Table III. A_0, A_{20}, and κ for the Lipid Mixtures GDNT and GDGT at Different Temperatures[a]

compd	temp, °C	A_0, Å²/ molecule	A_{20}, Å²/ molecule	$\kappa \times 10^3$, m/mN
GDNT	16	142.1 ± 1.1	124.2 ± 0.9	6.57 ± 0.07
	24	158.1 ± 2.6	130.8 ± 1.7	8.90 ± 0.57
	30	220.1 ± 1.5	150.8 ± 0.3	15.8 ± 4.2
GDGT	16	157.5 ± 2.0	134.3 ± 2.0	7.94 ± 0.45
	22	164.3 ± 4.1	132.3 ± 0.5	9.79 ± 0.87
	30	207.5 ± 8.1	155.7 ± 4.5	12.0 ± 0.3

[a] The data reported are the averaged values of at least three separate experiments. The values for A_0 and κ are determined from eq 1. The area per molecule at a surface pressure of 20 mN/m, A_{20}, is a directly measured experimental value.

ing" in analogy to hydrophobic compounds according to heat capacity measurements of aqueous solutions of saccharides.[44] Thus, the glucose head groups form bulky hydrophobic hydration structures[45] at low surface pressures, which are destabilized with increasing pressure. Rolandi et al.[20] also observed greater expansion in the GDNT lipids than the GDGT lipids on the buffered subphases at pH 7.4.

Conclusions

The hydrolyzed lipids GDNT and GDGT extracted from the thermoacidophile *S. acidocaldarius* do not form sta-

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ble monolayer films at the air/water interface; i.e., the films will not sustain any pressure. Hence, all the values reported (e.g., A_0 and ΔV) are dynamic rather than equilibrium values. As in other cases, methyl branching and cyclopentane rings in GDNT and GDGT lipids result in expanded monolayer films. The chain–chain interactions are not as strong as in straight-chain molecules. The pressure/area isotherms of the hydrolyzed lipid mixtures are representative of liquid-expanded films. The isotherms for both lipids are similar, suggesting that the molecular packing depends primarily on the alkyl chain–chain interactions. The areas per molecule are consistent with an upright orientation of the lipids with only one polar head group at the lipid/water interface. The hypothesis that a substantial fraction of the lipids is in an n-shaped configuration is not needed to explain the data. The responses of the hydrolyzed archaebacterial lipid films to temperature, ionic strength, and pH of the aqueous subphase provide strong evidence that the head groups at the lipid/water interface are the glycerol for GDGT and the nonitol for GDNT.

Electrochemical and Vibrational Spectroscopic Studies of Coadsorption: Formation of Mixed Monolayers of Methylene Blue and Long-Chain Dithioethers at Sulfur-Modified Polycrystalline Gold Surfaces[†]

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Molecular conformation and order within mixed monolayers of methylene blue, sulfide, and the long-chain dithioether $C_{14}H_{29}SC_2H_4SC_{14}H_{29}$ adsorbed onto polycrystalline evaporated gold films are studied by using electrochemical methods and ex situ vibrational spectroscopy. The methylene blue dye molecules directly chemisorb onto the sulfur-modified gold surface and do not significantly partition into the alkyl portions of the monolayer. However, upon reduction to leucomethylene blue, the dye molecules do partition into the alkyl subphase. Repeated electrochemical reduction and oxidation of the chemisorbed methylene blue result in an ordering of the adsorbed alkyl chains from a liquid-like structure to a close-packed configuration. The presence of a partial dithioether monolayer also leads to the formation of a stabilized leucomethylene blue film. The variations of the molecular structure observed in these mixed systems arise from the competing processes of chemisorption, aggregation, and hydrophobic solubilization occurring within the thin film.

Introduction

The formation of molecular monolayers at electrode surfaces has proven to be an effective strategy for the

control of surface chemistry in a variety of applications such as chemical sensors, electrochromic displays, semiconductor photoelectrochemical devices, and electrocatalytic schemes.[1-5] The adsorption of molecules onto electrodes can occur either through a direct chemical bonding to the surface or via the partitioning of species into a previously deposited monolayer subphase. As the com-
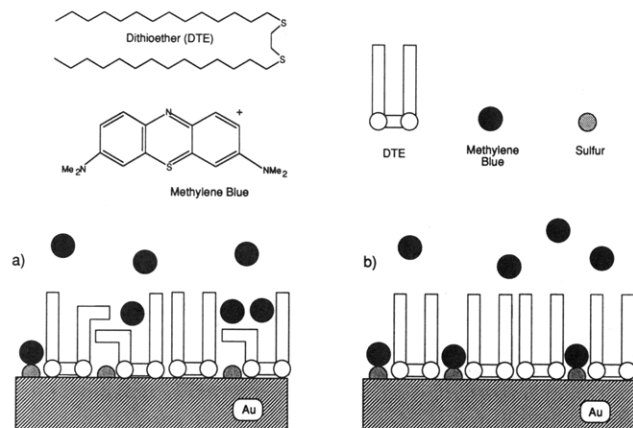
Figure 1. Methylene blue and long-chain dithioether (DTE) coadsorption at a sulfur-modified electrode: (a) a disordered DTE monolayer; (b) electrochemically organized DTE monolayer after cycling in the presence of methylene blue.

plexity of these systems increases, it becomes essential to utilize a variety of spectroscopic methods in conjunction with electrochemical measurements to monitor the chemical content and form of the monolayer. The spectroscopic studies can elucidate the relation of surface concentrations, molecular orientations, and molecular organization within a monolayer to the macroscopically observable properties of a given electrochemical device. In particular, vibrational spectroscopy is an excellent probe for the molecular structure of monolayer and multilayer films and has been applied effectively to molecules at electrochemical surfaces both ex situ[6] and in situ.[7] In this paper, we examine the formation of a complex model electroactive monolayer with a combination of electrochemical methods and ex situ vibrational spectroscopy.

