Formation and Stability of Hexadecanethiolate SAMs Prepared in Aqueous Micellar Solutions of $C_{12}E_6$

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Self-assembled monolayers (SAMs) prepared by the adsorption of hexadecanethiol ($C_{16}SH$) onto gold exhibit infrared and impedance spectra that are consistent with a greater overall chain density when prepared in aqueous micellar solutions of hexaethylene glycol monododecyl ether ($C_{12}E_6$) than when prepared in ethanol or isooctane, although the initial step of the assembly process is much slower in the micellar solution. On the basis of ex situ infrared spectra taken at different adsorption times, SAMs prepared in $C_{12}E_6(aq)$ undergo a more thorough structural transformation to likely minimize collapsed chains and other defects within the film. These water-borne SAMs are greatly resistant to structural changes when immersed in blank solvents ($C_{12}E_6(aq)$, ethanol, and isooctane), but changes in the IR spectra suggest that a small fraction of thiolate molecules desorb from the surface when exposed to a solution containing $C_{16}SH$ in ethanol. Conversely, when ethanolic SAMs are exposed to a solution of $C_{16}SH$ in $C_{12}E_6(aq)$, changes in the IR spectra are consistent with a net adsorption of thiols to increase the adsorbate density. SAMs prepared in isooctane exhibit significantly less stable structures when exposed to blank solvents as compared to SAMs prepared in $C_{12}E_6(aq)$ and ethanol. Combined, these results reveal that solvent–adsorbate and solvent–film interactions play an important role in defining the structure of a SAM and that the use of weaker solvents to prepare the SAMs yields more densely packed films with fewer defects that are more stable against desorption.

Introduction

The ability to prepare self-assembled monolayers (SAMs) with highly crystalline structures and ultralow defect densities is crucial in applications where SAMs are used as molecular resists,[1–3] corrosion inhibiting coatings,[4–8] and electron tunneling barriers.[9,10] While several manuscripts[4,8,11–15] have addressed the effect of the molecular composition of the adsorbates on the structure and barrier properties of the film, there has been less effort focused on the use of solvent and assembly conditions to affect the properties of the SAMs. To advance the applications of SAMs as barrier films, an improved understanding of

molecular film formation, including the dynamics of the assembly process and the dependence of SAM structure and stability on solvent and adsorption time, should be established. In addition, the development of environmentally friendly processes to prepare high-quality SAMs will likely become important if these films are adopted into large-scale materials fabrication.

We have recently reported the preparation of *n*-alkanethiolate self-assembled monolayers (SAMs) onto gold from aqueous micellar solutions of nonionic poly-(oxyethylene) monododecyl ethers ($C_{12}E_j$; j = 6 and 7)[11,16] and alkyltrimethylammonium bromides.[17] The micellar cores provide hydrophobic domains to solubilize alkanethiols and deliver them to a metal surface to assemble the film. Interestingly, we have found that the SAMs formed from these environmentally benign aqueous micellar solutions exhibit greater overall chain densities than SAMs formed from traditional organic solvents such as ethanol.[11] This greater chain density for the water-borne SAMs is attributed to hydrophobic interactions between alkyl chains during assembly. Consistent with a more defect-free structure, the water-borne SAMs exhibit greater resistances against the diffusion of redox probes than SAMs formed in ethanol.[11]

To investigate the mechanism of SAM formation in aqueous micellar solutions, we have developed the use of in situ capacitance measurements to assess the kinetics of SAM formation in $C_{12}E_6(aq)$ and $C_{12}E_7(aq)$.[16] The kinetics of micelle-assisted SAM formation is consistent with a diffusion-limited process where the thiols are released from the micelles through an activated diffusion process to admicelles that are present on the gold surface (at low coverage of thiolate) or atop growing islands of thiolates (at high coverage). At the surface, the thiols then displace surface micelles and adsorb to the surface through a gold–thiolate interaction. The rate of SAM formation

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via this micellar delivery process depends on the temperature and selection of surfactant, both of which govern the aggregation number and diffusional properties of the micellar vehicles, the chain length of the alkanethiol, which affects its release rate from the micelle, and the concentration of solubilized alkanethiols. The kinetics data in $C_{12}E_f$(aq) are well-described by a diffusion-limited, second-order Langmuir adsorption process[16] in contrast to SAM formation in organic solvents that can be approximated by a first-order Langmuir adsorption process.[18]

These kinetics results provide very useful information for the early stage of SAM formation. However, the capacitance measurements are not sensitive to the film ordering process that occurs over hours to days after exposure of the gold substrate to the thiol-containing solution. Therefore, these capacitance measurements provide no explanation as to why SAMs formed in aqueous micellar solutions are more densely packed, electrochemically blocking films than those prepared in other solvents. The use of a more structure-sensitive technique such as reflectance-absorption infrared spectroscopy (RAIRS) is more appropriate for investigating such fine structural details. RAIRS has been widely used as an analytical tool for probing the structure and conformation within SAMs.[19,20] For alkanethiolate SAMs on gold, results from RAIRS analyses have indicated that the alkyl chains are highly trans-extended with an average molecular cant of ~30°.[20,21] These results are consistent with those obtained with more sophisticated surface analytical techniques such as electron,[22] X-ray,[23] and He[24] diffraction and scanning probe microscopies,[25,26] which indicate that the alkanethiolate adsorbates form a $(\sqrt{3} \times \sqrt{3})R30°$ overlayer on Au-(111) with an interchain spacing of 5.0 Å. This adlayer is consistent with the sulfur atoms binding in the 3-fold hollow sites on the Au(111) surface.

