

## Notes

## Kinetics of Alkanethiol Adsorption on Gold

W. Pan,<sup>†</sup> C. J. Durning,<sup>‡</sup> and N. J. Turro<sup>\*,†</sup>

Department of Chemistry and Department of Chemical Engineering, Materials Science and Mining, Columbia University, New York, New York 10027

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## 1. Introduction

The molecular self-assembly of long-chain alkanethiols (HS(CH<sub>2</sub>)<sub>n</sub>X) on Au has drawn considerable attention during the past decade.<sup>1–5</sup> Such assembly results in surface monolayers with order comparable to Langmuir–Blodgett (LB) films. The end functional group X populates the outer surface of the layer, so that by manipulating X, substrates with designed surface chemistry can be obtained.<sup>6–9</sup> These provide model systems for studying wettability, surface reactions, adsorption, and adhesion.

While there has been considerable work on the structure and properties of equilibrated alkanethiol assemblies on Au, there have been relatively few studies of the kinetics of the formation process. Although gas phase deposition processes are of interest, alkanethiol self-assembly from liquid solution is the more common method of preparation and is the focus here. Previous works on the subject are not entirely consistent. Bain et al.<sup>3</sup> studied layers of octadecanethiol formed from quiescent ethanol solutions at room temperature for bulk concentrations,  $c_b$ , ranging from 10<sup>-4</sup> to 1 mM. The adsorption kinetics were followed *ex situ* by measuring the layer thickness via ellipsometry and the wettability of the layer by contact-angle measurements. The data for  $c_b > 0.1$  mM<sup>10</sup> indicate that a monolayer develops in two stages: In the initial stage, there is fast growth of the film thickness to 80–90% of the final value, typically within a few minutes; following this is a slow process in which both the thickness and wettability approach the equilibrium value in about 10–20 h. Bain et al. proposed that, at first, an imperfect, partial molecular assembly forms and this relatively disordered structure reorganizes in the second stage into a more perfectly ordered monolayer. The kinetics were sensitive to the bulk concentration,  $c_b$ , with both the thickness and the wettability showing large induction times (10–100 min) for  $c_b < 0.1$  mM.<sup>10</sup> The kinetics

were also sensitive to preadsorbed contaminants, which retard the process, presumably because displacement is required.

Quartz crystal microbalances (QCMs) have been used more recently to study the layer formation process *in situ*. Shimazu et al.<sup>11</sup> studied layers formed from stirred ferrocenylundecanethiol in hexane at room temperature for  $c_b = 0.5$  mM and found results reminiscent of Bain et al.'s:<sup>3</sup> 40–50% of the adsorption occurred very rapidly, within ~10 s. This was followed by slow adsorption, completing in about 10–100 min. The total frequency shift suggested a monolayer formation. Karpovich and Blanchard et al.<sup>12</sup> studied two alkanethiols, octadecanethiol and octanethiol, adsorbing from stirred hexane and cyclohexane solutions at room temperature, over a broad range of compositions (10<sup>-3</sup> to 10<sup>-1</sup> mM). They reported quite different observations from those of Shimazu et al.: The adsorption of both thiols from either solvent was very rapid, apparently complete within seconds, and there was no subsequent long time-scale process. They verified that a monolayer of alkanethiol was formed using infrared reflection and showed that the kinetics were adequately described by the simple reversible Langmuir adsorption model.

