Probability theory of desorption kinetics of self-assembled alkanethiols stabilized with pair interaction

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Abstract

An electrode kinetic theory is presented for the reductive desorption of self-assembled monolayers of alkanethiols adsorbed on a Au(111) surface by taking account of the probability of pair interaction between closest neighboring alkyl chains. The model of the desorption is a honeycomb-arrangement unit of adsorption sites, the center of which is occupied by the alkanethiol to be desorbed. The six surrounding sites are occupied or not by alkyl chains, depending on the pair interaction energy. The probability of de-stabilizing the alkyl chains on the six sites is calculated for all the possible arrangements. On the assumption that the desorption kinetics have an exponential dependence on the potential, a non-linear kinetic equation is derived, from which voltammograms are obtained in terms of the interaction energy and two kinetic parameters. The peak potential varies linearly with the logarithm of the potential sweep rate. With a negative increase in the interaction energy, the desorption wave shifts linearly in the negative direction and it becomes narrower. Voltammograms for alkanethiols with several chain lengths were analyzed on the basis of these variations. The transfer coefficient is determined from the variation of the peak potential with the sweep rate. The pair interaction energy is evaluated from the variation of the peak potential with the chain length. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Alkanethiols spontaneously adsorbed on the gold crystal surface form a monomolecular film with a highly ordered structure [1], called a self-assembled film. The ordered state has been demonstrated by images from STM/AFM techniques [2–4] and grazing angle X-ray diffraction [5,6]. It results from not only the strong adsorption of alkanethiols on the gold but also the interaction between the alkyl chains, overcoming entropic effects. Formation of the ordered structure requires a long time of soaking the gold substrate in a thiol solution, typically 1 day [7–11]. If the diffusion of alkanethiols in the solution to the gold surface was the rate-determining step of the monolayer formation, the time, t, required for covering the surface could be estimated from the equation for chronocoulometry:

\[ q = (2/\sqrt{\pi})F \epsilon^* \sqrt{D} t \]

where q is the charge density of the alkanethiol. The calculation shows that the adsorption should be completed to the monolayer coverage in a few tens of milliseconds. Thus, most of the time of completing the adsorbed layer is spent on reorganization of the adsorbed chains, so that the ordering energy reaches a minimum. The state at the minimum is attained by the balance of configuration, orientation and location of all the adsorbed molecules, which is known as a cooperative phenomenon [13].

Self-assembled films on the gold surface have the following features relevant to adsorption and desorption:
(a) strong adsorption on the gold from the aqueous solution
(b) desorption associated with electrochemical reduction:

$$\text{MS}^- \text{Au} + e^- \rightarrow \text{MS}^- + \text{Au}$$  \hspace{1cm} (1)

where M denotes the alkyl chain.
(c) compact film with slight defects
(d) very slow adsorption kinetics in comparison with rapid desorption
(e) sharp desorption voltammograms

These features should be ascribed to the interactions of adsorbed alkanethiols with the electrode, the other neighboring alkanethiol molecules, and solvent molecules or ions. Features (a) and (c) indicate that the first two interactions are predominant. Of interest are the highly irreversible properties (d, e), which bring about the drastic desorption like a phase transition.

The features of the phase transition-like desorption should be related not only to the equilibrium properties in ordered states but also to kinetic behavior such as the time-variation of adsorption and desorption, [14–17], as exemplified by (d) and (e). The very slow step of the adsorption kinetics suggests that a huge ($10^9 \text{cm}^{-2}$) number of alkanethiol molecules are rearranged and oriented until the total Gibbs energy reaches a minimum. In contrast, the rapid desorption kinetics imply that the molecule is influenced by the close neighbor interaction rather than long-range interaction. Therefore, the desorption kinetics are much simpler than the adsorption kinetics in the context of the interaction.

Several attempts [11,18,19] have recently been made to elucidate the mechanism of the reductive desorption. Unfortunately, the simple desorption kinetics with Frumkin’s adsorption isotherm have not explained the voltammetric behavior successfully [18]. The elucidation of the complication requires phenomenological theory combining nucleation and diffusion [19]. This paper deals with a theory of the desorption of alkanethiols on the Au(111) surface by applying the concept of the probability for the interaction [20] in a honeycomb model.