Terrill et al.[27] have used ex situ RAIRS to monitor the time-dependent structure of alkanethiolate SAMs on gold during formation from ethanol. Their results indicate an increase in crystalline content within the film and a decrease in the average cant angle of the adsorbates as the assembly time is increased. Himmelhaus et al.[28] used IR–visible sum frequency generation (SFG) to conclude that the structure of the monolayer transitions from that containing a high number of gauche defects to an all trans-extended film as the last few percent of the thiol molecules adsorb. Combined with other kinetics studies using ellipsometry[29] and wetting measurements,[30] these results

suggest that the formation of a SAM can be characterized by two stages: an initial rapid adsorption of molecules to the surface, in which the fractional coverage increases from 0 to ~0.9, followed by a slow adsorption of remaining molecules as the coverage approaches unity and the film orders on a macroscopic scale. Himmelhaus et al.[28] have concluded that the slow stage actually consists of two steps: the straightening of polymethylene chains to form a highly trans-extended structure and the subsequent reorientation of the terminal $-CH_2CH_3$ groups. From a microscopic perspective as obtained with in situ scanning probe microscopy,[26,31,32] this first stage of SAM growth is consistent with the rapid growth of domains of chemisorbed alkanethiolates, and the latter stage is consistent with the fusion of domains and the gradual minimization of defect sites (domain boundaries, adsorbate vacancies, missing rows, etc.) as the remaining alkanethiols adsorb to the surface. The selection of solvent is known to have a significant effect on both stages of SAM formation since, during the initial stage, alkanethiols must displace these solvents from the surface prior to adsorption,[18,33] and during the latter stage, interactions of the solvent with the adsorbates and with the assembling film are important as the remaining surface sites are filled.[28,34]

In this manuscript, we use RAIRS to study the structural evolution of hexadecanethiolate SAMs during the assembly process in aqueous micellar solutions of $C_{12}E_6$ (10 mM), based on adsorption times ranging from 1 min to 100 h. We compare the short-term kinetics and the long-term structural evolution for SAMs formed in $C_{12}E_6$(aq) with those for SAMs formed in ethanol to assess the key differences in the assembly of the films in these solvents. We also investigate the structural stability of preformed SAMs upon exposure to different solvents in the presence and absence of alkanethiols. Through these results, we seek to infer the effects of solvent–adsorbate and solvent–film interactions on the equilibrium structures of SAMs. These studies also provide clues as to why weak alkanethiol solvents such as $C_{12}E_6$(aq) provide superior media for forming high-quality SAMs.

Results and Discussion

Effect of Solvent on the Initial Stage of SAM Formation. We have used in situ capacitance measurements to monitor the early stage of SAM formation in $C_{12}E_6$(aq) and ethanol. While interfacial capacitance measurements are not sensitive to the ordering of the film near the limit of surface saturation, these measurements are quite sensitive to the initial stage of SAM formation. Figure 1 shows the time dependence for coverage after a step change in $C_{16}SH$ concentration from 0 to 1 mM in ethanol with 50 mM LiClO$_4$ as supporting electrolyte or in an aqueous solution with 10 mM $C_{12}E_6$ and 50 mM NaF. The time-dependent coverage ($\theta(t)$) of the film during the assembly process is estimated from in situ impedance measurements on the basis of[16]

$$\theta(t) = \frac{C_d + \dfrac{1}{2\pi f Z(t)(\sin\Phi)(t)}}{C_d - C_m} \tag{1}$$

where C_d represents the interfacial capacitance before the thiol molecules are introduced, C_m is the final capacitance of the formed monolayer, f is the fixed

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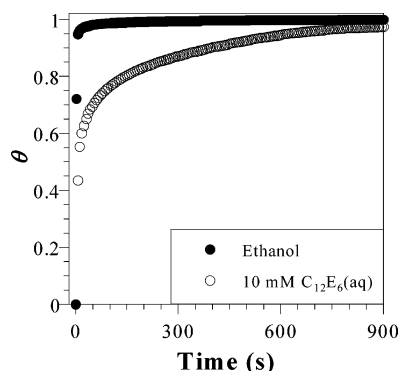
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Figure 1. Time dependence of surface coverage after a step change in $C_{16}SH$ concentration from 0 to 1 mM in ethanol with 50 mM $LiClO_4$ or in 10 mM $C_{12}E_6(aq)$ with 50 mM NaF.

frequency (100 Hz), $Z(t)$ is the impedance modulus, and $\Phi(t)$ is the phase angle. Figure 1 shows that the initial kinetic rate of SAM formation from $C_{16}SH$ onto gold in ethanol is much faster than that in $C_{12}E_6(aq)$. The coverage of the film reaches 90% within ~6 s in ethanol but requires 400 s in $C_{12}E_6(aq)$. The slower film growth in $C_{12}E_6(aq)$ is consistent with the slower diffusion of the micellar vehicles and the activated release of alkanethiols from the micelles.[16] After about 15 min (900 s), the coverage is close to unity in both solvents and continues to increase very slowly with time. This slow change in coverage is indicative of the film ordering process as the density of defects—adsorbate vacancies, domain boundaries, etc.—within the film is gradually reduced. The coverages based on capacitance are less sensitive to this latter (high-coverage) stage of SAM formation. In the remainder of this manuscript, we investigate the effect of solvent on the high-coverage stage of SAM formation using RAIRS.