Schneider and Buttry et al.<sup>13</sup> also studied the adsorption kinetics of an alkanethiol on gold *in situ* using a QCM, but they did so under potential control in an electrochemical cell with a background of electrolyte. The work showed that the kinetics depend strongly on the solvent. They studied dodecanethiol adsorption from dimethylformamide and acetonitrile at room temperature over a broad range of bulk concentrations (10 μM to 10 mM) with 0.1 M tetrapropylammonium perchlorate electrolyte. In acetonitrile, a multilayer of up to 15 layers formed first, followed by a relatively slow (~10 h) reorganization, which eventually led to monolayer formation. When adsorbed from dimethylformamide under the same conditions, no initial multilayer formation was observed, and the adsorption process was much more rapid, resembling that seen by Shimazu et al.<sup>11</sup> There was no clear mechanistic explanation advanced for the rather dramatic solvent effect. Using *ex situ* measurements of mass loading via a QCM, Bard et al.<sup>14</sup> reported results very different from those of Bain et al.,<sup>3</sup> Shimazu et al.,<sup>11</sup> and Karpovich and Blanchard.<sup>12</sup> They studied octadecanethiol adsorption on Au from solution in ethanol (1 mM) and reported that it took ~O(100 min) to form, and prolonged contact (> 10<sup>3</sup> min) led to multilayers.

The discrepancies among these reports may reflect artifacts of the different experimental techniques used (e.g. differences in Au surface preparation or whether *in situ* or *ex situ* methods were applied to track the kinetics) or the inherent sensitivity of alkanethiol adsorption to solvent, and external hydrodynamic conditions. They are sufficient to raise the following questions: (1) Does exposure of "clean" Au to alkanethiol solutions at room temperature lead to spontaneous formation of monolayers, or to multilayers? (2) What is the time scale for the

<sup>†</sup> Department of Chemistry.<sup>‡</sup> Department of Chemical Engineering, Materials Science and Mining.(1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.(2) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45.(3) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.(4) Tupper, K. J.; Colton, R. J.; Brenner, D. W. *Langmuir* **1994**, *10*, 2041.(5) Mar, W.; Klein, M. L. *Langmuir* **1994**, *10*, 188.(6) Erdelen, C.; Haussling, L.; Naumann, R.; Ringsdorf, H. *Langmuir* **1994**, *10*, 1246.(7) Tsukuk, V. V. *Langmuir* **1994**, *10*, 996.(8) Carey, R. I.; Folker, J. P.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2228.(9) Rowe, G. K.; Creager, S. E. *Langmuir* **1994**, *10*, 1186.(10) For the kinetic experiments in ref 3, bulk concentrations  $\geq 0.1$  mM provided an essentially infinite supply of thiol for adsorption; i.e., the bulk concentration can be considered constant during the process. For bulk concentrations below this range, significant depletion of thiol from the bulk occurs during adsorption, affecting the adsorption kinetics.(11) Shimazu, K.; Yag, I.; Sato, Y.; Uosaki, K. *Langmuir* **1992**, *8*, 1385–1387.(12) Karpovich, D. S.; Blanchard, G. J. *Langmuir* **1994**, *10*, 3315.(13) Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391.(14) Kim, Y.-T.; McCarley, R. L.; Bard, A. J. *Langmuir* **1993**, *9*, 1941.

**Table 1. Contact Angles<sup>a</sup> of Water and Hexadecane (HD) on Au and Alkanethiol-Coated Au**

surface	$\theta_{\text{H}_2\text{O}}$	$\theta_{\text{HD}}$
Au—as received	76.5	<i>b</i>
Au—cleaned	15.5	5.5
Au/HS(CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub>	103.0	28.5
Au/HS(CH <sub>2</sub> ) <sub>11</sub> OH	13.0	5.0

<sup>a</sup> Average value for four measurements using procedure B in ref 3. <sup>b</sup> Acceptable droplet could not be produced.

adsorption process? (3) Do the adsorption kinetics follow a simple law (e.g. reversible Langmuir kinetics)?

We report here new kinetic data on two alkanethiols adsorbing from ethanol using a QCM *in situ* which address these questions. To answer the first question, a calibration of the QCM is carried out, using a series of viscous fluids. This enables accurate calculation of the equilibrium absorbance from the ultimate frequency shift and a judgement of whether multilayer or monolayer coverage is achieved. For both systems, the ultimate coverage corresponds to about 1.2 monolayers. Regarding the remaining questions, nonlinear least squares fittings of real-time frequency shift data are carried out. The frequency shifts during adsorption follow a simple exponential relaxation, suggesting Langmuir kinetics. This agrees with the observations by Karpovich and Blanchard,<sup>12</sup> but we find rate constants 2–3 orders smaller than those in their study.