The model coadsorbed monolayers are comprised of two molecules, the first of which is the electroactive thiazine dye methylene blue (Figure 1). Methylene blue is a typical aromatic dye molecule of the type required in any electrochemical–optical device. The molecule possesses both a large ground and first excited state dipole moment as well as a large transition dipole moment between the two states. The large transition dipole moment leads to a strong optical response at visible wavelengths, and the permanent dipole moments result in the aggregation of methylene blue in solution. Both moments depend upon the local environment and should therefore be sensitive to any modifications in the structure of the chemisorbed monolayer that occur electrochemically.

In addition to its spectroscopic utility, methylene blue can be electrochemically reduced to leucomethylene blue in aqueous solution. A recent detailed electrochemical examination of the adsorption of methylene blue was performed by Clavilier et al. in a series of papers on thermally treated gold electrodes.[8–10] The presence of a zero-

valent sulfur monolayer at the electrode surface was shown to enhance the adsorption of a monolayer of methylene blue as well as subsequent monolayers of leucomethylene blue molecules plated out from solution. This chemisorption was detected electrochemically by the presence of an adsorption postwave for the adsorbed species; the enhanced adsorption onto the sulfur-modified gold surface was attributed to a nonbonding sulfur–sulfur interaction that held the molecules in place. This methodology for chemisorbed sulfur-containing molecules is attractive in its specificity and simplicity; we have recently demonstrated that this coadsorption strategy can be used in the chemisorption of methylene blue at sulfur-modified *platinum* electrodes and have measured in situ the molecular orientation of the adsorbed dye molecules with optical second harmonic generation.[11] However, evidence of the specific sulfur–sulfur interaction has yet to be established spectroscopically.

The second molecule in the model monolayer system is the long-chain dithioether (or dialkyl sulfide), $C_{14}H_{29}SC_2H_4SC_{14}H_{29}$, which will be denoted as DTE (see Figure 1). The adsorption of long-chain alkyl species has been employed frequently in electrochemical applications to create membrane-like structures on surfaces which can partition molecules from aqueous solution.[12] The aliphatic layers can be deposited either by direct adsorption from solution[13] or by the Langmuir–Blodgett dipping technique.[14] In the former process, the aliphatic monolayer is irreversibly adsorbed onto the surface by reaction with a chlorosilane, carboxylic acid, thiol, disulfide, or sulfide (thioether) group. Depending upon the type of chemisorbed molecule, the aliphatic "subphase" can either spontaneously organize to form a very close-packed structure or remain in a more liquid-like disordered state. A number of researchers have shown how these aliphatic monolayers can be loaded with or chemically modified to contain long-chain electroactive species;[5,12,15] other groups are interested in the more rigid self-assembled monolayers for molecular recognition schemes and the control of the electrochemical activity of the surface.[16] The number of aliphatic monolayers which have been created is quite large; for dialkyl sulfides alone Troughton et al. have demonstrated that a wide variety of both close-packed and disordered monolayers with specific chemical properties can be synthesized.[17] The DTE molecule chosen for this study can potentially lead to a more liquid-like, disordered aliphatic monolayer on the electrode surface; this structure is more

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appropriate for coadsorption studies which require room to accommodate additional partitioned species.

In this paper, we demonstrate that these two adsorbates can be combined to form mixed monolayers with varying conformational and thin-film growth characteristics. Through a combined spectroscopic and electrochemical study, the formation of mixed monolayers of chemisorbed sulfur, methylene blue, and long-chain dithioethers at evaporated gold film electrodes is documented. Vibrational spectroscopy (Fourier transform infrared (FTIR) and resonance Raman scattering) is used to characterize the thin films ex situ. The presence of the aliphatic molecules can be detected both directly by FTIR reflection–absorption measurements and indirectly by changes in the subsequent methylene blue electrochemistry at the electrode surface. Electrochemical cycling in the presence of methylene blue leads to an ordering of the alkyl chains of the DTE molecules. While only a small amount of methylene blue is found to partition into the alkyl subphase, the reduced form of the dye, leucomethylene blue, strongly partitions into the alkyl regions. In addition, the formation of a stabilized leucomethylene blue multilayer is observed with the mixed monolayers.

Experimental Section

The electrodes employed in these studies were formed by evaporating 200 nm of gold onto 0.75-in. square substrates cut from silicon (100) wafers (obtained from Monsanto). The thin-film deposition was accomplished at room temperature with a Balzers (Model 170H) turbomolecular-pumped vacuum deposition system. A very thin (2-nm) layer of Cr was deposited on the silicon prior to the gold evaporation in order to increase the adhesion of the gold film to the substrate; the gold films were deposited at an average rate of 0.5 Å s⁻¹ in order to create films which were resistant to Cr diffusion to the surface.

For the electrochemical experiments, the gold films were mounted with an O-ring seal into a Teflon cell with a solution volume of approximately 5 mL. This small volume cell facilitated the flushing and introduction of adsorption solutions while maintaining potentiostatic control. An IBM Instruments potentiostat (Model EC/225) was employed in a three-electrode configuration with a Pt counter electrode and a saturated NaCl calomel reference electrode (SCE) that was isolated from the solution compartment. All potentials are reported vs SCE; all scans were initiated at approximately +0.200 V, scanned negatively to approximately –0.500 V, and then returned to the initial potential at a constant sweep rate of 50 mV s⁻¹. The electrochemical solutions were buffered with phosphate to a pH of 7.9 and contained a supporting electrolyte of 1.0 M NaF.

Methylene blue obtained from Kodak was used after recrystallization from ethanol/water solutions. The DTE was provided by Prof. Sam Gellman at the University of Wisconsin. The water employed in the solutions was Millipore-filtered and then doubly distilled. The methylene chloride was obtained from Burdick and Jackson. All other chemicals were of puriss (Fluka) purity.

