Electrochemical Measurement of the Free Energy of Adsorption of *n*-Alkanethiolates at Ag(111)

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Abstract: The oxidative adsorption of *n*-alkanethiolates ($C_{n_c}H_{2n_c+1}S^-$) at Ag(111) in aqueous and methanolic solutions containing 0.5 M NaOH has been investigated by cyclic voltammetry and in-situ surface-enhanced Raman spectroscopy (SERS). Reversible adsorption of $C_{n_c}H_{2n_c+1}S^-$ under active potential control in solutions containing millimolar concentrations of $C_{n_c}H_{2n_c+1}S^-$ provides a means to control the deposition of *n*-alkanethiolate monolayers, and allows for the direct voltammetric measurement of the free energy of monolayer formation. Oxidative adsorption of short chain alkanethiolates ($n_c \leq 6$) in aqueous 0.5 M NaOH is characterized by two voltammetric waves, demonstrating that monolayer formation involves at least two energetically distinct chemical steps. The first voltammetric wave corresponds to the reversible and rapid adsorption of $C_{n_c}H_{2n_c+1}S^-$ at submonolayer coverages. The redox potential of this wave ($E^{\mathrm{I}}_{1/2} = -1.19 \pm 0.02$ V vs Ag/AgCl) is independent of n_c, suggesting that the interactions between adsorbed molecules are minimal at low surface coverages and that the energetics of adsorption are determined primarily by the strength of the Ag(111)−S bond. A second voltammetric wave is observed at more positive electrode potentials, corresponding to further adsorption of $C_{n_c}H_{2n_c+1}S^-$ to yield a complete monolayer ($\Gamma_{\max} \sim 7.7 \times 10^{-10}$ mol/cm^2). The redox potential for the second wave, $E^{\mathrm{II}}_{1/2}$, is a function of chain length, shifting to more negative potentials with increasing n_c. The dependence of $E^{\mathrm{II}}_{1/2}$ on n_c reflects the influence of hydrophobic interactions and intermolecular forces between the hydrocarbon chains. For $n_c > 6$, $E^{\mathrm{II}}_{1/2}$ shifts to potentials negative of $E^{\mathrm{I}}_{1/2}$, and the two voltammetric waves merge into a single wave, suggesting that the more structurally ordered monolayer is energetically favored for longer chain lengths (*i.e.,* $n_c > 6$). In-situ SERS is used to establish the potential-dependent adsorption isotherm of *n*-hexanethiolate adsorbed on roughened Ag electrodes. The potential dependence of the SERS intensities of the trans and gauche ν(C−S) stretching modes provides a means to monitor the structural ordering of the alkanethiolate monolayer during electrochemical deposition. The electrochemical data are used to separate the total adsorption free energy (ΔG_{ads}) into the individual contributions associated with the formation of the Ag(111)−S bond (−22.8 and −16.6 kcal/mol for the low- and high-density structures, respectively) and that associated with hydrophobic interactions and intermolecular forces between hydrocarbon chains (-1.02 ± 0.04 kcal/mol per n_c). Voltammetric data and ΔG_{ads} values are also reported for the adsorption of $C_{n_c}H_{2n_c+1}S^-$ ($2 \leq n_c \leq 16$) onto Ag(111) from basic methanolic solutions.

Introduction

Earlier reports from our laboratories have described the electrochemical deposition of hydrosulfide (HS^-)[1] and ethanethiolate ($CH_3CH_2S^-$)[2] monolayers at Ag(111) surfaces. The oxidative adsorption, eq 1, of HS^- and $CH_3CH_2S^-$ (which represent the $n_c = 0$ and 2 structures in the alkanethiolate series, $C_{n_c}H_{2n_c+1}S^-$) from aqueous solutions is characterized by reversible multiple-wave voltammetric responses that provide fundamental insight into the mechanism of the formation of alkanethiolate monolayers. The voltammetric data also provide a means to evaluate monolayer energetics and surface coverages. For instance, oxidative adsorption of $CH_3CH_2S^-$ at Ag(111) in aqueous 0.2 M NaOH solutions results in two well-resolved and reversible voltammetric waves with redox potentials $E^{\mathrm{I}}_{1/2} = -1.17$ V and $E^{\mathrm{II}}_{1/2} = -0.95$ V vs Ag/AgCl, corresponding to the formation of energetically distinct surface phases of $CH_3CH_2S^-$. The two-wave voltammetric response, in conjunction with measurements of the potential-dependent adsorption isotherm using electrochemical quartz crystal microbalance methods and in-situ surface-enhanced Raman spectroscopy, demonstrates the existence of a disordered low-coverage phase and a more highly ordered full monolayer. The phase transition between these structures, which is qualitatively depicted in Scheme 1, is attributed to a rapid increase in intermolecular interactions between adsorbed molecules at a critical potential-dependent surface coverage. Qualitatively similar conclusions regarding the multistep nature of alkanethiol monolayer assembly on Au surfaces recently have been presented by Poirier and Pylant[3] and Troung and Rowntree.[4]

$$\mathrm{Ag(111)} + C_{n_c}H_{2n_c+1}S^- \rightleftharpoons \mathrm{Ag(111)}{-}SC_{n_c}H_{2n_c+1} + e^- \quad (1)$$

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(1) (a) Hatchett, D. W.; Gao, X.; Catron, S. W.; White, H. S. *J. Phys. Chem.* **1996**, *100*, 331. (b) Hatchett, D. W.; White, H. S. *J. Phys. Chem.* **1996**, *100*, 9854.

(2) (a) Hatchett, D. W.; Stevenson, K. J.; Lacy, W. B.; Harris, J. M.; White, H. S. *J. Am. Chem. Soc.* **1997**, *119*, 6596. (b) Stevenson, K. J.; Hatchett, D. W.; White, H. S. *J. Isr. Chem.* In press.

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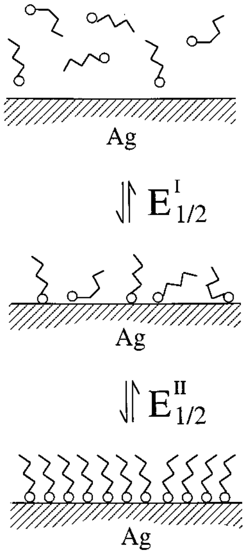
Scheme 1. Two-Step Mechanism of *n*-alkanethiolate Deposition on Ag(111) Electrodes[a]



[a] The half-wave potentials $E^{I}_{1/2}$ and $E^{II}_{1/2}$ correspond to the formation of low- and high-density monolayer structures, respectively.