Effect of Solvent on the Structural Evolution of SAM Formation. While the surface coverage of alkanethiolates begins to approach saturation within a few seconds to minutes as evidenced by in situ measurements, the addition of thiol molecules to fill the last few percent of surface sites and the corresponding evolution of film structure to form a crystalline, densely packed monolayer has been observed to require several hours.[9,18] In contrast to capacitance measurements, RAIRS-based intensities and positions are extremely sensitive to the structural changes within the film as the limiting coverage is approached. In a RAIRS measurement, p-polarized infrared light reflects from the gold surface to generate an electric field gradient normal to the surface.[35] The intensity of a given band in the IR spectrum is proportional to the square of the component of its transition dipole moment oriented along the surface normal,[19]

$$I \propto \cos^2 \theta_{mz} \qquad (2)$$

where I is the spectral intensity and θ_{mz} is the average angle between the transition dipole moment (m) and the surface normal (z). The wavenumber of the band is also related to the crystalline packing of the hydrocarbon chains within the SAM. Thus, by monitoring the intensities and positions of methylene ($-CH_2-$) and methyl ($-CH_3$) stretching bands as a function of adsorption time in the high-coverage state, we can qualitatively assess relative differences in the packing density and crystallinity of the SAM.

Infrared spectra for SAMs formed onto gold from $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$ and ethanol at different adsorption
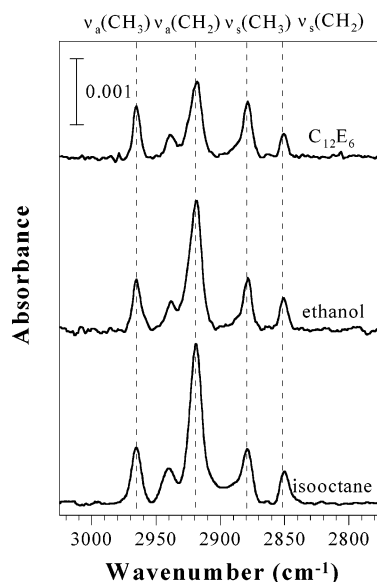
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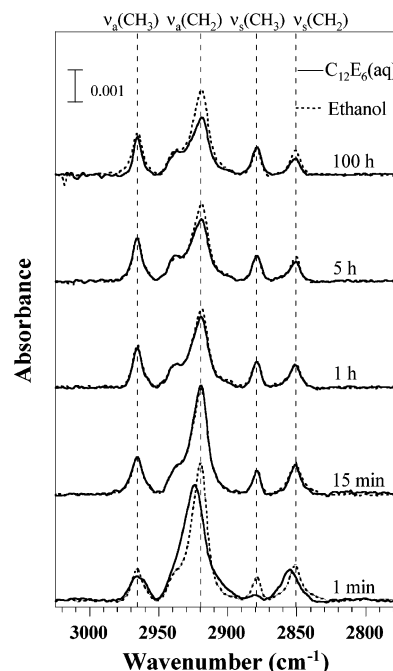
Figure 2. Reflectance infrared spectra of the C−H stretching region for SAMs formed by exposure of gold to 1 mM $C_{16}SH$ solutions in ethanol (dotted line) or 10 mM $C_{12}E_6(aq)$ (solid line) for different adsorption times. The dashed lines indicate the positions of the primary methyl and methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_3) = 2965$ cm^{-1}; $\nu_a(CH_2) = 2918$ cm^{-1}; $\nu_s(CH_3) = 2879$ cm^{-1}; $\nu_s(CH_2) = 2851$ cm^{-1}. The spectra for each adsorption time have been offset for clarity. The bar represents a scale for the absorbance.

times are shown in Figure 2. After 1 min of adsorption, the SAM prepared in ethanol exhibits well-defined bands for asymmetric ($\nu_a(CH_2)$) and symmetric ($\nu_s(CH_2)$) methylene stretching absorption at 2919 and 2851 cm^{-1}, respectively, whereas those for the SAM prepared in $C_{12}E_6(aq)$ are broader and shifted to higher wavenumber. The asymmetric ($\nu_a(CH_3)$) and symmetric ($\nu_s(CH_3)$) methyl stretching vibrations at 2965 and 2879 cm^{-1}, respectively, are also broader and less detailed in the water-borne SAM. These observations suggest that the water-borne film is less complete after this short exposure than the ethanolic SAM and exhibits a more heterogeneous distribution of chain orientations. These results agree with the in situ kinetics results (Figure 1) and confirm that the initial stage of formation for C_{16} SAMs is significantly faster in ethanol than in $C_{12}E_6(aq)$.

After adsorption for 15 min, the IR spectra for SAMs prepared in both solutions are nearly identical, indicating similar average structures. The SAM formed in ethanol exhibits a ~20% reduction in $\nu_a(CH_2)$ intensity and a slight increase in both $\nu_a(CH_3)$ and $\nu_s(CH_3)$ intensities between 1 and 15 min, consistent with the addition of thiol molecules to the surface to produce a more densely packed film in which the hydrocarbon chains exhibit a lower average cant angle. During this same time, the water-borne SAM undergoes a dramatic growth and ordering process as the methylene and methyl stretching modes exhibit narrowed peak widths and positions nearly identical with those of the ethanolic SAM.