The resonance Raman scattering measurement on the gold films was obtained from a spectrometer system consisting of (i) an excitation source that consisted of a dye laser (Coherent Model CR599) pumped by a 4-W Argon ion laser (Lexel Model 95) plus a prism filtering arrangement to remove any residual fluorescence from the laser beam, (ii) an f/1 collection lens and a 0.85-m double monochromator (Spex Model 1403) for collection and separation of the Raman scattered light, and (iii) a detection system consisting of a Hamamatsu R928 PMT cooled to –20 °C and amplification, discrimination, and photon-counting electronics that were constructed in-house. The dye laser was focused onto the electrode at an angle of incidence of 70° with respect to the surface normal, and the collection angle for the Raman scattering was 60° in a plane perpendicular to the plane of incidence for the laser in order to minimize back-
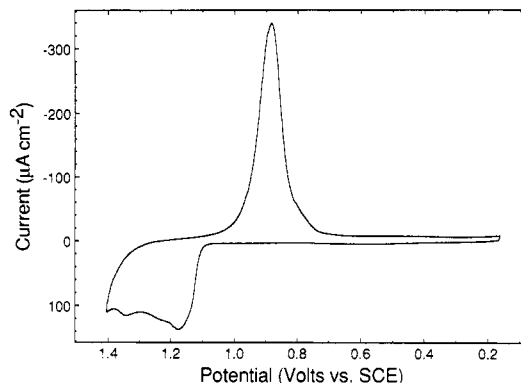

Figure 2. Cyclic voltammetry of an evaporated gold thin-film electrode in 0.5 M sulfuric acid. The electrochemical scan reveals the oxidation chemistry of the polycrystalline gold surface.

ground scattering. All spectra were taken with a slit width of 400 μm, which roughly corresponds to 4-cm⁻¹ resolution at 600 nm.

FTIR reflectance measurements were performed with a Mattson Cygnus 100 spectrometer at a nominal resolution of 2 cm⁻¹, using a narrow-band HgCdTe detector. The infrared beam was p-polarized, and the angle of incidence was 70°. A background spectrum was obtained from a companion evaporated gold film that was created simultaneously with the electrode.

Results and Discussion

A. Methylene Blue Monolayer Formation. The adsorption of methylene blue onto sulfur-modified evaporated gold films was accomplished by following the procedure of Clavilier et al.[8] Prior to the electrochemistry, the thin-film gold electrodes were dipped in a 1 mM sodium sulfide solution and then rinsed thoroughly with water. Exposure to the sulfide solution resulted in a monolayer of irreversibly chemisorbed zerovalent sulfur on the gold surface.[18] The presence of this monolayer was verified by its oxidation to sulfate on the first electrochemical cycle. Subsequent scans in 0.5 M sulfuric acid revealed the oxidation–reduction electrochemistry of the bare gold surface (Figure 2). These electrochemical scans suggest that the evaporated gold films on Si(100) were nearly polycrystalline[19] (as compared to the ordered gold(111) films that grow epitaxially on mica substrates).[20] However, the methylene blue electrochemistry on these films was not the same as that observed on alumina-polished polycrystalline electrodes, indicating differences in either roughness or cleanliness between the two surfaces.

Following exposure to the sulfide solution, a monolayer of methylene blue was electrochemically adsorbed onto the surface. The gold electrodes were placed into an electrochemical cell containing a methylene blue solution with a concentration varying from 1 to 100 μM; the CV of a gold thin film in a 80 μM methylene blue solution without the sulfide pretreatment is shown in Figure 3a and with the sulfide pretreatment in Figure 3b. As in the case of the thermally treated electrodes employed by Clavilier et al., the CVs exhibit a solution wave at –0.265 V and an adsorption postwave at –0.450 V. The shape of the solution wave indicates that the leucomethylene blue generated at the electrode formed a thin film on the electrode surface, and the presence of an

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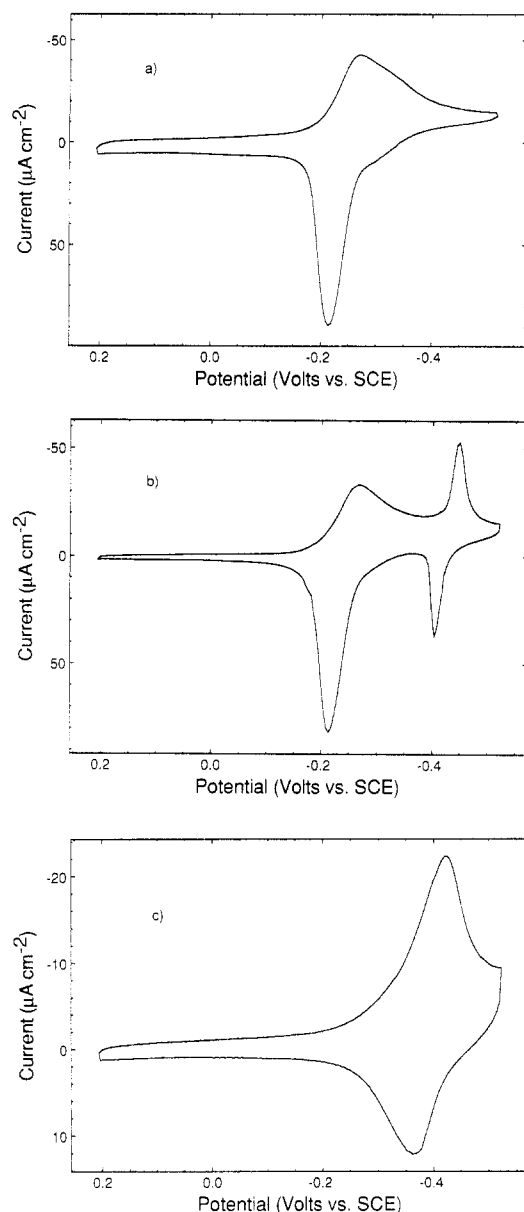(20) Scherson, D. A.; Kolb, D. M. *J. Electroanal. Chem.* **1984**, *176*, 353.