2. Theory

Charge neutrality associated with electrode reactions is usually satisfied with an excess of supporting electrolytes. However, this is not the case for reaction (1), because the charge neutrality at the oxidized sulfur may be blocked by the orientation of the alkyl chains. In order for reaction (1) to proceed, cations should penetrate the rigid ordered layer to reach the sulfur [21]. Therefore, the first rate-determining step of reaction (1) is the generation of defects in the ordered layer [21]. The reactant in Eq. (1) is not an isolated MS–Au but one of the assembly (MS–Au)$_N$ stabilized by the interaction with a large number of N alkanethiols. Thus, we consider a series of the two processes:

1. kinetics of the generation of the defect to maintain the electric neutrality by the insertion of cations, and
2. the electrode reaction to yield MS$^-$ associated with interactions.

Once the desorption occurs, cations can approach the electroactive site (sulfur) without blocking due to the rigid film. Thus the generation rate of the defect is not a function of the surface concentration of MS–Au, but is related with a degree of thermal fluctuation of the alkyl chains. Since the applied negative potential attracts cations electrostatically to the outside of the film, it can develop the defect which has been generated incidentally by thermal fluctuation. We can predict intuitively that the insertion of cations is increasingly activated by a more negative electrode potential, $E$. A part of the electrode potential, $\alpha'$, may participate in the generation rate of the defect. From the conventional concept of the activation energy, we can express the generation rate as

$$v_1 = k_1 \exp[-\alpha' F (E - E^0)/RT]$$  \hspace{1cm} (2)

where $k_1$ is the rate constant, and $E^0$ is the standard potential of reaction (1).

The electrode reaction rate of a given MS–Au depends on whether the MS–Au has MS–Au or solvent (water) as its closest neighboring molecules, because the energy of the reactant depends on the nature of the neighboring molecules through the interaction. The interaction to be considered is the pair energy for the neighbors (MS–Au)/(MS–Au) and (MS–Au)/(water). Since the former interaction is much lower than the latter, the MS molecule is more likely to be located next to other MS to yield an assembly (MS–Au)$_N$. A theoretical approach to predicting the assembly lies in evaluating the partition function for all the possible combinations of pair interactions as a function of $E$ [15,16]. Unfortunately, the formalism is possible only for the equilibrium state. Since the desorption occurs locally and rapidly, short-range interaction is predominant over the long-range interaction. As the simplest formulation of the closest neighboring interaction, we propose a honeycomb model composed of the seven sites, as shown in Fig. 1. This configuration is in harmony with the surface pattern of the Au(111) active sites. The center of the seven sites is occupied by an MS which is about to desorb. The six surrounding sites are occupied either by molecules of MS or by water.

The rate of reaction (1) is assumed to be a Tafel type:

$$v_2 = k_2 a \exp[(\alpha'' F (E - E^0)/RT]$$  \hspace{1cm} (3)

where $a$ is the activity of the MS which can undergo the charge transfer, and $\alpha''$ is the transfer coefficient. If
there were no interaction, \( a \) might be equivalent to the surface concentration of MS. The explicit form of \( a \) can be derived as follows: we introduce the pair interaction energy \( u_\text{V} \) between the MS and one of the closest neighboring MS, and the pair interaction energy \( u_\text{M} \) between the MS and a water molecule on a vacant site. Let the normalized surface concentration be \( x \), which is equivalent to the probability of locating an MS molecule at any site. Then the configurational probability that the MS at the center is surrounded with six vacant sites (Fig. 1A) is given by \( x(1-x)^6 \). This MS experiences the interaction from six vacant sites to be de-stabilized is given by \( 6x(1-x)^5 \). The factor 6 is the number of events of the instability: \( \exp[(6x(1-x)^5)] \). In general, the configurational probability of surrounding the MS with \( n \) MS molecules and \( 6-n \) vacant sites is given by \( \exp[(6x(1-x)^5)] \). The summation is reduced to

\[
a = \sum_{n=1}^{6} \binom{6}{n} x^n (1-x)^6-n \exp\left[\frac{(6-n)u_\text{V} + nu_\text{M}}{k_B T}\right] \Gamma
\]

The desorption is the two sequential steps, namely expressed by the product of \( v_1 \) and \( v_2 \). The simple product means the independence of the two processes. The independence may be valid except for small values of \( x \) or except for the voltammetric potential domain after the peak. Combining Eqs. (2), (3) and (5), we obtain the kinetic equation for the desorption:

\[
\frac{dx}{dt} = -k e^{-\frac{x}{kT}} \left( x(w+1)^6 \right)
\]

where \( k = k_1k_2 \) for the negative potential sweep, where \( E_i \) is the initial potential and \( v \) is the potential sweep rate. Replacing \( r \) by \( \zeta \), separating the variables and integrating the resulting equation from infinity to \( \zeta \) for the dimensionless potential or from unity to \( x \) for the concentration, we obtain

\[
\int_{\zeta}^{x} \frac{kRT}{Fv} e^{-z} \, dz = \int_{1}^{x} x^{-1}(w+1)^{-6} \, dx
\]

