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Stability and Self-Exchange in Alkanethiol Monolayers

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Abstract: Alkanethiols bearing radiolabeled (^{35}S) head groups have been incorporated into self-assembled monolayers (SAMs) on a variety of substrates to determine coverage, thermal- and photostability, and surface roughness. Spontaneous desorption of octadecanethiol SAMs immersed in solvent under ambient conditions is observed for all substrate/solvent combinations, including gold, silver, platinum, and copper and water, ethanol, tetrahydrofuran and hexane. A quantitative analysis of desorption suggests pseudo-first-order kinetics with rate constants in the range of 10^{-5} s^{-1} for THF. Evidence for multilayering on copper is found. Molecular hydrogen is not involved in the rate-determining step for desorption. Self-exchange of surface-labeled thiol with solution unlabeled thiol is also described by first-order kinetics. Both desorption and self-exchange experiments yield residual thiols at the surface which cannot be exchanged, and which are presumed to result from stronger binding at defect sites. Similarities in kinetics for exchange and desorption point toward a common mechanism for surface detachment, postulated to be a rate-limiting desorption step as a disulfide. Estimates for free energies of adsorption of a thiol generating molecular hydrogen and adsorption of a disulfide yield −5.5 and −24 kcal mol^{-1}, respectively. In conjuction with recent evidence that thiols are actually adsorbed as disulfides, $RSSRAu_{2(s)}$, the desorption is represented by $RSSRAu_{2(s)} \rightarrow RSSR + 2Au_{(s)}$ (slow). For exchange this is followed by $2RSH + 2Au_{(s)} \rightarrow RSSRAu_{2(s)} + H_2$ (fast), with some contribution from direct thiol/disulfide interchange for high concentrations of solution thiol, viz: $RS^*SRAu_{2(s)} + RSH \rightarrow RSSRAu_{2(s)} + R^*SH$. On clean gold surfaces, adsorption is shown to be diffusion limited. Finally, strategies for enhancing the stability of SAM monolayers made from thiols are discussed.

Introduction

Chemisorption via metal−sulfur interactions has proven a convenient means for attaching species to the surface of metals such as gold. Typically, a clean metal is immersed in a dilute solution of thiols or disulfides to produce well-defined, organized structures at the metal/liquid interface. Such "self-assembly" of monolayers is discussed in an abundance of work[1−11] on the adsorption of systems ranging from straight-chain alkanethiols to more complex molecules such as thiol-bearing porphyrins[12,13] and C_{60}.[14] Many recent studies have focussed on ways of chemically derivatizing self-assembled monolayers (SAMs) to build new structures with novel properties.[15−18] Much of the innovative work on SAMs is driven by the technological implications of being able to control the properties of interfaces. SAMs offer straightforward regulation of surface wetting[6,7] and have been used for corrosion protection.[19] They also provide for lithographic patterning,[20] promote selective adhesion of cells,[21] have been employed in interfaces capable of molecular recognition,[22] and have been used to build photoresponsive structures.[23]

Although organized structures form on a variety of surface morphologies,[17] the integrity and durability of monolayers are key to successful implementation of the SAM strategy for

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surface-confinement. Clues that the stability of SAMs is not complete, however, are to be found in the literature. For example, some loss in electroactivity for a ferrocenyl alkanethiol SAM soaking in hexane was observed by Hickman *et al.*,[24] although Collard and Fox[25] did not observe spontaneous detachment of a similar monolayer immersed in ethanol. Other studies on electroactive SAMs in nonaqueous electrolytes also indicate instability.[26] However, solvent systems for SAM deposition and electrochemical characterizations have mostly been limited to ethanol and water, respectively.[25,27] Results from our work will show prior use of aqueous systems is somewhat fortuitous, since spontaneous loss of material is minimized with water.

Loss of surface thiol is to be expected, since it is a manifestation of the reversible nature of thiol (RSH) adsorption as usually written:

$$\mathrm{RSH} + \mathrm{Au}_{(s)} \rightleftharpoons \mathrm{RS{-}Au}_{(s)} + {}^{1}/_{2}\mathrm{H}_2 \qquad (1)$$

where $\mathrm{Au}_{(s)}$ is an adsorption site. A dynamic and reversible adsorption process is part of the mechanism for attaining equilibrium adsorption coverage by maximizing packing density. Reaching equilibrium conformation (extended chains) requires additional time: Hahner et al.[28] have shown that initial rapid adsorption is followed by a reorganization period which takes days. Another way the dynamic nature of the equilibrium has been demonstrated is by exchange: Chidsey *et al.*,[27a] for example, studied the exchange of *n*-alkanethiols with ferrocene-labeled alkanethiols. Collard and Fox[25] examined the exchange kinetics of similar systems in greater detail. For practical applications, exchange with impurities with surface affinity, such as halide and sulfide ions, should also be considered. Self-exchange of isotopically labeled compounds

$$\mathrm{RS{-}Au} + \mathrm{R^{*}SH} \rightleftharpoons \mathrm{R^{*}S{-}Au} + \mathrm{RSH} \qquad (2)$$

where *S is labeled sulfur (^{35}S), represents a refinement over systems based on redox-tagged thiols exchanging with untagged thiols. Radiolabeling allows one to determine surface coverage with great accuracy and precision (±5% of a monolayer or better), the area occupied by all molecules is the same, and there is no possibility for preferential adsorption or phase separation of dissimilar species at the surface. In addition, ferrocene-labeled alkanethiols exhibit stable aqueous electrochemistry only at low pH in the absence of nucleophilic anions.[29] These restricted conditions are required due to the reactivity of the oxidized (ferrocenium) species toward even weak nucleophiles. A radiolabel does not suffer from such problems associated with chemical side reactions.

In the present work we use a range of solvents to study the desorption of alkanethiol SAMs from a variety of substrates. Our objectives are to provide a model for the stability of monolayers and to assess the kinetics and thermodynamics of the adsorption process. Several labeling schemes employing redox-active moieties attached to the distal end of alkanethiols have been employed.[27,29] Since the C−S bond is only a little stronger than the C−H bond, questions concerning possible cleavage of C-S have been raised.[30] Our studies are the first in which the sulfur head group has been labeled, and, as such, we are able to compare our surface coverages with those from redox-labeling studies to determine whether the C−S bond is labile.

Results and Discussion

Surface Roughness, Thermal Stability, and Photostability. Synthesis of radiolabeled octadecanethiol proceeded with good yield to give monolayers that exhibited count rates ranging from 2 to 20 counts s^{-1} cm^{-2}. Plastic scintillator consists of polystyrene having primary and secondary dyes dissolved therein, and has counting efficiency and speed performance characteristics similar to those for liquid scintillation counting. The penetration length for 0.167 MeV electrons (^{35}S) is ca. 20 μm in plastic. It is possible to use ^{14}C as a secondary standard once the system has been calibrated with ^{35}S. Due to a relatively short half-life for ^{35}S (87.4 days) the activity decreases significantly following an initial investment in isotope. Limited supplies of labeled thiol meant that we could not do exchange of unlabeled thiol on the surface with labeled thiol in solution.