Figure 3. Methylene blue electrochemistry at an evaporated gold film electrode. Cyclic voltammetry; (a) an 80 μM methylene blue solution in the absence of the adsorbed sulfur; (b) an 80 μM methylene blue solution after exposure of the electrode to a 1 mM sodium sulfide solution; (c) the electrode from part b in a phosphate buffer solution after rinsing. Integration of the adsorption postwave yields a surface charge density of 29 μC cm^{-2}.

adsorption postwave in Figure 3b indicates that for the sulfur-modified electrode the first monolayer of methylene blue molecules was strongly chemisorbed onto the surface. This adsorption postwave is greatly shifted from the small adsorption postwave observed for the case of methylene blue at a bare gold electrode[9] (Figure 3a); the increased separation of the adsorption postwave and the solution wave reflects the strong interaction of the dye molecule with the sulfur-modified gold surface. This interaction has been attributed by Clavilier et al. to a specific sulfur–sulfur interaction.

An estimate of the surface coverage of methylene blue chemisorbed onto the sulfur-modified gold electrode was obtained from the amount of charge passed during the reduction of the monolayer to leucomethylene blue. The integrated charge of the surface wave was found to be approximately 29 μC/cm^2. A space-filling model suggests that a charge density of 25 μC/cm^2 corresponds to

a flat orientation of the dye molecules' aromatic plane with respect to the electrode surface.[9] The amount of methylene blue chemisorption (as well as the exact nature of the leucomethylene blue monolayer) is highly dependent upon the solution concentration of dye and the supporting electrolyte. Clavilier et al. have observed in certain instances on thermally treated gold electrodes surface charge densities of up to 50 μC/cm^2, suggesting a more perpendicular orientation of the aromatic rings of the chemisorbed molecules.[9] The implication from the electrochemical measurements that the methylene blue molecules were oriented with their aromatic planes parallel to the electrode surface is indirectly supported by the failure to observe any CH stretching bands in ex situ FTIR measurements. A similar lack of infrared bands for molecules oriented parallel to the electrode surface (due to the absence of s-polarized light fields at the surface for infrared wavelengths) was observed by Hubbard et al. for hydroquinone chemisorbed onto a platinum surface.[21] In addition to the FTIR experiments, no fluorescence was observed from the chemisorbed monolayer. The quenching of the fluorescence from the chemisorbed methylene blue reflects a strong interaction of the dye molecules with the metal surface.

The chemisorption of the first methylene blue monolayer was found to be of intermediate reversibility. The methylene blue did not irreversibly decompose on the surface as in the case of aromatic molecules on platinum electrodes;[22] however, the dye molecules would not reversibly desorb from the surface. If the electrode was removed from solution, rinsed thoroughly, and then replaced in the electrochemical cell with a buffer solution containing no methylene blue, electrochemical cycling demonstrated that the methylene blue was still present on the surface (Figure 3c). Integration of the reduction wave of the adsorbed molecules again yielded a surface charge density of 29 μC/cm^2. Although the methylene blue was very strongly adsorbed onto the sulfur-modified gold surface, a repeated cycling of the electrode or flushing of the electrochemical cell with buffer while holding at a potential negative of the reduction potential for the chemisorbed methylene blue removed all of the dye molecules from the electrode. This indicated that in the leucomethylene blue form the adsorbed monolayer was unstable and tended to desorb.

B. Dithioether Monolayer Formation. The chemisorption of methylene blue onto sulfur-modified gold electrodes can provide a measure of the electrochemically available surface area (for a molecule of its size). The chemisorption of other, electroinactive molecules will block the methylene blue adsorption and result in a diminution of the charge passed in the adsorption postwave. We have found that other sulfur-containing dye molecules (e.g., Stains-All) will adsorb onto the electrode with sufficient strength and/or irreversibility to prevent the methylene blue chemisorption and completely suppress the methylene blue surface wave. This suppression suggests that the amount of current observed in the adsorption postwave can be employed as an indirect measure of surface coverage for electroinactive species. We wish to explore the use of the methylene blue chemisorption to study the formation of an adsorbed monolayer of the long-chain dithioether DTE on evaporated gold films.

To adsorb the alkyl molecules onto a gold film, the freshly prepared electrode was immersed in a 0.5 mM