With increasing adsorption time beyond 15 min, the spectra of both SAMs show less intense methylene stretching bands and sharpened $\nu_a(CH_3)$ bands, consistent with the gradual evolution to a more densely packed film of trans-extended hydrocarbon that exhibits a more homogeneous orientation of the terminal methyl groups in either solvent. A physical interpretation of these

Figure 3. Reflectance infrared spectra of the C—H stretching region for SAMs formed by exposure of gold to 1 mM solutions of $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$, ethanol, or isooctane. The dashed lines indicate the positions of the primary methyl and methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_3)$ = 2965 cm^{-1}; $\nu_a(CH_2)$ = 2918 cm^{-1}; $\nu_s(CH_3)$ = 2879 cm^{-1}; $\nu_s(CH_2)$ = 2851 cm^{-1}. The spectra for each solvent have been offset for clarity.

changes in IR spectra that is in line with both in situ microscopy studies[26] and ex situ SFG studies[28] is that thiols adsorb at domain boundaries and defect sites to facilitate the fusion of domains and the ordering of the film. The alkanethiolates in the vicinity of these boundaries and defect sites have fewer neighboring adsorbates and are likely to be highly canted with gauche conformers. These canted, gauche chains should exhibit CH_2 transition dipole moments that are more normal to the surface and therefore are more pronounced in the IR spectrum (eq 2). The ability to heal these defects by the adsorption of additional alkanethiols can greatly enhance the overall chain density on the surface and reduce the methylene absorbances in the IR spectrum.

On the basis of the exposure of gold to the $C_{16}SH$ solutions for ≥1 h, the IR spectra reveal that the SAM formed in $C_{12}E_6(aq)$ exhibits a markedly lower $\nu_a(CH_2)$ intensity and a slightly lower $\nu_s(CH_2)$ intensity in comparison with those for the SAM formed in ethanol. These reduced methylene intensities are consistent with the formation of a more densely packed SAM in aqueous micellar solutions in comparison with that in ethanol. We have previously shown that this enhanced packing in $C_{12}E_6(aq)$ results in improved barrier properties.[11] Considering that the $\nu_a(CH_2)$ intensity for the ethanolic C_{16} SAM changes very little from 1 to 100 h of exposure in contrast to the more significant changes in $\nu_a(CH_2)$ intensity for the water-borne C_{16} SAM over the same time range, these results suggest that the healing of defects and the filling in of the remaining surface sites are more extensive (and perhaps more energetically favorable) in the aqueous solvent.

To further explore the effect of solvent on the structure of SAMs, we compare the IR spectrum for a SAM formed from a 100 h exposure to $C_{16}SH$ (1 mM) in isooctane, a strong solvent for this alkanethiol, with those for C_{16} SAMs formed in 10 mM $C_{12}E_6(aq)$ and ethanol for 100 h (Figure 3). In these spectra, the peak positions of the various C—H stretching modes are all similar (within 0.5 cm^{-1}) and

consistent with those reported for highly crystalline monolayers.[20] The key difference in these spectra is the higher $\nu_a(CH_2)$ intensities as solvent strength is increased (isooctane > ethanol > $C_{12}E_6(aq)$), consistent with a higher average cant angle and lower average chain density. The ratio of the absorbance of $\nu_a(CH_2)$ to that for $\nu_s(CH_2)$ is known as the dichroic ratio, which is a parameter that is useful in describing the average twist angle of the alkyl chains within the SAM.[20] For the spectra in Figure 3, the dichroic ratio is 4.9 (isooctane), 4.0 (ethanol), and 3.2 ($C_{12}E_6(aq)$), which reflects a greater average twist angle as solvent strength is increased. The line width of the $\nu_a(CH_3)$ mode at 2965 cm^{-1} also increases with solvent strength, suggestive of a more heterogeneous orientation of the methyl groups for the SAM formed in isooctane. These structural differences correlate to measurable changes in electrochemical impedance as the water-borne film exhibits higher charge-transfer resistance (2.9 MΩ· cm^2) against the diffusion of water-soluble redox probes ($K_4Fe(CN)_6$ and $K_3Fe(CN)_6$) than the SAMs prepared in ethanol (1.8 MΩ·cm^2) and isooctane (0.7 MΩ·cm^2) do. These higher charge-transfer resistances are consistent with a film that contains fewer defects.[8] Collectively, these results reveal that the selection of solvent plays an important role in defining the structures of SAMs and suggest that the use of weaker solvents, those that are less solvating of the alkanethiols, yields SAMs with more densely packed structures and fewer defects.

Effect of a Solvent Switch on the Structure of Monolayer Films in the High-Coverage State. The structural evolution of a SAM on a particular metal surface is affected by the metal—adsorbate interaction,[20,36,37] while other interactions—interchain (van der Waals and hydrophobic),[11,29,38] adsorbate—solvent,[18,28,39] and SAM—solvent interactions[28,34,40] are postulated to play a role. We assert that these latter two interactions (adsorbate—solvent and SAM—solvent) can provide perturbation of attractive interchain interactions and thereby disrupt the formation of densely packed domains of alkanethiolates. Given this rationale, strong (highly solvating) solvents would be expected to produce SAMs with less well-defined domain structure and more defects. Due to the unfavorable interaction of water molecules with hydrocarbon chains of the alkanethiols and the strong, attractive hydrophobic interactions of these hydrocarbon chains in the presence of water,[38] there is perhaps a greater energetic penalty to have defects within these water-borne SAMs that increase the surface area of contact between the hydrocarbon chains of the alkanethiols and the aqueous solution. Therefore, SAMs prepared in aqueous solution are likely crystallized into a more well-defined domain structure with relatively few defects compared to SAMs formed in hydrocarbon solvents.

