

Characterization of Self-Assembled Monolayers Formed from Sodium *S*-Alkyl Thiosulfates on Copper

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We report the formation of self-assembled monolayers (SAMs) from sodium *S*-alkyl thiosulfates ($\text{CH}_3(\text{CH}_2)_{n-1}\text{S}_2\text{O}_3^-\text{Na}^+$) onto copper in aqueous and organic solvents. These ionic compounds are considerably more soluble in water than alkanethiols, and they adsorb to the copper surface primarily as thiolates. Characterization by electrochemical impedance spectroscopy (EIS) reveals that SAMs formed from longer-chained thiosulfates ($n = 12, 14$) exhibit comparable barrier properties to those of thiol-based SAMs when formed in organic solvents but diminished effectiveness when formed in aqueous solution. However, the water-borne thiosulfate-based SAMs do provide an increase in corrosion resistance by ~ 2 – 3 orders of magnitude compared to that of uncoated copper. Analysis by infrared (IR) spectroscopy indicates that the thiosulfate-based SAMs are less crystalline and less densely packed than thiol-based SAMs. Wetting measurements suggest that the surfaces of thiosulfate-based SAMs expose a greater number of methylene groups in comparison to that for the well-ordered methyl structure of alkanethiol-based SAMs. The combination of these analyses leads to a proposed structure for thiosulfate-based SAMs on copper in which the films contain molecular-scale defects, lower adsorbate density, and more disordered alkyl chains than SAMs formed from alkanethiols. A comparison of thiosulfate-based SAMs to those formed from benzotriazole (BTAH), a widely used corrosion inhibitor for copper, shows that longer-chained thiosulfates may be useful in inhibiting the corrosion of copper in aqueous environments.

Introduction

The formation of self-assembled monolayers (SAMs) onto copper has been used to provide a molecule-thick barrier against corrosion and oxidation.^{1–7} Primarily formed from alkanethiols, these SAMs exhibit dense molecular packing and highly crystalline structures to limit the diffusion of oxygen,¹ water,² and aqueous ions.^{3–5} The structure, stability, and barrier properties of these SAMs depend greatly on the extent of intermolecular interactions within the film, with longer-chained adsorbates yielding more protective SAMs that better maintain their crystalline structure through enhanced van der Waals interactions.⁵ Additional stability of these films can be achieved by cross-linking the adsorbates through siloxane bonds.^{6,7}

Because of the dramatic increase in corrosion resistance achieved using alkanethiolate SAMs,⁵ it is desirable to investigate these films and their precursors as in situ corrosion inhibitors in practical applications. This is particularly true for copper, due to its wide use in chemical process industries and microelectronics applications. In most previous studies, SAMs have been formed from solutions using organic solvents such as isooctane and hexane because of their ability to solvate long-chain alkanethiols.^{1,2,5} For many applications, water would be

the solvent of choice because of its ubiquitous use, particularly in chemical processing. Water is also environmentally benign and does not present problems of waste disposal encountered when using large quantities of organic solvents. However, one of the limitations of using *n*-alkanethiols as a SAM precursor is their extremely low solubility in water.

Alkyl thiosulfates (Bunte salts) provide a potential alternative to the use of alkanethiols for forming SAMs.^{8–10} Alkyl thiosulfates have the general formula RSSO_3M , where R is an aliphatic or aromatic group and M is a monovalent cation. These compounds possess several properties that are advantageous for aqueous self-assembly. The presence of an ionic headgroup greatly improves their solubility in water relative to those of alkanethiols, and they can be synthesized through a relatively simple one-step process. Because of these properties, other investigators have examined the effectiveness of alkyl thiosulfates as a means for forming SAMs onto gold nanoparticles⁸ and surfaces.⁹ In addition to traditional assembly methods, thiosulfates have also been examined as a self-assembly species through electrochemical oxidation.¹⁰ For traditional self-assembly, it is believed that the species adsorb on the surface in a manner similar to that reported for disulfides.^{9,11} After diffusion of the thiosulfate to the surface, the sulfur–sulfur bond is broken, yielding an adsorbed thiolate species and a weakly bound sulfite species that desorbs from the surface or is displaced by the adsorption of another thiosulfate.⁹ In all these studies, the adsorption of alkyl thiosulfates has been conducted either in an organic

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solvent or in an organic/water mixture. To our knowledge, there has been no report of the adsorption of these compounds directly from aqueous solution or onto copper substrates.