We now wish to report the results of an investigation of the electrochemical deposition of a series of *n*-alkanethiolates onto Ag(111) electrodes from both aqueous ($2 \leq n_c \leq 10$) and methanolic ($2 \leq n_c \leq 16$) solutions. Specifically, we demonstrate that adsorption free energies for *n*-alkanethiolates at Ag(111) can be directly obtained from voltammetric measurements of the redox reaction expressed by eq 1 when the measurement is made in solutions containing millimolar concentrations of $C_{n_c}H_{2n_c+1}S^-$. Schlenoff, Li, and Ly computed the free energy of adsorption of dodecanethiol on Au from methanolic solutions[5] using the electrochemical data of Weisshaar, Lamp, and Porter.[6] However, to our knowledge, a systematic study of the free energy of adsorption of *n*-alkanethiolates from solution (on any metal surface) has not been previously reported, despite the high level of interest in monolayers synthesized with use of these molecules. The heats of adsorption of methylthiolate and hexadecanethiolate at Au(111) have been previously estimated by Nuzzo et al. using vacuum temperature programmed desorption methods.[7] On the basis of data for methylthiolate, where lateral interactions between methyl groups are anticipated to be minimal, these researchers estimated the strength of the Au−S bond to be ~28 kcal/mol. In addition, Widrig et al.[8] measured the potential for reductive desorption of self-assembled monolayers of *n*-alkanethiolates from Ag and Au; however, these authors specifically ruled out the possibility that the potential of reductive desorption corresponds to the reversible potential of eq 1.

Because of the amphiphilic nature of *n*-alkanethiolates, the free energy of adsorption for these molecules at metal surfaces from aqueous solutions is anticipated to be dominated by hydrophobic interactions, attractive lateral forces between hydrocarbon chains, and the formation of the metal−sulfur bond. The spontaneous assembly of amphiphilic molecules into monolayers, bilayers, and micelles is driven by the strong self-association of water molecules, which inhibits the mixing of water and amphiphile. The energy gained by transferring amphiphilic molecules from water into a hydrocarbon phase is a linear function of the number of carbon atoms in the hydrocarbon chain, n_c, and can expressed as:[9],[10]

$$\Delta G \approx A - 1.4RTn_c \tag{2}$$

where the constant *A* depends on the nature of the polar headgroup and may be either positive or negative, but is generally on the order of a few kilocalories per mole. Equation 2 is also useful for estimating the adsorption energy of amphiphilic molecules from bulk water onto a surface, as recently discussed by Wängnerud and Jönsson.[10] Equation 2 indicates that the free energy of adsorption at 25 °C decreases by ca. 0.83 kcal/mol per unit increase in n_c. For a long-chain *n*-alkanethiolate, e.g., $n_c = 16$, the energy associated with the hydrophobic effect (10−20 kcal/mol) is within the same order of magnitude as estimates by Nuzzo et al. for the interaction of the sulfur headgroup with a Au surface.[7] Thus, it is clear that both the formation of the metal−sulfur bond and the hydrophobic effect are anticipated to contribute significantly to the overall thermodynamic stability of *n*-alkanethiolate monolayers.

In this report, we describe measurements of the free energy of adsorption of *n*-alkanethiolates at Ag(111). We show that the two-wave voltammetric response described above for ethanethiolate ($n_c = 2$) is also observed for short to intermediate length *n*-alkanethiolates ($n_c \leq 6$). For longer chain molecules ($n_c > 6$), the voltammetric waves collapse into a single wave, a consequence of increased hydrophobic interactions and stronger lateral intermolecular forces between hydrocarbon chains. Both forces tend to drive the monolayer into the more densely packed high-coverage phase. The electrochemical data are employed to quantitatively evaluate the contributions to the overall free energy of adsorption resulting from Ag(111)−S bond formation, hydrophobic interactions, and intermolecular forces within the monolayer.

Experimental Section

Ag(111) Electrodes. Thin films (~3500 Å) of Ag were thermally evaporated onto mica with use of a procedure recently reported.[11] The Ag films were thermally annealed under vacuum to produce (111)-oriented films that displayed 100 nm wide atomically flat terraces by scanning tunneling microscopy.[11] An apparent surface roughness of $R = 1.04 \pm 0.02$ was determined by Coulometric measurement of the charge associated with deposition of a monolayer of Pb onto the Ag(111) surface.[11] Surface coverages reported herein for the *n*-alkanethiolate monolayers are corrected by using this roughness factor.

Materials and Electrochemical Apparatus. Water was purified by using a Barnstead "E-pure" system. NaOH (Mallinckrodt), *n*-alkanethiols ($n = 2, 3, 5, 6, 7, 8, 10, 12, 16$, Aldrich; $n = 4$, Kodak Chemicals), isobutanethiol, and *tert*-butanethiol (Aldrich) were generally used as received. However, some select *n*-alkanethiols ($n = 2, 5, 10$) were purified by distillation. The voltammetric responses of Ag(111) in solutions prepared with purified *n*-alkanethiols were found to be indistinguishable from those obtained with solutions prepared from the "as received" *n*-alkanethiols.

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(3) Poirier, G. E.; Pylant, E. D. *Science* **1996**, *272*, 1145.

(4) Truong, K. D.; Rowntree, P. A. *J. Phys. Chem.* **1996**, *100*, 19917.

(5) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 7, 12528.

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

(7) (a) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 9, 733. (b) Nuzzo, R. G.; Zegarski,B. R.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

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

(9) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes;* John Wiley and Sons Inc.: New York, 1973.

(10) Wängnerud, P.; Jönsson, B. *Langmuir* **1994**, *10*, 3268.

(11) Stevenson, K. J.; Hatchett, D. W.; White, H. S. *Langmuir* **1996**, *12*, 2, 494.

A one-compartment, three-electrode Pyrex glass cell was used for all electrochemical measurements. Pt wire and Ag/AgCl (3 M NaCl) electrodes were employed as the counter and reference electrodes, respectively. Ag(111) film electrodes were prepared by cutting the larger mica/Ag(111) substrates into ∼1 cm × 1 cm samples. A small spring-loaded Cu clip was used to make electrical contact with one end of the sample. The electrode was immersed to a depth of ∼0.5 cm into the solution, taking precaution not to contact the Cu clip. Solutions were bubbled for ∼20 min with N_2 before electrochemical analysis to remove O_2, and a positive pressure of N_2 was maintained over the solution during the measurements. The cell temperature was 25 ± 2 °C. Voltammetric measurements were performed with an EG&G Princeton Applied Research model 173 potentiostat/galvanostat, model 175 universal programmer, and a Kipp & Zonen model BD 90 XY recorder.