The integrand on the right hand side was rewritten as a sum of the partial fractions, which were integrated term by term. Then we have

\[
\frac{kRT}{Fv} e^{-z} = \ln \left( \frac{xw+1}{w+1} \right) - \sum_{n=1}^{5} \left( \frac{1}{n(w+1)^n} - \frac{1}{n(w+1)^n} \right)
\]

This gives the kinetic relation between the potential and the concentration.

The current density is expressed by \( j = F \Gamma (dx/dt) \). Inserting Eq. (7) into this equation, we obtain

\[
j/FkT = -x(w+1)^6 e^{-\zeta} \]

Eliminating \( x \) implicitly from Eqs. (11) and (12), we obtain the relation of dimensionless current \( j/FkT \) with the dimensionless potential \( \zeta + \ln(zFv/kRT) \) as a function of \( u/k_B T \).

Some kinetic equations for an adsorbed monolayer have been proposed in the context of interaction and phase transition [22,23], and have been reviewed especially for upd [24]. Since these authors are interested in the adsorption and deposition of ions, the analysis is mostly directed to growth of films and diffusion. The basic equation reported so far is of the type: \( dx/dt = -k e^{-x} \). It is different from Eq. (7) in that successive desorption steps have been taken into account.

3. Results and discussion

Eq. (11) was calculated for various values of \( u/k_B T \) and the curves were plotted in Fig. 2. As values of
Fig. 2. Dimensionless linear sweep voltammograms for $u/k_B T = (a) - 0.5$, (b) - 0.4, (c) - 0.3, (d) - 0.2, (e) - 0.1 and (f) 0.0. The arrow indicates the direction of the potential sweep.

Fig. 3. Dependence of the dimensionless peak on $u/k_B T$ (solid curve) computed from Eqs. (11) and (12), and (dotted curve) calculated from the approximate Eq. (14).

Fig. 4. Dependence of the peak potential on $u/k_B T$ (solid curve). The dotted line is from Eq. (15).

$u/k_B T$ decrease, the peak gets sharper, shifting in the negative direction. Since the dimensionless current has the independent variable $\alpha' + \ln(xFv/kRT)$, an increase in $v$ by one decade shifts the peak in the negative direction by $2.3RT/xF$ or 59 mV at 25°C. Thus, $z$ can be estimated from variation of the peak potential with the sweep rate. At $u = 0$, corresponding to negligible effects of the interaction, Eq. (11) becomes

$$jRT/xF^2e^T = - \exp(-z - e^{-z})$$  \hspace{1cm} (13)

where $z = \alpha' + \ln(xFv/kRT)$. This ((f) in Fig. 2) agrees with the equation for the totally irreversible surface wave without any interaction [25].

The peak width at the half height, $W$, was evaluated for various values of $u/k_B T$, as shown in Fig. 3. For $u/k_B T < -1.0$, the width becomes very sharp as $u$ decreases. A decrease in $u$ causes more de-stabilization of the chain/water pair relative to the chain/chain pair. An extreme is a case of $u_M = u_V$ [18]. Then, the gold surface is either completely covered with the film or completely naked. Consequently, the film is desorbed drastically at a given potential, as for a phase transition. From the curve in Fig. 3, it is possible to estimate $u$ from a measured value of $W$ with a known value of $z$. In order to evaluate $u$ conveniently, we obtained an empirical approximate equation:

$$u/k_B T = 0.776 \log\left(\frac{xFW}{RT} + 0.025\right) - 0.366$$  \hspace{1cm} (14)

Fig. 4 shows variation of the dimensionless peak potential $\zeta_p = (E_p - E^0)/RT$ with $u/k_B T$. The stabilization of a chain/chain pair shifts the peak potential linearly in the negative direction. Thus, it retards the electrode reaction like an overpotential. For $u/k_B T < 0$, the peak potential can be expressed approximately by

$$\alpha_p + \ln\left(\frac{xFv}{kRT}\right) = 4.1 \frac{u}{k_B T} + 0.035$$  \hspace{1cm} (15)

The difference in the peak potential $\Delta E$ is related to the difference $\Delta u$:

$$xF(\Delta E) = 4.1N_A \Delta u$$  \hspace{1cm} (16)

where $N_A$ is the Avogadro constant. The factor 4.1 implies that 4.1 chain/chain pairs in effect retard the electrode reaction. This is the average number of surrounding alkanethiol molecules when the current reaches the peak.