The purpose of our research is to investigate the viability of alkyl thiosulfates as an alternative to alkanethiols for self-assembly onto copper. These SAMs can be formed in aqueous solution without the addition of surfactant species that are necessary to solubilize alkanethiols.¹² Our primary objective is to compare the structure and barrier properties of thiosulfate-based SAMs with those from corresponding alkanethiols, which have been previously documented.¹³ We have characterized the structure of these SAMs on copper using infrared (IR) spectroscopy, the wetting properties using contact angle measurements, and the barrier properties using electrochemical impedance spectroscopy (EIS). We have also characterized the SAMs with X-ray photoelectron spectroscopy (XPS) to determine the composition of sulfur species on the surface. Most of our experiments involve the use of sodium *S*-dodecyl thiosulfate (C₁₂TS) because of its use in previous studies and the extensive examination of dodecanethiol as a means of comparison. Thiosulfates of other alkyl chain lengths (8, 10, and 14) were also investigated to explore the effect of chain length on the performance of the SAMs as a corrosion barrier.

Experimental Section

Materials. Copper shot (99.99+%) and silicon [100] wafers were obtained from Aldrich Chemical and Montco Silicon, respectively. Chemicals used for the synthesis of the sodium *S*-alkyl thiosulfates, including 1-bromooctane (99%, Aldrich), 1-bromodecane (98%, Aldrich), 1-bromododecane (99%, Aldrich), 1-bromotetradecane (99%, Aldrich), and sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O, Aldrich), were used as received. Solvents including absolute ethanol (AAPER), toluene (Fisher), tetrahydrofuran (Fisher), and ethyl acetate (Fisher) were used as received. Other chemicals, including benzotriazole (Aldrich), sodium sulfate (Fisher), and hexadecane (Aldrich) were all used as received. Distilled water was deionized (16.7 MΩ) with a Modu-Pure system.

Synthesis of Bunte Salts. The sodium *S*-alkyl thiosulfates were prepared according to the procedure described by Shon et al.⁸ Briefly, 25 mmol of the 1-bromoalkane and 25 mmol of Na₂S₂O₃·5H₂O were dissolved in 50 mL of ethanol and 50 mL of deionized water, respectively. The solutions were combined in a 250-mL round-bottom flask and heated to reflux for 3 h. After cooling, the solvents were removed by vacuum filtration, and the crude product was collected and recrystallized in absolute ethanol.

Sample Preparation. Si [100] wafers were rinsed with absolute ethanol and dried in a nitrogen stream. The wafers were then placed in a diffusion-pumped thermal evaporator (CVC Products, Inc.) along with ~1 g of copper shot and a chromium rod. After evacuation of the chamber to an operating pressure of 3×10^{-6} Torr, the Si wafers were coated with 100 Å of chromium and 1000 Å of copper in succession at deposition rates of 1–3 Å/s. After evaporation, the wafers were cut into 1 cm × 3 cm samples and stored.

Before immersion in solution for SAM preparation, copper samples were reduced via cyclic voltammetry to remove any oxide present on the surface. This reduction was carried out in an 0.1 M aqueous solution of Na₂SO₄ using a potential range of –0.7 to –0.3 V versus the open circuit potential (E_{oc}) and a scan rate of 40 mV/s. Potentials were measured with an Ag/AgCl/saturated KCl reference electrode, and a gold-coated silicon sample was used as the counter electrode. Samples were held at –0.7 V versus E_{oc} until removal. After reduction, the samples were quickly rinsed with deionized water and ethanol, dried under nitrogen,

and immediately placed in vials containing 10 mL of solution at a 1 mM thiosulfate concentration. All solutions were deaerated with nitrogen prior to immersion in order to prevent etching, which has been reported for gold surfaces exposed to thiosulfate solutions containing an oxidizing species.¹⁴ Assembly times ranged from 2 min to 24 h for various studies,¹⁵ and adsorption temperatures ranged from 23 to 60 °C.¹⁶ Upon removal, samples were rinsed with ethanol and dried in a nitrogen stream.