The next section gives the key experimental details, including characterization of the Au surfaces by contact-angle measurements. Following that we discuss calibration of the QCM. Then the frequency shift data are presented and analyzed. Finally the results are discussed in light of previous work.

## 2. Experimental Section

**2.1. Materials.** 1-Dodecanethiol (HS(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>) was purchased from Aldrich. 11-Mercaptoundecanol (HS(CH<sub>2</sub>)<sub>11</sub>OH) was synthesized and purified according to the procedure reported in ref 3. Anhydrous absolute ethanol from Pharmaco Products Inc. was used as the solvent for the alkanethiol solutions. A series of alkanes (hexane, isooctane, dodecane, tridecane, pentadecane, hexadecane, heptadecane) were purchased from Aldrich and used as received for calibration of the quartz crystal microbalance.

AT cut, plano-plano quartz crystal plates with opposing surface electrodes were supplied by International Crystal Manufacturing (Oklahoma City, OK) with a nominal resonance frequency of 10 MHz. The crystal surfaces were “overtone” polished to remove large scale roughness. The vapor-deposited electrodes were 135 Å of Cr beneath 1500 Å Au. The diameters of the crystal and electrodes were 1.5 and 0.5 cm, respectively.

The as-received crystals were rinsed first with several aliquots of ethanol and then deionized water, before immersion in 1:3 (v/v) H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> (“piranha” solution<sup>15</sup>) for 5–10 min at room temperature. They were subsequently rinsed thoroughly in deionized water and then ethanol and finally dried with argon. The cleaning protocol was carried out on each crystal immediately before its use.

To check the effectiveness of cleaning, we did contact-angle measurements on the Au surfaces before and after the procedure. The contact angles of water and hexadecane (HD) were measured by procedure B in ref 3 using a contact-angle goniometer (Rame-Hart Inc., Mountain Lakes, NJ); Table 1 shows the results. Before cleaning, the Au surfaces are clearly hydrophobic, indicating the presence of adsorbed organic contaminants, while after cleaning, the surfaces become hydrophilic, indicating contaminant removal. Our contact angles lie below the typical range reported in ref 3 for “clean” Au.

**2.2. Quartz Crystal Microbalance (QCM).** The microbalance used was an Elchema model EQCN-500 (Potsdam, NY),

(15) “Piranha” solution reacts violently with many organic materials and should be handled with great care.

whose feedback-loop oscillation circuit outputs the working crystal's resonance frequency relative to an internal reference oscillator. The output is read by a frequency counter (Phillips, Model PM6673) interfaced to an IBM PC AT equipped with a data acquisition board (Metra-byte, Model MBC-488) sampling the output at 10 Hz. A point grouping technique was used to smooth the output over prescribed intervals.

The working crystal is mounted in a thermostated (25 ± 0.1 °C) glass cell between opposing O-ring seals, similar to the cell described in ref 16. The electrodes were connected to the circuit by short (<10 cm) shielded leads terminated with spring clips. The oscillation circuit and cell are housed in a Faraday cage.

The typical stability of the balance with the cell filled with liquid solvent (alkanes, various alcohols), including pure EtOH, is ±1 Hz over time scales ~1 h and about ±5 Hz over times scales ~24 h. We did *not* find exceptionally large fluctuations for contact in EtOH, as reported in ref 12.

**2.3. Procedures.** To monitor the adsorption process *in situ* in the QCM, the following procedure was adopted. After cleaning and mounting the crystal in the cell, the output frequency for the crystal against air was recorded for 1–2 h to establish a stable baseline. Then, a small amount of ethanol (~0.05 mL) was introduced into the cell. After the frequency restabilized, 1 mL of 5 mM alkanethiol in ethanolic solution was added. The frequency output was recorded continuously during the process. Transfer of liquids into the cell was done using glass syringes with Teflon-tipped needles; every effort was made to minimize the mechanical disturbance involved.

