

Quantitating the Balance between Enthalpic and Entropic Forces in Alkanethiol/Gold Monolayer Self Assembly

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Received May 10, 1996[⊗]

Abstract: We have studied the temperature and adsorbate concentration dependence of alkanethiol/gold monolayer formation *in situ* and in real time using a quartz crystal microbalance to monitor the rate of reaction. The temperature dependence of the experimental rate constants, for a given concentration, demonstrates that the formation of these monolayers is not diffusion rate limited for the conditions we report here. Our data are modeled accurately by the Langmuir adsorption isotherm and, using this model, we have determined the adsorption and desorption rate constants for monolayer self assembly. We have extracted from these data the thermodynamic quantities ΔG_{ads} , ΔH_{ads} , and ΔS_{ads} for monolayer formation. For 1-octadecanethiol adsorption from *n*-hexane onto gold, ΔG_{ads} is temperature dependent and is *ca.* -5.5 kcal/mol, $\Delta H_{\text{ads}} = -20 \pm 1$ kcal/mol, and $\Delta S_{\text{ads}} = -48 \pm 1$ cal/(mol·K). These data have direct bearing on the broader field of interface chemistry because they underscore the dominant role that entropy plays in determining the course of chemical reactions at interfaces and the robustness of the resulting molecular assembly. We discuss the implications of these data on the stability of the monolayers and the limits that these values place on the extent of experimental control available over their formation.

Introduction

The self assembly of alkanethiol monolayers onto gold has been studied extensively^{1–47} due to the potential applications

of these interfaces to important technologies such as chemical sensing, microdevice patterning, and surface lubrication.^{48–53} The extensive literature that exists on these systems is aimed

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⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1996.

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largely at understanding the steady state properties of the monolayers once they have formed, and from these studies has emerged a reasonably consistent picture. For long-chain *n*-alkanethiols ($\geq C_{10}H_{21}SH$), the aliphatic chains are densely packed with a 5-Å interchain spacing on Au(111), once formed and annealed.^{54,55} These chains are in a predominantly all-*trans* conformation, and the thiol head groups exist in a ($\sqrt{3} \times \sqrt{3}$)-*R30°* configuration on the hexagonal close-packed Au(111) surface.^{3,9} Recently, it has become increasingly clear that these monolayers are highly dynamic,^{17,18,56,57} with desorption and structural rearrangement playing an important role in determining the evolution of the macroscopic properties of the interfaces. Despite this significant level of understanding, there remain several substantial open questions in this field relating to the mechanism of monolayer formation and the extent to which surface defects mediate the dynamics of the monolayers, once they have formed.

The prospect of using self-assembled monolayers for patterning and in chemical sensing applications requires that monolayers possessing functionalities more complex than that available with simple aliphatic thiols be synthesized.^{4,5,27,43,50,58–60} The details of the interaction between the thiol head group and the Au surface remain, to some extent, uncertain and in addition, it has been demonstrated that the “tail group” can alter the organization of the formed monolayer if the organic tail contains chemically active or bulky termini. Thus there is a competition between different regions of the monolayer to determine the macroscopic organization of the system. In order to understand the balance that exists between the thiol head group interactions with the metal surface and organic tail group interactions with adjacent adsorbates, there needs to be a better understanding of the initial self-assembly process, and that is the focus of this work.

We have reported before on a method to monitor, *in situ*, the adsorption of alkanethiols onto gold using a quartz crystal microbalance (QCM) fabricated with evaporated gold electrodes that are predominantly Au(111).^{18,61} We were able to monitor the mass change of the QCM resulting from the adsorption of alkanethiols onto the gold electrodes with subsecond time resolution, allowing access to direct information on the formation of the monolayer. Earlier studies of alkanethiol/gold monolayer formation, performed *ex situ* with techniques such as external reflection FT-IR,⁶² optical ellipsometry,^{6,8} radio isotope labeling,⁶³ and liquid contact angle measurement,^{6,8} were limited to time resolution on the order of minutes to hours. Our *in situ* data demonstrate a kinetic response fully consistent with that predicted by the Langmuir adsorption isotherm,^{64–66} and by modeling the experimental adsorption data using this isotherm, we were able to determine the free energy of adsorption for the monolayer. The values we obtained for ΔG_{ads}