As an estimate of accuracy, a 1 cm^2 monolayer-covered gold foil, specific activity 1.4 Ci mol^{-1}, gave a count rate of ca. 20 counts s^{-1}, or 12 000 counts for 10 min for a counting error of 1%. The main source of error is thus from the syringe used for addition of an aliquot of standard. We obtained accuracy and precision of ±5% of a monolayer ($\pm 4 \times 10^{-11}$ mol cm^{-2}) for full coverage, with a detection limit of 2% monolayer (2×10^{-11} mol cm^{-2}). A higher specific activity would yield a lower detection limit.

The first issue addressed experimentally was that of surface roughness (roughness factor, R = actual/geometric surface area). Apparent surface coverages must be corrected for R if true packing densities and surface geometries are to be deciphered. Various techniques to prepare nominally smooth gold are available, including evaporation, sputtering, and mechanical polishing. Surface morphologies are dependent on the substrate (for vacuum deposition) and annealing, if performed. Methods for determining R for gold include using the electrochemistry of adsorbed iodine,[31] surface oxide electroactivity,[32] the underpotential deposition of silver and copper,[33] and scanning tunneling microscopy.[34] Recently, Porter *et al.* described reductive desorption of alkanethiolates as a method for determining surface coverage.[35] For work related to alkanethiol monolayers, R values from 1.2 to 2.0[36-39] have been employed for evaporated gold, 2[37] has been found for a polished gold disk,

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Table 1. Roughness Factors of Various Gold Substrates Using the Adsorption of ^{35}S-Labeled Octadecanethiol

substrate	roughness factor
polished Au	1.44 ± 0.1
polished Au with annealing	1.20 ± 0.05^{a} 1.27 ± 0.05^{b}
evaporated Au on mica	$1.7_8 \pm 0.1$
evaporated Au on mica with annealing	1.15 ± 0.05
sputtered Au on glasss	$2.0_9 \pm 0.1$
sputtered Au on plastic	$2.0_6 \pm 0.1$

[a] Annealed at 800 °C for 30 min. [b] Annealed at 400 °C for 30 min.

Table 2. Surface Coverage of Octadecanethiol Monolayers on Au, Pt, Cu, Ag, and GaAs[a]

substrate	coverage (mg m^{-2})	roughness factor
Au	3.3	1.44
Pt	3.8	
Ag	5.1	1.6
Cu	20–65	multilayers
GaAs	2.7	

[a] The coverages are uncorrected for surface roughness. Multilayers (10–30 layers) are formed on copper under the conditions employed for deposition.

and annealed gold usually gives a roughness factor of ca. 1.1[31,40] (although gold on mica annealed at excessively high temperatures yields inferior monolayers[27j]). The use of radiolabeled alkanethiol affords the possibility for accurate and precise surface roughness determination. We obtain an "operational" roughness factor that applies to adsorbed alkanethiols, since not all surface sites may be accessible to long chains. The use of surface oxide and iodine desorption electrochemistry may involve surface reconstruction and may not accurately indicate the area that is available to alkanethiols (although we are not able to exclude the possibility of reconstruction in our experiments). If electrochemistry is to be employed it is possible to use reductive desorption of alkanethiolate monolayers,[35b] although it is claimed that a significant fraction of charge passed during reductive desorption originates from charging the electrical double layer.[41] STM estimates for rough surfaces may be on the low side, since "overhangs" of grains or deep crevasses may obscure surface. Notwithstanding these potential pitfalls, it will be shown that reasonably good agreement, for smooth gold, is obtained between our results, STM, and iodine desorption.

All roughnesses are calculated from the observed surface coverage and an area per molecule of 21.7 Å^2, corresponding to a coverage of 4.6×10^{14} molecules cm^{-2}.[34,42–44] Labeled thiols were adsorbed from hexane and rinsed in hexane.[45] During this rinsing period spontaneous desorption is negligible (*vide infra*). Various substrates were examined: mechanically polished gold, evaporated gold on mica, and sputtered gold on plastic and glass. Some samples were annealed at temperatures stated. As seen in Table 1, *R* ranged from 1.1 to 2.1 for these nominally "smooth" gold surfaces. Several points of interest may be noted: the smoothest film was Au on mica after annealing with R of 1.15, in reasonable agreement with Atomic Force Microscopy (AFM) and iodine desorption (R = 1.1);[46] sputtered gold was somewhat rougher on the atomic scale. We were surprised that gold foil polished manually according to the procedure outlined in the experimental section (graded polishing with alumina powders) gave roughness factors less than evaporated and sputtered gold (although inspection with a microscope revealed surface scratching, as expected). Surfaces of polished samples appeared reasonably reproducible: six individual polished gold foils gave a mean R of 1.44 with a standard deviation of 0.07 (5%). Annealing gold foils in ambient at 400 °C or 800 °C caused the surface roughness to approach that for annealed mica substrates.

It should be noted that if the area per molecule were higher than 21.7 Å^2, or if gross packing defects were to occur, *R* would be proportionately higher. We were also concerned that bilayers or multilayers might be forming,[47] where the long aliphatic hydrocarbon tails of adsorbed thiols could interdigitate with solution thiols and cause the surface concentration of $C_{18}H_{37}$SH to be higher than expected (*R* would thus be larger) through this physisorption process. Experiments with a 10-fold excess of octadecyl alcohol added to the adsorbing thiol produced the same surface coverage. If bilayer formation were a problem we would expect the $C_{18}H_{37}OH$, with similar polarity to $C_{18}H_{37}$SH, to displace physisorbed thiol and lead to a lower observed surface coverage. These experiments do not rule out multilayer formation in solution: it may be that the rinsing step is sufficient to quantitatively remove physisorbed material.

Recent work by Zhong and Porter[30] described S–C cleavage in organosulfides (thioethers, R–S–R) on adsorption to gold producing monolayers identical to those resulting from S–H breaking in the corresponding thiol (R–S–H) or disulfide (RS–SR). These findings precipitate concern as to whether C–S bonds are broken in alkanethiols, leading to adsorbed sulfide (S^{2-}) or thiolate (SH^-) ions rather than alkanethiols. If this were the case, one would expect greater apparent coverages from head labeling (^{35}S) than from tail labeling (ferrocene group). Our coverages (not corrected for roughness) are 6.6×10^{14} cm^{-2} for octadecanethiol and $3.0 \pm 0.3 \times 10^{14}$ cm^{-2} for ferrocenethiol,[25,27] slightly smaller than the 3.9×10^{14} cm^{-2} calculated for densely-packed ferrocene head groups[27a] (with *R* = 1.44). Thus, if any C–S cleavage occurs it is minimal.