As an independent check of alkylation, a separate set of crystals were coated for contact-angle measurements. Cleaned crystals were immersed in the ethanolic solutions for 24 h at room temperature, rinsed with ethanol and deionized water, and finally dried with an Argon stream. Table 1 lists the contact angles on the coated surfaces. The contact angles of water (13.0) and HD (5.0) on HS(CH<sub>2</sub>)<sub>11</sub>OH-treated surfaces are in agreement with those reported for the same alkanethiol in refs 3 and 17, ≤15. For the HS(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>-treated surface, our values also compare well with the literature values:<sup>17</sup> 113 and 98 for advancing and receding contact angles of water, respectively, and 45 and 30 for those of HD. The data confirm an effective alkylation with both alkanethiols.

## 3. Results and Discussion

**3.1. QCM Calibration.** The deposition of a thin rigid overlayer with areal density  $A(\text{g}/\text{cm}^2)$  onto a resonating crystal increases its inertia and lowers the resonance frequency by  $\Delta f_M$ ; Sauerbrey<sup>18</sup> derived

$$\Delta f_M = -a\beta A \quad (1)$$

where  $a = 2\pi f_s [T^{-1}]$  and  $\beta = f_s/\pi Z_d [L^2/\text{M}]$ , with  $Z_d$  being the acoustic impedance of quartz ( $8.839 \times 10^5 \text{ g}/(\text{cm}^2 \text{ s})$ ). Sauerbrey's equation has been verified for  $\Delta f_M$  measured in feedback-loop oscillators to within a prefactor ~O(1); i.e., one should consider the “sensitivity”  $\beta$  as an instrument constant varying somewhat with the fixtures and feedback circuit used.

When a resonating crystal contacts a Newtonian liquid, the crystal's effective inertia also increases, since the vibrating crystal drags liquid in a narrow boundary layer near the surface. Kanazawa and Gordon<sup>19,20</sup> first calculated the frequency shift because of this damping,  $\Delta f_D$ , for hydrodynamically smooth crystals,<sup>21</sup> assuming no “slip” and continuity of the shear stress at the fluid–solid interface

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(18) Sauerbrey, G. Z. *Phys.* **1959**, *155*, 206.

(19) Kanazawa, K. K.; Gordon, J. G. *Anal. Chem.* **1985**, *57*, 1770.

(20) Kanazawa, K. K.; Gordon, J. G. *Anal. Chim. Acta* **1985**, *175*, 99.

(21) Hydrodynamically smooth means that the scale of roughness lies considerably below the depth of the liquid boundary layer near the crystal surface.

$$\Delta f_D = -b\beta(\rho\eta)^{1/2} \quad (2)$$

where  $b = (f_s\pi)^{1/2} [\text{T}^{-1/2}]$ . Bruckenstein<sup>22</sup> arrived at essentially the same result by a dimensional argument. Equation 2 has been verified experimentally for hydrodynamically smooth crystals (e.g. ref 23) to within a prefactor  $\sim O(1)$ , dependent on the fixtures and the circuit. Again,  $\beta$  ought to be considered an instrument constant  $\sim O(f_s/Z_d)$ .

Martin et al.<sup>24</sup> derived from a piezomechanical model that the total frequency shift,  $\Delta f_T$ , for simultaneous deposition and liquid damping on smooth crystals is the sum of eqs 1 and 2

$$\Delta f_T = \Delta f_M + \Delta f_D = -\beta[aA + b(\rho\eta)^{1/2}] \quad (3)$$

which was verified in carefully controlled experiments. In practice, additional contributions to  $\Delta f_T$  can arise.<sup>23,25,27,28</sup> Yang and Thompson<sup>27</sup> articulate the possibilities

$$\Delta f_T = \Delta f_M + \Delta f_D + \Delta f_X + \Delta f_A \quad (4)$$

where  $\Delta f_A$  is due to mechanical stress on the crystal when mounted in a liquid cell and  $\Delta f_X$  accounts for all "nonshear couplings" between the liquid and the oscillating crystal.

