

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231668914>

Direct Measurement of the Adsorption Kinetics of Alkanethiolate Self-Assembled Monolayers on a Microcrystalline Gold Surface

ARTICLE *in* LANGMUIR · SEPTEMBER 1994

Impact Factor: 4.46 · DOI: 10.1021/la00021a066

CITATIONS

329

READS

143

2 AUTHORS, INCLUDING:



Gary J Blanchard

Michigan State University

186 PUBLICATIONS 3,957 CITATIONS

SEE PROFILE

Direct Measurement of the Adsorption Kinetics of Alkanethiolate Self-Assembled Monolayers on a Microcrystalline Gold Surface

D. S. Karpovich and G. J. Blanchard*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322

Received June 15, 1994®

We report measurements on the adsorption kinetics of alkanethiolate monolayers onto a microcrystalline gold surface. Our data indicate that the formation of this monolayer is rapid and is described by the Langmuir adsorption isotherm. The concentration dependence of the monolayer formation rate indicates that there exists an equilibrium for the adsorption/desorption process. We determine from these measurements $\Delta G_{\text{ads}} = -5.5$ kcal/mol for 1-C₁₈H₃₇SH in *n*-hexane and cyclohexane adsorbing onto gold and $\Delta G_{\text{ads}} = -4.4$ kcal/mol for 1-C₈H₁₇SH in *n*-hexane adsorbing onto gold.

Introduction

The study of organic interfacial monolayer systems has attracted a great deal of research attention over the past decade because of the potential utility of these interfaces in materials science and chemical separation applications. Initial work on the structural and chemical properties of interfacial organic monolayers supported on amorphous substrates required statistical treatment to understand the role of their intrinsic heterogeneity. Recent chemical advances in the formation of single molecular layers on highly ordered metal¹⁻⁴ and dielectric⁵⁻¹² surfaces have allowed the structure of these assemblies to be examined more directly by removing structural variability induced by the surface. Much of the recent work on self-assembling organic monolayers at metal surfaces has focused on the alkanethiolate/gold system, where alkanethiols adsorb spontaneously onto the metal surface to form a highly ordered array.¹³⁻²⁵ A variety of tools have been applied in studies of these self-assembled monolayers to elucidate

their molecular-scale structural properties. FTIR spectroscopy has been used most commonly for the examination of molecular ordering in these films, and these results have shown that the interface is composed of densely packed, virtually all-*trans* aliphatic chains that are tilted at $\sim 30^\circ$ with respect to the surface normal.¹⁵ Ellipsometric and contact angle measurements have indicated that these films are uniform over macroscopic distances (several micrometers), and recent atomic scale microscopy has demonstrated the existence of highly regular structure on molecular length scales.²⁶⁻²⁹ Based on this large body of information, the alkanethiolate/gold system has come to be viewed as largely immobile, once formed.

McCarley's recent scanning probe microscopy work has called into question the extent to which these monolayers are "fixed" in place subsequent to adsorption.²⁹ The island structures formed by the alkanethiolate monolayers on an evaporated gold substrate exhibited macroscopic shape changes over periods as short as minutes, and the McCarley group has concluded that these shape-changes are associated with mobile defects in the gold surface and that the Au-S bond is labile.²⁹ This finding indicates that either the formation of the alkanethiolate monolayer has a substantial effect on the mobility of the surface gold atoms or that the overlayer itself exhibits structural mobility.

Virtually all examinations of the alkanethiolate/gold monolayer system have been performed on monolayers that were formed prior to examination, and little effort has been spent on understanding the elementary steps in the formation of the monolayers. We have chosen to examine the formation of these monolayers gravimetrically. We have measured the rate at which these monolayers form in real time by monitoring the change in mass of a quartz crystal microbalance made with evaporated gold electrodes. These data show that the alkanethiolate/gold system exhibits a measurable equilibrium between adsorbed thiolate and the free species. From our data we have determined that the free energy

* Author to whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts*, August 1, 1994.

- (1) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45.
- (2) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52.
- (3) Sondag, A. H. M.; Raas, M. C. *J. Chem. Phys.* **1989**, *91*, 4926.
- (4) Chau, L. K.; Porter, M. D. *Chem. Phys. Lett.* **1990**, *167*, 198.
- (5) Lee, H.; Kepley, L. J.; Hong, H. G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618.
- (6) Lee, H.; Kepley, L. J.; Hong, H. G.; Akhter, S.; Mallouk, T. E. *J. Phys. Chem.* **1988**, *92*, 2597.
- (7) Cao, G.; Mallouk, T. E. *J. Solid State Chem.* **1991**, *94*, 59.
- (8) Akhter, S.; Lee, H.; Mallouk, T. E.; White, J. M.; Hong, H. G. *J. Vac. Sci. Tech. A* **1989**, *7*, 1608.
- (9) Hong, H. G.; Mallouk, T. E. *Langmuir* **1991**, *7*, 2362.
- (10) Cao, G.; Rabenberg, L. K.; Nunn, C. M.; Mallouk, T. E. *Chem. Mater.* **1991**, *3*, 149.
- (11) Kepley, L. J.; Sackett, D. D.; Bell, C. M.; Mallouk, T. E. *Thin Solid Films*, **1992**, *208*, 132.
- (12) Hong, H. G.; Sackett, D. D.; Mallouk, T. E. *Chem. Mater.* **1991**, *3*, 521.
- (13) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 570.
- (14) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.
- (15) Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, *93*, 767.
- (16) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682.
- (17) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujscu, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301.
- (18) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.*, **1989**, *111*, 321.
- (19) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155.
- (20) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir*, **1988**, *4*, 365.
- (21) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
- (22) Whitesides, G. M.; Laibinis, P. E. *Langmuir*, **1990**, *6*, 87.

- (23) Camillone, N., III; Chidsey, C. E. D.; Liu, G.-Y.; Putvinski, T. M.; Scoles, G. C.; Wang, J. *J. Chem. Phys.* **1991**, *94*, 8493.
- (24) Chidsey, C. E. D.; Liu, G.-Y.; Wang, J. *Langmuir*, **1990**, *6*, 1804.
- (25) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5852.
- (26) Widrig, C. A.; Alves, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 2805.
- (27) Liu, G.-Y.; Salmeron, M. B. *Langmuir* **1994**, *10*, 367.
- (28) McCarley, R. L.; Kim, Y.-T.; Bard, A. J. *J. Phys. Chem.* **1993**, *97*, 211.
- (29) McCarley, R. L.; Dunaway, D. J.; Willicut, R. J. *Langmuir* **1993**, *9*, 2775.

of adsorption of the alkanethiol on gold is ~ -5 kcal/mol, and this value depends slightly on the aliphatic chain length of the alkanethiol adsorbate. It is therefore expected that, at any given time, a significant fraction of surface active gold sites will be exposed and thus macroscopic shape changes in the appearance of the surface are likely to occur. Our findings also imply that the rate of electron transfer across these monolayers is mediated by the equilibrium dynamics of the interface.