Electrochemical Impedance Spectroscopy. Impedance spectra of SAM-coated copper samples were measured with a CMS300 electrochemical impedance system (Gamry Instruments, Inc.) interfaced to a personal computer. A glass cell was filled with an oxygenated aqueous solution of 0.1 M Na₂SO₄ as the supporting electrolyte. The cell was equipped with a gold-coated silicon wafer as a counter electrode, an Ag/AgCl/saturated KCl reference electrode, and a copper-coated silicon wafer as the working electrode. Measurements were made at frequencies ranging from 50 mHz to 5 kHz at open circuit potential with a 5-mV ac signal. Resistance and capacitance values were determined by fitting the impedance data with an appropriate equivalent circuit model using the Framework software package provided by Gamry.

Infrared Spectroscopy. IR spectra were obtained with a Bio-Rad Excalibur FTS-3000 infrared spectrometer in single reflection mode containing a Universal Reflectance Attachment. The p-polarized light was incident on the sample at 80° from the surface normal. Reflected light was detected with a narrow-band MCT detector cooled with liquid nitrogen. Spectral resolution was 2 cm^{–1} after triangular apodization. Each sample was subjected to 1000 scans. Spectra were referenced against a copper sample with a SAM prepared from octadecanethiol-*d*₃₇.

Contact Angles/Wetting Properties. Contact angles were measured using a Rame-Hart manual goniometer. Advancing and receding contact angles for water and hexadecane were measured on both sides of a static ~5 μL drop at two different locations on each sample. The drops were advanced or receded prior to measurement at a rate of approximately 1 μL/s. The pipet tip remained in the drop during measurement. Errors reported in the results represent the standard deviation of the four measurements taken on each sample.

X-ray Photoelectron Spectroscopy. XPS spectra were obtained with a Kratos XSAM800pci spectrometer using a Mg Kα X-ray source (spot diameter = 1000 μm) and a concentric hemispherical analyzer (pass energy = 20 eV). The detector angle with respect to the surface normal was 0°. Spectra for sulfur were accumulated over ~20 min with a 20-eV window. XPS spectra were obtained at low resolution to improve sensitivity and enable shorter acquisition times to reduce the amount of X-ray beam damage to the sample. The binding energies are referenced to C(1s) at 284.8 eV.

Results and Discussion

Solvent Effects on Thiosulfate SAM Formation.

To investigate the effect of solvent on the assembly of C₁₂TS onto copper, we compared the performance of SAMs prepared from water with the performance of those prepared from common organic solvents. Toluene, ethyl acetate, tetrahydrofuran (THF), and ethanol were chosen in order to examine a set of solvents with a wide range of polarity. Figure 1 presents impedance spectra (Bode magnitude plots) obtained for SAMs formed on copper

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(15) Studies of immersion time with IR spectroscopy and EIS indicated that a 15-min exposure provided sufficient time to produce a monolayer film from C₁₂TS onto copper in water at 40 °C or in ethanol at 23 °C. Longer exposures (~30 min) resulted in no significant improvement in barrier properties. Exposure times could not be greatly increased due to the observation of multilayers for times greater than 45 min.

(16) SAMs formed in water at 40 °C resulted in films with comparable resistance and improved capacitance in approximately one sixth the time required for films formed in water at room temperature. Additional studies at 50 and 60 °C showed little improvement over 40 °C, as indicated by comparable IR spectra and resistance/capacitance values from EIS spectra.