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Figure 5. FTIR spectra of an irreversibly adsorbed monolayer of DTE on an evaporated gold film: (a) before electrochemical cycling; (b) after electrochemical cycling in an 80 μM methylene blue solution.
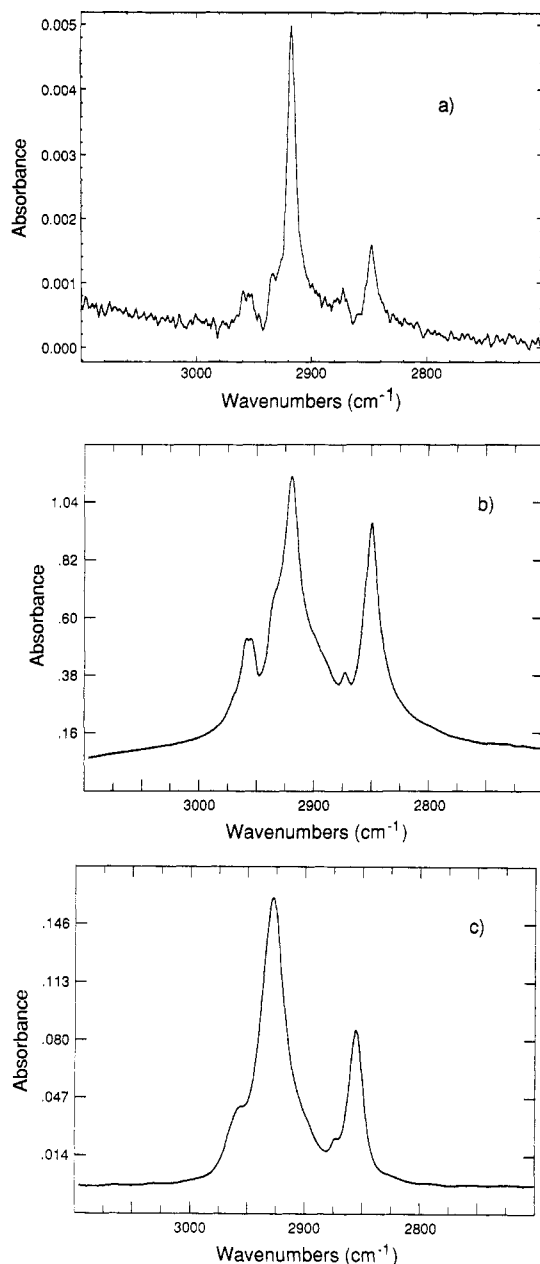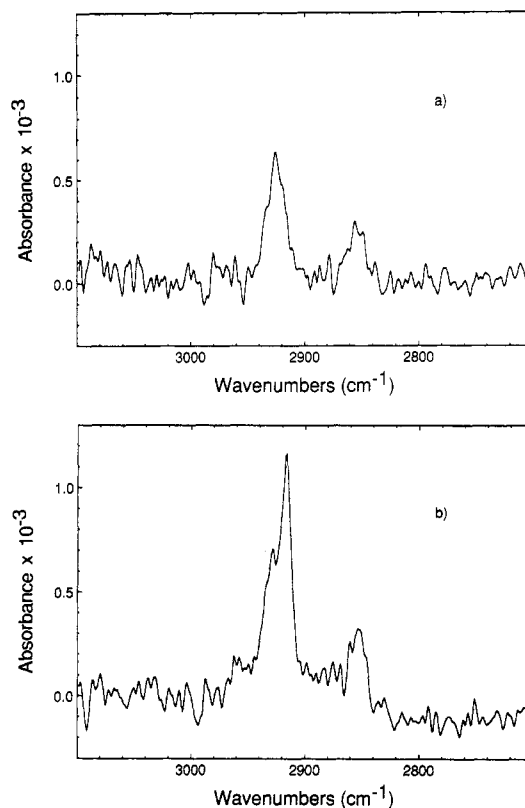
Figure 4. FTIR spectra of the dithioether $C_{14}H_{29}SC_2$-$H_4SC_{14}H_{29}$ (DTE): (a) a thin film of weakly adsorbed DTE on an evaporated gold film; (b) solid DTE in a KBr pellet; (c) 1 mM DTE solution in CCl_4.

DTE solution in methylene chloride. If the electrode was carefully removed from solution after 5 min and not rinsed, the FTIR reflectance spectrum of the surface revealed the presence of a thin multilayer film of DTE on the surface. Figure 4a shows the CH stretching region of the FTIR reflectance spectrum of this thin film; the most intense band at 2917 cm^{-1} is the asymmetric methylene CH stretch, and the band at 2848 cm^{-1} is assigned to the symmetric methylene CH stretch.[23] The ratio of intensities of these two bands is approximately 3.5:1. For comparison, the CH stretching region of the infrared spectrum of solid DTE and of DTE dissolved in CCl_4 is shown in parts b and c of Figure 4, respectively. The asymmetric methylene CH stretching frequency in the thin-film spectrum is the same as that in the solid, as compared to the broader 2927-cm^{-1} band that is observed from DTE

in CCl_4 solution. The fact that the ratio of intensities of the 2917-cm^{-1} band to the 2848-cm^{-1} band differs for the thin film as compared to the solid suggests that although the thin film is crystalline in nature, the thin film is not composed of small DTE crystallites randomly oriented with respect to the surface. This multilayer film is only weakly adsorbed to the gold electrode; FTIR measurements demonstrate that rinsing with hexane completely removes the alkyl molecules from the surface.

If, however, the electrode was immersed in a 0.5 mM DTE solution for 30 min or more and then rinsed thoroughly with hexane, a FTIR spectra indicative of an irreversibly adsorbed DTE monolayer was obtained (Figure 5a). This spectrum differs from the thin-film spectrum of Figure 4a and is similar to the FTIR spectra obtained by Troughton et al. for a variety of dialkyl sulfides.[17] In particular, note that the ratio of intensities between the asymmetric and symmetric methylene stretches has changed and that the frequency of the asymmetric stretch has shifted to 2927 cm^{-1}. Since the asymmetric stretch of DTE in solution is at 2927 cm^{-1} (Figure 4c), the FTIR reflectance spectrum of the monolayer suggests that the irreversibly adsorbed DTE is significantly conformationally disorded and liquid-like in structure.

Although most experiments yielded an irreversibly adsorbed DTE monolayer that was disordered, on occasion a more crystalline adsorbed monolayer was created on the gold surface. For example, the FTIR spectrum of an electrode that had been immersed in a 0.5 mM DTE solution for 2 days exhibited an asymmetric CH stretching band at 2919 cm^{-1}. The shift in this stretching frequency from the disordered monolayer suggested that the irreversibly adsorbed DTE molecules on the surface had assumed a packed structure similar to that in the weakly adsorbed multilayer film. For the monolayer spectra, the ratio of the intensities of the asymmetric and symmetric

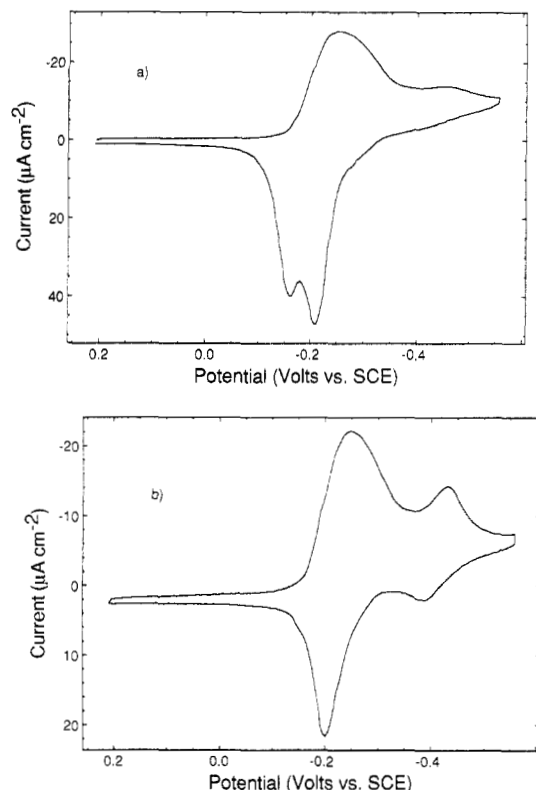(23) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta Part A* **1978**, *34*, 395.