Surface coverages for alkanethiols on gold, platinum, silver, and copper are summarized in Table 2. Also given is the coverage on GaAs(001).[48] Values in Table 2 have not been corrected for surface roughness, since gold is the only substrate for which we have an area per molecule. Structural studies of

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(44) The area per molecule is for Au(111). This is expected to differ slightly for other textures of Au.

(45) Ethanol is usually employed for alkanethiol adsorption. We chose hexane since there is evidence that a fraction of a monolayer of gold dissolves when octadecanthiol adsorbs from ethanol (see: Edinger, K.; Gölzhäuser, A.; Demota, K.; Wöll, Ch.; Grunze, M. *Langmuir* **1993**, *9*, 5–8). Additionally, our prior *in situ* quartz crystal microbalance studies showed better behavior for octadecanethiol adsorbing to gold from hexane (Schlenoff, J. B.; Dharia, J. R.; Xu, H.; Wen, L.; Li, M. *Macromolecules* **1995**, *28*, 4290–4295).

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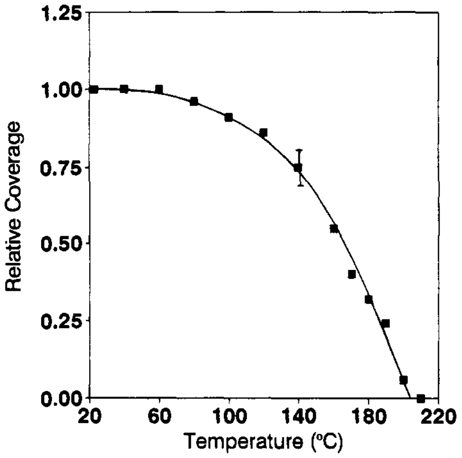

Figure 1. Thermal desorption of radiolabeled octadecanethiol from gold under ambient conditions. Heating rate 2 °C min^{-1}. The solid line is a guide to the eye.

alkanethiols on silver[49] suggest a tilt of 13° from the surface normal with an interchain packing distance of 4.1 Å, compared with a 30° tilt and 5.0-Å spacing for gold. From this we estimate 49% more molecules per unit area for silver (1.1×10^{-9} mol cm^{-2}) than for gold (7.64×10^{-10} mol cm^{-2}), and the surface roughness for our polished silver would be about 1.6. A range of very high coverage was seen on copper, consistent with multilayering via copper thiolate complexes observed previously.[50]

The thermal stability of $C_{18}SH$ monolayers under ambient conditions (i.e. not in high vacuum) was evaluated by placing labeled monolayers on gold in an oven and gradually increasing the temperature. (Counting was performed at room temperature). As shown in Figure 1, the point for 50% loss is about 160 °C under a slow-temperature ramp of ca. 2 °C min^{-1}. This finding is in general agreement with the results of Nuzzo et al.,[2] who demonstrated, using ESCA, loss of sulfur from the surface in a $C_{16}H_{33}SH$ monolayer on gold over the range 170–230 °C. Nuzzo *et al.*[51] also performed temperature-programmed desorption of methanethiolate on gold and found a desorption maximum at ca. 220 °C. A detailed mass spectroscopic study of *tert*-butanethiol desorption from gold, performed by Jaffey and Madix,[52] revealed a maximum for desorption at *ca.* 200 °C. Our results demonstrate complete loss of surface sulfur by 210 °C. It should be noted that the region for desorption in Figure 1 covers a wide temperature range with some loss occurring at 100 °C. Non-negligible thermal sensitivity of thiol-coated metals at these temperatures would have significant implications for projected applications. A recent STM/XPS study on the thermal stability of self-assembled monolayers[53] illustrates surface phase changes that occur to accommodate this loss of thiol. The profusion of metastable crystalline structures on progressive desorption of thiol indicates that structural studies requiring annealing to remove disorder should be interpreted with care, since, as shown here, annealing at temperatures close to 100 °C will lead to low-coverage phases. In a recent helium diffraction study an upper limit for temperature cycling of 50 °C was quoted for stability of observed structures.[54]

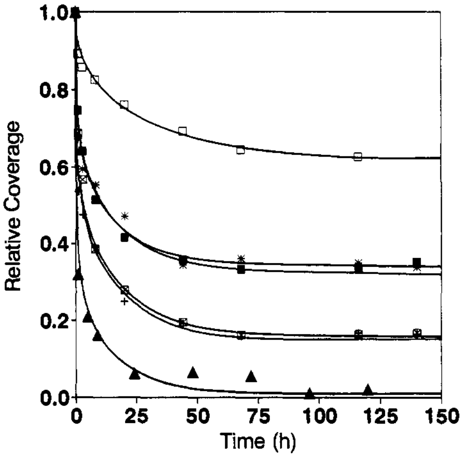

Figure 2. Self-exchange of labeled octadecanethiol on a gold surface. The normalized coverage is shown as a function of exposure time for samples immersed, at room temperature, in 0.001 M (■), 0.01 M (*), 0.1 M (+), and saturated (0.5 M) (x in a square)) octadecanethiol in hexane. Immersed in pure solvent (□) and in pure thiol (▲) at 41 °C. All $C_{18}H_{37}SH$ coverages are normalized to an intitial coverage of 7.6 ± 0.8×10^{-10} molecules cm^{-2}.

We performed two further experiments that would be of general interest. The first involved exposing a monolayer of thiol to "piranha", which is commonly used to clean gold surfaces prior to monolayer deposition (see Experimental Section). Ten minutes of soaking in piranha at room temperature was sufficient to remove >98% (±2%, i.e. all detectable) of the thiol on the gold. In the second experiment we exposed a $C_{18}H_{37}SH$ monolayer to ultraviolet radiation from a mercury UV lamp (medium pressure Hg lamp, total spectral power density at the sample was ca. 2 W cm^{-2}) for 30 min. It has been shown that exposure to UV under ambient conditions causes oxidation of thiol sulfur to sulfoxides,[20c,d] and eventually to sulfate ion[20e] which may subsequently be removed by rinsing in aqueous solution.[55] Selective area oxidation of thiols may be employed in surface patterning for microscale processing. Rinsing our photooxidized sample in dilute sulfuric acid effected complete (>95%) removal of adsorbed thiol. While these two experiments result in one extreme of residual thiol (i.e. approaching zero) they demonstrate the great utility of radiolabeled thiols in "assays" of surface coverage.

Self-exchange of surface-labeled for solution-unlabeled $C_{18}H_{37}SH$ at gold immersed in hexane solutions of unlabeled thiols is summarized in Figure 2. Exchange takes place over *ca.* 24 h. These results are qualitatively consistent with those of Collard and Fox,[25] who used ferrocenyl groups to tag thiols in exchange experiments. Perhaps the most noteworthy result is that a significant fraction of thiols remains non-exchanged at long times—unexpected in view of the $>10^6$-fold excess of unlabeled thiol in the reaction system. Clearly kinetic limitations to exchange of all thiols exist, and only when pure $C_{18}H_{37}SH$ is used (albeit at a slightly higher temperature) can all thiols be exchanged. There is very little dependence of the rate and extent of exchange on thiol concentration. Most revealing was the finding that significant loss of adsorbed thiol occurred in pure solvent.