Experimental Section

Kinetic Measurements. We used a quartz crystal microbalance (QCM) to study the adsorption kinetics of alkanethiols onto gold. A quartz crystal microbalance with a resonance frequency of ~ 6 MHz is sensitive to mass changes as small as several nanograms.³⁰ The electrodes of the QCM we use are vapor deposited gold that yields a polycrystalline, predominantly (111), surface. There are several factors in addition to the mass loading of the QCM that affect its oscillation frequency. The resonance frequency of the QCM depends on mass loading according to the Sauerbrey equation.³¹ This relationship holds well for gas-phase measurements, but *in situ* solution phase measurements using the QCM are, in many cases, only semi-quantitative due to capacitive and colligative effects arising from the presence of the solvent and the adlayer(s). We discuss this point below and note that only certain solvents are amenable to these measurements. Ethanol, for example, yields a QCM response dominated by large frequency fluctuations ($\Delta\nu \sim 150$ Hz) which we attribute to the complexity of ethanol's dielectric response and the hydrophilic nature of the clean QCM gold electrode surfaces. Our primary focus in this work lies in determining the rate of QCM frequency change associated with the formation of the alkanethiolate monolayer, and we do not attempt to extract absolute mass change information from our data.

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 QCM devices were sufficiently robust to avoid breakage from the spring clip pressure required to ensure reliable electrical contact. The QCM was connected to a 6-MHz oscillator circuit (Maxtek part number 124200-4). 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 this frequency counter was sent to a computer for data processing and storage. For all adsorption rate measurements the data were acquired at a rate of ten readings per second to ensure adequate sampling of the kinetic response. All electrical connections were made using shielded coaxial cables to minimize QCM frequency instability arising from electrical interference.

The resonant frequency of a QCM 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. Measurements were performed in a 150-mL jacketed beaker connected to a flowing liquid temperature controller (Neslab Model RTE-110) set to 293.00 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.

Glassware was cleaned using a chromic acid solution and rinsed with distilled water and subsequently the solvent of interest prior to each measurement. The QCMs were cleaned with piranha solution (1:3 H_2O_2 (30%)/ H_2SO_4) for 5 min,³² rinsed with deionized water, and dried in a stream of high-purity N_2 . The

cleaned QCMs were then rinsed with tetrahydrofuran to remove any residual water and then with the solvent to be used in the experiment (*n*-hexane or cyclohexane) and used immediately thereafter. Prolonged exposure to piranha solution damaged the QCM electrodes, and this damage was manifested by an increase in frequency fluctuations for the baseline readings. A new crystal was used approximately every 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 high enough thiol concentration to allow small injection volumes, minimizing mechanical disruption of the contents of the reaction vessel. For 10^{-4} M thiol final concentration, 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 from injection.

External Reflection FTIR Measurements. We obtained infrared spectra of the adsorbed films via external reflection infrared spectroscopy using a Nicolet 520 Fourier transform infrared spectrometer. The spectrometer was equipped with a cooled MCT detector. The external reflection sample mount and optics used were obtained from Harrick Scientific Corp. and the polarization of the IR light was controlled using a Cambridge Physical Sciences broad band IR polarizer. The light was p-polarized and was incident at 75° with respect to the surface normal of the QCM. Achieving an 86.5° incidence angle to maximize the signal was not possible because of the geometric constraints imposed by the QCM electrode dimensions. Spectral resolution was 2 cm^{-1} for the scans we report here.

Chemicals. The alkanethiols 1-octadecanethiol and 1-octanethiol were purchased from Aldrich Chemical Co. and were used as received. These thiols were tested by gas chromatography and mass spectrometry to determine the presence of the corresponding dialkyl disulfide, and none was detected. The solvents *n*-hexane and cyclohexane were purchased from Baxter (Burdick and Jackson) and were used without further purification.

Results and Discussion

Despite extensive investigation of equilibrated alkanethiol monolayers, there is little fundamental information on the kinetics or energetics of their formation. Methods used commonly for the examination of alkanethiolate-gold monolayers, such as external reflection infrared spectroscopy, contact angle measurement, and optical ellipsometry, are sensitive to structural properties on a length scale many times longer than the aliphatic chains that comprise the monolayer, but, more importantly, these methods have been used to measure the response of an equilibrated chemical system. In the work we report here, we determine the rate of mass change of the alkanethiolate-gold interface resulting from adsorption of alkanethiol from solution onto gold. This kinetic response, arising from systems that are initially far from equilibrium, provides fundamental information on the initial steps of the alkanethiolate monolayer self-assembly process.

To provide a frame of reference, we briefly recap what is known about alkanethiolate monolayers. Diffraction and scanning microscope measurements have shown that these systems form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ monolayer structure on Au(111) surfaces,^{23,27,33,34} with infrared measurements showing that all-*trans* aliphatic chains of the alkanethiolate are oriented at $\sim 30^\circ$ with respect to the gold surface

(30) Guilbault, G. G. *Methods and Phenomena 7: Applications of Piezoelectric Quartz Crystal Microbalances*; Elsevier Science Publishing Co.: New York, 1984; p 252.

(31) Sauerbrey, G. Z. Z. Phys. 1959, 155, 206.

(32) We caution that $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ solution is hazardous and corrosive. Contact with organic matter, especially when the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ solution is hot, can result in a rapid oxidation reaction.

(33) Strong, L.; Whitesides, G. M. *Langmuir* 1988, 4, 546.

(34) Chidsey, C. E. D.; Liu, G.-Y.; Rowntree, P.; Scoles, G. J. *Chem. Phys.* 1989, 91, 4421.