Electrode Preparation and Instrumentation for SERS. *In-situ* SERS measurements were performed by using an electrochemically roughened polycrystalline Ag disk-shaped electrode. Construction of the electrode and electrochemical roughening of the electrode surface have been described previously.[2a]

The 647.1 nm line from a krypton ion laser (Coherent, Innova 90-K) was focused to a spot diameter of ca. 25 μm with an angle of incidence of 35° relative to the surface normal. The incident laser power was typically on the order of 50−100 mW. Removal of the incoherent laser plasma lines was accomplished by passing the beam through a dove prism (Newport Corporation), a 3 nm band-pass interference filter (Oriel), a plano-convex lens ($f = 1.0$ m, Newport Corporation), and a 0.5 mm pinhole aperture. Raman scattering was collected with a 10× microscope objective lens (Baush and Lomb) and focused onto a fiber optic bundle (Fiberguide Industries) containing 44 low hydroxyl quartz fibers (100 μm diameter) contained in a circular pattern. The output fibers were arranged in a linear array to match the entrance slit of a $f/7$ single stage spectrograph (0.5 m, Spex, Model 1870C). The transmitted radiation was collected and collimated by an $f/1.3$ camera lens (JML Optics) and focused onto the spectrograph entrance slit by a plano-convex lens ($f = 100$ mm, Newport Corporation). A holographic notch filter (Kaiser Optical Systems) was placed between the collection and focusing lenses to remove Rayleigh and specular scattering. The Raman signal was detected with a water-cooled 512 × 512 CCD (EG&G PARC, model 1530-P/PUV). Integration times for the SERS spectra were typically on the order of 17 s. Factor analysis was used to resolved the potential-dependent spectra from the background to determine the intensity and peak position of the chemisorbed alkanethiolate Raman bands.,[12] [13]

Results and Discussion

Voltammetric Response of Ag(111) in Aqueous Solutions of n-Alkanethiolate. The voltammetric behavior of Ag(111) electrodes immersed in aqueous 0.5 M NaOH solutions containing 5 mM *n*-alkanethiolates is shown in Figure 1. As previously reported, the voltammetric curve for ethanethiolate ($n_c = 2$) consists of two well-resolved waves with half-wave redox potentials $E^{\mathrm{I}}_{1/2} = -1.18$ V and $E^{\mathrm{II}}_{1/2} = -0.98$ V vs Ag/AgCl.[14] Previous electrochemical quartz microbalance (EQCM) and in-situ SERS measurements indicate that *both* waves correspond to $CH_3CH_2S^-$ adsorption at Ag(111).[2a] In addition, $CH_3CH_2S^-$ is completely desorbed from Ag(111) at potentials negative of $E^{\mathrm{I}}_{1/2}$, as indicated by a decrease in SERS intensities to background levels. The voltammetric wave at −1.18 V corresponds to adsorption of ca. one-half of a monolayer of $CH_3CH_2S^-$ as determined by Coulometric and EQCM measurement.[2a] This low-coverage structure is energetically favored at electrode potentials, E, between $E^{\mathrm{I}}_{1/2}$ and $E^{\mathrm{II}}_{1/2}$. The wave at $E^{\mathrm{II}}_{1/2}$ corresponds to further adsorption of $CH_3CH_2S^-$ to yield a complete monolayer ($\Gamma = 7.7 \times 10^{-10}$ mol/cm^2). Scheme 1 depicts the transitions between the bare Ag(111) surface ($E < E^{\mathrm{I}}_{1/2}$), the intermediate low-coverage structure ($E^{\mathrm{I}}_{1/2} < E < E^{\mathrm{II}}_{1/2}$), and the full monolayer ($E > E^{\mathrm{II}}_{1/2}$).

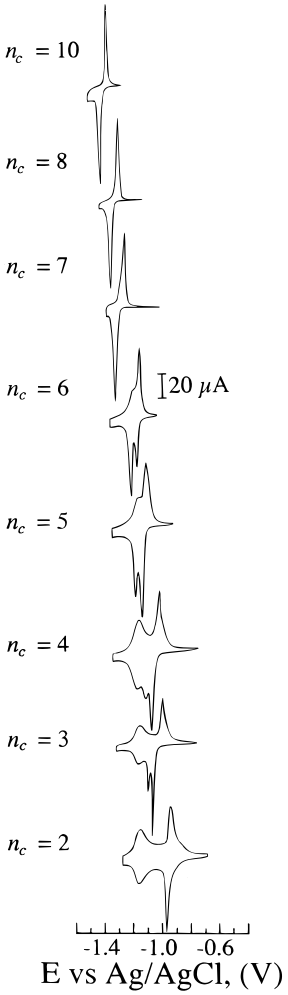

Figure 1. Voltammetric responses of Ag(111) electrodes immersed in aqueous 0.5 M NaOH solutions containing 5 mM $C_{nc}H_{2nc+1}SH$. Scan rate = 100 mV/s. Electrode area = 0.65, 0.50, 0.55, 0.45, 0.30, 0.28, 0.26, and 0.24 cm^2 for n_c = 2, 3, 4, 5, 6, 7, 8, and 10, respectively.

The two-wave voltammetric response is observed for *n*-alkanethiolates with $2 < n_c \leq 6$. However, as apparent in Figure 1, the second voltammetric wave shifts to more negative potentials as the length of the hydrocarbon tail increases. Specifically, $E^{\mathrm{II}}_{1/2} = -0.98$ V for $n_c = 2$, −1.07 V for $n_c = 3$, −1.10 V for $n_c = 4$, and −1.14 V for $n_c = 5$, with an estimated error of ±0.01. On the other hand, the redox potential for wave I, $E^{\mathrm{I}}_{1/2} = -1.19 \pm 0.02$ V, is independent of n_c. As $E^{\mathrm{II}}_{1/2}$ shifts to more negative values, the two waves merge and a single voltammetric wave is obtained for $n_c > 7$. This single wave continues to shift to more negative potentials with increasing chain length. Qualitatively similarly behavior is observed for adsorption of *n*-alkanethiolates from basic methanolic solutions, as discussed in a later section.

Although the voltammetric waveshape for *n*-alkanethiolates is strongly dependent on n_c, the surface coverage, $\Gamma = 7.7 \pm 0.3 \times 10^{-10}$ mol/cm^2, obtained by coulometric integration of the voltammetric waves and assuming the reaction stoichiometry of eq 1, is independent of n_c. This value is in agreement with

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[12] Lawton W. H.; Sylvestre E. A. *Technometrics* **1971**, *13*, 617.

[13] Malinowski E. R.; Cox R. A.; Haldna U. L. *Anal. Chem.* **1984**, *56*, 778.

[14] The potentials reported in ref 2a correspond to measurements in 0.2 M NaOH solutions and are slightly positive ($E^{\mathrm{I}}_{1/2} = -1.17$ V and $E^{\mathrm{II}}_{1/2} = -0.95$ V vs Ag/AgCl) of the values reported here.

the surface coverages obtained by Porter and co-workers for the reductive desorption of *n*-alkanethiolate monolayers from Ag electrodes (7.0×10^{-10} mol/cm^2).[8] Our measured value is also in agreement with the theoretical value ($\Gamma = 7.6 \times 10^{-10}$ mol/cm^2) predicted for a $\sqrt{3} \times \sqrt{3}(R)$ 30° structure deposited on Ag(111).

