

Measurement of the sticking probability of self-assembled 1-octadecanethiol on polycrystalline Au surface

Ehab AlShamaileh, Department of Chemistry, The University of Jordan, Amman 11942, Jordan
e-mails: ehab@ju.edu.jo , ehabju@gmail.com.

Abstract

The sticking probability of self-assembled 1-octadecanethiol on the surface of polycrystalline Au was measured using cyclic voltammetry. A Langmuir-like adsorption kinetics was observed for the 1-octadecanethiol adsorption on Au at high micro-molar concentrations which became more precursor-like at $7.0\text{-}10.0 \times 10^{-4}$ mM concentrations. At 5.0×10^{-4} mM concentration, the adsorption isotherm revealed an additional feature which could be explained by the initial adsorption of the solvent methanol or one of its by-products and subsequent removal by the strong Au-S bond formation. It could be also explained by the formation of a "lying down" phase of the 1-octadecanethiol on Au surface. This phenomenon was reproducibly observed for the 1-octadecanethiol and results compare well with other methods reported in the literature.

Keywords: sticking probability, self-assembly, 1-octadecanethiol, Au, cyclic voltammetry.

1. Introduction

The most fundamental way to express an adsorption rate constant is in terms of a sticking probability, defined as the probability that a molecule will adsorb upon its collision with a surface. Organic monolayer formation is generally performed by two methods: Langmuir-Blodgett or self-assembly, the latter yielding more stable mono layers [1]. An understanding of the growth and the structures of self-assembled mono layers (SAM's) is a prerequisite for a successful use in technical applications. Such applications include corrosion protection, wetting control, friction and lubrication control, adhesion, use as model systems for surface chemistry, biomolecule immobilisation and non-linear optical applications [2]. Of the wide variety of SAM's studied [1,3], *n*-alkanethiols have attracted the most attention due to their stability, ease of preparation and availability [4]. Alkanethiolate SAM's are densely packed films and their structure has been well established [1]. Kinetics of their assembly from solution have been investigated by a wide range of spatially averaging in-situ and ex-situ techniques [2]. Recent Atomic Force Microscopy (AFM) [5] and Scanning Tunneling Microscopy (STM) [6] studies revealed that assembly occurs in a number of steps: (1) growth of a 'lying down' phase in which molecules are aligned parallel to the surface; (2) 'standing up' island formation of tilt angle $25\text{-}30^\circ$ from the surface normal, and (3) a slow consolidation phase. Evolution of these phases has generally revealed Langmuir adsorption kinetics occurring, in which the growth rate is proportional to the number of unoccupied adsorption sites. Experimental conditions have often precluded observations of the initial phase during assembly from solution [2].

Sticking probabilities are dimensionless with values ranging from 0 to 1. The accurate use of sticking probabilities was, until recently, restricted almost exclusively to adsorption from the gas phase, in which initial sticking probabilities of alkanethiols on low index gold faces approached unity [7]. A more recent report by Jung and Campbell employed the gas phase adsorption equation for sticking probability determination for alkanethiol assembly from ethanol on thin Au films, monitored by in-situ Surface Plasmon Resonance (SPR). Initial sticking probabilities were shown to range from 10^{-8} to 10^{-6} for alkanethiol chains possessing 3 to 19 carbons, accounting for diffusion depletion in a quiescent assembly solution [8].

Copper underpotential deposition (upd) onto Au low index surfaces by cyclic voltammetry has been well-established [9]. Copper upd forming [10] and fully formed [11] SAMs has revealed a blocking capability of the SAM towards copper and this feature is utilised in this paper. Unlike the STM analysis of copper deposited during SAM assembly by Sun and Crooks [10], a more straightforward analysis of copper deposited was performed in this work. Sole use of the versatile, convenient and relatively inexpensive technique of cyclic voltammetry, compared to the more sophisticated SPR technique,

permitted the evaluation of sticking probability under a range of different conditions for the 1-octadecanethiol assembly at room temperature from methanol onto a polycrystalline Au electrode.