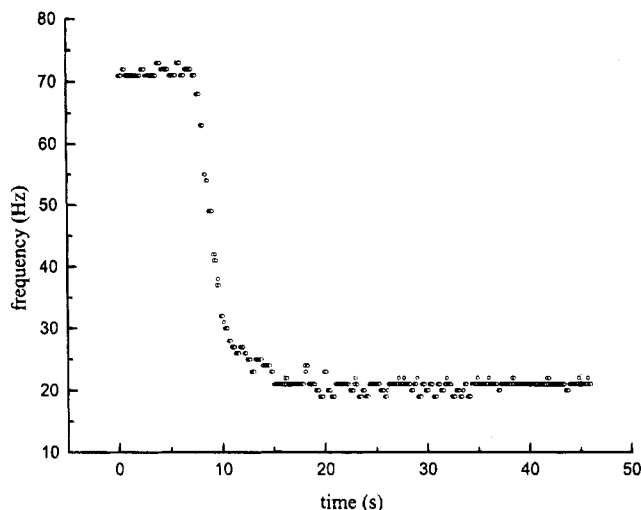
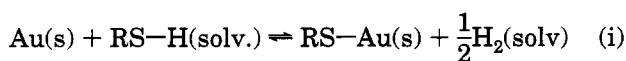


Figure 1. Representative raw data of QCM oscillation frequency vs time subsequent to thiol injection. Injected solution was $C_{18}H_{37}SH/n$ -hexane. See text for a detailed discussion of these data.

normal and are rotated $\sim 55^\circ$ with respect to the plane formed by the surface normal and the orientation vector of the chain.¹⁵ These monolayers are densely packed, with an interchain spacing of ~ 5 Å, established by He diffraction measurements and corroborated by STM data.^{23,26,33} While thought to be comparatively rigid until recently, McCarley's STM measurements have provided compelling evidence for structural mobility within these monolayers.²⁹ In addition, several recent studies of electron transfer across these monolayers have suggested that the rate of transfer is mediated by the density of defect sites. The data that we present in this paper provide an explanation for these recent observations and demonstrate that the apparently labile nature of these monolayers is a natural consequence of the strength of the bond responsible for the initial formation of the monolayer.

We have examined the formation kinetics for the alkanethiolate-gold monolayer from two different solvents and for two different alkanethiol aliphatic chain lengths. 1-Octadecanethiol was adsorbed onto the QCM electrodes from both *n*-hexane and cyclohexane and 1-octanethiol was adsorbed from *n*-hexane. For each of these chemical systems, data were collected over an alkanethiol concentration range large enough to establish the region in which the Langmuir isotherm predictions hold. Raw data (QCM resonant frequency vs time after thiol introduction) for the adsorption of 1-octadecanethiol from a 10^{-4} M solution in *n*-hexane are shown in Figure 1. It is immediately apparent from these data that a chemical equilibrium is achieved within a very short time (< 1 min) following thiol introduction. Further, the rate at which this equilibrium is achieved depends on the concentration of the thiol (Figure 2), and it is information from this concentration dependence that yields the free energy of adsorption for these systems. The adsorption reaction we detect is believed to be³⁵



This reaction proceeds at a gold surface where the thiols react with the metal to form a gold thiolate monolayer ($Au-SR$) and hydrogen. Our experimental data show that the Langmuir isotherm can be used to describe the kinetic

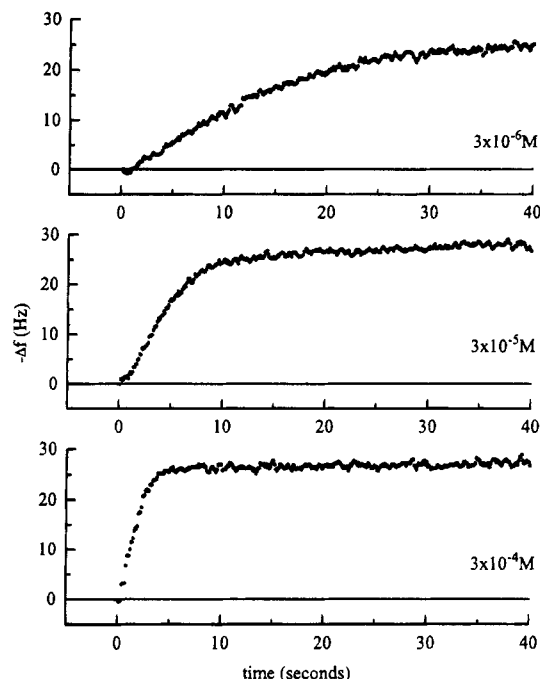


Figure 2. Thiol concentration dependence of QCM frequency change for 1-octadecanethiol in *n*-hexane. The top panel is data for a 3×10^{-6} M final thiol concentration, the center panel is for a 3×10^{-5} M final thiol concentration, and the bottom panel is for a 3×10^{-4} M thiol concentration.

response of this reaction over a substantial concentration range. The Langmuir isotherm is based on the assumptions that adsorption is limited to one monolayer, all surface sites are equivalent, and adsorption to one site is independent of the occupancy condition of the adjacent sites. The first assumption is clearly valid based on the chemical identity of the adsorbate species. An equivalent expression of the second assumption is that the surface is defect-free. Clearly this assumption is not physically realistic. While there are a variety of defects at the gold surface associated with grain boundaries, step edges, adatoms, and vacancies, the resultant modulation of surface site energies is apparently small enough that the Langmuir approximation holds. The physical and chemical bases for a third assumption are also open to significant question. The adsorbate alkyl chains interact with each other, but this interaction is likely only significant for nearly complete surface coverage because of the inherently short range nature of dispersive forces. In addition, it is likely that the time scale over which these interchain interactions proceed is significantly longer than the time scale associated with the formation of the gold-thiolate bond. We note also that the Langmuir isotherm was derived initially for physisorption, not chemisorption, but the bond strength of the alkanethiolate-gold bond is apparently small enough that this condition is not violated seriously (*vide infra*).

The effects of exposing the QCM electrodes to liquids have been studied by Thompson's group using network analysis as well as conventional series frequency measurements.^{36,37} Network analysis involves measurement by standard circuit analysis of four impedances in an equivalent circuit. These impedances are the static capacitance C_0 , the motional resistance R_m , the motional inductance L_m , and the motional capacitance C_m . The static capacitance describes the QCM response at frequencies far from the resonant frequency where it is a

(35) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.

(36) Yang, M.; Thompson, M. *Langmuir* **1993**, *9*, 802.