We shall apply the present analysis to the experimental results of the desorption voltammograms of $CH_3(CH_2)_nSH$ for $n \leq 17$ [11]. Since all the characteristic values include $z$ as a parameter, we should first evaluate $z$ by the variation of the peak potential with potential sweep rates. The peak potential shifted 70 mV negatively when the sweep rate increased from 2 to 20 mV [11]. From the relation $59/z = 70$ mV, we obtain $z = 0.84$. Since $z$ is the sum $z' + z''$, the value is usual. As alkyl chains were longer, the peaks became nar-
rower. This accords with the variation in Fig. 3. The peak width for \( n = 15 \) and 17 ranged from 15 to 20 mV. Inserting the values of \( W \) and \( z \) into Eq. (14), we obtained \( u = -1.4 \pm 0.1 \text{ kJ mol}^{-1} \). Since this value is the interaction energy of the chain/chain pair, the chain should acquire \( 6u = -8.4 \pm 0.6 \text{ kJ mol}^{-1} \) from the six closest neighbors before the desorption. The absolute value is unfortunately smaller than the enthalpy of fusion even of n-undecane (22 kJ mol\(^{-1}\)) [26]. There are four possible reasons for the smaller value. (A) All the methylene groups do not participate in the chain/chain interaction, especially groups near the sulfur. (B) The determined value is of kinetic significance like the activation energy, while the value obtained in crystallization is for equilibrium. (C) The peak width corresponds to the second derivative of the surface concentration with respect to the potential (the current is the first derivative). It is natural that higher order derivatives should lack accuracy. (D) Values of \( k_1 \) and \( x' \) at the first step of the generation of the defect may vary with \( x \), especially for small values of the surface concentration.

More reliable experimental data come from the variation of the peak potential with the length of alkyl chains. As \( n \) increased, the peak potential shifted linearly in the negative direction with coefficient 15 mV per methylene unit when \( 5 \leq n \leq 17 \) [11]. The linearity can be predicted from the curve in Fig. 4. Inserting \( \Delta E = 15 \text{ mV} \) in Eq. (16), we obtain \( \Delta u = 0.3 \text{ kJ mol}^{-1} \) per methylene. For the alkanethiol surrounded with six other alkanethiols, the interaction energy per methylene unit is 1.8 kJ mol\(^{-1}\). This is smaller than the literature values 2.9 kJ mol\(^{-1}\) [11], 3.8 \( \pm \) 0.8 kJ mol\(^{-1}\) [27,28] and 3.3 kJ mol\(^{-1}\) [29]. The first literature value was obtained by applying the current–potential curve proposed by Angerstein-Kozlowska et al. for oxide formation [30] and by regarding Frumkin’s interaction parameter as the interaction energy, while the value obtained in crystallization is determined value is of kinetic significance like the activation energy. The second was obtained from the thermal desorption of an aliphatic alcohol from platinum. The third was from temperature-programmed desorption of a hexadecanethiol monolayer on Au(111). A reason for the small value is that 4.1 pairs participate in the shift of the peak. Actually, the correction 1.8 \( \times \) (6/4.1) leads to 2.6 kJ mol\(^{-1}\), which is close to the literature values.

The value 1.8 \( \times \) 17 = 30.5 kJ mol\(^{-1}\) for \( n = 17 \) should be consistent with the value \( 6u = 8.4 \pm 0.6 \text{ kJ mol}^{-1} \) obtained by the peak width. Reasons (A) and (B) in the previous paragraph are common to the peak width and the peak shift. The discrepancy may be caused by reason (D).

4. Conclusion

In the present hexagonal model on Au(111), a given alkanethiol to be desorbed interacts with at most six surrounding alkanethiols by the amount of \( \exp(u/k_B T) \) per alkanethiol. Each step of the desorption interacting with one to six alkanethiols has been taken into account. Since the voltammetric shape depends on the course of a reaction rather than the initial and final states, the present model may be more advanced than the model of Angerstein-Kozlowska et al. A key point of the present theory is to evaluate the activity from the probability of the adsorption of the alkanethiols by regarding the surface concentration as the probability.

The route of data analysis is first to determine \( z \) from the variation of the peak potential with the sweep rate, and then to estimate \( u \) from the dependence of the peak potential on the length of alkanethiols.

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