The stress effect,  $\Delta f_A$ , can be minimized or eliminated by a well designed cell and careful technique.<sup>24,25</sup>  $\Delta f_X$ <sup>28</sup> includes effects related to surface roughness and molecular-level interfacial interactions. We adopt Martin et al.'s<sup>25</sup> treatment,<sup>26</sup> which attributes  $\Delta f_X$  to the effects of surface roughness, mediated by incomplete wetting in cases with unfavorable interfacial interactions. For roughened crystals in contact with wetting liquids eq 2 is replaced by

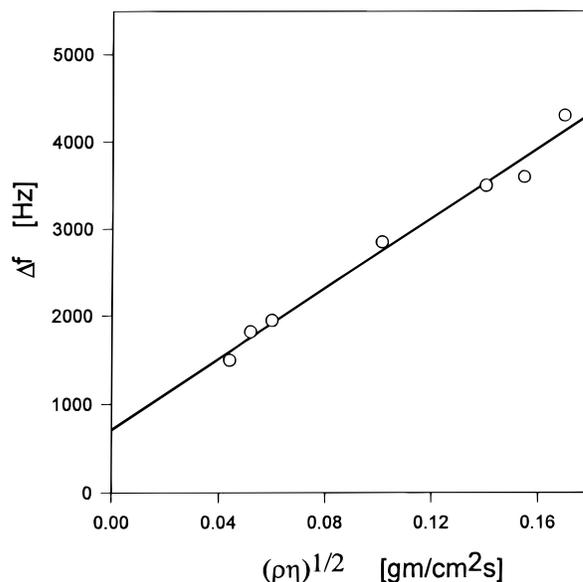
$$\Delta f_D + \Delta f_X = -\beta[b'(\rho\eta)^{1/2} + c\rho] \quad (5)$$

where the first term on the right is the same contribution described in eq 2 but for an effectively larger surface area, while second term on the right accounts for acoustic effects. The coefficient  $b'$  exceeds  $b$ , retains its frequency dependence ( $\sim f_s^{1/2}$ ), and increases linearly with the scale of roughness;  $c$  scales linearly with  $f_s$  and algebraically with the roughness. Consequently, for adsorption of a thin layer onto a rough crystal from a wetting solution we expect

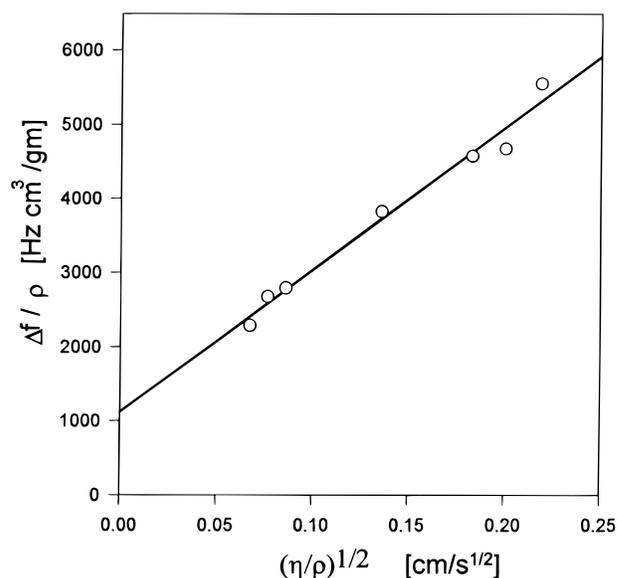
$$\Delta f_T = \Delta f_M + \Delta f_D + \Delta f_X = -\beta[a'A + b'(\rho\eta)^{1/2} + c\rho] \quad (6)$$

with  $a'/b' = a/b = 2(\pi f_s)^{1/2}$ , if the stress effect is minimal ( $\Delta f_A \approx 0$ ). Equation 6 provides a basis for quantitative analysis of  $\Delta f_T$  for  $A$  after calibration to determine  $\beta b'$  and  $\beta c$ .