Figure 6. Methylene blue electrochemistry at a sulfur-modified gold film electrode with a partial monolayer of irreversibly adsorbed DTE: (a) initial electrochemical scan; (b) 25th CV after electrochemical cycling.

Figure 7. Plot of surface charge density of chemisorbed methylene blue for a mixed monolayer electrode as a function of the number of electrochemical cycles.

methylene stretch was approximately 2:1 as compared to the 3.5:1 or greater ratio for the multilayer film. A number of FTIR studies on the adsorption of long-chain alkyl sulfides,[17] alkanethiols,[24] and alkyl disulfides[25] have shown that in some instances an adsorbed monolayer of these molecules can spontaneously organize from dilute solution and form a tightly packed structure in which the long alkyl chains assume an all-trans conformation. It is likely that the crystalline spectra that we occasionally observed for the irreversibly adsorbed DTE monolayer represented a spontaneously organized film, but for a molecule as complex as DTE this spontaneous organization from dilute solution must be described as at best a slow, haphazard process. In general, adsorption from solution resulted in a monolayer of disordered DTE molecules on the gold surface.

C. Methylene Blue–Dithioether Coadsorption. Because there are two sulfur attachment points connected by an ethylene bridge in the DTE molecule, these irreversibly adsorbed monolayers should not easily form a tightly packed structure. A portion of the electrode surface should still remain accessible to electroactive solution species; the methylene blue electrochemistry can be employed to measure how effectively the DTE monolayer blocks the electrode surface. After formation of the DTE monolayer, the electrodes were dipped in 1 mM sulfide solution and then cycled electrochemically in the presence of methylene blue (Figure 6a). Three changes are observed in the CV: (i) the methylene blue adsorption postwave is altered, (ii) the shoulder on the methylene blue reduction wave differs in shape from that observed at a bare gold surface or at a sulfur-modified gold sur-
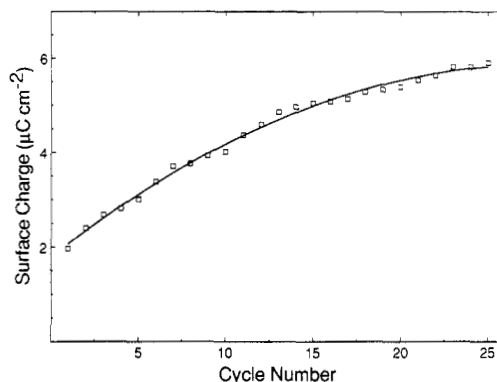
face, and (iii) the characteristics of the leucomethylene blue film formation are modified. Changes ii and iii are discussed further in subsection D. As expected, the methylene blue adsorption postwave is present but greatly depressed as compared to the case when no DTE is adsorbed onto the surface (as described in subsection A). The residual surface charge density on the mixed monolayer electrodes varied from 1 to 8 $\mu C/cm^2$, corresponding to approximately 3–28% of a full monolayer. This residual surface charge density confirms the view that the monolayer is a disordered, liquid-like structure that allows molecules the size of methylene blue to see a portion of the electrode surface (see Figure 1a).

Surprisingly, the residual surface charge density was found *not* to be constant with electrochemical cycling. Figure 7 plots the residual surface charge density obtained from a methylene blue–DTE monolayer film as a function of the number of electrochemical cycles experienced by the electrode. The surface concentration of chemisorbed methylene blue increased as the cycling continued, rising from a surface charge density of about 2 to 6 $\mu C/cm^2$ in 25 cycles (Figure 6b plots the 25th CV). A subsequent FTIR spectrum of the electrode revealed that the increase was due to a restructuring of the DTE monolayer. Figure 5b plots the FTIR spectrum of a methylene blue–DTE monolayer which has experienced electrochemical cycling. The antisymmetric CH stretch is clearly changing, with the broader band at 2927 cm^{-1} that matches the asymmetric methylene CH stretching frequency in solution being replaced by the sharper band at 2917 cm^{-1} that was observed in the crystalline monolayer and multilayer spectra. As in the case of the DTE organized monolayer spectra, the ratio of intensities for the asymmetric and symmetric methylene CH stretch was 2:1. Further cycling led to an almost complete disappearance of the 2927-cm^{-1} band. If the chemisorbed methylene blue is removed from the surface electrochemically (as described in subsection A), FTIR measurements showed that the DTE on the gold surface remained in the crystalline state.

Both the electrochemical measurements and the FTIR spectra are consistent with the view that an electrochemical organization of the DTE monolayer has occurred. The cyclical reduction and oxidation of the chemisorbed methylene blue organize the DTE molecules on the surface, forcing them into a crystalline structure similar to that which occurs in the solid. As the DTE molecules organize, chemisorbed sulfur sites that were previously unavailable to the methylene blue become open for adsorption (see Figure 1b). Note that if desorption of the DTE had occurred rather than organization, bare gold sites

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(25) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.

rather than sulfur-modified sites would have been created. That would have led to an increase in the shoulder on the methylene blue solution wave at −0.265 V; instead, a decrease in the shoulder on the methylene blue solution wave and an increase in the adsorption postwave at −0.450 V were observed.

