N_0 is not predetermined by the physical properties of the monolayer (or of the metallic substrate). This variation of N_0 can be rationalized by assuming that the presence of a sufficiently negative potential drop across the monolayer is just a prerequisite for the appearance of active sites in the monolayer, their actual number being determined by both E_{fin} and the experimental time scale, since a finite time is required for the electrolyte to penetrate the monolayer to create an active site. Upon application of a negative enough desorption potential, a number of defect sites (such as the borders between domains) will be almost instantaneously permeated, but as time progresses permeation will extend over the entire monolayer. Keeping in mind that both k_N and ν increase with overpotential, this situation leads quite naturally to

(42) Sluyters-Rehbach, M.; Sluyters, J. H. *Electrochim. Acta* **1988**, *33*, 983.

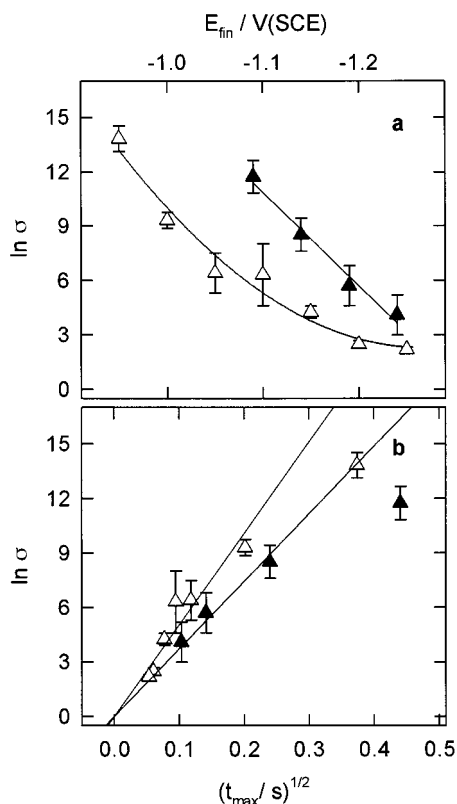


Figure 8. (a) Dependence of the number of active sites per domain on the desorption potential. (b) Dependence of the number of active sites per domain on the time of appearance of the chronoamperometric maximum. Open and solid triangles correspond to butanethiol and nonanethiol monolayers, respectively. Solid lines are eye guides.

a progressive nucleation regime ($k_N \rightarrow 0$, $v \rightarrow 0$, and $N_0 \rightarrow \infty$, see eq 4) at low overvoltages and to an instantaneous nucleation regime, modified by radial shrinking of the thiol domains, at high overvoltages ($k_N \rightarrow \infty$, $v \rightarrow \infty$, $N_0 \rightarrow 0$, see eq 3). Between these two extreme regimes, the increase in the number of active sites while the chronoamperogram is being recorded would lead to higher current densities than those predicted by our model, as observed in parts b and c of Figure 5 for butanethiol monolayers. The improved quality of the fits for nonanethiol monolayers in Figure 6 is likely to be due to an increased difficulty of the electrolyte to permeate the monolayer, which results in a lower rate of formation of active sites, as illustrated in Figure 8b.

It may also be of interest to note that we have observed⁴³ the appearance of delayed transients, obeying the classical progressive nucleation limit, for the reductive desorption of 2-mercaptoethanesulfonate monolayers from an Au(111) electrode at lower overpotentials than those considered in Figures 5 and 6. This result can be understood on the basis of our previous discussion since (a) the presence of an induction time is to be expected from a combination of low permeation and desorption rates and (b) an expanded time scale ($N_0 \rightarrow \infty$) and a low k_N value set up the necessary conditions for the progressive nucleation regime.

Recently, Vinokurov et al.³⁵ have offered an alternative explanation for the chronoamperometric shape obtained for the reductive desorption of nonanethiol monolayers. They have adopted an expression analogous to our eq 1

to describe the nucleation rate, though N_0 represents the total number of adsorbed and detachable molecules in their formulation and have assumed that the chronoamperometric broadening is due to a low diffusional rate of the reduced thiol molecules. They obtained good fits of the four chronoamperograms reproduced in Figure 6, except for the $t \rightarrow 0$ limit, which necessarily gives $I = 0$ in their model. However, a detailed assessment of the relative merits of the work of Vinokurov et al. and our own theoretical approach will have to wait until a larger body of chronoamperometric data has become available.

Conclusions

The present model, which describes the thiol monolayer desorption as a combination of a radial shrinking of thiol patches and the concurrent formation of holes inside the receding domains by a nucleation and growth mechanism, accounts satisfactorily for the shape of the chronoamperograms on overpotential for butanethiol and nonanethiol monolayers. Both the radial desorption rate and the nucleation rate constant were found to increase as the desorption potential was made more negative. The variation of the radial desorption rate appears to be related to the acceleration of the reductive charge transfer step, whereas that of the nucleation rate constant is likely to be due to the presence of a stronger electric field inside the monolayer, which facilitates ionic permeation at certain "weak spots" as a prerequisite to form a critical hole. When the overpotential is made more negative, the decrease in the number of active sites per domain leads to the radial desorption becoming the predominant mechanism of film removal, which results in the observed broadening of normalized chronoamperograms and the simultaneous increase of the initial current. This decrease in the number of active sites could tentatively be explained in terms of the shorter time available for the electrolyte ions to permeate the monolayer, and it would anticipate (correctly) the appearance of delayed transients, approaching the limit of progressive nucleation, at less negative overpotentials. Incorporation of the dynamic aspects of nucleation into the above model is currently underway.