2. Experimental

2.1 Materials and Apparatus

Doubly distilled water was used in all preparations. All chemicals used in this study were of the highest purity possible. Sulfuric acid (95-97%, Allied Signal), KMnO_4 (99.8% purity, Aldrich), H_2O_2 (30%, Aldrich). All glassware was submerged and soaked overnight in a concentrated sulfuric acid- KMnO_4 mixture and then rinsed thoroughly and partially filled with doubly distilled water. Glassware was placed on a heating block to boil for one hour allowing a steaming process to remove any trace acid wash.

The three-electrode electrochemical cell was placed on a specially constructed conical flask with a narrow neck, partially filled with doubly distilled water. Steam was allowed to pass through the cell for around forty-five minutes. Glassware was filled with doubly distilled water and covered until use during the experiment and the process was repeated as required during the work. All electrochemical experiments were performed in a two-compartment conventional three-electrode Pyrex glass cell constructed according to designs in the literature. One compartment of the cell contained the polycrystalline Au rod as the working electrode (Goodfellow, Cambridge, UK). A 0.25 mm diameter of 99.999% pure Pt wire (Goodfellow, Cambridge) supported on a Teflon plug connected to a Pt mesh was used as the auxiliary electrode. The second compartment contained a 99.999% pure Cu wire (Goodfellow, Cambridge) as the reference electrode.

All electrode potentials were measured and are quoted against the $\text{CuO}/\text{Cu}^{2+}$ reference electrode. The supporting electrolyte used in all electrochemical reactions was 0.1 M H_2SO_4 , prepared using ultra pure grade sulfuric acid (99.99% purity, Aldrich). The 1 mM Cu^{2+} solution was prepared by dissolving 0.0624 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.99% purity, Aldrich) in 250 cm^3 of 0.1 M H_2SO_4 . The electrolyte in the working and counter electrode compartment was de-oxygenated for 10 minutes, followed by de-oxygenating the reference electrode compartment for 10 minutes and finally the working and counter electrode compartment for a further 5 minutes with high purity N_2 gas (National Gas Company, filtered through a Supelco filtering system). The solution was blanketed using the high purity N_2 gas during all readings through the use of a N_2 flow-rate low enough so as to avoid noise creation but high enough as to facilitate rattling of a glass stopper placed in the working electrode cell compartment. The alkanethiol used was obtained from Aldrich and used directly without further purification.

Stock solutions were prepared in the fume hood using HPLC grade methanol (99.9% purity, LabScan) from which serial dilutions were accordingly prepared. 0.1 M 1-octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$) (99% purity, Aldrich) such that due to the lower apparent solubility stirring on a hotplate and sonication (at 35 °C) has been applied. HPLC grade methanol was never reused but discarded into a non-chlorinated waste container. Diluted alkanethiol solutions were used as dipping solutions in the preparation of self-assembled mono layers, such that all beakers and volumetric flasks were rinsed with HPLC grade methanol prior to stock or dilution preparation and uptake experiments.

A cumulative dipping method was performed in each experiment in which the electrode was initially flame-annealed only at the start of each run. The Au electrode was extracted from the electrolyte, dipped in the dilute alkanethiol solution while stirring as constantly and rapidly as possible without touching the Au sample off the assembly beaker walls for a defined period recorded using a digital timer, washed immediately for a few seconds with doubly distilled water then immersed in the electrolyte. In the dipping interval, a glass stopper was placed onto the working electrode compartment in an effort to prevent atmospheric air overcoming the N_2 flow out of the cell and the cyclic voltammogram was commenced immediately.

To assist the reproducibility of electrode area in contact with the electrolyte, the insulating outer layer of the working electrode crocodile clip was fixed to the Teflon plug by an adhesive tape without contacting the metal clip or the Pt wire leading to the Au sample. The polycrystalline Au electrode with a strong Au(111)-like surface was cleaned each time the electrochemical cell was cleaned using a two step methods. The first step involved the flame annealing and subsequent immersion in concentrated nitric acid (69% purity, Analar grade, Allied Signal) removing Cu deposits which could alloy with the Au sample on subsequent flaming and was then rinsed in doubly distilled water using a blue flame. The electrode was heated to ~ 1000 K by passing it through the flame so the electrode spent no more than 1 second in

the flame in each passing until it just glowed red. The electrode was then cooled under a stream of N₂ for a long period until it was assumed to have cooled to room temperature such that it was believed that the electrode would first cool rapidly from ~1000 K to ~380 K and then slowly to room temperature.