A possible interpretation of this solvent-dependence on the structural properties of SAMs is that a fraction of adsorbed thiolates, most likely those at domain boundaries and other sites where the number of nearest neighbors is reduced, exists in equilibrium with thiols in solution. Assuming a simple first-order, reversible Langmuir
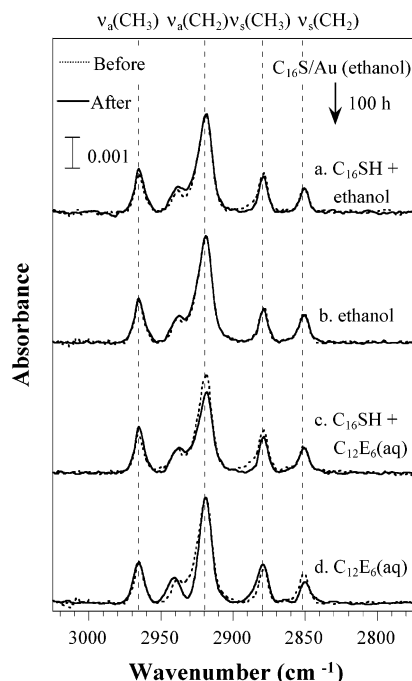
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$\nu_a(CH_3)$ $\nu_a(CH_2)\nu_s(CH_3)$ $\nu_s(CH_2)$

Figure 4. Reflectance infrared spectra of the C–H stretching region for SAMs formed by exposure of gold to 1 mM $C_{16}SH$ in ethanol for 100 h before (dotted line) and after (solid line) exposure to (a) 1 mM $C_{16}SH$ in ethanol, (b) ethanol without thiol, (c) 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$, and (d) 10 mM $C_{12}E_6$-(aq) without thiol, for an additional 100 h. The dashed lines indicate the positions of the primary methyl and methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_3)$ = 2965 cm^{-1}; $\nu_a(CH_2)$ = 2918 cm^{-1}; $\nu_s(CH_3)$ = 2879 cm^{-1}; $\nu_s(CH_2)$ = 2851 cm^{-1}. The spectra for each experiment have been offset for clarity.

adsorption isotherm, the equilibrium constant is defined as[41]

$$K = \frac{k_{ads}}{k_{des}} = \frac{\theta'}{(1 - \theta')C} \qquad (3)$$

where θ' is the coverage at or near these defect sites, k_{ads} and k_{des} are adsorption and desorption rate constants, respectively, and C is the concentration of alkanethiol in solution. We would expect K to be larger for SAM formation in $C_{12}E_6(aq)$ than in ethanol and significantly larger than in isooctane, where the driving force for adsorption is lower and that for desorption is higher because of more favorable solvent–adsorbate interactions. On the basis of this argument, questions arise regarding the reversibility of this process: Can a SAM originally formed in ethanol become more densely packed if it is exposed to a thiol-containing solution in $C_{12}E_6(aq)$? Likewise, does a SAM formed in $C_{12}E_6(aq)$ lose adsorbates if it is exposed to a thiol-containing solution in ethanol? What effect does blank solvent (without thiol) have on the structures of preformed SAMs?

To determine if the SAM structure is reversible, depending on the solvent it is contacted with, we have exposed SAMs formed in one solvent for 100 h to another solvent for an additional 100 h (with and without thiols) or to the same solvent with and without thiols. We chose 100 h for these exposure times to allow sufficient time for the SAMs to achieve a nearly equilibrium structure. Figure 4 shows the IR results of this experiment in which SAMs

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formed in 1 mM $C_{16}SH$ in ethanol were exposed to (a) 1 mM $C_{16}SH$ in ethanol, (b) ethanol without thiol, (c) 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$, or (d) 10 mM $C_{12}E_6(aq)$ without thiol. Upon exposure for 100 h to blank ethanol (Figure 4b) or to the same ethanolic $C_{16}SH$ solution (Figure 4a), the IR spectra (before and after) remain nearly constant, suggesting no significant structural changes within the film. These results suggest that a 100 h adsorption time is sufficient to produce an essentially equilibrium film structure that does not gain additional adsorbates upon continued exposure to a thiol-containing solution. This film also does not appear to lose adsorbates when exposed to a solution of blank ethanol for 100 h, indicating that the idea of a simple equilibrium between specific molecules on the surface and those in solution (eq 3) is too simplistic. In agreement with Dannenberger et al.,[18] the desorption rate must decrease significantly as the final coverage is approached and the film orders.