We were compelled by these observations to undertake a systematic survey of the stability of $C_{18}H_{37}SH$ on metals commonly used for SAM work: gold, silver, platinum, and copper. The solvents were chosen to represent a range of

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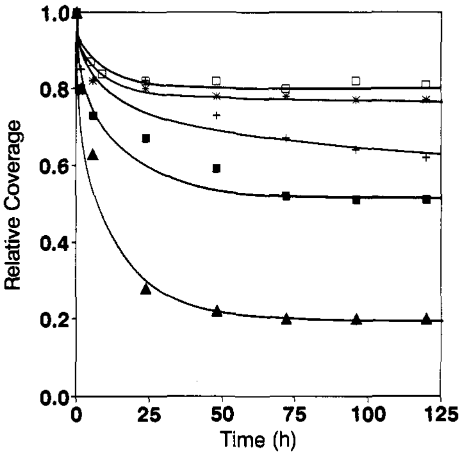

Figure 3. Surface coverage of ^{35}S-labeled octadecanethiol monolayers on gold as a function of immersion time in various pure solvents at room temperature: water (*); hexane (+); ethanol (■); THF (▲); 0.1M aqueous $HClO_4$ (□).

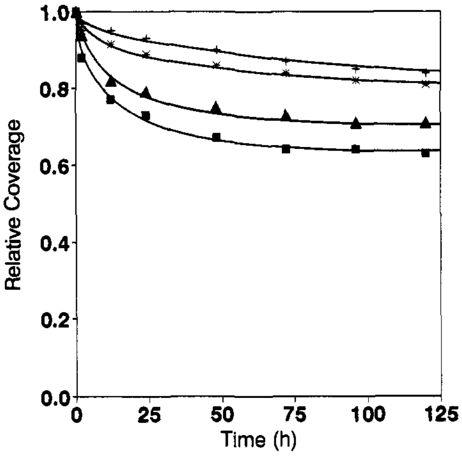

Figure 4. Surface coverage of labeled octadecanethiol monolayers on silver as a function of time immersed in water (*), hexane (+), ethanol (■), and THF (▲).

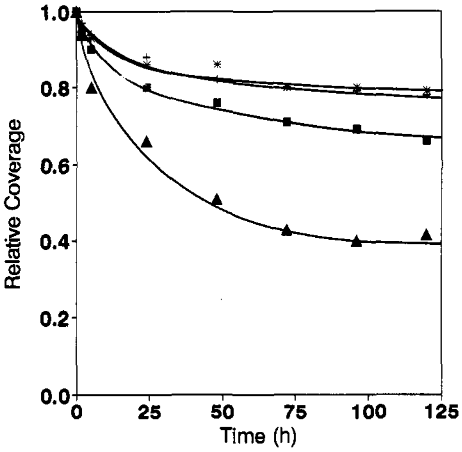

Figure 5. Surface coverage of labeled octadecanethiol monolayers on platinum as a function of immersion time in pure water (*), hexane (+), ethanol (■), and THF (▲).

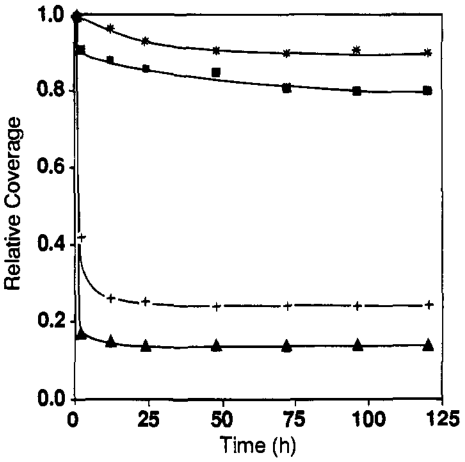

Figure 6. Coverage of labeled ocatdecanethiol multilayers on copper as a fuction of immersion time in water (*), hexane (+), ethanol (■), and THF (▲).

polarities, and comprised water, ethanol, THF, and hexane. Normalized coverage as a function of exposure time in these pure solvents is given in Figures 3–6. Some general trends are seen. First, the quasi-steady-state limiting coverages reached after long immersion times are a strong function of substrate and solvent.[56] Mono(multi)layers appear to be least stable when deposited on copper,[57] and most stable in water. Second, for gold, the time scales for desorption are similar to those for exchange, pointing toward a similarity in mechanism. In the discussion that follows we evaluate mechanisms for exchange and desorption and their importance in the stability of monolayers.

Adsorption/Desorption Thermodynamics. The equilibrium distributions for species in eq 1 will be determined by the net energy for adsorption. An estimate of this parameter may be made by considering the bond energies for RS–H, H_2, and RS–Au. Literature values for RS–H and H_2 are listed as 87 and 104 kcal mol^{-1}, respectively, while the strength of the RS–Au bond is estimated to be roughly 40 kcal mol^{-1}.[7b,8] The net energy would be ca. −5 kcal mol^{-1} (exothermic). An alternate route to a more precise estimate of $\Delta G°_{adsorption}$ may be made using the data from Weisshaar *et al.*[35c] concerning the chemically reversible electrodeposition of thiols from alkaline solutions

$$RSAu_{(s)} + e^- \rightleftharpoons RS^- + Au_{(s)} \qquad (3)$$

A potential of −0.76 V vs SHE is determined for 10 mM dodecanethiol after examination of Weisshaar et al. $E°$ would thus be −0.88 V.[58] Summation of the following yields the desired overall reaction:

$$\text{(i)}\quad RS^- + Au_{(s)} \rightleftharpoons RSAu_{(s)} + e^-$$

$$\text{(ii)}\quad e^- + H^+ \rightleftharpoons {}^1/_2H_2$$

$$\underline{\text{(iii)}\quad RSH \rightleftharpoons RS^- + H^+}$$

$$\text{net}\quad RSH + Au_{(s)} \rightleftharpoons RSAu_{(s)} + {}^1/_2H_2$$

where $Au_{(s)}$ is an adsorption site on gold. Reactions (i) and (ii) give an $E°_{cell}$ of 0.88 V with a corresponding $\Delta G°$ of −20.2 kcal mol^{-1}, while reaction (iii), using a K_a of 1.4×10^{-11},[59] would have $\Delta G° = +14.7$ kcal mol^{-1}.[60] The overall $\Delta G°_{adsorption}$ is thus −5.5 kcal mol^{-1}, which compares well with the estimate above and implies that 40 kcal mol^{-1} is a reasonable value for

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(56) The desorption rate was the same in the presence and absence of ambient air (oxygen) and light.

(57) The physisorbed multilayers on copper would be more easily removed by rinsing in solvent.