The second electrochemical step involved the investigation of the contamination from glassware or electrolyte solution by flame annealing and cooling the Au sample, running a couple of cyclic voltammograms, leaving the sample in meniscus contact but at a potential that no Cu adsorbs (+550 mV for 10 minutes) and any organics would slowly adsorb, so when the cyclic voltammograms were re-run the integrated area would decrease and the shape of the cyclic voltammogram would change. Initial cyclic voltammograms after flame annealing exactly reproduced those after a long quiet time. Where the cell was not washed prior to an alkanethiol uptake run, the first cleaning step (flame annealing) was performed only. At the end of each daily analysis of Cu uptake, the electrode was flame annealed and scanned by cyclic voltammetry ensuring a typical Cu adsorption/desorption cyclic voltammogram and was revealed prior to storage in doubly distilled water overnight. The copper reference electrode was cleaned by a quick immersion in a separate concentrated nitric acid beaker to that used to clean the Au sample, and then rinsed immediately with doubly distilled water.

Cyclic voltammetry was performed using a Voltalab-10 potentiostat (Radiometer, France). General parameters employed for Cu upd/probing experiments were: initial potential: 550 mV; upper potential limit: 550 mV; lower potential limit: 0 mV; scan rate: 20 mV.s⁻¹; number of segments: 2; initial direction: negative; quiet time: 5 s; sensitivity: 10 mA/V. For Cu uptake experiments or Au oxidation/reduction cycling, the same analyses as above were employed, except different potentials were scanned as indicated on the abscissa of voltammograms. For Cu uptake experiments, only 0.1 M H₂SO₄ was present in the cell. The initial sticking probability of 1-octadecanethiol was measured by following the change in the fractional coverage of the 1-octadecanethiol molecule at different concentrations taking into account the possible diffusion depletion during the solution phase assembly using the electrochemical method of copper underpotential deposition (Cu *upd*) with sulfate co-adsorption or sulfate anion deposition.

2.2 Data analysis

Cyclic voltammograms were produced and treated using the software provided by Voltalab-20. Microcal™ Origin data analysis software was used to treat all results. Absolute integrated areas at positive and negative sides of the zero current line between the potentials limits of 0 mV and 550 mV were obtained. Subsequent processing of the integrated areas involved normalising, i.e. the highest initial area made equal unity, and lower subsequent areas calculated relatively; averaged normalised area between replicate runs plotted against the corresponding averaged dipping times and areas used to determine the average fractional coverage of alkanethiol adsorbed on the Au surface, assumed to be inversely proportional to the Cu deposition/desorption peak area (i.e. the blocking of copper interaction signal with Au decreasing with increasing alkanethiol adsorbed. Fractional coverage was calculated using the equation [8]:

$$\text{Fractional coverage}_{t=n} = \left(\frac{\text{Integrated area}_{t=0} - \text{Integrated area}_{t=n}}{\text{Integrated area}_{t=0}} \right) \times \left(\text{Coverage of one alkanethiol monolayer} \right)$$

where the coverage of one monolayer was assumed to be 4.8×10^{14} alkanethiol molecules.cm⁻² [8]. Averaged normalized areas and fractional coverages were then plotted against the corresponding average dipping times. A polynomial was fitted to the data points whose equation was employed to obtain fractional coverage, and through differentiation, the slope at any dipping time. The slope equaled the rate of adsorption (R_{ads}) and was converted from molecules.cm⁻².s⁻¹ into moles.m⁻².s⁻¹. The latter was used to calculate the sticking probability (S) of alkanethiol onto the Au surface at any dip time where the initial sticking probability at time zero is denoted S_0 using the following equation [8]:

$$S = \frac{R_{ads}}{J_s} = \frac{R_{ads}}{C_s} \sqrt{\frac{2\pi m}{k_B T}}$$

where J_s = collision frequency, i.e. the number of specific alkanethiol molecules assuming negligible impurities which collide with the surface per second per unit area; C_s = the concentration of the solute in that liquid nearest to the electrode surface (moles/m³); k_B = Boltzmann's constant (1.3807×10^{-23} J.K⁻¹); T = temperature (assumed 298 K); m = mass of alkanethiol surfactant (kg/atom). Ensemble averaging of normalized area and fractional coverage data decreased the signal to noise ratio by \sqrt{n} where n is the number of runs averaged.