For $n_c = 3$, 4, and 5, we occasionally observe an extraneous reductive wave or current spike at potentials between waves I and II (see Figure 1 for $n_c = 3$ and 4). We believe that the presence of an additional reductive peak is due to subtle variations in monolayer domain size and structure, which are reflected in the dependence of desorption rates and energetics on these variations. For instance, molecules located at higher-energy domain boundaries should desorb at more positive potentials than those positioned within the domains. Zhong and Porter have reported similar voltammetric responses for the reductive desorption of dodecanethiol and hexadecanethiol at Au(111) electrodes.[15] We note that the multiple-wave voltammetric response observed for *n*-alkanethiolate adsorption on Ag(111) is not the result of adsorption at defect sites or different crystallographic orientations. In particular, we find that thermal annealing of the Ag(111) electrodes results in a significant improvement in the resolution of the multiple-wave voltammetric response.[2a]

We attribute the shift of wave II with increasing n_c to the increased hydrophobicity of the molecules. The deposition of the high-coverage structure ($\Gamma = 7.7 \times 10^{-10}$ mol/cm^2) requires that the *n*-alkanethiolate molecules are transferred completely out of the aqueous phase as they are adsorbed onto the surface. The free energy associated with this transfer should follow the chain length dependency indicated in eq 2, and indeed, we observe that a plot of $E^{\mathrm{II}}_{1/2}$ vs n_c has a slope of $\sim 1.4RT/F$. The analysis of adsorption free energy is described in detail below. The fact that $E^{\mathrm{I}}_{1/2}$ is independent of n_c suggests that the low-coverage phase of adsorbed $C_{n_c}H_{2n_c+1}S^-$ comprises molecules that remain fully in contact with water.

The finding that a single voltammetric wave is observed for longer chain *n*-alkanethiolates ($n_c > 6$) is not surprising, since it is well established that these molecules spontaneously self-assemble into organized monolayers under open-circuit conditions. Self-assembly of *n*-alkanethiolates is a redox process in which the electrical charge generated by oxidative adsorption is balanced by the charge associated with a reductive reaction, e.g., the reduction of H_2O or O_2. The deposition of *n*-alkanethiolates by electrochemical methods involves the same chemical process as that for conventional self-assembly, except that the electrochemical potential of the electron in the metal is externally controlled. Thus, the driving force for adsorption can be independently varied by changing the electrode potential. The electrochemical deposition of *n*-alkanethiolate monolayers onto Hg electrodes was first demonstrated by Birke and Mazorra[16] and more recently by Weisshaar, Lamp, and Porter using Au electrodes.[6] The observation of a two-wave response at Ag(111) for $n_c \leq 6$, however, is surprising, since this indicates that the low-coverage structure is more stable for short-chain *n*-alkanethiolates than for the full monolayer. The energy difference between these structures is not large ($\Delta G = -nF(E^{\mathrm{II}}_{1/2} - E^{\mathrm{I}}_{1/2}) \sim 4$ kcal/mol for $n_c = 2$ and smaller for longer chain molecules) and should reflect either repulsive interactions between the sulfur headgroups or an energy cost associated with displacing solvent dipoles from the electrically charged metal surface as the alkanethiolate monolayer is formed. Hydrophobic interactions and intermolecular forces between hydrocarbon chains apparently become sufficiently large at $n_c = 7$ to make the high-coverage structure the more energetically favored structure at all electrode potentials.

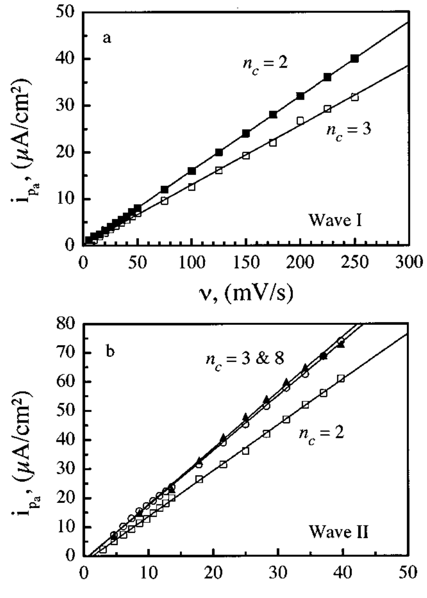

Figure 2. (a) Dependence of the anodic peak currents (i_{pa}) of wave I ($n_c = 2$ and 3) on the voltammetric scan rate (ν). (b) Dependence of i_{pa} for wave II ($n_c = 2$, 3, and 8) on the voltammetric scan rate raised to the 2/3 power, ($\nu^{2/3}$). All measurements correspond to Ag(111) electrodes immersed in aqueous 0.5 M NaOH solutions containing 5 mM $C_{nc}H_{2nc+1}SH$ (n_c indicated on the figure).

The dependence of voltammetric peak currents on scan rate, ν, for the deposition of several *n*-alkanethiolates is presented in Figure 2. The peak currents for wave I increase linearly with ν, indicative of a fast, reversible surface redox process, and consistent with the formation of a low-density phase of noninteracting adsorbates, Scheme 1. In contrast, the peak current for wave II increases in proportion to $\nu^{2/3}$ for both the short-chain and long-chain *n*-alkanethiolates. The 2/3 power dependence is consistent with voltammetric behavior associated with nucleation and growth (or dissolution) of two-dimensional molecular films.[17] [18]

Influence of Steric Forces on the Electrochemical Deposition of *n*-Alkanethiolates. The oxidative adsorption of the three structural isomers of butanethiolate was investigated to examine the influence of steric forces on monolayer formation. We hypothesized that if wave II is associated with the formation of a dense and ordered monolayer, then the branching of the alkane group should be reflected in the voltammetric responses for the structural isomers. Conversely, the redox potential of wave I should not change for the different isomers if the adsorbed molecules are solvent separated and weakly interacting. In addition, since the hydrophobicity of the three isomers is approximately the same, we anticipate that $E^{\mathrm{II}}_{1/2}$ should also be essentially independent of the isomer.

Figure 3 shows the voltammetric response for Ag(111) electrodes immersed in aqueous 0.5 M NaOH solutions containing 5 mM *n*-butanethiol, isobutanethiol, or *tert*-butanethiol. The shape of wave I, which is associated with the formation of the low-density monolayer, remains relatively unchanged with

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[15] Zhong, C.-J.; Porter, M. D. *J Electroanal. Chem.* **1997**, *425*, 147.

[16] Birke, R. L.; Mazorra, M. *Anal. Chim. Acta* **1980**, *118*, 257.

[17] Maestre, M. S.; Rodriguez-Amaro, R.; Munoz, E.; Ruiz, J. J.; Camacho, L. *J. Electroanal. Chem.* **1994**, *373*, 31.

[18] Fletcher, S. *J. Electroanal. Chem.* **1981**, *118*, 419.