Calibration consisted of measuring the frequency shifts upon damping with wetting, viscous liquids (alkanes).  $\Delta f_T$  is plotted against  $(\rho\eta)^{1/2}$  in Figure 1, together with a linear regression fit; the nonzero intercept indicates the contributions  $\Delta f_A$  and/or  $\Delta f_X$ . Figure 2 shows a plot of  $\Delta f_T/\rho$  against  $(\eta/\rho)^{1/2}$  suggested by eq 5. The linear regression slope and intercept permit calculation of  $b'$  ( $=1.05b$ ) and



**Figure 1.** Frequency shift  $\Delta f$  versus  $(\rho\eta)^{1/2}$  for a series of seven alkanes, indicating the contributions  $\Delta f_X$  and/or  $\Delta f_A$ .



**Figure 2.**  $\Delta f/\rho$  versus  $(\eta/\rho)^{1/2}$  for a series of seven alkanes, confirming eq 5 and  $\Delta f_A \approx 0$ .

$c$  ( $=311$  cm/s). Comparing with the correlations determined by Martin et al.<sup>25</sup> for the dependence of  $b'$  and  $c$  on  $f_s$  and roughness, one finds these values correspond to an unstressed crystal ( $\Delta f_A \approx 0$ ) with roughness of 100–200 nm. This is consistent with the manufacturer's estimate and is close to the hydrodynamically smooth limit.

**3.2. Adsorption Kinetics.** Following eq 6, we subtract from  $\Delta f_T$  the contribution from the liquid reservoir,  $\Delta f_D + \Delta f_X$ , given by eq 5 to obtain  $\Delta f_M$  during adsorption. In our adsorption experiments, we used 5 mM alkanethiol solutions, which have nearly the same density and viscosity as pure EtOH. Thus  $\Delta f_D + \Delta f_X$  was treated as a constant offset equal to the frequency shift caused by the contact of the electrode with pure EtOH.<sup>29</sup> We measured a reproducible shift of  $\Delta f_D + \Delta f_X = 2.520 \pm .005$  kHz for EtOH, within 5% of the prediction from eq 5 using  $\beta b'$  and  $\beta c$  from Figure 2 and literature values of  $\rho$  and  $\eta$ .

(29) The difference estimated between the frequency shift caused by pure ethanol and that by 5 mM alkanethiol in ethanol is only a few hertz, based on eq 5 and the data for changes in  $\rho$  and  $\eta$  with alkanethiol concentration given by Shimazu et al.<sup>11</sup>

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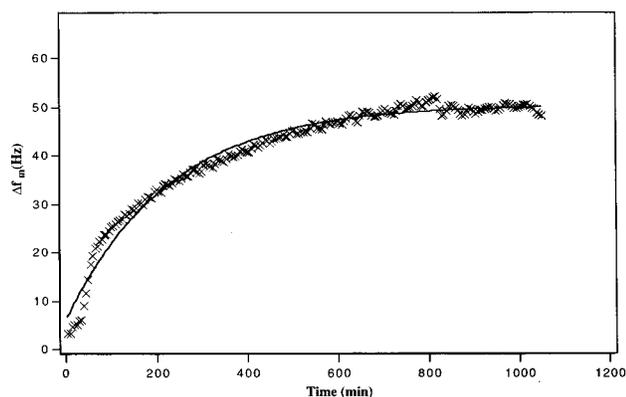
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(26) The effects contributing to  $\Delta f_X$  are still a matter of debate. Surface roughness clearly plays an important role<sup>23,25,27</sup> but the nature of the contribution from interfacial interactions is still under study.<sup>25,28</sup>

(27) Yang, M.; Thompson, M. *Langmuir* **1993**, *9*, 1990.