(58) All $E°$ values are vs SHE. A shift of -2×0.059 V converts the E measured in 10 mM thiol to the $E°$ for standard conditions (1.0 M).

(59) K_a for 1-propanethiol is 1.4×10^{-11}, see: *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985; pp 5–54.

the RS−Au bond. The equilibrium constant, K

$$K = \frac{[\mathrm{RSAu}_{(s)}]p_{\mathrm{H}_2}^{\ 1/2}}{[\mathrm{RSH}][\mathrm{Au}_{(s)}]} \qquad (4)$$

would be *ca.* 1.1 × 10^4. The quantities $[\mathrm{RSAu}_{(s)}]$ and $[\mathrm{Au}_{(s)}]$ are treated as fractions of a monolayer. K is not particularly large—for example, in 1 atm of hydrogen with 10^{-4} M thiol one would expect a coverage of approximately half a monolayer ($[\mathrm{RSAu}_{(s)}] = [\mathrm{Au}_{(s)}]$).

While the above discussion of thermodynamics is useful for equilibrium conditions, further analysis is required for desorption or self-exchange kinetics. If a monolayer is immersed in pure solvent the concentration of thiol in the solution approaches zero and coverage is controlled by the kinetics of desorption. Treatment of the kinetics of thiol adsorption has been sparse and even less is known about the rates of desorption. According to time-resolved studies, adsorption to form almost a full monolayer is rapid.[4,61] A quantitative treatment of kinetics according to eq 5 is possible:

$$k_{\mathrm{on}}[\mathrm{RSH}][\mathrm{Au}_{(s)}] = k_{\mathrm{off}}[\mathrm{RSAu}_{(s)}]p_{\mathrm{H}_2}^{\ 1/2} \qquad (5)$$

at equilibrium, where k_{on} and k_{off} are adsorption and desorption rate constants, respectively, and $K = k_{\mathrm{on}}/k_{\mathrm{off}}$. According to the time-resolved data of Rubini[61b,62] and Karpovich and Blanchard,[61d,63] it takes approximately 2 s to form half a monolayer ($[\mathrm{Au}_{(s)}] = 0.5$; 0.5 monolayer = 3.8×10^{-10} mol per actual cm^2 or 5.7×10^{-10} mol per geometric cm^2, using R of 1.5) of alkanethiol from a 3×10^{-4} M solution. If we use the expression

$$\mathrm{flux}_{\mathrm{on}}(\mathrm{mol\ dm}^{-2}\ \mathrm{s}^{-1}) = k_{\mathrm{on}}[\mathrm{RSH}][\mathrm{Au}_{(s)}] \qquad (6)$$

and substitute [RSH] = 3×10^{-4} mol dm^{-3}, a value of $k_{\mathrm{on}} = 1 \times 10^{-4}$ dm s^{-1} obtains. k_{off} would thus be *ca.* 9×10^{-9} mol dm^{-2} s^{-1} atm$^{-1/2}$. Using a similar expression for the adsorption rate

$$\mathrm{flux}_{\mathrm{off}} = k_{\mathrm{off}}[\mathrm{RSAu}_{(s)}]p_{\mathrm{H}_2}^{\ 1/2} \qquad (7)$$

with $[\mathrm{RSAu}_{(s)}]$ = 1 monolayer, we obtain a desorption rate of 6×10^{-12} mol dm^{-2} s^{-1} if a value for the ambient partial pressure of hydrogen of 0.5 ppm is inserted.[64] If a monolayer is approximately 1×10^{-7} mol dm^{-2} the desorption time would be in the range of 10^4 s, or a few hours—certainly within an order of magnitude of the observed initial desorption and self-exchange rates. If the desorption mechanism described by eq 1 were in operation one would expect faster loss of surface-bound thiol in the presence of hydrogen. Figure 7 compares the rates of desorption of ferrocenethiol on gold in aqueous solution in the absence and presence of 1 atm of hydrogen. No significant difference in rates is seen.

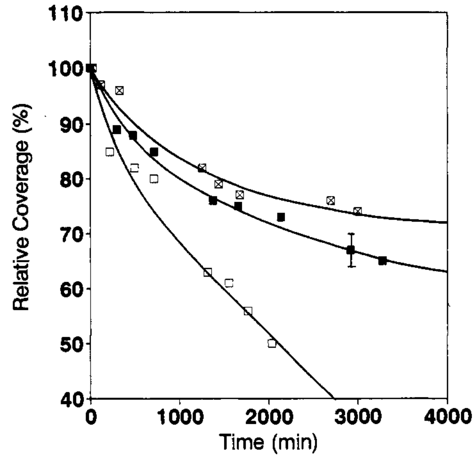

Figure 7. Relative coverage vs time for ferrocenylalkanethiol monolayers on gold. SAMs are immersed in aqueous 1 M $\mathrm{HClO_4}$ at room temperature: unannealed wire under ambient conditions (■) and with 1 atm of hydrogen (× in a square) and annealed wire under ambient conditions (□). The initial coverage (uncorrected for surface roughness) for alkanethiol SAMs was 5 ± 0.5 × 10^{-10} mol cm^{-2}.

At this point it is important to discuss possible flaws in the preceding argument, and to clarify the significant gaps in the present understanding of the alkanethiol/gold adsorption system. The treatment above invoked a bimolecular type reaction where hydrogen assisted the desorption of alkanethiolate. Inserting the ambient concentration of hydrogen into eq 7 is not particularly satisfactory, since this quantity varies widely. In reality, the rate of desorption appears to be *independent* of hydrogen concentration. Indeed, the role and fate of hydrogen in the adsorption of alkanethiols is poorly understood. While there is no proof, to our knowledge, that $\mathrm{H_2}$ is generated on chemisorption of alkanethiols to gold, the S−H bond is not observed in Raman scattering studies of thiols adsorbed on silver and gold.[65] Thus, there is strong evidence that adsorption is a chemically irreversible process involving loss of $\mathrm{H_2}$. The Porter group has shown that adsorption of solution thiolate (eq 3) is reversible,[35] but this process does not involve hydrogen.

A re-evaluation of data on adsorption kinetics suggests very strongly that adsorption is, in fact, diffusion controlled. For example, in the references quoted above half a monolayer (6×10^{-10} mol cm^{-2}) forms in about 2 s for [RSH] = 3×10^{-4} M. In the regime of diffusion-limited transport to a planar surface the surface coverage as a function of time, t, would be given by[66]

$$\text{no. of moles/area} = \frac{2D^{1/2}_{\mathrm{RSH}}C_{\mathrm{RSH}}t^{1/2}}{\pi^{1/2}} \qquad (8)$$

Using a value of 10^{-6} cm^2 s^{-1} for D_{RSH}, the diffusion coefficient, and 3×10^{-7} mol cm^{-3} for the concentration of RSH we obtain 5×10^{-10} mol cm^{-2} in 2 s. The agreement with the experimental values is close enough to indicate that, in all likelihood, adsorption of alkanethiols under these conditions is controlled by diffusion and not by Langmuir adsorption kinetics, as concluded previously.[61a,b,d] This would make the numbers determined for k_{on} and k_{off} lower boundaries, the real values being significantly higher.[67]

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(60) Note that the thiolate oxidation half-cell occurs in ethanol, whereas the other two reactions used in this scheme are aqueous. We assume the thiolate redox potential would be the same in aqueous solution if it were reversible.