at 293 K were -5.6 ± 0.4 kcal/mol for 1-octadecanethiol adsorption onto gold from *n*-hexane, -5.5 ± 0.2 kcal/mol for formation of 1-octadecanethiol/gold from cyclohexane, and -4.4 ± 0.2 kcal/mol for formation of 1-octanethiol/gold from *n*-hexane.¹⁸ These modest free energies, on the order of the hydrogen bond strength characteristic of liquid alcohols,⁶⁷ demonstrated that these systems are highly labile, a finding at odds with the then-prevailing thought that, once formed, the monolayers exhibited few dynamics. Studies of the mobility of alkanethiol/gold monolayers by the McCarley and Tarlov groups using scanning probe microscopy have revealed the presence of mobile defect sites, providing a different indication of the labile nature of these monolayers.^{17,56} In that work, it was shown that the rate at which these defects migrated across the surface was independent of alkanethiol chain length, suggesting that the thiol head group plays the dominant role in mediating the adsorption and desorption steps,¹⁷ and that the first layer of Au atoms was apparently involved in the monolayer rearrangement directly.⁵⁶ The relatively small free energies of adsorption we obtained in our earlier work indicated that alkanethiols are not bound to the surface strongly, but it was not clear, based on a single quantity (ΔG_{ads}), whether the labile nature of these films was a consequence of chemically weak interactions between the adsorbate and the surface or the counter-balance of two significant but opposing forces, specifically the enthalpy and entropy of adsorption. The answer to this question was indicated by earlier work on the thermal desorption of a monolayer of alkanethiols from Au. Nuzzo and co-workers desorbed a dimethyl disulfide monolayer from gold thermally, recovering a heat of desorption (ΔH_{des}) of 28 kcal/mol.⁶⁸ The implied heat of adsorption, $\Delta H_{\text{ads}} = -28$ kcal/mol, was determined in the absence of solvent and using a different adsorbate, and while leading, the utility of this value for comparison with our experimental data on ΔG_{ads} is limited due to the unknown solvent–thiol contribution to our data. In order to determine the enthalpic and entropic contributions to the small ΔG_{ads} we measure for adsorption from solution, we have measured these quantities directly through the temperature dependence of k_a and k_d , the adsorption and desorption rate constants for monolayer assembly. Our data indicate that the formation of these monolayers is spontaneous by ~ -5.5 kcal/mol at room temperature because of the offsetting effects of large enthalpic and entropic forces. In this paper, we focus on 1-octadecanethiol/gold monolayer formation from *n*-hexane. We measure the temperature dependence of the equilibrium constant K_{eq} to determine the enthalpy of adsorption, ΔH_{ads} . From $\Delta G_{\text{ads}}(T)$ and ΔH_{ads} we determine the entropy of adsorption, ΔS_{ads} . These thermodynamic quantities underscore the high degree of molecular organization characteristic of self-assembled monolayers and serve to place limits on the ultimate structural robustness and chemical “tunability” attainable with a thiol/gold monolayer assembly approach.

Experimental Section

Kinetic Measurements. We have reported previously on the microbalance apparatus used to measure monolayer adsorption kinetics¹⁸ and recap only the essential details here. The QCM was suspended in solution with isolated electrical connections for both gold electrodes using a modified spring clip. AT-cut quartz crystal microbalances (6 MHz resonance frequency) with vapor deposited gold electrodes were obtained from McCoy Electronics (part number 78-18-4). These QCMs were sufficiently robust to avoid breakage resulting from the contact pressure required to ensure reliable electrical contact. The QCM was

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connected to a ~6 MHz oscillator tank circuit (Maxtek part number 124200-4) and a frequency counter (Phillips model PM 6673) was used to monitor the QCM oscillation frequency. This frequency counter has 1-Hz resolution with a gate time of 280 ms. The analog output of the frequency counter was routed to a computer for acquisition, A/D conversion, and storage. For all adsorption rate measurements, the data were acquired at ten readings per second to ensure adequate sampling of the QCM kinetic response. Electrical connections between components were made using shielded coaxial cables to minimize QCM frequency instability arising from electrical interference.

QCMs with a resonance frequency of ~6 MHz are sensitive to mass changes as small as a few nanograms. Several factors, in addition to the mass loading of the device surfaces, can affect its oscillation frequency. The resonance frequency of the QCM is related to mass loading according to the Sauerbrey equation.⁶⁹ This relationship holds quantitatively for gas-phase measurements, but *in situ* solution-phase measurements using the QCM are, in many cases, only semiquantitative due to the complex dielectric response of the solvent and the presence of the adlayer(s). The basis for complications associated with QCM mass measurement in liquids is discussed in detail elsewhere,^{70,71} and is not directly relevant to the focus of this work. Our primary objective here is to determine the rate of mass change associated with the formation of the alkanethiol monolayer. We do not attempt to extract absolute mass change information from our data and thus many of the complications associated with the operation of a QCM in solution for quantitative applications do not play a role in our measurements.

In addition to the several material factors that contribute to the experimental response of the QCM, the resonant frequency of these devices depends sensitively on temperature. To minimize QCM frequency drift associated with thermal fluctuations, the temperature of the solution and QCM was controlled to within ± 0.05 K for a given set point. Measurements were performed in a 150 mL jacketed beaker connected to a flowing liquid temperature controller (Neslab model RTE-110). The temperature was varied from 288 to 303 K in increments of 5 K. Total solution volume in the jacketed beaker was 100.0 mL for each measurement. Stirring was accomplished with a magnetic stirrer and a Teflon coated stir bar. The stirring speed was set to be as fast as possible without introducing fluctuations to the QCM baseline frequency.

The jacketed beakers and other glassware used for the measurements were cleaned using chromic acid solution and rinsed with distilled water, tetrahydrofuran (THF), and *n*-hexane prior to each measurement. The QCMs were cleaned with piranha solution (1H₂O₂ (30%):3H₂SO₄) for 5 min, rinsed with deionized water, and dried in a stream of high-purity N₂. The cleaned QCMs were then rinsed with THF to remove any residual water, then with *n*-hexane and used immediately thereafter. Prolonged exposure to piranha solution damaged the QCM electrodes, as evidenced by an increase in frequency fluctuations for the baseline readings. The mechanism of the damage is likely the attack of the Cr bonding layer between the quartz and the Au. Typically, a new QCM was used each third run, as determined by the stability of the baseline frequency. Individual monolayer adsorption measurements began with pure solvent in the temperature-controlled vessel to establish a stable QCM baseline oscillation frequency. An aliquot of stock thiol solution was then introduced by syringe. The stock solutions were of sufficiently high thiol concentration to allow small injection volumes, minimizing mechanical disruption of the contents of the reaction vessel. For a 10⁻⁴ M thiol final concentration, for example, 99.0 mL of solvent was introduced to the jacketed beaker and, after thermal equilibration, with stirring, data were collected for 10 s to establish a QCM baseline frequency. Injection of 1.0 mL of stock 10⁻² M alkanethiol yielded a 10⁻⁴ M final concentration in the reaction vessel. The stock solutions were maintained at the same temperature as the solvent in the reaction vessel to avoid thermal disruptions resulting from injection.