The electrochemical organization of the monolayer of DTE always required the presence of chemisorbed methylene blue on the electrode surface. Moreover, the number of electrochemical cycles required for the organization decreased as the surface concentration of chemisorbed methylene blue increased. Although the formation of a spontaneously organized monolayer from dilute methylene chloride solution was an uncontrollable process, the observation of an increasing methylene blue surface concentration during electrochemical cycling of a disordered DTE monolayer reliably yielded a partial monolayer of organized DTE molecules.

D. Leucomethylene Blue Multilayer Formation. In the previous subsection, we observed that electrochemical reduction and oxidation of the chemisorbed methylene blue in a mixed methylene blue–DTE monolayer alter the conformational order of the adsorbed DTE. Conversely, we have also observed that the presence of the irreversibly adsorbed DTE alters the electrochemistry of the methylene blue at the electrode surface. Two types of electroactive leucomethylene blue films are observed on the mixed monolayer electrodes, and with continuous cycling a stabilized leucomethylene blue film that can be removed from solution is eventually formed. While a leucomethylene blue film can exist in the absence of DTE on a gold electrode in solution under potentiostatic control, the electrode normally cannot be removed from solution with the adsorbed leucomethylene blue multilayer intact (it readily converts back to methylene blue, which dissolves into the buffer).

Figure 6a reveals that *two* types of leucomethylene blue films were formed on the mixed monolayer electrodes. At both bare and sulfur-modified gold electrodes, leucomethylene blue forms a conductive film on the surface that can be reoxidized at −0.210 V (Figure 3a and 3b). On bare gold electrodes, a second type of leucomethylene blue film can also be formed on the surface by holding the electrode potential negative of −0.500 V.[10] This film can be reoxidized at −0.150 V and is thought to be a different polymorphic structure of leucomethylene blue. The second type of film structure does not occur on sulfur-modified gold electrodes.[9] The first CV of the mixed monolayer electrode (Figure 6a) exhibits both of these oxidation waves; the amount of the second leucomethylene blue film depended upon the negative limit of the electrochemical scan. The presence of the second type of leucomethylene blue film suggests that there are some electroactive methylene blue molecules at the surface *within* the disordered DTE chains and not interacting with any sulfur-coated gold sites. Further evidence for these molecules is the appearance of a shoulder on the solution methylene blue reduction wave at −0.265 V; a similar shoulder/postwave occurs in the absence of sulfur (Figure 3a).

The formation of both types of leucomethylene blue films decreased under repeated electrochemical cycling. Figure 8 plots the 5th, 10th, 15th, and 20th CVs for the electrode whose 1st and 25th CV are plotted in Figure 6. As noted in subsection C, the charge in the adsorption postwave at −0.450 V increased during electrochemical cycling due to the organization of the adsorbed DTE molecules. As the electrode is cycled electrochemically, the second type of leucomethylene blue film (as character-
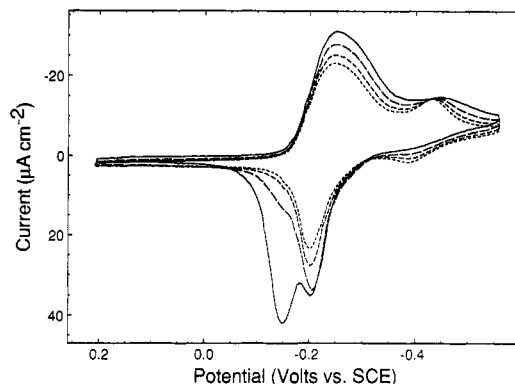

Figure 8. Methylene blue electrochemistry at a sulfur-modified gold film electrode with a partial monolayer of irreversibly adsorbed DTE: (—) 5th CV; (− −) 10th CV; (- - -) 15th CV; (· · ·) 20th CV.

ized by its oxidation wave at −0.150 V) rapidly disappears, and the shoulder on the methylene blue solution reduction wave at approximately −0.300 V is lost. The disappearance of these features can be attributed to the loss of methylene blue surface molecules within the chains as the DTE compacts on the surface. Further cycling leads to continued loss of current of the methylene blue solution reduction wave at −0.265 V and the leucomethylene blue reoxidation wave at −0.210 V. This suggests that the now-organized DTE has blocked the methylene blue from a portion of the electrode surface. However, if the electrode was held at 0.200 V after 25 CVs and the methylene blue solution was flushed from the cell and replaced by a phosphate buffer, the CV remained the same as that in Figure 6b. The persistence of the methylene blue and leucomethylene blue waves in the CV indicated that the electrode was coated with a stable dye multilayer film; repeated cycling of the electrode in the buffer solution eventually removed the film and yielded a CV similar to that in Figure 3c.

Removal and inspection of the electrode after the electrochemical cycling in methylene blue revealed that an inhomogeneous film had formed on the surface. Rinsing with water would not remove the film; a portion of the infrared spectrum of the film is shown in Figure 9a. In addition to the bands shown in Figure 9a, an NH stretching band was observed at 3400 cm⁻¹ that is indicative of the leucomethylene blue molecule. Methylene blue is also present within this thin film; the infrared absorption band at 1600 cm⁻¹ is characteristic of the oxidized form of the dye molecule. The presence of methylene blue in the film is confirmed by the observation of a methylene blue resonance Raman scattering spectrum (with an excitation wavelength of 594.2 nm[26]) from a freshly removed multilayer film; the ex situ Raman spectrum is plotted in Figure 10. The fluorescence background in the resonance Raman scattering spectrum is much smaller than in solution or in the solid, demonstrating that the multilayer film is interacting with the metal surface through the DTE monolayer. The leucomethylene blue film can also be oxidized by oxygen back to methylene blue. If the film was kept in the FTIR spectrometer under nitrogen purge overnight, the spectrum slowly changed from a predominantly leucomethylene blue spectrum to a spectrum resembling solid methylene blue as trace atmospheric oxygen oxidized the sample (Figure 9b and 9c). Upon conversion to methylene blue, the dye multilayer