Acknowledgment. This work was supported by the Spanish DGICYT under Grant PB98-1123.

Appendix

The above model can be easily extended to account for a continuous distribution of the domain sizes. We can define a size distribution function $g(R)$, so that the number of domains whose radii values lie within a given interval dR may be expressed as

$$dN_d(R) = N_d g(R) dR \quad (\text{A1})$$

Now, the thiol surface coverage $1 - S(t)$ can be obtained by adding the contributions from all individual domains, as stated in eq 7, therefore

$$1 - S(t) = \int_{vt}^{\infty} \pi(R - vt)^2 \exp(-S_x(t)) N_d g(R) dR \quad (\text{A2})$$

The lower limit of integration is vt because, at a given time t , domains with $R \leq vt$ have been swept out and no longer contribute to the current.

To explore qualitatively the influence of size distribution, a function $g(R)$ has been chosen that combines convenient analytical properties and a not too unrealistic

(43) Calvente, J. J.; Andreu, R. Unpublished results.

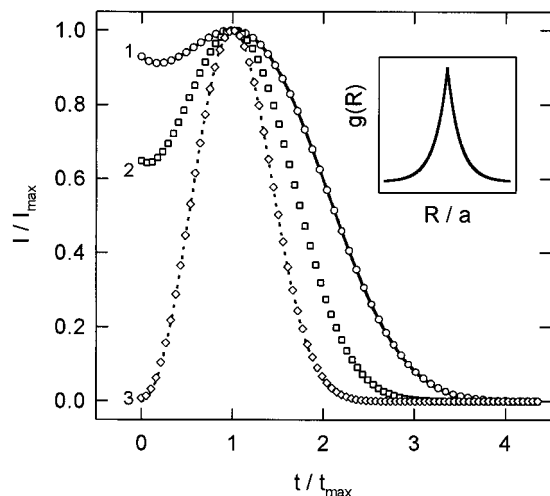


Figure 9. Influence of the domain size polydispersity (inset) on the theoretical chronoamperograms: (1) $\sigma^* = 30$, $\gamma^* = 1$, $\omega^* = 0.01$; (2) $\sigma^* = 30$, $\gamma^* = 1$, $\omega^* = 10$; (3) $\sigma^* = 30$, $\gamma^* = 1$, $\omega^* = 10^5$. The solid line has been computed from the isodisperse model for $\sigma = 30$ and $\gamma = 1$. The dotted line has been computed from the uniform film model for $\sigma = 30$ and $\gamma = 1$.

appearance, as follows

$$g(R) = \frac{b \exp(-b|R - a|)}{2 - \exp(-ba)} \quad (\text{A3})$$

so that the most frequent radius corresponds to $R = a$ and the half-height width of the distribution is $2 \ln 2/b$ (see inset in Figure 9). After substituting eq A3 into eq A2 and integrating we obtain

$$1 - S(t) = \frac{2\pi N_d e^{-S_x(t)} [(ba - bvt)^2 + 2 - e^{-(ba-bvt)}]}{b^2(2 - e^{-ba})} \quad (\text{A4})$$

$$vt \leq a$$

$$1 - S(t) = \frac{2\pi N_d e^{-S_x(t)} e^{ba-bvt}}{b^2(2 - e^{-ba})} \quad (\text{A5})$$

$$vt \geq a$$

In the case where the monolayer consists of a set of domains, the sizes of which are distributed according to eq A3, eqs A4, A5, and 13 can be combined to give

$$i = \Omega_3 e^{-S_x(t)} \left[\frac{bv}{k_N} (2(ba - bvt) + e^{-(ba-bvt)}) + \frac{1}{k_N} \frac{dS_x}{dt} (2 + (ba - bvt)^2 - e^{-(ba-bvt)}) \right] \quad (\text{A6})$$

$$0 \leq t \leq a/v$$

$$i = \Omega_3 e^{-S_x(t)} e^{ba-bvt} \left(\frac{bv}{k_N} + \frac{1}{k_N} \frac{dS_x}{dt} \right) \quad (\text{A7})$$

$$t \geq a/v$$

where

$$\Omega_3 = (q_{\text{bare}}^M - q_{\text{ox}}^M - nFT_{\text{ox}}) \frac{\phi_{\text{init}} k_N}{2 + (ba)^2 - e^{-ba}} \quad (\text{A8})$$

$$\frac{dS_x}{dt} = 2\alpha k_N (k_N t - 1 + e^{-k_N t}) \quad (\text{A9})$$

and $\phi_{\text{init}} = \pi N_d \int_0^\infty R^2 g(R) dR$ is the initial thiol coverage.

Surface films with a polydisperse island distribution lead to normalized chronoamperometric transients whose shape is most easily analyzed in terms of the following parameters

$$\sigma^* = N_0 \pi a^2 \quad (\text{A10})$$

$$\gamma^* = a k_N / v \quad (\text{A11})$$

which are analogous to the σ and γ parameters that we have defined previously for the isodisperse islands case, and

$$\omega^* = \pi N_0 / b^2 \quad (\text{A12})$$

which is a measure of the polydispersity of the thiol domains in the monolayer.

For a particular choice of σ^* and γ^* , the value of ω^* modulates the chronoamperometric response between the limits corresponding to a uniform film ($\omega^* \rightarrow \infty$) and an isodisperse monolayer ($\omega^* \rightarrow 0$), as illustrated in Figure 9.

As compared with the isodisperse islands model, this new model introduces an additional parameter ω^* and, since no significant improvement in the quality of the fits to experimental data was observed, it was decided to perform our analysis in terms of the former model.

LA001283B