Conductivity Measurements. The conductivity of suspensions of Au dust in ethanol were measured before and after the addition of 1-octadecanethiol using a conductivity meter and cell (Cole-Parmer).

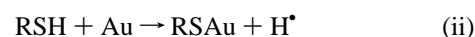
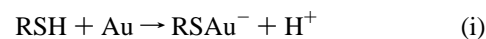
Chemicals. 1-Octadecanethiol was purchased from Aldrich Chemical Co. and used as received. The thiol was tested by gas chroma-

tography and mass spectrometry to determine the presence of the corresponding dioctadecyl disulfide, and none was detected. The solvent *n*-hexane was purchased from Baxter (Burdick and Jackson) and used without further purification. For conductivity measurements, 1–3 μ m Au dust was purchased from Aldrich Chemical Co. and used as received. For the conductivity measurements, anhydrous ethanol solvent was used.

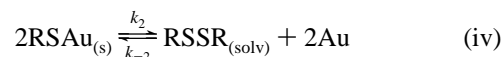
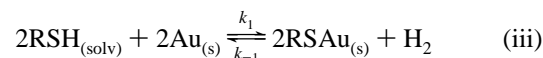
Results and Discussion

The Adsorption and Desorption Reactions. Before presenting our experimental data on the thermodynamics of monolayer formation, it is important to have a clear understanding of the chemical reaction to which these data apply. While the initial reactants are known and the product monolayer is comparatively well-characterized, the structural identity of monolayer constituents that desorb from the Au surface remains open to speculation and is awaiting direct experimental verification of their identity. Specifically, there are two points of uncertainty that exist in the literature. These are the fate of the thiol hydrogen and its role in desorption, and the competition between thiol desorption and disulfide desorption. We consider below the current understanding of these reactions, the possible desorption products, and the likely reaction scheme for our experimental conditions.

The initial adsorption reaction can, in principle, proceed either by ionic dissociation of the thiol or by formation of H[•],



and based on available electrochemical evidence^{18,19,24} as well as conductometric data,⁷² reaction ii is favored significantly over reaction i. This portion of the monolayer formation reaction is comparatively well understood, save for the fate of H[•] at the Au surface. The role of H[•] is different in the two most likely desorption reactions,



We consider first the enthalpic contributions to reactions iii and iv to estimate the course of the desorption, whether it is predominantly via k_{-1} or k_2 . Given the starting materials, RSH_(solv) and Au_(s), the forward reaction, with rate constant k_1 , is the starting point. In order to estimate the heat of reaction, we need first to understand the fate of H[•]. There is literature precedent for absorption of H[•] into thin Au films,⁷³ and such an absorption would be in competition with formation of H₂ from 2H[•]. For the reaction 2H[•] \rightarrow H₂, $\Delta H = -104$ kcal/mol,⁷⁴ and for H[•] + Au_(s) \rightarrow H[•]Au_(s), $\Delta H \cong -2$ kcal/mol.⁷³ The formation of molecular hydrogen will be favored over dissolution of H[•] into the Au matrix, although this is not necessarily the case for all metals, such as Pd or Pt. We must also consider the possibility that H₂ is stored as H₂O₂ if O₂ is available to the reaction at the time of monolayer formation. The enthalpy of

(72) We measured the conductivity of a suspension of 1–3 μ m of gold in anhydrous ethanol during the addition of ethanolic 1-octadecanethiol. We detected no change in the conductivity of the solution as a result of RSH/Au interaction (< 0.01 μ -mho). If the dissociation of H⁺ from RS⁻ were complete, for our experimental conditions we would expect the change in [H⁺] = 4.6×10^{-6} M. The corresponding change in conductivity of a 4.6×10^{-6} M ethanolic HCl solution relative to neat ethanol was measured to be 0.47 μ -mho.

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formation of H₂O₂ from H₂ and O₂ is ~ -45 kcal/mol, and the dissociation reaction of H₂O₂ to form H• + HO₂• yields -40 kcal/mol.⁷⁴ Thus the presence of O₂ at the surface has some effect on the availability of H• to the desorption but the energies are modest and the desorption to the thiol will still proceed because of the limited amount of O₂ available at the Au reaction site.