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

simple parallel-plate capacitor. The motional resistance is related to the liquid density and viscosity such that R_m increases with increasing viscosity and density. The motional inductance increases with the increase in plate thickness associated with external mass loading. The motional capacitance represents the elasticity of the QCM. Ideally, the above parameters, except the motional inductance, will remain constant for over the time course of our measurements.

Given the motional resistance, and the measured frequency shift (also called the series frequency Δf_s), the individual components of the frequency shift can be estimated^{36,37}

$$\Delta f_s = \Delta f_d + \Delta f_m + \Delta f_a + \Delta f_x$$

Where Δf_d is the portion of the frequency shift related to viscous damping, Δf_m is caused by adsorbed mass, Δf_a is surface stress, and Δf_x is caused by energy dissipation by nonshear couplings. We need to consider how the frequency shifts we report are affected by each of these components.

According to Thompson's experiments on a QCM in air with both bare gold and thiol-modified gold surfaces, the viscoelastic properties of the QCM did not change with adsorption and thus the motional capacitance and Δf_d did not change with the presence of the thiol monolayer.^{36,37} In other words, the thiol monolayer can be considered a rigid film for purposes of the QCM measurements. In a comparison of the thiol-modified QCM and the bare gold QCM, Thompson noted that upon immersion into polar solvents such as water, the frequency shifted more for the bare gold QCM than for thiol-modified QCM. This was attributed with the interfacial properties exhibited with water at the hydrophilic and hydrophobic surfaces which would affect Δf_m and Δf_x .

Thompson's work also involved a study of the effects of roughness of the QCM's surface on its behavior in liquids.^{36,37} He found that frequency shifts of polished surfaces upon immersion into liquids were less than those of unpolished surfaces in the same liquid. Electron microscopy showed that the polished and unpolished surfaces differed greatly in roughness, with the rough, unpolished surfaces possessing a higher number of adsorptive sites. The variability in surface roughness between individual QCM's introduces uncertainty in the number of active gold sites available for thiol adsorption. There is also a mechanical stress on our QCMs due to the spring clip used to hold the QCM. Although Δf_a would vary from one measurement to the next, this variation should not cause a frequency shift (Δf_s) error since Δf_a would remain constant through a single measurement. Changes in mechanical stress caused by the spring clip are the result of variability in the positioning of the spring clip, which would affect the amount of exposed gold surface available for the reaction.

The frequency changes we report for the formation of alkanethiol/Au monolayers are not simply due to the mass uptake of the surface. As a consequence of the adsorption, the interfacial monolayer is changing from hydrophilic to hydrophobic. The energy of interaction of the surface with solvent, which does affect the frequency, is therefore changing throughout the measurement in addition to the mass of the QCM. For our measurements, the frequency shift (Δf_s) is affected by changing Δf_m and Δf_x (the adsorbed mass and the energy dissipation by nonshear coupling) during a single measurement. The net result of this complex process is that the frequency shifts from our measurements are not representative of only the mass changes, and thus extraction of fractional coverage

information from these data is problematic at best. The time dependence of this response is, however, a direct result of the formation of the monolayer, which affects both the mass uptake and changing surface/solvent interactions. Our time domain measurements are sensitive to the kinetics of formation of the monolayer. The run-to-run variation in Δf_s for our experiments results from variable gold surface roughness of the QCMs (which affect Δf_m and Δf_x) and variability in positioning the spring clip onto the QCM resulting in variability in the area of the exposed gold.

We do not have a good gauge of the roughness of the gold surface at the atomic scale, and while this information is important, it is not critical to our experiment for the reasons we have discussed above. The coverage of the QCM electrode surface is expressed as a unitless quantity θ , the fraction of available sites that have reacted, or, equivalently, the fraction of a monolayer ($0 \leq \theta \leq 1$). The Langmuir isotherm dictates that the rate of surface reaction is given by

$$\frac{d\theta}{dt} = k_a(1 - \theta)c - k_d\theta \quad (1)$$

where θ is the fraction of surface covered, $(1 - \theta)$ is the fraction of surface exposed, C is the alkanethiol concentration, and k_a and k_d are the association and dissociation constants, respectively. Integration of eq 1 yields the time course of the monolayer formation

$$\theta(t) = \frac{C}{C + (k_d/k_a)} [1 - \exp(-(k_a C + k_d)t)] \quad (2)$$

This result can be simplified by the substitutions $k_{obs} = k_a C + k_d$ and $K' = C/(C + (k_d/k_a))$, giving

$$\theta(t) = K'[1 - \exp(-k_{obs}t)] \quad (3)$$

Notice from the raw data, shown in Figure 2, that the maximum initial rate of monolayer formation is not reached immediately upon injection. Depending on the volume and concentration of thiol aliquot injected, it may take up to several seconds to achieve the maximum adsorption rate because of limitations inherent to mixing of the solvent and the thiol aliquot. We have determined that the aliquot mixing time is substantially shorter than the monolayer formation time by measurement of the mixing time using a colored dye solution. The time required for thorough mixing is related to both the concentration and volume of the injected aliquot; as either of these quantities decreases, the mixing time increases correspondingly. The onset of the maximum initial rate is caused by the concentration gradient introduced by mixing. We account for this mixing effect by modifying the variable " t " in eq 3 to " $t - t_0$ " where t_0 is the time required to achieve a homogeneous solution

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

Fitting the portion of the curve from the onset of the maximum rate through a significant portion of equilibrium yields t_0 , the predicted time of injection if mixing were instantaneous, or equivalently, the time required for the thiol reactant to achieve a homogeneous distribution in the reaction vessel.

The raw data were fit to eq 4, and the agreement between fit and data is shown for a representative scan in Figure 3. The results of these fits are presented in Table 1. For the purpose of fitting the data, k_{obs} is independent of K' because the absolute frequency changes vary from one

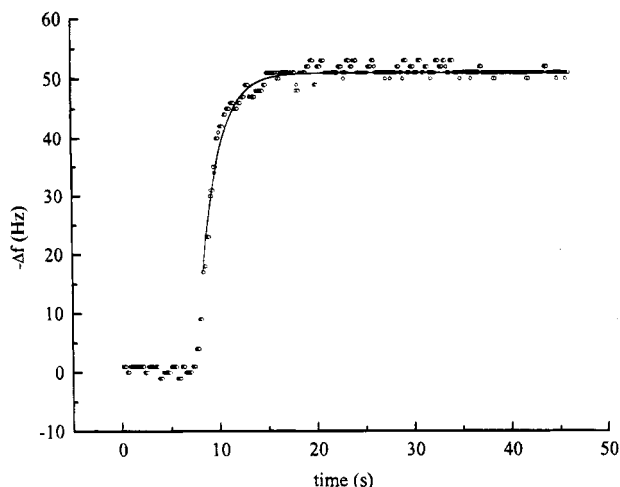


Figure 3. Fit of Langmuir adsorption isotherm (eq 4) to raw experimental data.