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**Figure 3.** Representative plot of  $\Delta f_M$  versus time during adsorption of  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$  from 5 mM ethanol solution.

Knowing the connection between  $A$  and  $\Delta f_M$  allows prediction of the  $\Delta f_M$  expected for an adsorbed monolayer. Assuming the adsorbed alkanethiol monolayers have a (3X3)R30 structure, the areal densities  $A$  for 1-dodecanethiol ( $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ ) and 11-mercaptoundecanol ( $\text{HS}(\text{CH}_2)_{11}\text{OH}$ ) are estimated as  $1.831 \times 10^{-7}$  and  $1.849 \times 10^{-7}$  g/cm<sup>2</sup>, respectively, and the corresponding frequency shifts are the same to the significant figures permitted by the instrument, at 41 Hz. This prediction accounts for the roughness.

Now, the frequency shifts during alkanethiol adsorption were fit with an exponential decay (see below):

$$\Delta f_M = k_1 - k_2 e^{-k_3 t} \quad (7)$$

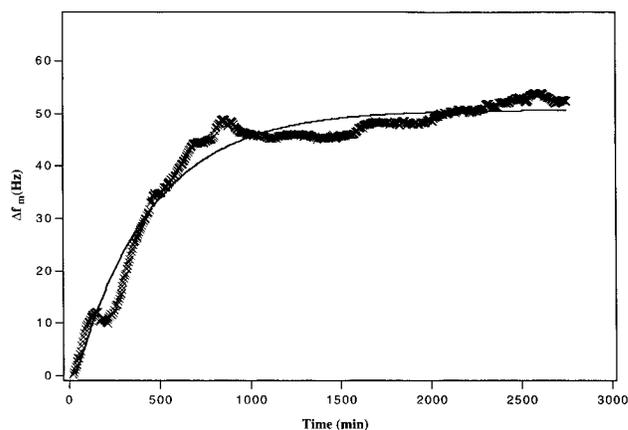
In the case where the formation of a layer obeys reversible Langmuir kinetics, the relationship between the surface coverage and the time is<sup>12</sup>

$$A(t) = A_\infty - A_\infty e^{-kt} \quad (8)$$

where  $A(t)$  is the surface coverage at time  $t$ ,  $A_\infty$  is the equilibrium coverage, and  $k$  is the combination  $k_a c_b + k_d$  with  $k_a$  being the intrinsic rate constant for adsorption,  $k_d$  being the intrinsic rate constant for desorption, and  $c_b$  being the bulk alkanethiol concentration. (The above presumes that  $c_b$  remains fixed during adsorption, which is the case in our system.<sup>30</sup>) Comparing eqs 7 with 8 gives  $k_1$  equal to  $k_2$ , consistent with a Langmuir rate law, with the values corresponding to the equilibrium surface coverage  $A_\infty$ . The constant  $k_3$  would then correspond to  $k$ .

Figure 3 shows the representative data for the frequency shift  $\Delta f_M$  during the formation of the thiol layer on Au from a 5 mM  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3/\text{EtOH}$  solution. The data are fitted by eq 3, with  $k_1 = 50 \pm 5$  Hz,  $k_2 = 45 \pm 5$  Hz, and  $k_3 = 0.01 \pm 0.003$  min<sup>-1</sup>. The difference between  $k_1$  and  $k_2$  is within the uncertainty dictated by the baseline stability of the instrument, which is suggestive that the adsorption can be described by a Langmuir rate law, in general agreement with the observations by Karpovich and Blanchard.<sup>12</sup> This conclusion is debatable however, as discussed below.

The frequency shift corresponding to the equilibrium surface coverage  $A_\infty$  is  $k_1 = 50 \pm 5$  Hz, while the estimated frequency shift for a monolayer is 41 Hz. The data indicate a positive deviation of the measurement from the estimate for a monolayer by about 25%. This may stem from either a contribution to  $\Delta f_M$  not accounted for by eq 6 (e.g.