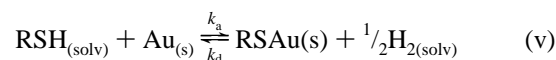
For the formation of the monolayer, where the bond dissociation energy for the RS–H bond is taken to be ~ 87 kcal/mol,²⁰ the RS–Au bond dissociation energy is ~ 40 kcal/mol,¹ and 2H• \rightarrow H₂ dominates over Au matrix absorption of H•, the calculated heat of this reaction is -5 kcal/mol. The heat of the reverse reaction, denoted by the rate constant k_{-1} in reaction iii, is 5 kcal/mol, if all of the reactants are available. We compare the desorptive reaction yielding starting materials to the formation of the disulfide, according to the reaction denoted by rate constant k_2 in reaction iv. The reaction to form RSSR involves the breakage of two RS–Au bonds (40 kcal/mol each) and the formation of a RS–SR disulfide bond (~ 74 kcal/mol for disulfide bond cleavage²⁰), yielding a net heat for the k_2 desorptive process of $+6$ kcal/mol. Note that this latter reaction does not require hydrogen to proceed, where the reaction to form thiol from the adsorbed monolayer does require a source of H₂. Based on enthalpic arguments alone, and given the presence of H₂ from the initial monolayer formation, we would predict that both desorption reactions will contribute to the monolayer dynamics.

The enthalpic contributions to the formation and dynamics of these monolayers do not provide a complete picture, however. In addition to enthalpic contributions to the reaction, there are also entropic considerations that are non-negligible (*vide infra*). As we detail below, our data indicate a large negative entropy associated with the formation of the monolayer. In other words, there is a significant increase in the order of the system in going from a clean metal surface and solvated thiols to an organized two-dimensional array of gold–thiol bound species. There is a significant entropic driving force for the desorption of the monolayer, and the expected entropic contributions for the two processes presented in reactions iii and iv need to be compared. We measure experimentally that $\Delta S_{\text{des}} > 0$, and argue that, on stoichiometric grounds, $\Delta S_{\text{des}}^{\text{RSH}} \sim 2\Delta S_{\text{des}}^{\text{RSSR}}$. Given that the enthalpic contributions to each desorption reaction are essentially identical, to within the uncertainty of the values used in these estimates, the difference in the free energy of desorption for the two processes will be determined by the entropic term,

$$\Delta G_{\text{des}}^{2\text{RSH}} - \Delta G_{\text{des}}^{\text{RSSR}} = -T\Delta S_{\text{des}}^{\text{RSSR}} \quad (1)$$

Equation 1 indicates that the energetic barrier for desorption of the monolayer back to thiol is smaller than that for desorption of a disulfide by an amount $\sim T\Delta S_{\text{des}}^{\text{RSSR}}$. For our experimental conditions, which we describe below, we estimate that desorption back to the thiol is favored over disulfide desorption by ~ 6 – 12 kcal/mol near 300 K.

As noted above, the dominance of desorption to yield the thiol requires the availability of H₂ and/or H•, and if these species are not available, then desorption to form disulfides in solution would dominate the reaction pathway. Given the presence of H₂ in the system by the formation of the monolayer, the solubility of H• in Au, and the presence of air, we believe that the dominant reaction for our experiments is



where k_{a} and k_{d} are the adsorption and desorption rate constants for monolayer formation. There are several conditions for which this could not be the dominant desorption pathway, such as when disulfides⁶⁸ or thioethers²⁰ are used in forming the monolayer. Under these conditions, where H₂ is not available as a product of the initial adsorption reaction, we expect that desorption of disulfides will be the primary reaction pathway. With the probable chemical reaction pathway determined for our measurements, we consider next the form and interpretation of the QCM kinetic data.

Experimental Data and Reaction Kinetics. The monolayer formation experiments yield information about the assembly of alkanethiol/gold monolayers based on *in situ*, real-time data (Figure 1). Noticeable is the short time it takes to achieve a steady state condition (seconds). Early studies reported that monolayers required formation times of hours to days.^{6,8,62} However, these *ex situ* studies were done using techniques that measured properties resulting from monolayer formation such as ellipsometric thickness, IR peak position, or solvent contact angle.^{6,8,62} It has since been found that the monolayer properties mentioned above are the result of ordering brought about by the structural annealing of the monolayer aliphatic chains. More recent studies have shown that there are two distinct processes associated with monolayer formation. The first process is adsorption of thiol head group to the Au surface and the second is structural annealing of the adsorbate aliphatic chains. There is some very recent and compelling evidence for cooperative interactions between head and tail groups in the formation of monolayers by UHV vapor phase adsorption.⁵⁷ Adsorption from solution, however, will be mediated by the solvent interactions with the thiol tail group, and the cooperative formation of highly organized islands of alkanethiols on Au for low fractional coverages from solution remains to be demonstrated. We consider for solution-phase processes that the adsorption and annealing processes can be treated separately to good approximation based on the significant body of experimental data indicating their widely differing time scales.^{6,8,18,62} An important factor in the acquisition of the raw data is the temporal resolution of the measurement. We designed our experiment so that we would have sufficient data for determination of the kinetic rate constants. The frequency counter we used had a gate time of 280 ms (~ 4 readings/s), and the computer data collection program acquired 10 readings/s. Oversampling in this manner ensures that the frequency counter time resolution is limiting for these experiments.

We next consider the interpretation of our raw kinetic QCM responses. We have provided a detailed explanation of the data processing and modeling elsewhere,¹⁸ and include only the essential aspects of this treatment here. The adsorption experiments were performed in solutions with concentrations ranging from 3×10^{-6} to 3×10^{-4} M 1-octadecanethiol in *n*-hexane. The adsorption kinetics exhibit a concentration dependence with the rates increasing in proportion to thiol solution concentration. Within the concentration range used here, we model our Δf vs. time data using the Langmuir adsorption isotherm,^{64–66}

$$\frac{d\theta}{dt} = k_{\text{a}}(1 - \theta)C - k_{\text{d}}\theta \quad (2)$$

where θ is the fraction of available sites, and the quantities k_{a} and k_{d} are the adsorption and desorption rate constants, respectively. As noted previously, there are several assumptions implicit in the use of the Langmuir adsorption isotherm for

(74) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990.