The $\nu_a(CH_2)$ intensity of C_{16} SAMs formed in ethanol decreases when exposed to 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6$-(aq) (Figure 4c), consistent with an increase in overall chain density and a net addition of thiol adsorbates to the surface. Upon exposure to the aqueous solvent, hydrophobic interactions between the alkyl chains in the film likely produce a more well-defined domain structure that allows easier access to available sites so that additional alkanethiols can adsorb and reduce unfavorable contact area between water and the hydrophobic film. Upon exposure of the ethanolic C_{16} SAM to blank $C_{12}E_6(aq)$ for 100 h (Figure 4d), a shift to higher wavenumber of the symmetric methyl Fermi resonance band at ~2940 cm^{-1} and an increased broadness of the symmetric methyl band at 2879 cm^{-1} suggests a restructuring of terminal methyl groups upon exposure to the aqueous solution. The decrease in $\nu_s(CH_2)$ absorbance and the absence of change in $\nu_a(CH_2)$ is consistent with a slightly altered orientation of the hydrocarbon chains to accomplish this restructuring. Nonetheless, there is no indication that a significant fraction of thiolates are desorbed from the surface during exposure to blank $C_{12}E_6(aq)$. There is also no spectral evidence to suggest that $C_{12}E_6$ molecules are retained in the film, based on the absence of an ether stretch at ~1130 cm^{-1}.

Figure 5 shows IR spectra for an experiment in which SAMs formed in 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$ for 100 h were exposed for an additional 100 h to (a) 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$, (b) 10 mM $C_{12}E_6(aq)$ without thiol, (c) 1 mM $C_{16}SH$ in ethanol, or (d) ethanol without thiol. Upon exposure of the C_{16} SAM prepared in 10 mM $C_{12}E_6$-(aq) to the same solution for another 100 h (Figure 5a), increases in the $\nu_a(CH_3)$ and methyl Fermi resonance band intensities and a slight decrease in the $\nu_s(CH_3)$ intensity suggest some ordering of the methyl termini. Nonetheless, we observed little or no change in the methylene modes, suggesting no real change in adsorbate density. These results indicate that the film achieves an equilibrium coverage during the first 100 h of adsorption. Exposure of the water-borne C_{16} SAM to blank $C_{12}E_6(aq)$ (Figure 5b) or blank ethanol (Figure 5d) for 100 h also did not produce significant changes in the IR spectrum, indicating that the alkanethiolates are irreversibly adsorbed when formed in $C_{12}E_6(aq)$ and do not desorb into solvent. However, upon exposure to a 1 mM $C_{16}SH$ solution in ethanol (Figure 5c), the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ intensities of the water-borne C_{16} SAM increase, consistent with a net desorption of alkanethiolates from the surface. The fact that this net desorption does not occur in blank ethanol suggests that alkanethiols in solution can facilitate the desorption of alkanethiolates bound at the surface. Previ-
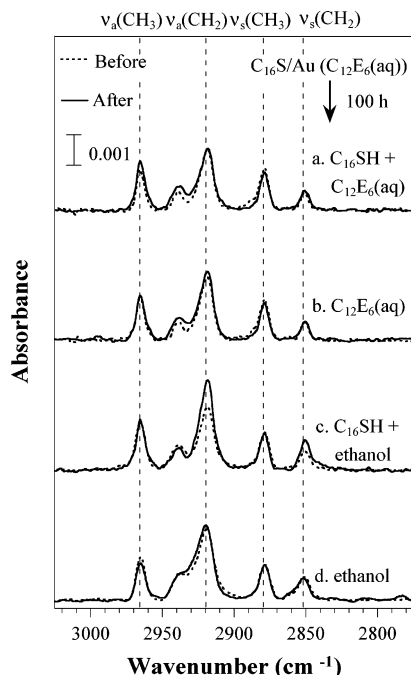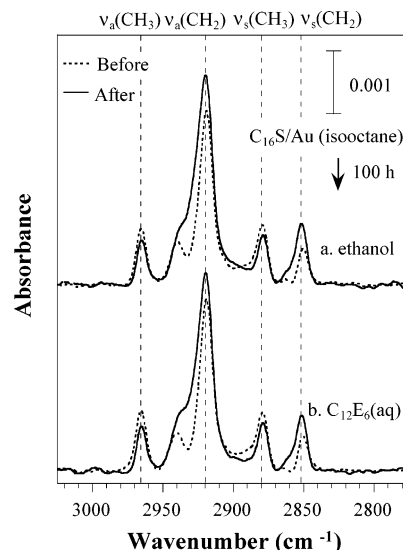
Figure 5. Reflectance infrared spectra of the C−H stretching region for SAMs formed by exposure of gold to 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$ for 100 h before (dotted line) and after (solid line) exposure to (a) 1 mM $C_{16}SH$ in 10 mM $C_{12}E_6(aq)$, (b) 10 mM $C_{12}E_6(aq)$ without thiol, (c) 1 mM $C_{16}SH$ in ethanol, and (d) ethanol without thiol, for an additional 100 h adsorption. The dashed lines indicate the positions of the primary methyl and methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_3) = 2965$ cm^{-1}; $\nu_a(CH_2) = 2918$ cm^{-1}; $\nu_s(CH_3) = 2879$ cm^{-1}; $\nu_s(CH_2) = 2851$ cm^{-1}. The spectra for each experiment have been offset for clarity.

ous studies have shown that the self-exchange of surface-bound alkanethiolates is much more rapid and extensive than their desorption into blank solvents.[42] Here, a highly dynamic self-exchange between adsorbates in solution with those at the surface is perhaps accompanied by a net desorption of these exchanging species at specific surface sites.