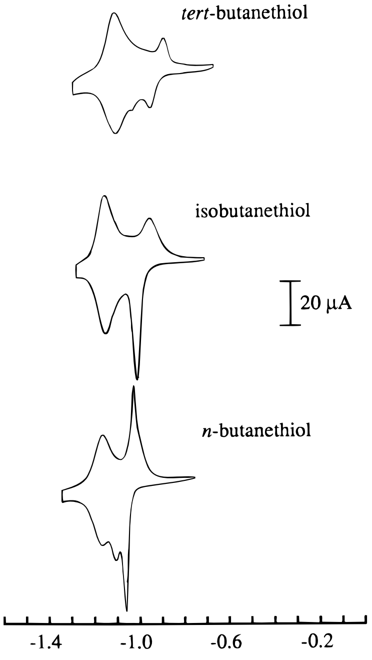

Figure 3. Voltammetric responses of Ag(111) electrodes immersed in 0.5 M NaOH solutions containing 5 mM of *tert*-butanethiol, isobutanethiol, and *n*-butanethiol. Electrode areas are equal to 0.55, 0.75, and 0.72 cm^2, respectively. Scan rate = 100 mV/s.

respect to the branching of the alkane chain. However, a small positive shift in $E^{\mathrm{I}}_{1/2}$ is observed for the deposition of *tert*-butanethiolate. The direction of the shift is opposite that from expectations based on electron inductive effects and, thus, most probably reflects small repulsive interactions between highly branched alkane groups. The surface coverages associated with wave I, however, are independent of the isomer structures. In contrast, voltammetric wave II is strongly dependent on the structure of the isomer. Figure 3 shows that the currents associated with this wave decrease significantly with increased branching. The surface concentrations for *n*-, iso-, and *tert*-butanethiolate monolayers, computed from integration of the areas beneath the anodic peaks of waves I and II, are $\Gamma = 7.5 \pm 0.3 \times 10^{-10}$, $6.8 \pm 0.2 \times 10^{-10}$, and $5.5 \pm 0.2 \times 10^{-10}$ mol/cm^2, respectively. The decrease in Γ with increased branching of the alkane group suggests that steric forces between adsorbates control the packing density of molecules on the Ag(111) surface.

In-Situ SERS Measurement of the Potential-Dependent Adsorption of *n*-Hexanethiolate. SERS was used to monitor the potential-dependent formation of *n*-hexanethiolate ($n_c = 6$) monolayers on Ag electrodes.[19] Figure 4 shows the voltammetric response of an electrochemically roughened polycrystalline Ag electrode immersed in an aqueous solution containing 0.5 M NaOH and 5 mM *n*-hexanethiol. As noted above, the two-wave voltammetric response in *n*-hexanethiol solution can be partially resolved at the highly ordered Ag(111) electrode (Figure 1); however, the voltammetric waves are not resolved for the electrochemically roughened Ag electrodes (Figure 4). The two spectral regions investigated include the range of frequencies previously reported for the ν(C−S) (600−750 cm^{-1}) and ν(C−C) (1000−1200 cm^{-1}) stretching modes of the trans and gauche conformers of *n*-alkanethiols adsorbed on Ag.[20] [21]

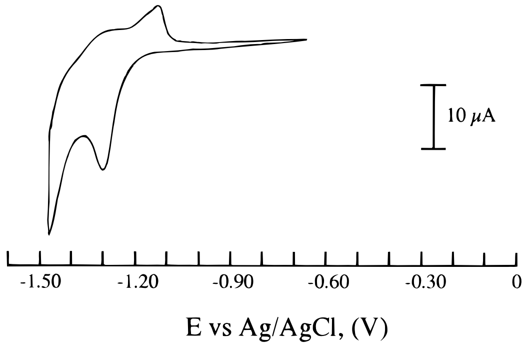

Figure 4. Voltammetric response of an electrochemically roughened Ag electrode immersed in a 0.5 M NaOH solution containing 5 mM *n*-hexanethiol. Scan rate = 100 mV/s. Electrode area = 0.031 cm^2.

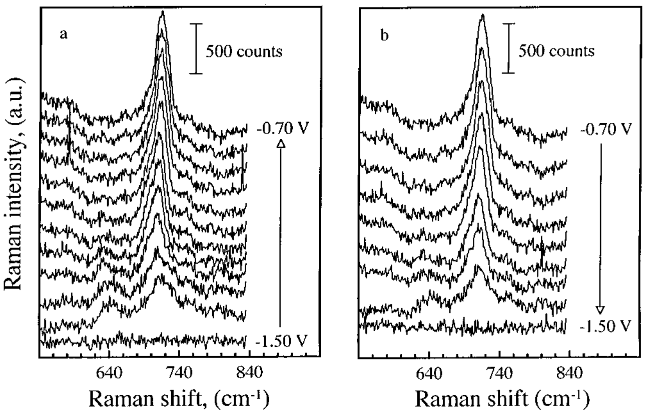

Figure 5. In-situ SERS spectra of the ν(C−S) stretching region recorded during the (a) adsorption and (b) desorption of *n*-hexanethiolate at an electrochemically roughened polycrystalline Ag electrode. Measurements made with use of a 0.5 M NaOH solution containing 5 mM *n*-hexanethiol. Applied potentials (from bottom to top): (a) −1.50, −1.45, −1.40, −1.35, −1.30, −1.25, −1.20, −1.15, −1.10, −1.00, −0.80, and −0.70 V; (b) −0.70, −0.90, −1.20, −1.25, −1.30, −1.35, −1.40, −1.45, and −1.50 V, respectively. The spectra represent an average of two individual measurements with integration times of 20 s.

Figure 5a shows in-situ SERS spectra recorded within the ν(C−S) stretching region. These spectra were obtained while stepping the potential in the positive direction, corresponding to adsorption of *n*-hexanethiolate (−1.50 to −0.70 V). Spectra were recorded after each potential step when the current had decayed to background values (<1 s). Figure 5b shows the same spectral region as the potential is stepped in the negative direction (−0.70 to −1.50 V), corresponding to desorption of *n*-hexanethiolate.

The SERS spectrum for an electrochemically roughened Ag electrode at an applied potential of −1.5 V shows no detectable Raman signal above the background, indicating that *n*-hexanethiolate is completely desorbed at this potential. (We previously reported that ethanethiolate is also desorbed from Ag(111) at potentials negative of −1.3 V.[2a]) As the electrode potential is stepped in the positive direction, two Raman bands appear at 645 and 720 cm^{-1}. These bands correspond to the gauche and trans conformers of the ν(C−S) stretching mode, respectively. The Raman band at 720 cm^{-1} is assigned to the trans ν(C−S) mode, which has been previously observed at 699 and 707 cm^{-1} in ex-*situ* (i.e., measured in air) spectra of *n*-butanethiol and *n*-decanethiol, respectively, adsorbed onto a roughened Ag surface.[19] The assignment of the gauche mode

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[19] Pemberton, J. E.; Guy, A. L.; Sobocinski, R. L.; Tuschel, D. D.; Cross, N. A. *Appl. Surf. Sci.* **1988**, *32*, 33.

[20] Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 3629.

[21] Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 8284.