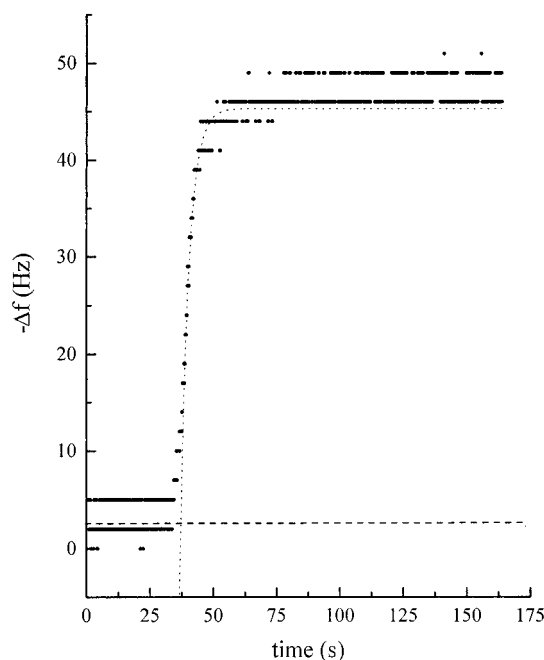


Figure 1. Raw QCM $-\Delta f$ vs time data for 1×10^{-5} M 1-octadecanethiol adsorption from *n*-hexane at 288 K. The actual QCM oscillation frequency is *ca.* 6 MHz higher than the frequency indicated on the ordinate. The fit of the data to eq 4 is shown (small dotted line), where $k_{\text{obs}} = 0.17 \pm 0.09 \text{ s}^{-1}$ and $t_0 = 3.0 \text{ s}$. The dashed line at $\Delta f \sim 3 \text{ Hz}$ indicates the pre-injection baseline for the fitting.

describing the formation and desorption of these monolayers. Based on our previous measurement of $\Delta G_{\text{ads}} \sim -5.5 \text{ kcal/mol}$ for these monolayers,¹⁸ the assumption of non-interacting adjacent adsorption sites is not violated seriously. In addition, the identity of the monolayer constituents precludes multilayer formation, at least in the concentration range used here. The Langmuir adsorption isotherm provides a framework for data interpretation that is consistent with our knowledge of this system. Integration of eq 2 yields the time dependence of monolayer formation, indicating exponential growth of the layer in time,

$$\theta(t) = \frac{C}{C + (k_d/k_a)} [1 - \exp(-k_a C + k_d)t] \quad (3)$$

We measure, for a given thiol concentration and temperature, a buildup of the monolayer in time that is fit best by a single rate constant, $k_{\text{obs}} = k_a C + k_d$. We also substitute $k' = C/(C + [k_d/k_a])$ into eq 3 because we are not attempting to quantitate the mass adsorbed. The term k' corresponds to the steady state fractional coverage of the monolayer, $\theta(\infty)$. To account for finite introduction time of the thiol into the reaction vessel, we incorporate a temporal offset (t_0) in our fitting equation. The simplified form of eq 3 used to fit the data is

$$\theta(t - t_0) = k' [1 - \exp(-k_{\text{obs}}(t - t_0))] \quad (4)$$

See Figure 1 for an example of the fit of eq 4 to the experimental data. Note that, as discussed above, we are not attempting to extract adsorbed mass information because of the complications associated with solution-phase measurements. We have determined the concentration and temperature dependence of k_{obs} (Table 1). For a given temperature, the dependence of k_{obs} on thiol concentration (Figure 2) provides information on the adsorption and desorption rate constants k_a and k_d (Table 2). These data can be used to calculate the equilibrium constant K_{eq} and thus the Gibbs free energy of adsorption, ΔG_{ads} , for

Table 1. k_{obs} Values Determined from Raw Data as a Function of Thiol Concentration

temp (K)	thiol concn (M)	$k_{\text{obs}} \pm 95\% \text{ C.I. (s}^{-1}\text{)}$
288	1×10^{-5}	0.17 ± 0.09
	3×10^{-5}	0.28 ± 0.10
	1×10^{-4}	0.96 ± 0.84
293	2×10^{-4}	1.44 ± 0.86
	1×10^{-5}	0.11 ± 0.04
	3×10^{-5}	0.15 ± 0.11
298	2×10^{-4}	0.51 ± 0.35
	3×10^{-4}	0.78 ± 0.46
	1×10^{-5}	0.16 ± 0.04
303	3×10^{-5}	0.25 ± 0.14
	1×10^{-4}	0.33 ± 0.22
	2×10^{-4}	0.53 ± 0.42
303	3×10^{-4}	0.84 ± 0.54
	1×10^{-5}	0.21 ± 0.08
	3×10^{-5}	0.40 ± 0.13
	1×10^{-4}	0.43 ± 0.20
	2×10^{-4}	0.71 ± 0.33