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

adsorbate/solvent	thiol concentration (M)	$k_{\text{obs}} \pm 95\% \text{ C.I.}$ (s^{-2})
1-octadecanethiol/ cyclohexane	1×10^{-5}	0.06 ± 0.02
	3×10^{-5}	0.23 ± 0.07
	1×10^{-4}	0.51 ± 0.16
	3×10^{-4}	0.58 ± 0.43
1-octadecanethiol/ <i>n</i> -hexane	1×10^{-6}	0.06 ± 0.04
	3×10^{-6}	0.14 ± 0.04
	1×10^{-5}	0.24 ± 0.06
	3×10^{-5}	0.23 ± 0.13
1-octanethiol/ <i>n</i> -hexane	1×10^{-4}	0.44 ± 0.16
	3×10^{-4}	0.75 ± 0.41
	1×10^{-5}	0.17 ± 0.03
	3×10^{-5}	0.44 ± 0.06
	1×10^{-4}	0.52 ± 0.11
	3×10^{-4}	0.70 ± 0.23
	1×10^{-3}	1.20 ± 0.34
	3×10^{-3}	0.90 ± 0.34

run to the next due to the sensitive impedance matching conditions required by the electronics and the variation of the gold surface morphology from one QCM to another. Because θ is unitless, the absolute mass change is not important to the determination of kinetic quantities k_a and k_d . The QCM oscillation frequency in solution prior to thiol introduction represents a baseline and plotting the (negative) QCM frequency change vs time subsequent to thiol introduction yields data of the form $z\theta(t)$ vs t where z is an arbitrary scaling factor.

Fitting the experimental data to eq 4 gives k_{obs} . Since $k_{\text{obs}} = k_a C + k_d$, a plot of k_{obs} vs C for a series of thiol concentrations gives a line with a slope of k_a and an intercept of k_d , as shown in Figure 4. The values of k_a and k_d obtained from these plots are presented in Table 2. The uncertainty in the values of k_a and k_d we obtain is significant, but, the data show unambiguously that desorption plays an important role in the formation of the alkanethiol monolayers, *i.e.* $k_d > 0$. This is an important finding in and of itself, because the existence of a nonzero k_d for alkanethiolate-gold self-assembled monolayers demonstrates that these are equilibrium systems, and therefore at any given instant in time, some fraction of the adsorbate sites on the surface is unoccupied.

The data we present in Table 2 allow the determination of the equilibrium constant, K_{eq} , for the monolayer system

$$K_{\text{eq}} = k_a/k_d \quad (5)$$

We can obtain two important physical quantities from

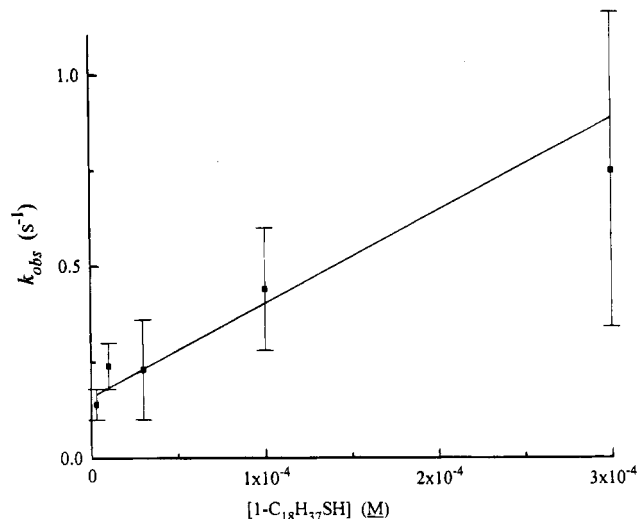


Figure 4. Concentration dependence of k_{obs} for 1-octadecanethiol in *n*-hexane in the concentration range over which Langmuir behavior is followed (see text for a discussion). The best fit line through the data has a slope of k_a and an intercept of k_d . See Table 2 for results of the fits to the data.

Table 2. k_a and k_d Determined from Concentration Dependence of k_{obs}

adsorbate/solvent	k_a ($\text{M}^{-1} \text{s}^{-1}$) $\pm 95\% \text{ C.I.}$	k_d (s^{-1}) $\pm 95\% \text{ C.I.}$
1-octadecanethiol/cyclohexane	2059 ± 1394	0.19 ± 0.09
1-octadecanethiol/ <i>n</i> -hexane	2440 ± 1074	0.16 ± 0.03
1-octanethiol/ <i>n</i> -hexane	811 ± 334	0.42 ± 0.06

Table 3. Fractional Surface Coverage as a Function of Thiol Concentration, Calculated Using Equation 6, for the 1-Octadecanethiol/*n*-Hexane System^a

thiol concentration (M)	$\theta(\infty)$
3×10^{-6}	0.04 ± 0.02
1×10^{-5}	0.13 ± 0.07
3×10^{-5}	0.31 ± 0.16
1×10^{-4}	0.60 ± 0.34
3×10^{-4}	0.82 ± 0.51

^a The uncertainty in $\theta(\infty)$ is determined by propagation of the uncertainty in k_a and k_d .