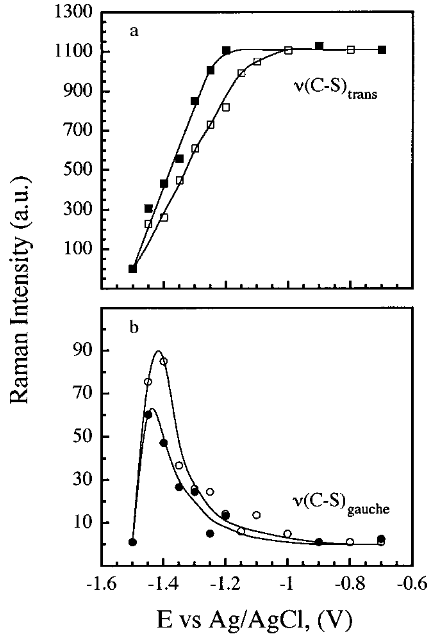

Figure 6. SERS intensity as a function of the applied potential for the trans and gauche ν(C−S) modes of *n*-hexanethiolate during adsorption (open symbols) and desorption (filled symbols). The data correspond to the spectra in Figure 5.

at 645 cm^{-1} is also based on the ex-situ Raman spectrum of *n*-butanethiol and *n*-decanethiol, which displays the gauche ν(C−S) mode at 630 and 636 cm^{-1}.[19] The ca. 15 cm^{-1} frequency shift for these bands is an effect of the overlaying solvent. We have previously observed that the in-situ gauche ν(C−S) mode for ethanethiolate monolayers on Ag is red shifted by ~12 cm^{-1} in comparison to the ex-situ value.[22]

Figure 6 presents a plot of the potential-dependent SERS intensities for the gauche and trans ν(C−S) modes. The SERS intensity for the trans ν(C−S) mode increases over the potential range from −1.5 to −1.10 V, which corresponds to the formation of the *n*-hexanethiolate monolayer in Figure 4. In contrast, the gauche ν(C−S) mode increases between −1.5 and −1.40 V and then rapidly decreases as the electrode potential is scanned to more positive values. Kabasawa et al. report a similar potential dependency for the gauche ν(C−S) mode for butanethiol adsorbed on Ag;[23] however, these researchers did not scan the electrode potential to values sufficiently negative to observe desorption, as would be evident by a decrease in the intensity of the trans ν(C−S) mode. Our results, and those of Kabasawa et al., indicate that electrochemically deposited *n*-alkanethiolate monolayers contain a significant fraction of both gauche and trans conformations at low coverages. The disappearance of intensity for the gauche ν(C−S) mode and increase in intensity for the trans ν(C−S) mode as the electrode potential is shifted toward positive values suggests that the gauche conformers are eliminated as the surface concentration increases. This behavior is consistent with a concentration-dependent transition between a disordered and ordered monolayer; unfortunately, the heterogeneity of the roughened, polycrystalline Ag electrode prevents a clear observation of the transition between the two phases by either electrochemical or spectroscopic methods.

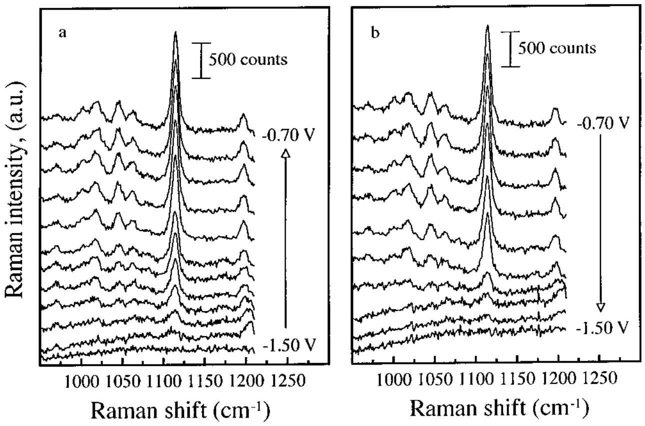

Figure 7. In-situ SERS spectra of the ν(C−C) stretch region recorded during the (a) adsorption and (b) desorption of *n*-hexanethiolate at an electrochemically roughened polycrystalline Ag electrode. Measurements made with use of a 0.5 M NaOH solution containing 5 mM *n*-hexanethiol. Applied potentials (from bottom to top): (a) −1.50, −1.45, −1.40, −1.35, −1.30, −1.25, −1.20, −1.15, −1.10, −1.00, −0.80, and −0.70 V; (b) −0.70, −0.90, −1.10, −1.20, −1.25, −1.30, −1.35, −1.40, −1.45, and −1.50 V, respectively. The spectra represent an average of two individual measurements with integration times of 15 s.

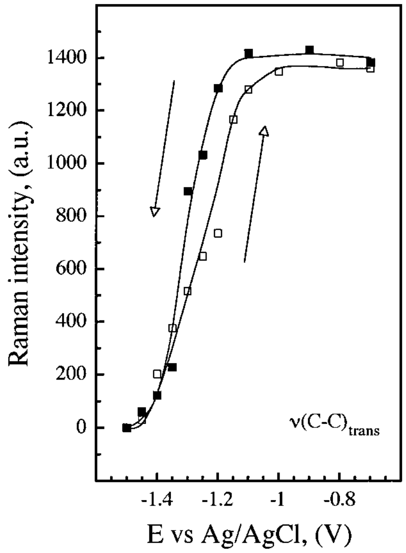

Figure 8. SERS intensity for the 1115 cm^{-1} ν(C−C) trans mode recorded as a function of the applied potential during adsorption (open squares) and desorption (filled squares) of *n*-hexanethiolate. The data correspond to the spectra in Figure 7.

Figure 7 presents the SERS spectra of the ν(C−C) region as a function of applied potential. The strong SERS intensity at 1115 cm^{-1} corresponds to the trans ν(C−C) stretching mode.[19,24] Figure 8 shows the corresponding potential-dependent intensity for this SERS peak. These data confirm our conclusion that the oxidative adsorption of *n*-hexanethiolate is a chemically reversible process.

Analysis of the Adsorption Free Energy. The redox potentials, $E^{\mathrm{I}}_{1/2}$ and $E^{\mathrm{II}}_{1/2}$, represent thermodynamic free energies of adsorption, and thus are directly related to the stability of *n*-alkanethiolate monolayers. Values of ΔG_{ads} were computed from the expression $\Delta G_{\mathrm{ads}} = -nFE_{1/2}$,[25] after coverting experimental $E_{1/2}$ values (measured vs Ag/AgCl) to the normal hydrogen electrode scale. Thus, the free energy data reported here correspond to the following reaction:

$$\mathrm{Ag(111)} + \mathrm{C}_{n_c}\mathrm{H}_{2n_c+1}\mathrm{S}^-(5\ \mathrm{mM}) + \mathrm{H}^+(a{=}1) \rightleftharpoons \mathrm{Ag(111)}{-}\mathrm{SC}_{n_c}\mathrm{H}_{2n_c+1} + {}^{1}\!/_{2}\mathrm{H}_2(a{=}1)$$

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[22] Lacy, W. B. Ph.D. Thesis, University of Utah, 1996.