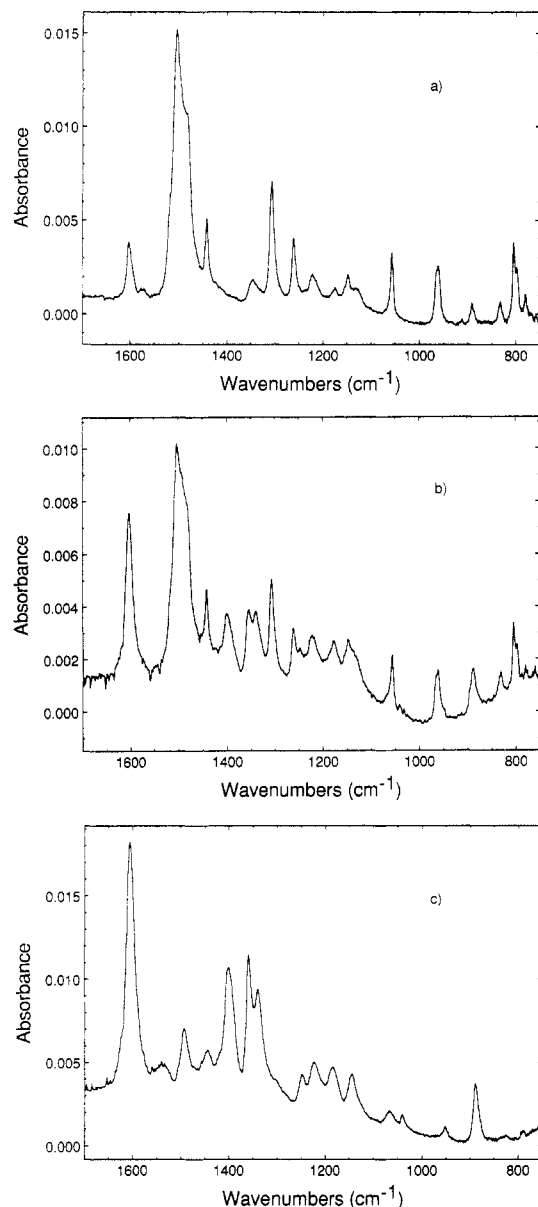(26) Yamada, H.; Nagata, H.; Kishibe, K. *J. Phys. Chem.* **1986,** *90,* 818.

Figure 10. Resonance Raman spectrum of the stabilized methylene blue/leucomethylene blue film immediately after removal from solution. The excitation wavelength is 594.2 nm. This spectrum demonstrates that from its formation a portion of the multilayer film exists in the oxidized methylene blue form.

nized DTE is adsorbed and creates an inhomogeneous film of leucomethylene blue. If the electrode is cycled in a buffer solution, the leucomethylene blue eventually diffuses back to the areas of the electrode which have methylene blue chemisorbed onto the surface, and the dye multilayer film can be removed.

Conclusions

In summary, the electrochemical preparation of a coadsorbed monolayer of methylene blue and DTE on thin-film gold electrodes exhibits two electrochemical processes that could not be obtained from monolayers of the individual molecules. The alkyl chains of the irreversibly adsorbed DTE become close-packed and conformationally ordered upon electrochemical cycling in the presence of methylene blue. This "electrochemical organization" should be possible for all long-chain alkyl molecules which are not already locked into a close-packed structure. A corollary of this effect is that long-chain alkyl monolayer films should *not* be thought of as impervious to the electrochemistry.

The partitioning of the leucomethylene blue into the DTE portions of the adsorbed monolayer also led to modifications in the electrochemistry of the methylene blue at the electrode surface. The incorporation of methylene blue into the disordered DTE film resulted in the formation of two types of conductive leucomethylene blue films, and continuous electrochemical cycling led to buildup of a stabilized dye multilayer film. These changes of the thin-film formation process in the presence of the mixed monolayer illustrate how a single monolayer can strongly alter the performance of an electrode by affecting the local solubility of the products at the surface.

Although we were able to spectroscopically monitor the DTE adsorbed onto the electrode and the leucomethylene blue and methylene blue in the multilayer films, we were unfortunately unable to spectroscopically observe the methylene blue that was directly chemisorbed onto the sulfur-modified gold surface. Future studies will explore the use of resonant optical second harmonic generation[11] to measure the molecular orientation of the chemisorbed dye molecules.

Figure 9. FTIR spectrum of a stabilized methylene blue/leucomethylene blue film formed on a partially DTE coated gold film electrode. FTIR spectrum of the leucomethylene blue film (a) immediately after removal from solution, (b) after partial conversion from leucomethylene blue to methylene blue, and (c) after complete conversion to the oxidized form.

film could be removed from the electrode by rinsing with water.

The formation of a stabilized leucomethylene blue film on the mixed monolayer electrode is a fascinating side consequence of the interaction of the leucomethylene blue and the irreversibly adsorbed DTE (the same interaction which leads to the conformational ordering described in subsection B). We hypothesize that the leucomethylene blue is created at the electrode surface and partitions into the DTE portions of the adsorbed monolayer. Upon reoxidation of the leucomethylene blue back to the methylene blue cation, the aromatic molecule moves out of the DTE subphase. This constant uptake and desorption slowly convert the DTE monolayer into a close-packed organized structure. As the DTE molecules compact, some of the solution leucomethylene blue which has partitioned into the alkyl regions is no longer in direct contact with the electrode surface and cannot be reoxidized. This surplus leucomethylene blue builds up over t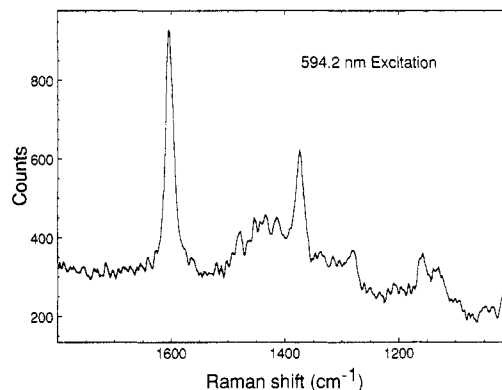he portions of the electrode onto which the now orga-