3. Results and Discussion

Figure 1 illustrates a set of cyclic voltammograms obtained for periodic Cu underpotential deposition (*upd*) during the adsorption 1-octadecanethiol (C_{18} -SH) at different dipping times. Hagenstrom *et al.* [12] and Oyamatsu *et al.* [11] detailed the kinetic hindrance effects of such adsorption. The disappearance of the absolute area under the curve was monitored as well as the area of the underpotential deposition peaks due to the difficulty of deposition/desorption peak separations.

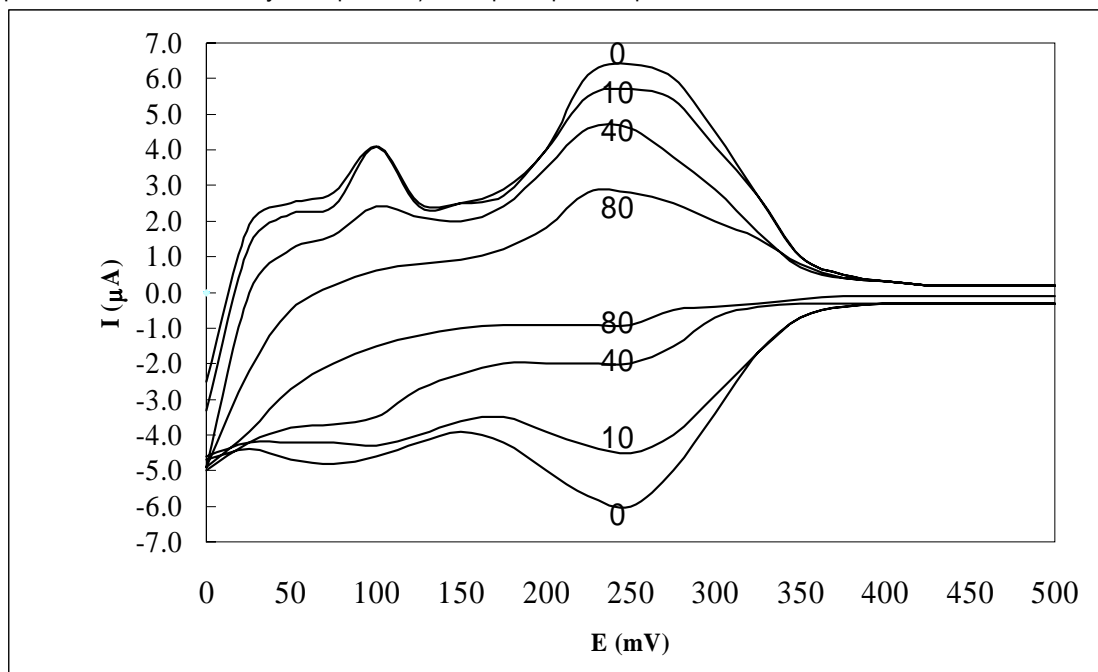


Figure 1. Cu *upd* cyclic voltammograms of 3×10^{-3} mM 1-Octadecanethiol on polycrystalline Au at dipping times of 0, 10, 40 and 80 seconds.

The averaged normalized integrated areas for the CV at different dipping times were evaluated and plotted in figure 2. It is clear that the monolayer formation starts around 40 seconds of dipping. These data were utilized to calculate the average fractional coverages.