[23] Kabasawa, A.; Matsuda, N.; Sawaguchi, T.; Matsue, T.; Uchida, I. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1992**, *60*, 986.

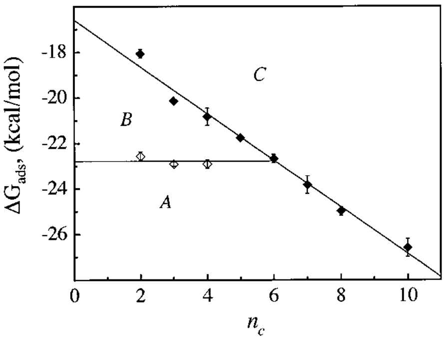

Figure 9. ΔG_{ads} vs n_c for the formation of the low-density (wave I, open diamonds) and high-density (wave II, filled diamonds) phases of $C_{nc}H_{2nc+1}S^-$ monolayers at Ag(111) in aqueous 0.5 M NaOH solutions. Region *A* corresponds to the bare Ag(111) surface, region *B* to the low-coverage phase, and region *C* to the full monolayer.

Adsorption free energies associated with the low-coverage (wave I) and full monolayer (wave II) are plotted as a function of n_c in Figure 9. The free energy data define three phases for the Ag(111)/$C_{n_c}H_{2n_c+1}S^-$ system. Region *A* corresponds to the "bare" Ag(111), where $C_{n_c}H_{2n_c+1}S^-$ is completely desorbed from the electrode surface. Region *B* corresponds to the low-coverage and disordered submonolayer. Region *C* corresponds to the high-density and more ordered monolayer.

ΔG_{ads} for the low coverage phase (open symbols in Figure 9) is independent of n_c, a finding that we previously attributed to negligible lateral interactions between solvent-separated hydrocarbon chains. As such, the measured free energy of −22.8 kcal/mol is dominated by the energy of formation of the Ag(111)−S bond in the absence of hydrophobic effects and lateral chain interactions. This free energy also includes the energy associated with displacing H_2O molecules from the surface and desolvation of the sulfide headgroup.

ΔG_{ads} for the high-coverage phase (filled symbols, Figure 9) is a linear function of n_c. Extrapolation of these values to $n_c = 0$ yields $\Delta G_{ads} = -16.6$ kcal/mol, which corresponds to the high-coverage Ag−S interaction in the absence of hydrophobic effects and lateral chain interactions. As previously mentioned, the difference between this value and that measured for the low-coverage structure (−22.8 kcal/mol) is probably due to increased repulsive interactions between sulfur headgroups or the energy associated with desorbing H_2O from the Ag(111) surface.

The chain length dependence of wave II for *n*-alkanethiolate adsorption indicates that the monolayer becomes increasingly more stable as n_c increases. ΔG_{ads} shifts from −18.1 to −26.6 kcal/mol as n_c increases from 2 to 10. We attribute this stabilization to the increased hydrophobicity of the molecules as n_c increases. We note that Birke and Mazorra[16] reported a similar shift in $E_{1/2}$ for the oxidative adsorption of *n*-alkanethiolates on Hg and attributed this to increased inductive effects of the alkane group, the larger alkane groups being more electron donating. However, it seems highly unlikely that inductive effects would give rise to a linear dependence of $E_{1/2}$ on n_c over the large range of chain lengths employed in this study.

The plot of ΔG_{ads} vs n_c for wave II, corresponding to formation of the full monolayer, has a slope of −1.02 ± 0.04 kcal/mol. Thus, the addition of one CH_2 group results in stabilization of the film by ~1 kcal/mol. For comparison, the free energy of transfer of simple hydrocarbons into water is reported to vary as −0.88 kcal/mol per CH_2.[9]

In summary, the free energy of adsorption of *n*-alkanethiolates at Ag(111) from aqueous 0.5 M NaOH solutions is given by the following expressions:

$$\Delta G_{ads} = -22.8 \text{ (kcal/mol)}$$

for the low-coverage phase, and

$$\Delta G_{ads} = -16.6 - 1.02n_c \text{ (kcal/mol)}$$

for the high-coverage phase.

In a related series of experiments, Porter,[8] Kakiuchi,[26] and their co-workers measured the voltammetric peak potential, E_{pc}, for the reductive desorption of self-assembled monolayers of *n*-alkanethiolates on Ag and Au. These researchers found that E_{pc} shifted negative in methanol solutions by 15−20 mV per n_c, corresponding to ca. −0.5 kcal/mol per CH_2. Because these measurements were made in solutions which did not contain dissolved *n*-alkanethiolate, i.e., conditions that correspond to a chemically irreversible redox system, it is difficult to ascertain whether E_{pc} corresponds to a true thermodynamic potential. Our measured values of the reversible half-wave potential, $E_{1/2}$, should be a good approximation of the true equilibrium potential of the redox reaction expressed by eq 1. Regardless, Porter and co-workers[8] ascribed the shift in E_{pc} with increasing n_c to the electric-field dependent transport of ions across the monolayer, while Kakiuchi and co-workers[26] concluded that the chain length dependence is dominated solely by lateral intermolecular forces. In contrast, we believe that the observed chain length dependence of $E_{1/2}$ in aqueous solutions must reflect, in part, if not entirely, the hydrophobic nature of *n*-alkanethiolate molecules.

Adsorption of *n*-Alkanethiolates from Methanol Solutions. If the −1.02 ± 0.04 kcal/mol per CH_2 group reflects the energy of transfer associated with hydrophobic forces, then this value should decrease when an organic solvent is used in place of water. Conversely, if lateral intermolecular forces are more important than the hydrophobic effect in determining the overall monolayer stability, then the nature of the solvent should have little, if any, effect on the measured adsorption free energies. To test these predictions, we measured the voltammetric response of Ag(111) in methanol/H_2O solutions (95% methanol by volume[27]) containing 0.5 M NaOH and 5 mM *n*-alkanethiol. Figure 10 shows that the two-wave voltammetric response is clearly present in this solvent, although not as clearly resolved as in aqueous solutions. As before, the two waves merge into a single wave as n_c increases.

Figure 11 shows values of ΔG_{ads} in methanol computed from the voltammetric data. ΔG_{ads} for the formation of the low-coverage phase is equal to −24.1 kcal/mol, approximately 2.5 kcal/mol lower in energy than that measured in aqueous solutions. The lowering of ΔG_{ads} in methanol is assumed to reflect a weaker interaction between methanol and the electrically charged Ag(111) surface. Thus, desorption of solvent molecules from the surface during monolayer formation is energetically less costly in methanol than in water.

ΔG_{ads} corresponding to the formation of the full monolayer in methanol decreases with increasing chain length by −0.45

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(24) (a) Sobocinski, R. L.; Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 6177. (b) Sandroff, C. J.; Garoff, S.; Leung, K. P. *Chem. Phys. Lett.* **1983**, *96*, 547.