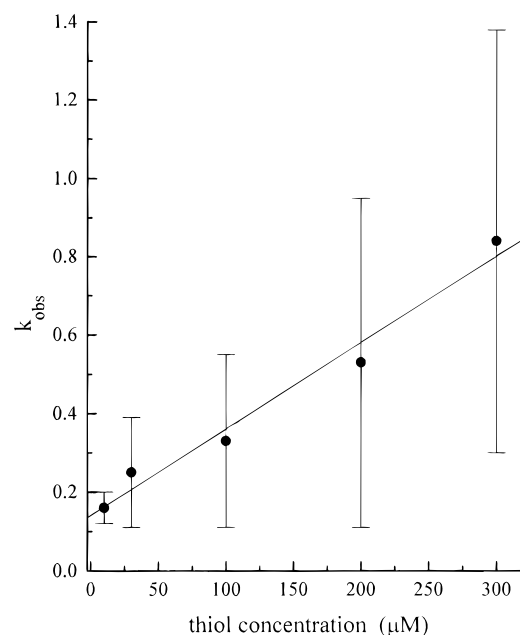


Figure 2. Concentration dependence of k_{obs} at 293 K. From these data we obtain best fit values of $k_a = 2278 \pm 92 \text{ M}^{-1} \text{ s}^{-1}$ and $k_d = 0.08 \pm 0.02 \text{ s}^{-1}$.

Table 2. Adsorption and Desorption Rate Constants (k_a and k_d) from Fits of Eq 4 and $k_{\text{obs}} = k_a C + k_d$ to the Experimental Data

temp (K)	$k_a (\text{M}^{-1} \text{ s}^{-1})$	$k_d (\text{s}^{-1})$
288	6871 ± 803	0.13 ± 0.09
293	2278 ± 92	0.08 ± 0.02
298	2201 ± 198	0.14 ± 0.03
303	2278 ± 537	0.24 ± 0.06

the adsorption reaction v ,

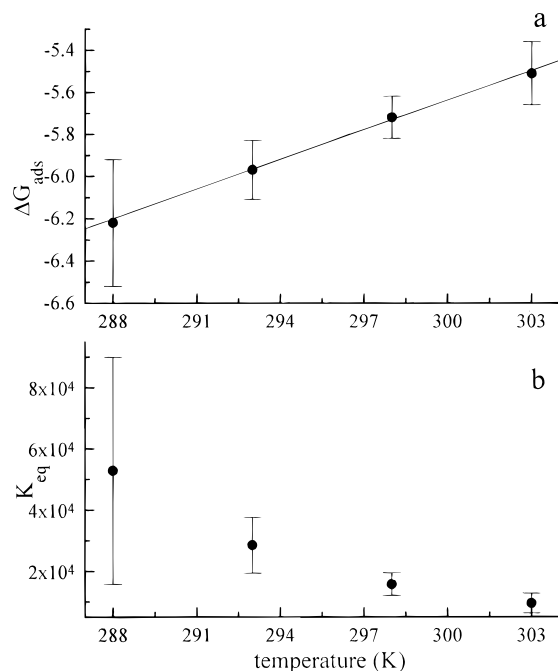
$$K_{\text{eq}} = k_a/k_d$$

$$\Delta G_{\text{ads}} = -RT \ln K_{\text{eq}} \quad (5)$$

By performing our experiments at specific temperatures in the range of 288–303 K, we have measured the temperature dependence of K_{eq} and ΔG_{ads} which we present in Table 3 and Figure 3. The data exhibit a substantial decrease in K_{eq} with increasing temperature; ΔG_{ads} becomes less negative with increasing temperature. Since a negative ΔG_{ads} indicates a spontaneous condition, the trend to less spontaneous ΔG_{ads} with

Table 3: Temperature Dependence of the Equilibrium Constant (K_{eq}) and the Gibbs Free Energy of Adsorption (ΔG_{ads})

temp (K)	K_{eq}	ΔG_{ads} (kcal/mol)
288	52854 ± 37100	-6.22 ± 0.30
293	28475 ± 9134	-5.97 ± 0.14
298	15721 ± 3653	-5.72 ± 0.10
303	9492 ± 3262	-5.51 ± 0.15

**Figure 3.** Temperature dependence of (a) ΔG_{ads} and (b) K_{eq} . The regressed line shown in part a yields a slope of $-\Delta S_{\text{ads}} = 48 \pm 1$ cal/(mol·K) and an intercept of $\Delta H_{\text{ads}} = -19.9 \pm 0.4$ kcal/mol.

increasing temperature indicates that the adsorption process we measure is exothermic. The temperature dependence of K_{eq} allows the calculation of the enthalpy of adsorption, ΔH_{ads} , using the van't Hoff equation,⁶⁶

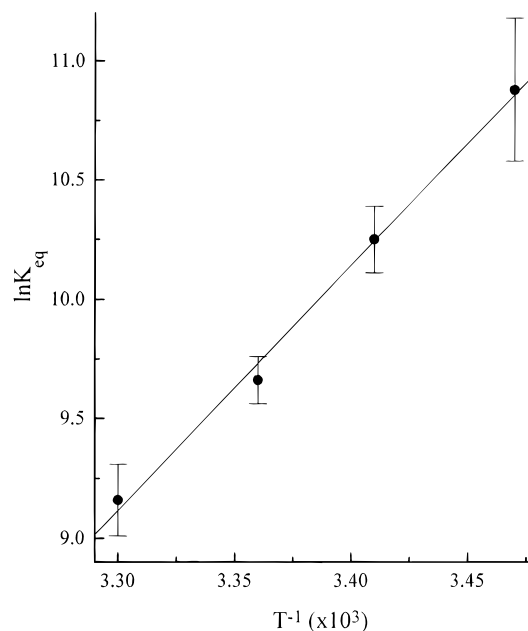
$$\frac{-\Delta H_{\text{ads}}}{R} = \frac{\ln K_{\text{eq}}}{T^{-1}} \quad (6)$$