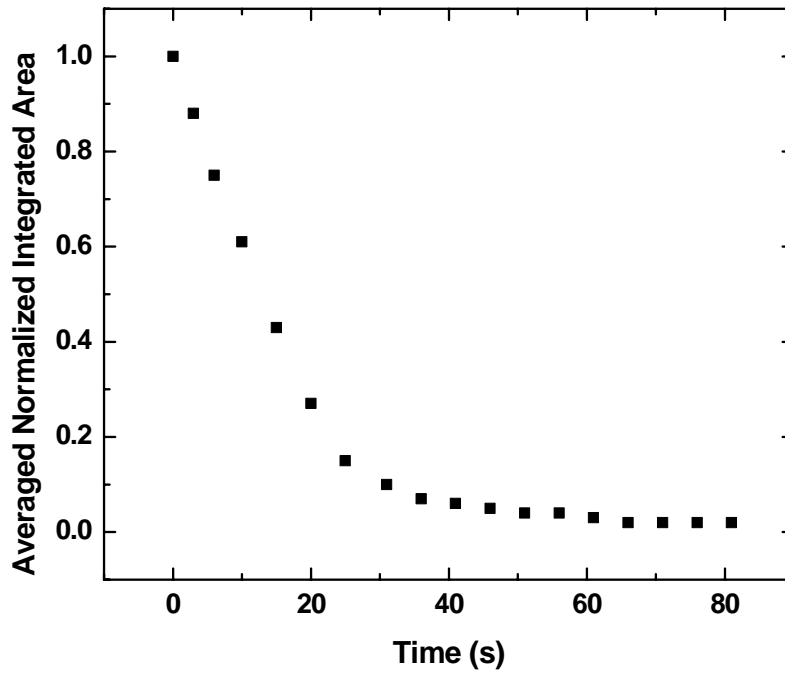


Figure 2. Average normalized integrated area as a function of dipping time.

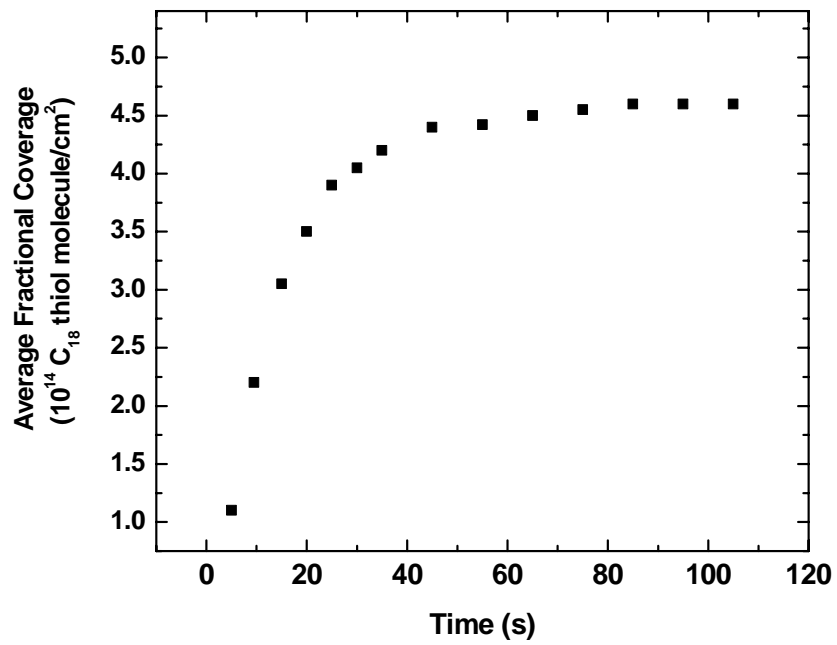


Figure 3. Average fractional coverage as a function of dipping time.

Figure 3 shows the fractional coverage function with time which appears to be in direct proportion similar to that found by Karpovich and Blanchard [13] who studied C₁₈-SH uptake from *n*-hexane, thus adopting

a Langmuir adsorption kinetics. A polynomial was fitted to the data as it endured easier integration than a Langmuir model. It can be seen that rapid initial near monolayer formation occurred followed by a slower rearrangement/crystallization process leading to a more consolidated monolayer and little coverage change [1].

The CV at dipping time of 80 and longer dipping times (not shown on the figure) revealed that the Cu *upd* signal never depleted completely but was still apparent in the nano-ampere range (nA) as was the case for all Cu probing uptake runs, probably due to a low density of pinhole defect sites as once suggested in the literature [14]. Saturation coverages were generally reached for all uptake runs at approximately 4.6×10^{14} Thiol molecule/cm² which is close to 95% of the full monolayer formation. All polynomials fitted to fractional coverage versus time data had high correlation coefficients ($R^2 > 0.99\%$) such that they were generally preferred to Langmuir model fits due to applicability and ease of differentiation.