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Table 1. Film Resistance and Capacitance Values for SAMs Formed from C₁₂TS and C₁₂SH on Copper^a

precursor	solvent	temp (°C)	log R_{ct} ($\Omega \cdot \text{cm}^2$)	capacitance ($\mu\text{F}/\text{cm}^2$)	log Z_W ($\Omega \cdot \text{cm}^2$)
none			2.78 ± 0.31	35.0 ± 4.3	2.61 ± 0.18
C ₁₂ TS	toluene	23	2.89 ± 0.23	6.08 ± 1.23	3.23 ± 0.14
	H ₂ O	23	3.41 ± 0.15	4.15 ± 0.92	3.38 ± 0.21
		40	4.43 ± 0.14	1.89 ± 0.19	
	ethyl acetate	23	5.08 ± 0.46	1.68 ± 0.30	
	THF	23	5.35 ± 0.21	2.18 ± 0.35	
C ₁₂ SH	ethanol	23	5.91 ± 0.10	1.74 ± 0.48	
	ethanol	23	5.99 ± 0.19	1.12 ± 0.16	

^a The \pm values represent one standard deviation from the sample mean.

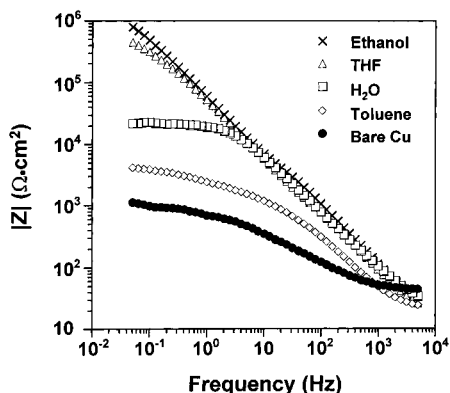


Figure 1. Electrochemical impedance spectra obtained in 0.1 M Na₂SO₄(aq) for SAMs formed from C₁₂TS on copper in various solvents. The spectrum for bare copper is shown as a reference. The SAMs were formed at 23 °C except for the one formed in water (40 °C).¹⁶

from 15 min¹⁵ exposure to 1 mM solutions of C₁₂TS in four of the solvents studied: toluene, THF, and ethanol, each at 23 °C, and water, at 40 °C.¹⁶ To illustrate the effectiveness of each SAM as a corrosion barrier, the spectrum for bare copper is included as a reference. The high-frequency region of the Bode plots in Figure 1 is dominated by the solution resistance. The linear region at intermediate frequencies is indicative of the capacitive property of the film ($Z \propto 1/(\omega C)$), and the low-frequency region corresponds to the charge-transfer resistance and/or Warburg impedance provided by the film.¹⁷ While all these SAMs provide an increase in impedance over that of uncoated copper at low and intermediate frequencies, the films formed in ethanol and THF provide the highest levels of protection. At intermediate frequencies, the higher impedances of the films formed in ethanol, THF, and water suggest considerably lower capacitances than that exhibited by the film formed in toluene. In the low-frequency region, the impedance generally increases in the order toluene \ll water \ll THF $<$ ethanol.

Table 1 presents the calculated resistance, capacitance, and Warburg impedance values for SAMs formed in each of the solvents studied. Spectra for the moderately to highly blocking SAMs were fit with an equivalent circuit that has been previously described,⁵ containing a solution resistance in series with a parallel combination of film capacitance (C_f) and charge-transfer resistance (R_{ct}). Spectra for the poorly blocking SAMs (toluene, water at 23 °C) and uncoated copper were fit with a similar equivalent circuit that contains one additional term, a Warburg impedance (Z_W) that is in series with the charge-transfer resistance.¹⁸ In this experiment, multiple samples

were prepared from each solvent, and errors reported in Table 1 represent one standard deviation from the sample mean. For the organic solvents, an increase in the dielectric constant effectively corresponds to the formation of a SAM with a higher charge-transfer resistance and a lower film capacitance. The poor quality of the film formed from toluene is a result of the relatively low solubility of C₁₂TS in toluene; all other solvents accepted C₁₂TS at 1 mM concentration. Films formed in aqueous solution are of a poorer quality than those formed from organic solvents (except toluene), while the film formed at 40 °C is superior to that formed at room temperature.¹⁶ The high capacitance and Warburg behavior of the SAMs formed in toluene and room-temperature water are indicative of incomplete films that enable facile permeation of water and electrolyte.