K_{eq} . The steady-state fractional coverage of the gold surface, $\theta(\infty)$, is given by

$$\theta(\infty) = \frac{C}{C + (1/K_{\text{eq}})} \quad (6)$$

We show in Table 3 the fractional coverage values calculated for the 1-octadecanethiolate-gold system using the experimental concentrations and equilibrium constant. The $\theta(\infty)$ values approach unity only at comparatively high thiol concentrations. The free energy of adsorption of the monolayer is also found directly from the equilibrium constant data.

$$\Delta G_{\text{ads}} = -RT \ln K_{\text{eq}} \quad (7)$$

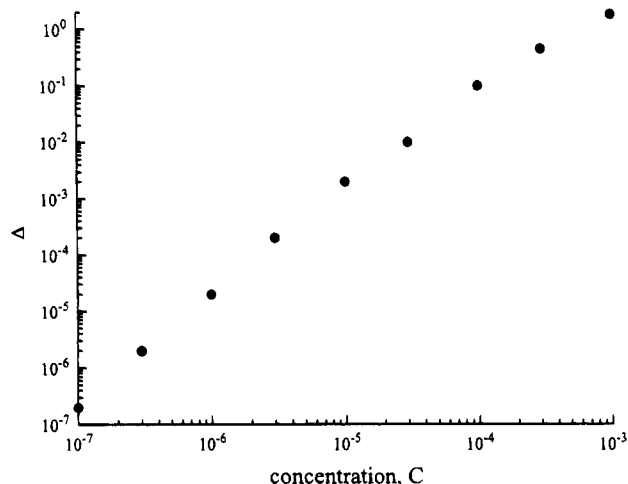
We show in Table 4 the free energies and equilibrium constants we have determined. Our data provide direct proof that the alkanethiolate-gold system is an equilibrium system. Recent atomic microscopy studies have shown that regions of the monolayers exhibit structural mobility,²⁹ and this finding is explained by the fact that the monolayer system is an equilibrium system.

Limits of Applicability for Langmuir Behavior. We observe a negative deviation from linearity for the relationship between k_{obs} and C for both high and low

Table 4. K_{eq} and ΔG_{ads} Determined from the Experimental Data^a

adsorbate/solvent	K_{eq} (M ⁻¹)	ΔG_{ads} (kcal/mol)
1-octadecanethiol/ <i>n</i> -hexane	15250 ± 7300	-5.6 ± 0.2
1-octadecanethiol/cyclohexane	10850 ± 8950	-5.5 ± 0.4
1-octanethiol/ <i>n</i> -hexane	1930 ± 840	-4.4 ± 0.2

^a Uncertainty in ΔG_{ads} is propagated from the uncertainty in K_{eq} .

**Figure 5.** Concentration dependence of Δ for $k_a = 2000$ M⁻¹ s⁻¹ and $k_d = 0.2$ s⁻¹.

thiol concentrations. We discuss below how the observed deviations do *not* indicate that these systems are ill-described by the Langmuir adsorption model, but, rather, demonstrate the limits intrinsic to this treatment of a complex equilibrium process.

The first deviation we consider is for low thiol concentrations. At low thiol concentration the perturbation introduced to the system by the thiol is small. In other words, for low thiol concentrations, the system remains in close proximity to equilibrium and the expected mass change for such conditions lies beneath our limit of detection ($\theta \ll 1$). At equilibrium, the net rate of reaction is zero, although there remains a nonzero adsorption and desorption rate for the thiolate.

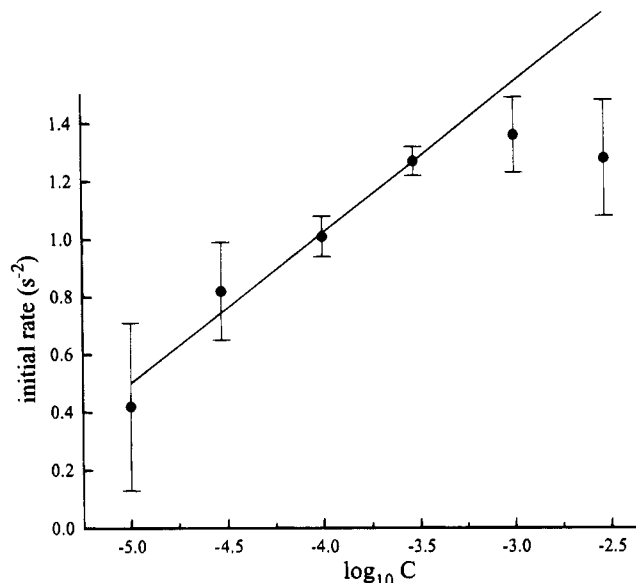
$$\frac{d\theta}{dt} = 0 = k_a(1 - \theta)C - k_d\theta$$

$$k_a(1 - \theta)C = k_d\theta \quad (8)$$

For small C , θ approaches zero, and the equilibrium rate of monolayer formation becomes very close to the initial rate of monolayer formation ($k_a C$). The perturbation from equilibrium introduced into the system by a low concentration of thiol is negligibly small, and the difference between the initial rate and the equilibrium monolayer formation rate tends to zero before $C = 0$. We define the quantity Δ to describe the displacement from equilibrium for low thiolate concentration. Δ is the difference between initial rate of adsorption and the equilibrium rate of adsorption.

$$\Delta = k_a C - k_a(1 - \theta)C = \frac{(k_a C)^2}{(k_a C + k_d)} \quad (9)$$

A plot of Δ vs C yields a line with a slope $\gg 1$, indicating that Δ becomes negligibly small as $C \rightarrow 0$ (Figure 5). Our data are explained by this prediction, and we expect a negative deviation from Langmuir behavior at low thiol concentrations.

**Figure 6.** Concentration dependence for initial rate of monolayer formation for 1-octanethiol adsorbed from *n*-hexane. Note the high concentration region where the rate becomes concentration independent.**Table 5.** Limiting Initial Rates of Monolayer Formation for High Thiol Concentration

adsorbate/solvent	initial rate (s ⁻²) ± 95% C.I.
1-octadecanethiol/ <i>n</i> -hexane	31 ± 12
1-octadecanethiol/cyclohexane	12 ± 4
1-octanethiol/ <i>n</i> -hexane	19 ± 9

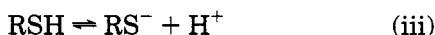
For high thiol concentrations we also observe a negative deviation from Langmuir isotherm predictions. At high thiol concentration the initial rate of adsorption approaches zeroth-order behavior, *i.e.* the initial rate of adsorption becomes concentration independent for high thiol concentrations (Figure 6). This change in behavior is indicative of the mechanism of monolayer formation. It is important to note that the initial rates in the zeroth-order regime are not the same for each system studied (see Table 5), suggesting that the onset of pseudo-zeroth-order behavior is not a stoichiometric effect. If stoichiometry were limiting, then the initial rates of adsorption would be independent of thiol and/or solvent identity. If an intermediate state plays a role in the adsorption reaction, then we would expect a solvent and alkanethiol dependence, as is seen. The solvent-dependence of the initial rates in the zeroth-order regime implies that the rate of monolayer formation is limited by the time required to form some intermediate state. Our data do not shed light on the structure of the intermediate state but do suggest its presence.