Error bars in the area/fractional coverage versus time plots were based on the deviation in the averaged replicate run data (three or more) and the reproducibility of dip height. Where only two runs were performed, a third area (the average) was included to calculate a standard deviation value. Averaging facilitated a decrease in the S/N ratio permitting less the influence of outlying points on the sensitive polynomial. Polynomial undulations produced at high dipping times were abandoned by selection of data close to the time at which near relative saturation coverage occurred. Fractional coverage data up to 50 seconds were employed to calculate the sticking probability which is illustrated in Figure 4, in which near linear associative Langmuir adsorption was followed up to ~ 3 to 4×10^{14} C₁₈ thiols/cm², followed by a second consolidation step.

Jung and Campbell [8] have found a similar S (sticking probability) versus θ (fractional coverage) plots for mM alkanethiol adsorption from ethanol. It was noticed immediately that unlike S_0 values from gas phase alkanethiol adsorption approximating unity [7,15], S_0 was approximately six orders of magnitude lower. This may be the result of large gas to liquid viscosity differences, a methanol solvation shell surrounding the alkanethiol, and the influence of methanol molecules which need to be physically displaced from the surface by incoming alkanethiol molecules.

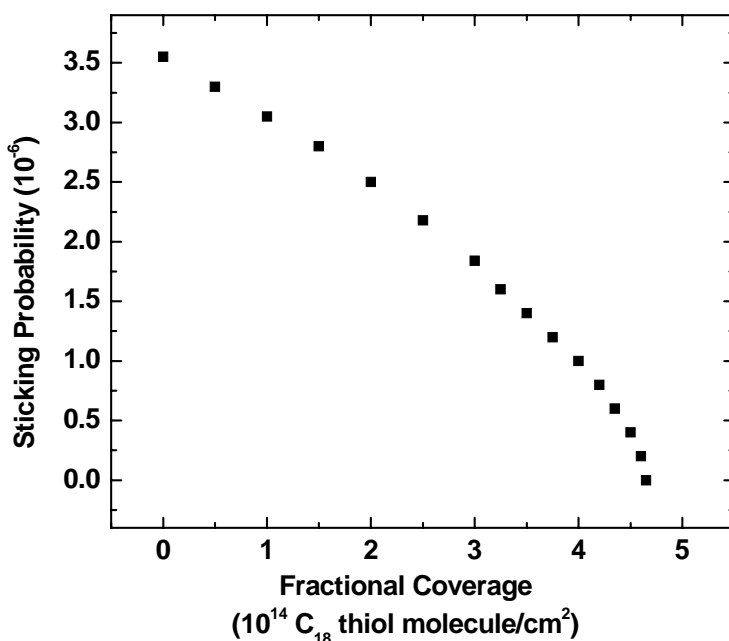


Figure 4. Sticking probability versus fractional coverage for the 1-octadecanethiol on Au.

The heat of desorption of a methanol molecule on a Cu(111) surface was estimated by density functional theory as 34.7 kJ/mol [16], such that displacement of one or two methanol molecules could cause S_{liquid}

to decrease to 8.27×10^{-7} or 6.84×10^{-13} of that S_{gas} value, respectively. This decrease was an estimate from theory, such that at 30 kJ/mol, $S_{\text{liquid}} = 5.51 \times 10^{-6} \times S_{\text{gas}}$. The activation energy of methanol desorption from Au(110) was estimated as 58 kJ/mol [17], translating to $S_{\text{liquid}} = 1.56 \times 10^{-9} \times S_{\text{gas}}$. These are merely simple estimates used in an effort to explain such a large decrease in S_0 observed here and by Jung and Campbell [8].