(25) $\Delta G_{rxn} = -nFE_{1/2}$ is used to compute the free energy of a half-cell reaction when the reaction is written as a *reduction* versus the normal hydrogen electrode (NHE). A negative value of $E_{1/2}$ corresponds to a positve value of ΔG_{rxn}. However, since adsorption of *n*-alkanethiolate corresponds to *oxidation*, the sign of this expression must be reversed., *i.e.*, oxidative adsorption at negative electrode potentials vs NHE corresponds to a negative adsorption free energy.

(26) Imabayashi, S.-I.; Iida, M.; Hobara, D.; Feng, Z. Q.; Niki, K.; Kakiuchi, T. *J. Electroanal. Chem.* **1997**, *428*, 33.

(27) The H_2O is added to this solution to increase the solubility of NaOH.

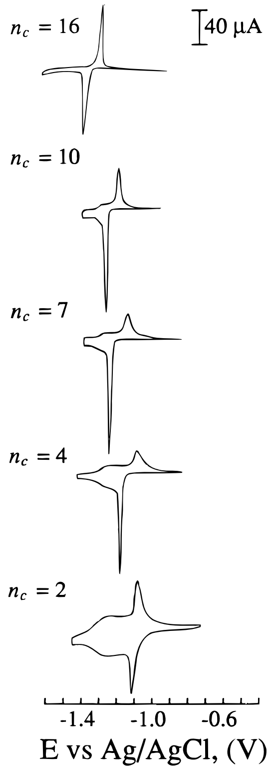

Figure 10. Voltammetric responses of Ag(111) electrodes immersed in methanolic 0.5 M NaOH solutions containing 5 mM $C_{nc}H_{2nc+1}SH$. Scan rate = 100 mV/s. Electrode areas = 0.80, 0.43, 0.30, 0.28, and 0.27 cm^2 for n_c = 2, 4, 7, 10, and 16, respectively.

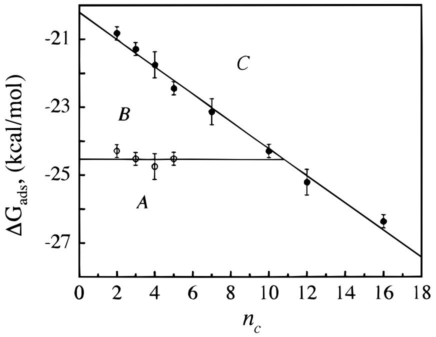

Figure 11. ΔG_{ads} vs n_c for the formation of the low-density (wave I, open circles) and high-density (wave II, filled circles) phases of $C_{nc}H_{2nc+1}S^-$ monolayers at Ag(111) in methanolic 0.5 M NaOH solutions. Region *A* corresponds to the bare Ag(111) surface, region *B* to the low-coverage phase, and region *C* to the full monolayer.

± 0.03 kcal/mol per CH_2. This value is about half as large as the corresponding value measured in aqueous solutions, clearly reflecting the fact that the thermodynamic stability is strongly dependent on the solubility of the molecule in the contacting solution, water being a much poorer solvent than methanol for the nonpolar *n*-alkanethiolate. However, the measured value of -0.45 kcal/mol per CH_2 is 2 to 3 times larger than values reported for transfer of simple hydrocarbons into methanol,[9] suggesting that intermolecular forces between the hydrocarbon chains contribute significantly to the overall stability of the monolayer, albeit to a smaller degree than the hydrophobic interactions.

Figure 12 shows a comparison of ΔG_{ads} values in methanolic and aqueous solutions for the formation of a full monolayer (wave II). Interestingly, the *n*-alkanethiolate monolayer is less stable in aqueous solutions than in methanol for $n_c < 6$, but more stable for $n_c > 6$. The lower stability of the short-chain molecular films in aqueous solutions is due to the higher energetic cost of displacing water, relative to methanol, from the Ag(111) surface. On the other hand, the hydrophobic effect makes a more significant contribution to ΔG_{ads} at larger n_c, making the longer chain ($n_c > 6$) *n*-alkanethiolate monolayer more stable in water than methanol.

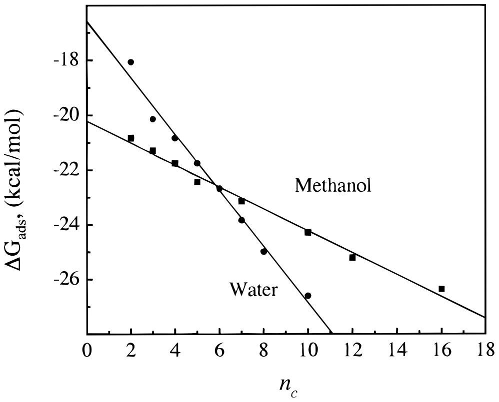

Figure 12. Comparison of ΔG_{ads} vs n_c for formation of full *n*-alkanethiolate monolayers (wave II) in water and methanol.

Finally, our voltammetric and SERS data unequivocally demonstrate that the adsorption of *n*-alkanethiolates at Ag(111) in either aqueous ($n_c = 2-10$) or methanolic solutions ($n_c = 2-16$) is a chemically reversible process at Ag(111). A similar conclusion regarding the reversibility of adsorption at Hg and Au surfaces is drawn from the voltammetric data presented in refs 15 and 16. Thus, monolayers of these *n*-alkanethiolates cannot be considered to be completely stable when placed in contact with aqueous or methanolic solutions which do not contain the adsorbing molecule. However, the potential of a metal surface resting at open-circuit in aqueous or methanolic solutions containing O_2 is typically ca. 1 V positive of $E^{I}_{1/2}$ or $E^{II}_{1/2}$. Such a large driving force would prevent significant desorption of the molecules.

Conclusions

Voltammetric measurement of the reversible oxidative adsorption of *n*-alkanethiolates provides a direct and quantitative method to determine the free energy of adsorption of these molecules on metal surfaces. Adsorption of *n*-alkanethiolates on Ag(111) is driven by hydrophobic interactions, intermolecular forces between hydrocarbon chains, and formation of the Ag(111)$-$S bond. Adsorption of short-chain molecules ($n_c < 7$) is characterized by two surface phases: a low-coverage and more stable structure in which adsorbate molecules are weakly interacting, and a high-coverage full monolayer in which hydrocarbon chain interactions are important. The high-coverage full monolayer becomes energetically more favorable for *n*-alkanethiolates with hydrocarbon chains containing 7 or more carbon atoms.

The free energy associated with formation of the Ag(111)$-$S bond in aqueous solutions is estimated to be -22.8 kcal/mol for the more stable low-coverage phase and -16.6 kcal/mol for the full monolayer. The hydrophobic effect and lateral intermolecular forces between hydrocarbon chains contribute -1.02 kcal/mol per CH_2 to the overall stability of *n*-alkanethiolate films in aqueous solutions. This value decreases to -0.45 kcal/mol per CH_2 in methanolic solutions due to the increased solubility of *n*-alkanethiolates in methanol.

Acknowledgment. This research was supported by the Office of Naval Research and by the U.S. Department of Energy.

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