Comparison to Electrochemical Data. An important question relating to these monolayer assemblies is the actual identity of the adsorbing and desorbing species. Specifically, is the labile hydrogen from the thiol eliminated as a proton or as a neutral hydrogen species? Recent electrochemical work by the Porter group indicates that neutral hydrogen is the product of this reaction, or H₂O₂ if oxygen participates in the reaction.^{35,38} Using data from their work, we can estimate ΔG_{ads} for the adsorption of alkanethiols onto gold for both possible chemical reactions. Porter *et al.* measured the potential corresponding to the desorption of alkanethiols from gold.

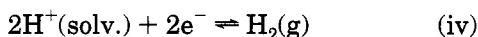
(38) Weishaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860.



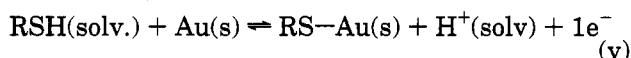
The potential reported was -1.25 V vs saturated Ag/AgCl, or -1.05 V vs SHE for 10^{-2} M thiolate in 0.5 M ethanolic KOH, and the variation of this potential with aliphatic chain length is small.³⁸ For adsorption to occur, the thiol must dissociate



There is little information in the literature on the pK_a of alkanethiols. Based on the limited information available, pK_a values in the range of 9 to 12 are expected, depending on the solvent.³⁹ For pK_a values of 9 and 12, we calculate the potential for thiol dissociation to be -0.53 and -0.71 V, respectively, vs SHE. The third reaction we must consider is the reduction of protons to hydrogen



We can estimate the half cell potential for this reaction by taking into account the proton concentration contributed from thiol dissociation and the partial pressure of atmospheric hydrogen in the air-saturated solution. For pK_a values of 9 and 12 we calculate half cell potentials of -0.23 and -0.31 V, respectively, vs SHE. From the above estimates we approximate the free energies for alkanethiol-gold adsorption for conditions of either the generation of a proton or of hydrogen. For the generation of a proton



we calculate a potential of $+0.43$ V vs SHE, corresponding to a $\Delta G_{\text{ads}} = -9.9$ kcal/mol. If instead, as indicated by the Porter group's data,^{35,38} the formation of the gold thiolate monolayer produces neutral hydrogen (eq i), we calculate a potential of $+0.16$ V vs SHE, giving $\Delta G_{\text{ads}} = -3.7$ kcal/mol. In addition to the ambiguity of the locations of the excess electron and proton generated in eq v, the calculated ΔG_{ads} for eq i is closer to the experimentally determined values we report here. We caution that the extent to which a comparison can be made between our data and the above estimate is limited because the experimental conditions and sources for the electrochemical and equilibrium data vary for parameters used in the approximation. Nonetheless, the agreement between our data and the estimate is quite good and provides further support, albeit only qualitative, for the monolayer formation proceeding according to eq i and not eq v.

Infrared Spectra. External reflection infrared spectroscopy has been used extensively to study macroscopic ordering in alkanethiolate self-assembled monolayers. The spectral positions of the methylene stretching modes for the alkanethiolate monolayers can be compared to those for *n*-alkanes which differ from liquid to crystalline environments (a trend to a more ordered environment). FTIR studies of self-assembled monolayers have shown that the alkyl chains exist in densely packed environments, where a high degree of crystallinity was assumed to be necessary to achieve the packing density. The band position(s) of these vibrational modes has been reported to evolve in time subsequent to monolayer formation, and this evolution time has been shown to be on the order of hours to days.¹⁸ The fact that we see chemical equilibration within 1 min suggests that the equilibrium achieved among the aliphatic chains can be largely separated from

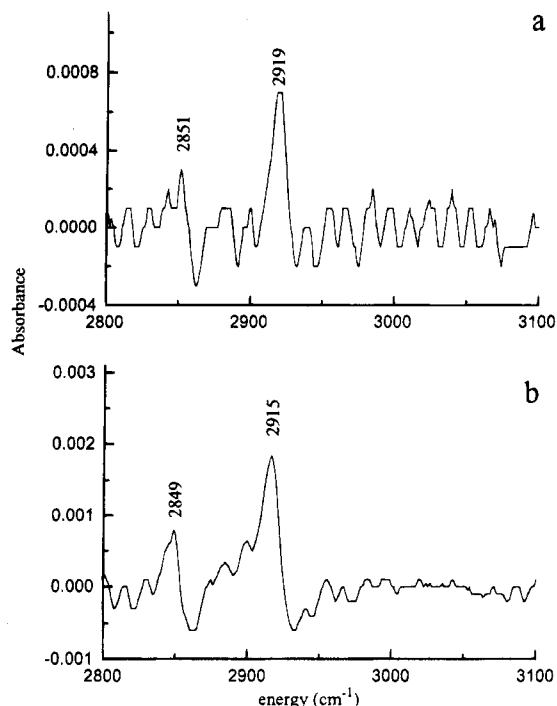


Figure 7. FTIR spectra of a 1-octadecanethiolate monolayer formed on the QCM surface, taken with 2 cm^{-1} resolution. (a) Spectrum recorded immediately after adsorption. (b) Spectrum recorded 2 weeks after adsorption.

the formation of the alkanethiolate monolayer.⁴⁰ In order to ensure the correspondence between our self-assembled monolayer systems and those studied earlier, we have examined the spectral evolution of the CH stretching region of the IR spectra of our films.

We show in Figure 7 the spectra for 1-octadecanethiolate monolayers on the QCM surface. The IR response of the 1-octanethiol monolayers was below our detection limit. The 1-octadecanethiol monolayers were formed by adsorption from a 3×10^{-4} M solution in *n*-hexane. Formation of the monolayer measured with the FTIR was determined to be gravimetrically complete based on the QCM response. The spectrum shown in Figure 7a was taken from a monolayer adsorbed immediately prior to the IR measurement. The symmetric and asymmetric methylene stretching modes occurred at 2851 and 2919 cm^{-1} , respectively. The spectrum of the same monolayer, stored in inert atmosphere for 2 weeks, is presented in Figure 7b. In this spectrum the symmetric and asymmetric methylene stretching modes appear at 2849 and 2915 cm^{-1} , respectively. Because the spectral resolution used in these measurements was 2 cm^{-1} , the red shifts we report are significant and indicate an approach to a more densely packed, and possibly crystalline, environment for the adsorbed alkanethiolate chains. We note the results for a monolayer that was aged for 24 h were identical to those we report in Figure 7b.