Figures 4b,d and 5b,d suggest that SAMs formed by 100 h exposures to $C_{16}SH$ in either ethanol or $C_{12}E_6(aq)$ do not exhibit appreciable desorption of the alkanethiolates into either of these blank solvents. This result is consistent with that of Himmelhaus et al.,[28] who studied $C_{22}S/Au$ SAMs, but contradicts that of Schlenoff et al.,[42] who quantified considerable loss of $C_{18}S$− upon exposure to solvents such as ethanol, hexane, and water. This discrepancy may be due to their use of hexane as solvent for forming their SAMs, their use of a gold foil as a substrate, rather than evaporated gold in our experiments, and/or their shorter adsorption times (5 h vs 100 h). In Figure 6, we show IR spectra for SAMs formed from $C_{16}SH$ (1 mM) in isooctane for 100 h before and after exposure to blank $C_{12}E_6(aq)$ or blank ethanol. These spectra reveal both an increased intensity and a significant broadening in the $\nu_a(CH_2)$ modes after exposure to the blank solvents and a decrease in $\nu_a(CH_3)$ and $\nu_s(CH_3)$ intensities. Similar, but more dramatic changes (not shown) were observed when the SAM prepared in isooctane was placed in blank isooctane for 100 h. The increased methylene intensities and decreased methyl intensities are consistent with desorption of alkanethiolates from the surface whereas the broadening indicates a more heterogeneous and

Figure 6. Reflectance infrared spectra of the C−H stretching region for SAMs formed by exposure of gold to a 1 mM $C_{16}SH$ solution in isooctane before (dotted line) and after (solid line) exposure to (a) ethanol without thiol and (b) 10 mM $C_{12}E_6(aq)$ without thiol. The dashed lines indicate the positions of the primary methyl and methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_3) = 2965$ cm^{-1}; $\nu_a(CH_2) = 2918$ cm^{-1}; $\nu_s(CH_3) = 2879$ cm^{-1}; $\nu_s(CH_2) = 2851$ cm^{-1}. The spectra for each experiment have been offset for clarity.

disordered conformation of alkyl chains within the SAM. Presumably, desorption of alkanethiolates is accompanied by the partial collapse of adjacent chains, which contributes to the growing heterogeneity within the film. If one assumes that the desorption of alkanethiolates is preceded by the solvation of the adsorbate, then those alkanethiolates at defect sites such as domain boundaries that allow facile permeation of solvent are likely desorbed preferentially over those in well-ordered domains. This result for 2-D SAMs is consistent with that for 3-D SAMs on gold nanoparticles as reported by Hostetler et al.,[43] where alkanethiolates at edge and vertex sites are more easily desorbed and exchanged than those at terrace sites. The significant loss of adsorbates for SAMs prepared in isooctane is similar to that reported by Schlenoff et al.[42] for SAMs prepared in hexane. The relative stability of SAMs prepared in $C_{12}E_6(aq)$ or ethanol versus those prepared in isooctane (here) or hexane[42] suggests that SAMs formed in weaker (more polar) solvents contain a more densely packed structure that more effectively inhibits solvent permeation. This comparison further indicates that the desorption rate of SAMs is greatly dependent on the limiting coverage and the defect density within the monolayer.

To further investigate the stability of SAMs to immersion in blank solvent, we exposed C_{16} SAMs prepared from a 100 h adsorption in either ethanol or $C_{12}E_6(aq)$ to blank isooctane for 100 h and collected IR spectra before and after the isooctane exposure (Figure 7). The IR spectra shown in Figure 7 indicate that the SAM formed in $C_{12}E_6(aq)$ is barely changed upon exposure to blank isooctane while the SAM formed in ethanol undergoes dramatic structural transitions as evidenced by the increased absorbance and broadening of the $\nu_a(CH_2)$ band and the sharp decrease in absorbance of the methyl modes. Similar to the SAMs formed in isooctane in Figure 6, these transitions are consistent with the loss of adsorbates from

(42) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528−12536.

(43) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3728−3789.
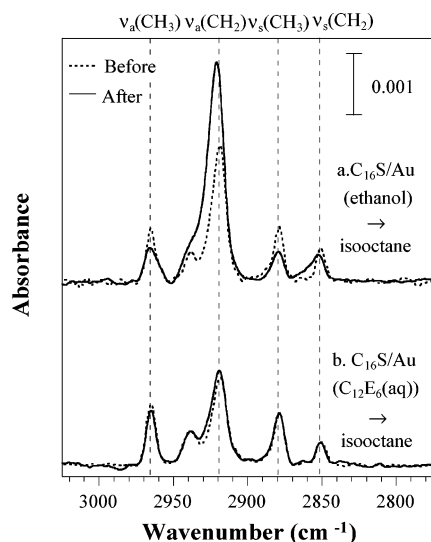
Figure 7. Reflectance infrared spectra of the C−H stretching region for SAMs formed by exposure of gold to a 1 mM $C_{16}SH$ solution in (a) ethanol or (b) 10 mM $C_{12}E_6$(aq) for 100 h (dotted line). These samples were then exposed to isooctane without thiol for 100 h (solid line). The dashed lines indicate the positions of the primary methyl and methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_3) = 2965$ cm^{-1}; $\nu_a(CH_2) = 2918$ cm^{-1}; $\nu_s(CH_3) = 2879$ cm^{-1}; $\nu_s(CH_2) = 2851$ cm^{-1}. The spectra for each experiment have been offset for clarity.

the surface, which in turn induces disorder in neighboring chains. The fact that the structure of the ethanolic SAM is largely unaffected by exposure to blank ethanol or to blank $C_{12}E_6$(aq) but is significantly altered upon exposure to isooctane suggests that the solvent strength plays a large role in the desorption of alkanethiolates. As hypothesized above, solvent molecules likely penetrate the SAM at defect sites and promote the desorption of the alkanethiolates. The IR spectrum for the SAM prepared in $C_{12}E_6$(aq) after isooctane exposure shows a slight increase in the broadness of the $\nu_a(CH_2)$ peak and a slight decrease in the $\nu_a(CH_3)$ intensity. The more constant structure exhibited by the water-borne SAM upon prolonged exposure to these different blank solvents attests to its more densely packed, highly defect-free structure that resists the permeation of solvent molecules.