We show in Figure 4 the linear dependence of $\ln K_{\text{eq}}$ on T^{-1} giving a slope of $-\Delta H_{\text{ads}}/R$. We obtain $\Delta H_{\text{ads}} = -20 \pm 1$ kcal/mol for the adsorption of 1-octadecanethiol/gold monolayers from *n*-hexane. From the $\Delta G_{\text{ads}}(T)$ and ΔH_{ads} , we obtain the entropy of adsorption,

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \quad (7)$$

The dependence of ΔG_{ads} on T is shown in Figure 3a. We find from a regression of these data that $\Delta S_{\text{ads}} = -48 \pm 1$ cal/(mol·K) and, as a comparison to the van't Hoff determination of ΔH_{ads} , we obtain $\Delta H_{\text{ads}} = -19.9 \pm 0.4$ kcal/mol. This alternate route to ΔH_{ads} serves as a useful self-consistency check on our results.

We note that, because the alkanethiol/gold system is an equilibrium system, the fractional coverage of the Au surface depends on the concentration of the thiol solution, and over the concentration range studied here the fraction of the surface, $\theta \sim 0.1$ (RSH = 1×10^{-5} M) to $\theta \sim 1$ (RSH = 3×10^{-4} M).¹⁸ This concentration-dependent surface coverage is expressed in the prefactor of eq 3 and is an expected result based on the predictions of the Langmuir adsorption isotherm. The phenomenon under examination in this work is the initial formation

**Figure 4.** Van't Hoff plot of $\ln K_{\text{eq}}$ vs T^{-1} . From these data we determine $\Delta H_{\text{ads}} = -20 \pm 1$ kcal/mol.

of the gold–thiol bond, which is expected to proceed more rapidly than rearrangement and annealing steps in the formation of the monolayer. The thermodynamic results on alkanethiol adsorption to Au are interesting in and of themselves and are consistent with the other, limited thermodynamic data that exist for these systems. We consider next the implications and chemical information content of these results.

Before discussing the chemical implications of these data, we need to consider whether or not the adsorption process is diffusion limited. Indeed, if the reaction under consideration is diffusion limited, then a Langmuir treatment of our data is inappropriate. We presume as a starting point that both adsorption and desorption occur, and this *ansatz* is supported by both McCarley's¹⁷ and Poirier's⁵⁶ atomic microscopy data. Recently, the Schlenoff group has suggested that the adsorption reaction is diffusion rate limited⁶³ based on initial rate data that we had reported previously.¹⁸ The temperature dependence of the observed rate constant for a fixed thiol concentration (Figure 5) demonstrates clearly that the adsorption reaction is not diffusion rate limited. Our basis for this statement is that a diffusion rate limited reaction should possess a rate constant that depends linearly on temperature,⁶⁵ and the data presented in Figure 5 are independent of T , to within the uncertainty of the measurement. We note that the data presented in Figure 5 are rate constants extracted directly from raw data and do not depend on the use of the Langmuir isotherm. Regardless of the isotherm under consideration, our data demonstrate that the adsorption of alkanethiols onto Au is not diffusion limited for these conditions.

There are two processes intrinsic to the formation of self-assembled monolayers, and they proceed on significantly different time scales. These processes are the initial adsorption of the thiol head group to the Au surface, which occurs within seconds of exposure, and subsequent to head group adsorption, the aliphatic chains anneal from an initially statistical distribution of conformers to a predominantly all-*trans* conformation over a period of hours to days. Our QCM-based kinetic studies yield information about thiol head group adsorption. Accordingly, we consider the processes of initial adsorption and aliphatic annealing separately and assume that they are significantly decoupled.

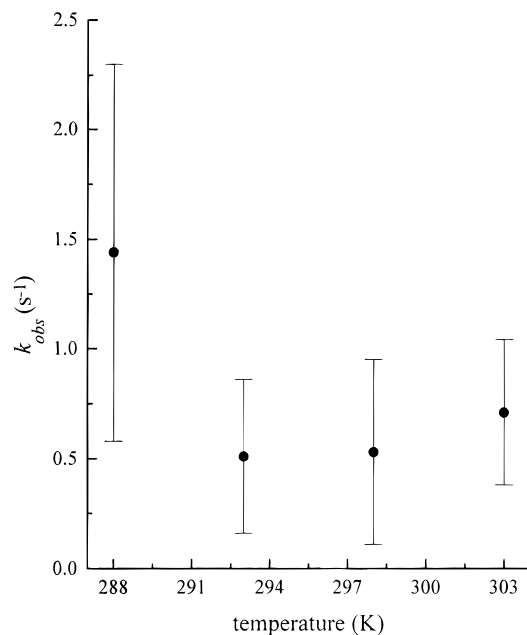


Figure 5. Temperature dependence of the observed rate constants, k_{obs} . These data are essentially temperature independent, to within the uncertainty of the measurements. No linear dependence of k_{obs} on T is detectable from these data.