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(62) Rubini used conductance changes in thin films of gold to follow mercaptoundecanoic acid adsorbing from ethanol.

(63) Karpovich and Blanchard used a quartz crystal microbalance to measure adsorption of octadecanethiol from hexane.

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Table 3. Second- and First-Order Rate Constants for Desorption of Octadecanethiol in THF and Exchange on Gold in Hexane (Figure 2)

system	*k*, 1st order (s^{-1})	correl coeff	*k*, 2nd order ($\text{monolayer}^{-1}\ s^{-1}$)	correl coeff
self-exchange	1.7×10^{-5}	0.982		
desorption[a] from Au	2.1×10^{-5}	0.986	2.0×10^{-5}	0.955
desorption from Ag	9.8×10^{-6}	0.960	1.7×10^{-6}	0.817
desorption from Pt	1.1×10^{-5}	0.982	5.3×10^{-6}	0.977

[a] Desorption in THF, room temperature.

Table 4. Room-Temperature Solubilities of Octadecanethiol in Water, Ethanol, THF, and Hexane

solvent	solubility (M)
C_2H_5OH	0.0049
water	<0.0005
hexane	0.51
THF	0.50

Possible mechanisms for desorption that do not involve hydrogen should be considered. In protic solvents one could conceive of the following:

$$RSAu_{(s)} + H^+ \rightleftharpoons RSH + Au_{(s)}^+ \tag{9}$$

with reduction of the oxidized gold site by some impurity. This (unlikely) mechanism can be discounted for aprotic solvents. Also, exposure of monolayers to conditions of high proton concentration had no effect on desorption rate (see Figure 3). We consider a more plausible explanation to be desorption via the formation of disulfide, similar to the desorption of methanethiolate from gold under UHV conditions.[51] Second-order kinetics for the bimolecular reaction

$$2RSAu_{(s)} \rightarrow RS{-}SR + 2Au_{(s)}$$

$$\text{rate (monolayer s}^{-1}) = k[RSAu_{(s)}]^2 \tag{10}$$

might be expected. Second-order plots ($1/C = 1/C_o + kt$) of octadecane thiol desorption[68] from gold, platinum, and silver in THF yield rate constants of magnitude ca. 10^{-5} monolayer^{-1} s^{-1} (Table 3). Data for these plots are taken over the first 48 h. Correlation coefficients, which are not high, reflect curvature in the plots. In reality, more complex behavior might be expected with superposition of several desorption rates corresponding to a range of binding site energies (*vide infra*). For completeness we should mention other possible unimolecular mechanisms for desorption, such as $RSAu_{(s)} \rightarrow RS^\bullet + Au_{(s)}$, and $RSAu_{(s)} \rightarrow RS^- + Au^+$, although such homolytic or heterolytic cleavage of the S−Au bond should be considered unlikely, as the products would quickly recombine.

One would expect desorption to be promoted by better solvents. From a thermodynamic standpoint, each factor of ten increase in the solubility of thiol in a solvent would lead to *ca.* 1.4 kcal decrease in the binding energy (Table 4). The trend does not strictly follow the order of solubility, however. For example, ethanol promotes more desorption than does hexane. Surface affinity or coordinating ability may play a key role in displacing surface-bound thiol. A general observation is that water is the worst solvent for octadecanethiol, and desorption in water is minimal, which has important practical implications. A small amount of water in an organic solvent has a strong impact on the desorption rate, as seen in Figure 8 which depicts the effect of adding water to THF.

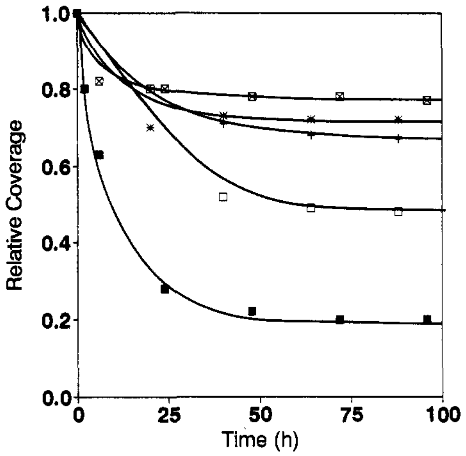
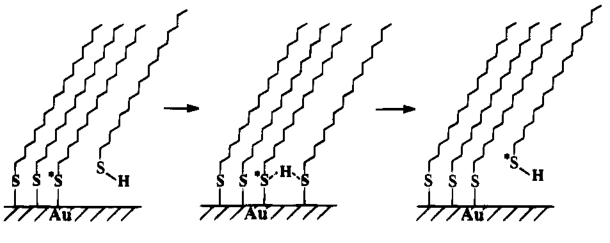


Figure 8. Coverage of radiolabeled octadecanethiol monolayers on gold as a function of immersion time in pure THF (■), 1 wt% H_2O in THF (□), 5% H_2O/THF (+), 10% H_2O/THF (*), and pure H_2O (× in a square).

Self-Exchange. Our analysis of self-exchange of bound alkanethiols parallels that for desorption, since the exchange and desorption rates appear to be similar and both share the feature that a pseudo-steady-state incomplete desorption/exchange plateau is reached. The rate of self-exchange shows little dependence on concentration, as seen in Figure 2, suggesting a bimolecular mechanism of the type



to be unlikely. The weak concentration dependence in kinetics for exchange was also observed by Collard and Fox for ferrocenylalkanethiols.[25] These workers inferred dissociation at the surface to be rate-limiting, and Hickman *et al.*[24] in their ferrocenylalkanethiol experiments concluded an "S_N1" mechanism to be in operation, where the replacement of one thiol proceeds via loss from the surface followed by uptake of a solution thiol. The rate of exchange is much too slow to be limited by diffusion, in contrast to adsorption kinetics. In the absence of hydrogen it is possible that exchange occurs via desorption as a disulfide (rate-limiting) followed by replacement by a thiol, in a manner analogous to desorption in pure solvent. A weak (or non-) dependence of rate on solution concentration of thiol would be expected.

$$\text{(i) } R^*SAu_{(s)} + RSAu_{(s)} \rightarrow 2Au_{(s)} + R^*S{-}SR \quad \text{(slow)}$$

$$\text{(ii) } 2Au_{(s)} + 2RSH \rightarrow 2RSAu_{(s)} + H_2 \quad \text{(fast)} \tag{11}$$

The overall concentration of surface thiol remains constant with a large excess of unlabeled thiol. Therefore pseudo-first-order kinetics are expected. A first-order plot of log [labeled thiol] vs t^{-1} gives a rate constant of 1.7×10^{-5} s^{-1} (Table 3).