Implications of the ΔG_{ads} Data. The magnitude of ΔG_{ads} we have measured for alkanethiolate/gold systems is important because it provides insight into the chemical processes relevant to the formation of this interface. We consider that there are two significant interactions that contribute to the formation of the observed monolayers. The first interaction is that of the thiol moiety with the gold surface to form a gold-thiolate bond. The second interaction is the intermolecular attraction between adjacent aliphatic chains that must also contribute to the

(39) Oae, Shigeru *Organic Sulfur Chemistry: Structure and Mechanism*; CRC Press: Boca Raton, FL, 1991.

(40) Hahner, G.; Woll, Ch.; Buck, M.; Grunze, M. *Langmuir* **1993**, *9*, 1955.

stability of the system. We consider the expected contributions from each of these interactions individually.

The first fundamental question to be addressed is the energy associated with bond formation for gold/thiolate systems. We are not aware of detailed thermodynamic measurements on this chemical system but note that Bockris has reported a free energy of formation for butanethiol on mercury of -4.9 kcal/mol.⁴¹ The similarity of this value to the ΔG_{ads} we measure indicates that the dominant contribution to the formation of this thiolate-metal bond is determined by the creation of the thiolate species. The strength of interaction between aliphatic chains must also be considered. Obtaining an estimate of this interaction energy is difficult, but we approximate this interaction through the viscous flow energy of the corresponding liquid *n*-alkanes. The comparison we make is between a three-dimensional liquid and a nominally two-dimensional interface. Such a comparison is directly relevant to the system under consideration because adsorption and desorption at the interface must involve adsorbate molecular translation in to and out of the plane of the interface. The "viscosity" exhibited by a given liquid can be considered as an activated process, and thus the temperature dependence will obey Arrhenius behavior.

$$\eta = A \exp(E_{\text{vis}}/RT) \quad (10)$$

The interaction energy, E_{vis} , is an energy of interaction between molecules, and while this energy may be expected to be slightly different for a two-dimensional interface than for a three-dimensional bulk liquid, we do expect this difference to be comparatively small, *i.e.* within a factor of ~ 2 of the interaction energy within the monolayer. Measurement of the viscous flow energy for a given solvent requires knowledge of the temperature dependence of the solvent bulk viscosity, and the pre-exponential factor A is strongly solvent-dependent. The viscous flow energy for a given liquid is typically $1/3$ to $1/4$ of the latent heat of vaporization for the liquid.⁴² Indeed, the qualitative reason for the relationship of E_{vis} to ΔH_v is not surprising, since the heat of vaporization is a measure of the energy required to overcome the collective attractive forces within the system, and those same attractive forces are responsible for viscous flow in the liquid. For *n*-octane and *n*-octadecane we estimate the viscous flow energies to be 3 and 6 kcal/mol, respectively. This energy is essentially the same, within the uncertainty of the estimate, to that of the measured ΔG_{ads} .

There are two possible explanations for the similarities of these two quantities. The first is that we are, in fact, measuring the net energy of adsorption of the gold-thiolate system, which is dominated by interchain interactions among the aliphatic chains of the alkanethiols. This explanation is not likely because, if true, it would imply that the attractive interchain forces would lead to the spontaneous formation of alkanethiol molecular assemblies in solution, and we do not observe this experimentally. The second possibility is that the quantity we measure is largely unaffected by these interchain

interactions because the thiolates that contribute to the observed equilibrium are not involved in the formation of the "bulk" monolayer, and thus exhibit a ΔG_{ads} characteristic of only the thiolate-gold bond. Such a condition could occur at interfaces between domains on the surfaces where an edge of a monolayer is at least partially exposed to the solvent overlayer. In addition, the time scales on which the interchain forces operate must necessarily be longer than that for the gold-thiolate bond formation because of the large number of possible conformers of the alkyl chains and the large amplitude motions required for the chains to achieve a predominantly all-*trans* conformation. We expect that it is not possible to separate the relative contributions to the observed ΔG_{ads} cleanly, and there is a contribution to the observed data from both interchain interactions and the gold-thiolate bond. Based on our estimates of the interchain interaction energy, we believe that at least some diminution of this interaction is required to measure a free energy of adsorption that is as small as we observe.

It is important to note that we measure the total free energy of the adsorption process and have not separated the entropic and enthalpic contributions. Previous measurements of the heat of desorption for alkanethiolate monolayers has provided a value of ~ 28 kcal/mol.⁴³ While it might be tempting to use this value for ΔH_{des} and infer the entropic contribution to the adsorption, this is not possible without knowing the heat of solution of the alkanethiolate in the solvents we use here. For our measurements we determine the adsorption from solution, and for the ΔH_{des} determination, desorption is from the surface into vacuum. Thus the heat of solution for the alkanethiolate is required in order to determine the entropic contribution to the formation of these monolayers.

Conclusions

We have presented kinetic measurements of the formation of alkanethiolate monolayers on microcrystalline gold. The adsorption behavior of these systems follows the predictions of the Langmuir isotherm over a limited concentration range, and the deviations observed from the Langmuir prediction are expected based on limits inherent to the assumptions of the Langmuir isotherm. Our data demonstrate that the alkanethiolate-gold system is in equilibrium with free gold sites and alkanethiolate moieties. From our data we derive $\Delta G_{\text{ads}} = -5.5 \pm 0.4$ kcal/mol for *n*-C₁₈H₃₇SH adsorption onto gold, and $\Delta G_{\text{ads}} = -4.4 \pm 0.2$ kcal/mol for *n*-C₈H₁₇SH adsorption onto gold. These values are virtually the same as our estimates for the aliphatic interchain interaction energies, indicating that the equilibrium behavior we observe proceeds predominantly at the edges of monolayers islands and/or at step edges and defect sites. The infrared data demonstrate that the mass equilibrium for alkanethiolate monolayers is achieved within ~ 1 min, but the structural equilibration of the aliphatic chains proceeds over a much longer time scale.

Acknowledgment. We are grateful to the National Science Foundation for support of this work through Grant CHE 92-11237 and to Professor M. D. Porter for several stimulating and insightful discussions of these data.

(41) Blomgren, E.; Bockris, J. O'M.; Jesch, C. *J. Phys. Chem.* **1961**, *65*, 2000.

(42) Moore, W. J. *Physical Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1963; p 724.

(43) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.