The 3×10^{-3} mM solution was then diluted to 2×10^{-3} mM C_{18} -SH. For the diluted slow blocking up to 15 seconds was observed leading to a large unexpected S increase (from $S_0 \sim 10^{-3}$) as the electrode initially offered the largest surface area. Three individual runs were performed and showed similar behavior. A sensitive polynomial thus yielded an S versus θ curve which behaved unlike even precursor state adsorption isotherms [18]. This behavior may have been due to (1) contaminant presence e.g. in glassware [5,19,20], (2) temperature variations in the electrode at early stages of uptake analysis or (3) thiol molecule break-up at special defect sites like kinks (dissociative adsorption). Thus, although thiol molecules hit and stick, because they break up, they do not block Cu *upd* like a full thiol molecule does. A Langmuir adsorption isotherm with near-linear S decrease versus θ up to 55 seconds dipping time was observed. This adjusted data was normalized with respect to time and fractional coverage, and was included in subsequent concentration versus S_0 profiling.

Analysis of 1×10^{-3} mM and 6.67×10^{-4} mM revealed non-Langmuir adsorption, but precursor state like kinetics [21]. Polynomial fitting revealed a more severe S increase initially with θ compared to the precursor adsorption recorded by Kreuzer [18]. At each of these concentrations, a linear trend line could almost be fitted up to ~ 80 and 100 seconds, respectively, which would result in S constancy prior to a sharp decrease towards the end. Precursor adsorption has not yet been shown in the literature for straight chain alkanethiol adsorption from solution/gas phases, but was proposed by Whelan *et al.* [22] for the formation of two dimensional benzenethiolate islands assembled from gas phase on Au(111) on increasing benzenethiol exposure. It was accepted that the technique in this work was subject to more noise and less accuracy in the data collected than by the use of *in-situ* techniques like SPR spectra which have been sampled at a rate of up to 300/minute [20]. However, the polynomial closely followed averaged data points picking up a small decrease in S at the start of assembly.

At 5×10^{-4} mM C_{18} -SH, this apparent initial S decrease became more noticeable, *i.e.* a linear Langmuir-like S decrease with θ , to $\sim 1.3 \times 10^{14}$ C_{18}/cm^2 followed by a similar S vs. θ shape as observed previously. Two possibilities were proposed for this occurrence: (1) the effect of methanol on the uptake becomes more apparent as the C_{18} -SH concentration is lowered and (2) an additional lying down phase formation occurred at the lower μM thiol concentration as has been more commonly observed for gas phase alkanethiol adsorption [4], and more recently reported by others from solution [5,6,23].

Using STM monitoring of decanethiol growth on thin Au film from heptane Uamada and Uosaki [23] revealed that at 3 μM the lying down phase was hardly observed and standing up islands covered the surface quickly which could support the lying down phase absence here at higher concentrations. Also at 0.2 μM decanethiol, island formation was suppressed facilitating STM investigation of the low coverage phases. At 0.5 μM decanethiol, stripe lines were observed but standing up phase STM imaging was not possible due to an insufficient tunneling gap impedance and the structure being destroyed by the tip. An 'S' shape in S versus θ was reproduced at a lower concentration in duplicate and runs performed on concentrations down to 5×10^{-4} mM were prepared from serial dilution of the 3×10^{-3} mM solution originally prepared, unlike the 2×10^{-4} mM solution which produced relative block times out of line with those expected. Figure 5 shows data at 2×10^{-4} mM C_{18} -SH. An inverse relationship between concentration and rate constants for adsorption has been employed similar to that reported by other research groups [6,24].