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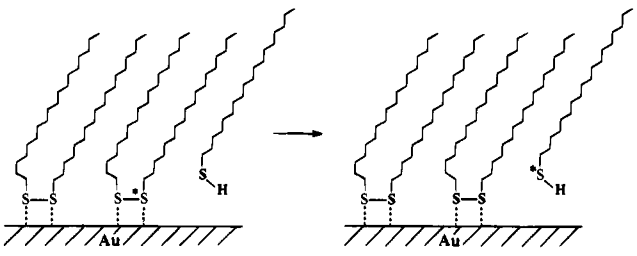
(67) Clean surfaces are required to observe diffusion-limited monolayer formation. It is possible to self-assemble alkanethiols at contaminated surfaces over more extended periods of exposure since the thiol aggressively displaces other species at the surface.

(68) Data have been corrected for residual thiol. Thiol was divided into two populations: desorbing (exchanging) and non-desorbing (non-exchanging). First- and second-order plots are of the desorbing (exchanging) thiols only.

The most puzzling features of exchange, noted originally by Chidsey *et al.*[27a] and confirmed by Collard and Fox,[25] is that a significant fraction of thiols is not exchangeable (or exchanges over a much longer time scale). For example, in Figure 2, 20–40% of labeled thiol remains on the surface after several days of soaking in unlabeled thiol over the concentration range 1 mM to 0.4 M. Only by immersion in pure thiol can all surface species be exchanged. A parallel effect is observed for the spontaneous desorption data—after an initial period of loss the surface concentration remains quite stable (Figures 3–6). The proposed explanation for non-exchanging thiol invoked defect sites in the form of crystal defects (steps, edges), crystalline boundaries, or impurities.[25,27a] Thiols at defect sites were proposed to exchange quickly.

As-made vapor-deposited surfaces with no annealing are defect rich. Defects are also generated on annealed gold when alkanethiol SAMs are deposited, but these "holes" are actually pits in the underlying gold[69] rather than vacancies in the SAM. Defects on untreated gold appear to be step-edges: Walczak et al.,[70] using electrochemical desorption of alkanethiolates and STM imaging of substrates, provide direct evidence for thiols bound at defect sites on unannealed gold evaporated onto silicon or glass. Thiols at step-type defects were shown to be bound up to 6 kcal more *strongly* than thiols on Au(111) terraces. Annealed gold on mica (more defect-free by STM) produced electrochemistry consistent with thiols having uniform binding energy.

If 6 kcal were to represent a slower k_{off}, the rate of exchange (and desorption) would be on the order of 10^4 times slower for the "defect" population - a rate which is not observable on the time scale of our experiments.[71] It is also seen from Figure 2, and from the results of Collard and Fox,[25] that the use of pure thiol as solution phase *does* promote quantitative exchange. In pure thiol, direct disulfide–thiol interchange is possible:[72]



(For an example of thiol–disulfide interchange at a surface see Yee *et al.*, ref 73).

In order to test the influence of the defect population on desorption we performed some preliminary experiments with annealed gold wires. In Figure 7 are presented the coverage vs time data for ferrocene-tagged monolayers on gold that has been annealed at 800 °C for 3 h. A faster rate of desorption is consistent with a smaller defect population.

Adsorption/Desorption as Disulfides. We wish to draw attention to recent structural studies by Fenter *et al.*,[74] who provide strong evidence that the sulfur head groups of adsorbed alkanethiol actually adopt a dimerized arrangement on the surface of Au(111), with an S–S distance (2.2 Å) that is short enough to imply a disulfide bond. A gauche defect at the S–C bond permits the hydrocarbon tails to assume the well-known $\sqrt{3} \times \sqrt{3}R30°$ hexagonal packing. It would appear, therefore, that adsorbed thiols are already "set up" for desorption as disulfides.

Adsorption energetics may be reevaluated in terms of this disulfide surface structure, although the evidence for such a structure in our studies is indirect. Electrochemical methods are unable to distinguish between thiolates and disulfides at the interface, since the number of electrons consumed in reaction (i) below and the reaction in eq 3 (thiolate reduction) is the same (both require one electron per surface sulfur). For this reason, the claim that sulfurs exist in dimerized form does not compromise the validity of using electrolytic desorption to determine surface coverage. After rewriting eq 3 to reflect the reduction of disulfides at the surface (eq (i) below), we sum the following:

$$\text{(i) } 2\text{RS}^- + 2\text{Au}_{(s)} \rightleftharpoons \text{RSSRAu}_{2(s)} + 2e^-$$

$$\text{(ii) } \text{RSSR} + 2e^- \rightleftharpoons 2\text{RS}^-$$

$$\text{net } \text{RSSR} + 2\text{Au}_{(s)} \rightleftharpoons \text{RSSRAu}_{2(s)}$$

using $E°$ for (i) of −0.88 V as before, and $E°$ for (ii) as −0.35 V from the cyclic voltammetry of hydroxyethyl disulfide at platinum,[75,76] we obtain −24 kcal mol^{-1} for $\Delta G°_{\text{adsorption}}$ (the net reaction). The adsorption energy is thus ca. −12 kcal per RS^-, or about twice as favorable as $\Delta G°_{\text{adsorption}}$ calculated for the thiol mechanism involving molecular hydrogen (eq 1).[77]

The desorption kinetics are now expected to be first order as opposed to second order. We employ the desorption results in THF, since the data are spread out over the surface coverage axis, and present the first-order rate constants in Table 3. Better correlation for the first-order mechanism supports the analysis above, although determination of desorption products would be more compelling evidence of desorption as disulfides.

For practical applications it would be useful to design strategies to improve the stability of surface-bound alkanethiol monolayers.[78] Clearly, a defect-rich (rough) surface would be advantageous for this purpose (as would the use of aqueous systems only). Since defects are likely to be 1-dimensional (step edges) rather than point-defects it is reasonable to expect molecules to adsorb at these locations also as disulfides rather than isolated thiolates. A preferred disulfide surface configuration can be viewed as a lower energy structure whereby significant electron density goes into the S–S bond rather than two isolated S–Au thiolate-type bonds. This kind of surface dimerization is akin to a Jahn–Teller[79] effect or Peierls distortion[80] in the solid state: both occur to lower the energy of the highest occupied states. This dimerization is unfortunate from a binding point of view, since a stronger S–Au bond would imply greater stability. It may be possible to prevent dimerization by designing thiol molecules where sulfurs are structur-

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(69) Schönenberger, C.; Sondag-Heuthorst, J. A. M.; Jorritsma, J.; Fokkink, L. G. J. *Langmuir* **1994**, *10*, 611–614.

(70) Walczak, M. M; Alves, C. A.; Lamp, B. D.; Porter, M. D. *J. Electroanal. Chem.* In press.