For 1-octadecanethiol/gold monolayer formation from *n*-hexane, $\Delta G_{ads} \cong -5.5$ kcal/mol depending on the temperature. The magnitude of ΔG_{ads} for the 1-octadecanethiol/gold monolayer is the same as that of a liquid alcohol hydrogen bond; the result of a close balance between the enthalpy and entropy of adsorption, both of which are significant for this reaction. The enthalpy of adsorption, ΔH_{ads} , was found to be -20 ± 1 kcal/mol. We note that this value does not correspond closely with the calculated quantities discussed above for the formation and desorption of the monolayer. We understand the differences between calculation and experiment based on our use of standard enthalpies in the calculations and the significant difference between our experimental conditions, which include solvation effects and standard conditions. We can compare our experimental value of ΔH_{ads} to the ΔH for desorption of a monolayer of 28 kcal/mol for desorption into air obtained by Nuzzo and co-workers.⁶⁸ Our data contain both solvation and adsorption information and their data are a direct measure of (reversible) desorption. The difference between their data and ours indicates the enthalpy of solvation, $\Delta H_{solv} \sim -8$ kcal/mol for 1-octadecanethiol in *n*-hexane because their data represent, almost exclusively, the gold–sulfur interaction. The enthalpy of solvation is both solvent and thiol dependent and thus -8 kcal/mol is a useful, but only qualitative, estimate for other systems. The adsorption enthalpy we measure, ΔH_{ads} (-20 kcal/mol), consists of the balance between the solvation enthalpy ΔH_{solv} (-8 kcal/mol) and the monolayer formation enthalpy ΔH_{ml} (-28 kcal/mol).

$$\Delta H_{ads} = \Delta H_{ml} - \Delta H_{solv} \quad (8)$$

The quantity ΔH_{ml} is dominated by Au–S bond formation and any energy associated with displacement of solvent from the Au surface during the formation of the monolayer. We expect that ΔH_{ml} will be largely independent of thiol chain length because the dominant process on these comparatively short time scales is the interaction between the thiol head group and the metal surface. We note that one potential solvent-dependent

contribution to ΔH_{ml} may be associated with the polarity of the transition state in the formation of the gold–thiol bond and the extent to which the solvent stabilizes or destabilizes that state,⁴⁰ but this effect is likely to be modest because of steric constraints in the formation of the monolayer and the presence of the metal interface.

The entropy of adsorption, ΔS_{ads} , is -48 ± 1 cal/(mol·K). This quantity is approximately four times larger than a typical ΔS_{fus} for a liquid-to-solid phase transition.⁷⁴ For the same reason that ΔH_{ml} is largely thiol independent, we expect the entropy of adsorption, ΔS_{ads} , to be substantially independent of thiol aliphatic chain length. This large entropic term is dominated by the change in system order associated with alkanethiols oriented randomly in solution going to produce a highly organized, two-dimensional crystalline array of thiol head groups on gold.

Given the predicted thiol independence of ΔH_{ml} and ΔS_{ads} , it is important to review our previous experiments indicating solvent- and thiol-dependent monolayer formation. We account for the thiol dependence of ΔG_{ads} we observed for monolayer formation from *n*-hexane based on different solvation enthalpies for the two thiols. For the adsorption of 1-C₁₈H₃₇SH, $\Delta G_{ads} = -5.6 \pm 0.2$ kcal/mol at 293 K, and for 1-C₈H₁₇SH monolayer formation, $\Delta G_{ads} = -4.4 \pm 0.2$ kcal/mol at the same temperature.¹⁸ As discussed above, we believe that the enthalpy of monolayer formation, ΔH_{ml} , is constant for all thiols at -28 kcal/mol. The solvation enthalpy ΔH_{solv} is, of course, solvent dependent. We calculate $\Delta H_{solv} = -8$ kcal/mol for 1-octadecanethiol in *n*-hexane and $\Delta H_{solv} = -9$ kcal/mol for 1-octadecanethiol in *n*-hexane. Invoking the thiol independence of ΔS_{ads} yields $\Delta H_{ads} = -19$ kcal/mol for the 1-octadecanethiol/gold monolayer. For alkanethiol monolayer formation on Au, the enthalpy of solvation, ΔH_{solv} , is the primary quantity under the influence of experimental control, and attempts to enhance the robustness of alkanethiol monolayers will ultimately be limited by the extent to which ΔH_{solv} can be adjusted.

Conclusions

We have measured the thermodynamics of 1-octadecanethiol/gold monolayer formation from *n*-hexane solution. Our data indicate that the comparatively small free energy of adsorption for this system is the result of a close balance between the enthalpic driving force for the reaction and an entropic penalty associated with the high degree of organization associated with self assembly. For our experimental conditions the dominant chemical reaction is the reversible adsorption of the alkanethiol, and the temperature dependence of the QCM kinetic response demonstrates that the reaction, for our conditions, is not diffusion rate limited. These data point collectively to the fact that there are limits to the robustness of alkanethiol/gold monolayers and that the ability to adjust the formation properties of this system is limited primarily by the solubility of the alkanethiol in the solvent from which the adsorption takes place. Because the formation of the thiol–Au bond is fast compared to the structural annealing of the organic tail group, these data may be of some utility in predicting the formation properties of other thiol/gold assemblies in the limit that steric contributions from the organic tail groups do not preclude significant monolayer formation.

Acknowledgment. We are grateful to The National Science Foundation for support of this work through Grant CHE 95-08763 and for the support of H.M.S. through the NSF REU Program at MSU. We are indebted to Professor J. Allison for several insightful suggestions on this work.