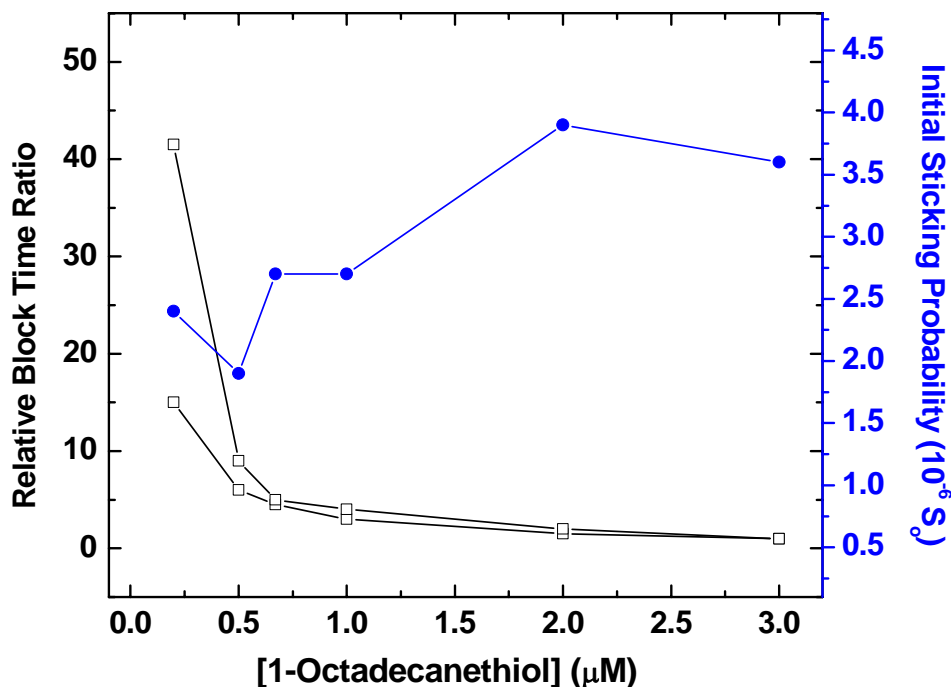


Figure 5. Expected and calculated relative block times versus 1-octadecanethiol concentration and change in the initial sticking probability versus concentration. Lines with square points represent the relative block time ratio and lines with circles represent the initial sticking probability.

Results of figure 5 were compiled by best eye-fit polynomial fitting and on the basis of highest correlation coefficient to data of each individual run. From 6.67×10^{-4} mM to 3.0×10^{-3} mM, 50% relative block time was found experimentally, generally at half of $\sim 4.6 \times 10^{14}$ molecules/cm² saturation coverage, which agreed well with those expected and calculated by inversely scaling up the 12 second average 50% relative block time at 3×10^{-3} mM, linearly with concentration although a small difference occurred at 5×10^{-4} mM (Figure 5), possibly due to a small plateauing effect, not observed at other concentrations.

S_0 at concentrations $< 2 \times 10^{-3}$ mM appeared to continually decrease to 5×10^{-4} mM, suggesting that in weaker solutions, the thiol concentration close to the Au surface may have been depleted to a small extent, *i.e.* the concentration assembled from, may not have been that of the bulk solution but of the solution close to the gold surface depleted in thiol.

It should be noted that thiol uptake from serially diluted solutions would presumably have some effect on this analysis. At each concentration analyzed, loss of $\sim 0.76\%$ (after 2 runs) to $\sim 1.15\%$ (after 3 runs) of the initial alkanethiol number of moles was incurred. Not accounting for alkanethiol coating of higher electrode areas during dipping, such that greater thiol loss would occur at successively lower concentrations whose block times were then compared to analysis of a solution in which no thiol loss had occurred. Methanol and ethanol have viscosities of 0.60 and 1.20 mNsec.m⁻², respectively [24,25]. S_0 was calculated as $\sim 1 \times 10^{-6}$ for C₁₈-SH adsorption at room temperature from ethanol accounting for diffusion depletion [8]. According to the inverse linear rate constant versus viscosity relationship by Dannenberger *et al.* [24], S_0 may be increased to $\sim 2 \times 10^{-6}$ to approximate the average S_0 value of 3.54×10^{-6} at 3×10^{-3} mM measured here. This further supports the absence of depletion at higher C₁₈-SH concentrations, where the rate at which depletion occurs appears to be slower than the speed at which the sample is moved in the assembly solution.

Finally, A preliminary analysis of the C₁₈-SH assembly onto the single crystal surface of Au(111) electrode from methanol resulted in large error bars in the data and were believed to have arisen from imperfection of crystal quality or problems with meniscus contact or electrode cleanliness. Therefore, polycrystalline Au data appear to be more convincing than the Au(111) and more research into this issue is recommended.

4. Conclusions

It has been demonstrated that the sticking probability of an alkanethiol can be calculated using the technique of cyclic voltammetry. The adsorption behavior of thiols on the surface of polycrystalline Au is shown to be highly dependent on its concentration and on the solvent interactions.

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