(71) Steady-state coverages are not under equilibrium control since replenishing solvent with fresh solvent did not result in further desorption.

(72) Adsorbed molecules are drawn as disulfides, consistent with Fenter *et al.* ref 74.

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(75) Liu, M.; Visco, S. J.; de Jonghe, L. C. *J. Electrochem. Soc.* **1989**, *136*, 2570–2575.

(76) Nichols and Grant (Nichols, P. J.; Grant, M. W. *Aust. J. Chem.* **1982**, *35*, 2455–2463) quote a value of −0.30 V for the thiophenolate/disulfide couple.

(77) These mechanisms are not competing since RSSR is not added to the solution.

(78) We saw no evidence for desorption in air at room temperature.

(79) Jahn, H. A.; Teller, E. *Proc. R. Soc.* **1937**, *A161*, 220.

(80) Peierls, R. E. *Quantum Theory of Solids*; Oxford University Press: London, 1955; Chapter 5.

ally constrained and held apart, either by making a rigid dithiol or a thiol with a bulky head group.

Another approach to improving stability would be to use multiple attachment points in a polythiol molecule. If desorption is "correlated," that is, either all thiols are adsorbed or all are desorbed, as in a rigid molecule, adsorption energy per molecule scales as the number of surface thiolate or disulfide groups. Roughly speaking, for N equivalent "stickers" per molecule, each having free energy of adsorption $\Delta G_{\text{adsorption},1}$, $\Delta G_{\text{adsorption},N} = N\Delta G_{\text{adsorption},1}$ and $K_N = K_1^N$, where K_1 is the equilibrium constant for a molecule with one attachment point. For "uncorrelated" desorption, such as widely spaced adsorbing groups on a flexible molecule (e.g. polymer), the adsorption can be treated statistically: the probability of a molecule having all adsorbing "feet" off the surface at one time, allowing for total desorption, scales as $(2^N - 1)^{-1}$.

In conclusion, thiol-based self-assembled monolayers are subject to equilibrium considerations, leading to spontaneous desorption in solvents containing no thiol. A quasi-steady-state surface coverage is achieved, the level of which is highly solvent dependent. Desorption is least pronounced in aqueous systems, a propitious attribute for practical applications. For example, if octadecanethiol is to be used for corrosion protection of copper, near quantitative loss of multilayered thiol is observed in THF, whereas only 10% desorbs in water. An analysis of desorption kinetics based on net adsorption energies per molecule suggests *significant advantages may be realized by using multiple attachment points for stabilizing monolayers.* Examples of polythiols, where the number of sulfhydryl (or sulfur) groups is greater than 2, include polymers containing thiols[61e,81] or disulfides,[82,83] or smaller molecules with several "sticky feet," such as a trithiol described recently.[84]

Experimental Section

Materials. Au and Pt foil and Au wire (>99.9%) were obtained from Hauser & Miller (St. Louis, Missouri) and Cu and Ag foil from Aldrich. Octadecanethiol (unlabeled, Aldrich) was recrystallized from ethanol. Hexane (Fisher Scientific, HPLC grade) and ethanol (Florida Distillers) were used as received. GaAs(001), p-doped ($n = 0.26-1.1 \times 10^{19}$ cm^{-3}), was supplied polished on one side.

^{35}S-Labeled Octadecanethiol. 1-Bromooctadecane (65.8 mg, 0.2 mmol, Aldrich) and ^{35}S-labeled thiourea (8.6 mg 0.11 mmol, specific activity ca. 10 Ci mol^{-1}, Amersham) were refluxed in 3 mL of methanol for 50 h under nitrogen. Octadecylthioureanium salt was precipitated, washed with hexane and water, and redissolved in a minimum of methanol. The salt was hydrolyzed by reflux with excess NaOH for 2 h under nitrogen and the reaction quenched with dilute HCl. Octadecanethiol was extracted with hexane. Yield 29 mg (90%). The NMR of the product was identical to that of an authentic sample.

11-Mercaptoundecanoylferrocene was synthesized according to the procedure of Hickman et al.[24]

Adsorption. Au and Pt foils and Au wires were prepared by manual polishing with graded alumina (Buehler Inc.) from 5.0 to 0.05 μm on Microcloth, treating with freshly prepared "piranha" (7:3 ratio of concentrated H_2SO_4 and 30% H_2O_2; *caution* piranha reacts violently with organic compounds and should not be stored in closed containers), and ultrasonicating in distilled, deionized water for 20 min. Ag and Cu foils were polished with alumina, ultrasonicated in water, and rinsed with acetone, methanol, then water. For metal foils, ^{35}S-labeled monolayers were prepared by soaking cleaned surfaces in a 1 mM hexane solution of labeled octadecanethiol for 5 h, followed by rinsing in hexane 3 times (with a total exposure time of <10 min). The exact concentration of labeled thiol solutions was determined by GC−MS and recrystallized octadecanethiol as standard. Ferrocene-labeled thiol monolayers were prepared by immersing the end of a 1 mm diameter cleaned gold wire in a 0.01 M solution of 11-mercaptoundecanoylferrocene for 12 h, followed by rinsing in pure ethanol. GaAs was rinsed with acetone, methanol, and water, dried in air, and exposed to 1 mM $C_{18}H_{37}SH$ for 5 h.

Surface Coverage. Coverage of radiolabeled thiols was determined by scintillation counting using plastic scintillator (SCSN 81, Kuraray Inc.).[85] Scintillation was detected using a RCA 8850 end-on photomultiplier tube (PMT) biased to 2200 V with a Bertan 313B high-voltage supply. Counts were collected with a Philips PM6654C frequency meter interfaced to a computer. The pulse-height threshold was set to 20 mV, resulting in a counting efficiency of 35%. The PMT was placed vertically in a light-tight box. Counting was performed by placing a sheet of plastic scintillator on the horozontal silica face of the PMT and placing the monolayer-modified metal foil on top of the plastic. The background was typically 4 counts per second using this apparatus. Samples were removed periodically, rinsed in pure solvent, dried, and counted. A solid-state scintillator-based method, as opposed to liquid, avoids exposure to solvent during the counting period. Known amounts of labeled octadecanethiol were introduced onto the plastic for calibration. Coverage for ferrocene-labeled thiols was determined electrochemically: cyclic voltammetry was performed in ambient using aqueous 1.0 M $HClO_4$. Voltammograms were recorded with a Princeton Applied Research 362 voltage sweep generator and a Recorder Company 200 XY recorder. The sweep rate was 50 mV s^{-1} and the reference electrode was a double-junction calomel electrode. The scan range employed was 0.3 to 0.9 V vs SCE. Ferrocene was actively maintained in the reduced form by holding the potential at 0.3 V between scans. Voltammograms were symmetric and resembled literature electrochemistry[25,27] closely. Coverage was determined from the charge under the oxidation peak.

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