Conclusions

The results of this manuscript show that the structural properties and stability of a SAM are greatly affected by the solvent from which it is prepared. SAMs prepared from weaker solvents exhibit more densely packed structures that are more stable upon exposure to blank solvents. These results suggest that interactions between the solvent and adsorbates in solution and within the monolayer film can greatly influence the equilibrium structure and properties of the SAM. Weak solvent−adsorbate interactions can drive the adsorption of alkanethiols at the surface, much like in a crystallization process. At the surface, hydrophobic interactions between the adsorbed alkanethiolates in $C_{12}E_6$(aq) produce a well-defined, densely packed domain structure that allows the adsorption of additional alkanethiols at domain boundaries and defect sites. The more effective minimization of defects within these water-borne SAMs reduces permeation by other molecules, thereby producing a film that is more stable upon exposure to blank solvents.

Experimental Section

Materials. Gold shot (99.99%) and silicon(100) wafers were obtained from J&J Materials (Neptune City, NJ) and Silicon

Sense (Nashua, NH), respectively. All chemicals, including hexadecanethiol (Aldrich), hexaethylene glycol monododecyl ether ($C_{12}E_6$; Fluka), sodium fluoride (Fisher), lithium perchlorate (Alfa), isooctane (Fisher), and 100% ethanol (AAPER) were used as received. Deionized water (16.7 MΩ) was purified with a Modu-Pure system.

Sample Preparation. Gold substrates were prepared by evaporating ~1500 Å of gold at a rate of 3−5 Å/s onto silicon [Si(100)] wafers inside a diffusion-pumped chamber with a base pressure of 4×10^{-6} Torr. Prior to the evaporation of gold, a 100 Å layer of chromium was evaporated onto silicon to serve as a primer.

SAM Preparation for ex Situ Studies. SAMs were prepared by immersing evaporated gold films into solutions containing 1 mM alkanethiol in 10 mM $C_{12}E_6$(aq), ethanol, or isooctane at room temperature for various times. Upon removal, the samples were rinsed with fresh solvent ($C_{12}E_6$(aq), ethanol, or isooctane) followed by water and then dried in a stream of nitrogen. The samples were then characterized by RAIRS. For the solvent switch experiments, after characterization by RAIRS, the samples were placed into either ethanol or $C_{12}E_6$(aq) with and without $C_{16}SH$ or blank isooctane for 100 h. Upon removal, the samples were rinsed as before and recharacterized by RAIRS.

SAM Preparation for in Situ Studies. Capacitance measurements were taken with a CMS300 electrochemical impedance system (Gamry Instruments) interfaced to a personal computer. Measurements were taken inside a Teflon cell containing a gold working electrode with a 1 cm^2 fixed area. NaF was used as electrolyte in aqueous solutions, and LiClO$_4$ was used as electrolyte in ethanol. The cell initially contained 1 mL of 50 mM electrolyte in either 10 mM $C_{12}E_6$(aq) or ethanol. After a stable capacitance was obtained, a 6 mL solution of 1 mM alkanethiol in either 10 mM $C_{12}E_6$(aq) or ethanol and 50 mM electrolyte were added. Capacitance readings were recorded every 3 s and were obtained from the imaginary impedance at 100 Hz. We have described the physical underpinnings of this method in a separate paper.[16]

Reflectance-Absorption Infrared Spectroscopy. IR spectra were obtained in a single reflection mode with a Bio-Rad Excalibur infrared spectrometer equipped with a Universal reflectance attachment. The polarized light was incident at 80° from the surface normal. The reflected light was detected with a narrow-band MCT detector cooled with liquid nitrogen. Spectral resolution was 2 cm^{-1} after triangular apodization. Spectra were referenced to those of SAMs prepared on gold from octade-canethiol-d_{37}, and 1000 scans of both sample and reference were collected. All reported IR spectra were repeated at least twice using independent sample preparations. The estimated error in reported spectra on the basis of the standard deviations of band absorbances measured after these independent preparations was less than 10%.

Electrochemical Impedance Spectroscopy (EIS). Electrochemical impedance measurements of SAM-coated gold samples were performed with a CMS300 electrochemical impedance system (Gamry Instruments) interfaced to a personal computer. A Teflon cell equipped with a gold-coated silicon counter electrode and a Ag/AgCl/saturated KCl reference electrode contained an aqueous solution of 0.1 M Na$_2$SO$_4$, 1 mM K$_3$Fe(CN)$_6$, and 1 mM K$_4$Fe(CN)$_6$·3H$_2$O. The area of the working electrode in contact with the aqueous solution was a confined circle with an area of 1 cm^2. The measurements were made at the open circuit potential with a 5 mV ac perturbation that was controlled between 50 mHz and 20 kHz. Film resistance and capacitance values were determined by fitting the EIS data with a Randles model equivalent circuit[4] using software provided by Gamry.