**Figure 4.** Representative plot of  $\Delta f_M$  versus time during adsorption of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  from 5 mM ethanol solution.

interfacial ordering of ethanol) or adsorption in excess of a monolayer. The latter explanation seems more likely, since the Au surfaces here are polycrystalline, with many steps, ledges, and defects, offering high energy adsorption sites, and the solutions were not degassed, leaving open the possibility of disulfide formation as a route to partial formation of multilayers.

The characteristic time for the layer formation in Figure 1,  $3k^{-1} \approx 300$  min, is comparable with that found by ellipsometry by Bain et al.<sup>3</sup> for the same thiol from EtOH at similar bulk concentrations but is somewhat longer than what is observed for monolayer formation in similar systems using the QCM, in studies by Shimazu et al.<sup>11</sup> (10–100 min), and is much longer than that reported by Karpovich and Blanchard<sup>12</sup> (~10 s). Examination of Figure 3 indicates that the exponential fit is not a very precise representation: There appears to be a fast process in the early stages followed by a slower process, exactly as described by Bain et al. and Shimazu et al. It appears that in our measurements we are tracking the same process observed by Bain et al. and probably by Shimazu et al.

When a 5 mM  $\text{HS}(\text{CH}_2)_{11}\text{OH}/\text{EtOH}$  solution was used, we found similar results. Figure 4 shows typical data;  $k_1 = 51.0 \pm 5$  Hz,  $k_2 = 56 \pm 5$  Hz, and  $k_3 = 0.02 \pm 0.004$  min<sup>-1</sup>. This is in line with expectations from previous work, where the X group did not exhibit a dramatic influence on the kinetics.<sup>3</sup> Essentially the same equilibrium frequency shift is found, leading to about 1.2 monolayers. The time scale is, again, quite long compared to that found by Karpovich and Blanchard<sup>12</sup> but is in the same range detected by Bain et al.<sup>3</sup> The exponential representation is clearly an approximation; in fact, the data give the impression of a two-step process (fast stage followed by a slow stage), in agreement with refs 3 and 11.

For both systems examined here, prolonged exposure to alkanethiol solution did not cause further deposition of alkanethiol on the already formed layer.

#### 4. Conclusions

There are substantial differences among reports in the literature regarding the kinetics of alkanethiol adsorption onto Au from liquid solution. The most important factors affecting the kinetic features appear to be the presence of preadsorbed contaminants, the solution phase hydrodynamics, and solvent effects. We revisited this issue by examining the process for two alkanethiols at conditions closely resembling those used in ref 3, using an *in situ* technique, and careful cleaning the gold surfaces prior to adsorption.

(30) For example, it requires  $\sim O(10^{-9})$  mol of thiol for ten layers of coverage over the entire crystal surface, an amount negligible compared to  $\sim O(10^{-3})$  mol of thiol in 1 mL of 5 mM solution.

We found that alkanethiols in ethanol solution adsorb on Au to form layers about 20% in excess of a monolayer. These were stable under prolonged exposure to the alkanethiol solution; there was no evidence for a multilayer formation process. The adsorption process can be described very roughly by simple Langmuir adsorption kinetics, but there appear to be systematic deviations from exponential fits, suggesting an initial fast process followed by a slower one, as reported in ref 3. The characteristic times for adsorption are on the same order as those in ref 3 but are longer than those reported in ref 11, by about an order of magnitude. This is likely due to a combination of different hydrodynamic conditions (we employed a quiescent solution; stirred solutions were employed in ref 11) and a solvent effect (we studied adsorption from

ethanol while in ref 11 hexane was used). However, even these considerations do not account for the difference between our results and those in ref 12, where characteristic times more than two orders of magnitude smaller are reported. The difference encourages re-examination of the process under tight control with particular attention to the cleaning protocols and hydrodynamic conditions used.

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