Comparison of Thiosulfate- and Thiol-Based SAMs on Copper. To determine the effectiveness of alkyl thiosulfates as a precursor for SAMs on copper, the properties of SAMs formed from C₁₂TS were compared against those of SAMs formed from dodecanethiol (C₁₂-SH). In this study, thiosulfate SAMs were formed by exposing copper to 1 mM C₁₂TS in water at 40 °C or ethanol at 23 °C for 15 min. These conditions were chosen because of the particular interest in C₁₂TS as a precursor to SAMs in aqueous solution and because of the superior quality of the SAMs formed in ethanol (as shown in Table 1). Thiol-based SAMs were formed by exposing copper to 1 mM C₁₂SH in ethanol at ambient temperature for the same immersion time.

Figure 2 shows the infrared spectra for the SAMs described above. Results from the IR analysis indicate dramatic differences in the structure of these SAMs. The spectrum obtained for the C₁₂SH-based SAM contains features consistent with a highly crystalline monolayer with trans-extended alkyl chains, as indicated by the positions of the $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ peaks at 2851 and 2919 cm⁻¹, respectively, and the positions of the $\nu_s(\text{CH}_3)$ and $\nu_a(\text{CH}_3)$ peaks at 2879 and 2965 cm⁻¹, respectively. The relatively low intensities of the methylene stretching modes are consistent with a densely packed monolayer in which the molecules are oriented nearly normal to the surface.¹⁹

The spectrum for a SAM formed from C₁₂TS in ethanol shows an increase in methylene intensity and a slight decrease in $\nu_s(\text{CH}_3)$ intensity in comparison to those for the C₁₂SH-based SAM. These changes in intensity are indicative of a greater tilt of the chain axes away from the surface normal¹³ and thus a decrease in overall adsorbate density on the surface. In addition, the asymmetric methylene mode shows a pronounced increase in broadness, partially masking the Fermi resonance component of the CH₃ stretching mode at 2938 cm⁻¹. This peak is also

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(19) For a highly crystalline alkanethiolate SAM on copper, the average molecular cant is approximately 12° from the surface normal (see ref 13).

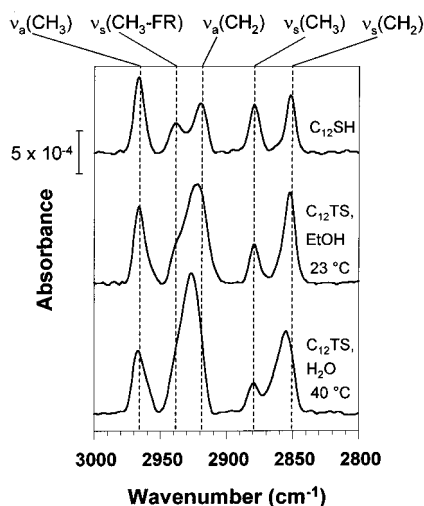


Figure 2. Reflectance infrared spectra of the C-H stretching region for SAMs formed from $C_{12}SH$ (in ethanol) and $C_{12}TS$ (in ethanol or water) on copper. SAMs were formed by a 15-min immersion in 1 mM solution. The dashed lines indicate the positions of the methyl and methylene modes for a trans-extended monolayer with no gauche defects: $\nu_a(CH_3) = 2965\text{ cm}^{-1}$, $\nu_s(CH_3-FR) = 2938\text{ cm}^{-1}$, $\nu_a(CH_2) = 2918\text{ cm}^{-1}$, $\nu_s(CH_3) = 2879\text{ cm}^{-1}$, and $\nu_s(CH_2) = 2851\text{ cm}^{-1}$. The spectra have been offset for clarity.

Table 2. Advancing and Receding Contact Angles (in deg) for SAMs on Copper Formed from 15-min Exposure to 1 mM Solutions^a

sample	water		hexadecane	
	θ_a	θ_r	θ_a	θ_r
$C_{12}SH$, ethanol	114 ± 2	95 ± 2	44 ± 1	22 ± 3
$C_{12}TS$, H_2O	110 ± 3	90 ± 3	<10	<10
$C_{12}TS$, ethanol	115 ± 5	80 ± 2	25 ± 5	<10
$C_{14}TS$, H_2O	113 ± 2	85 ± 4	20 ± 2	<10
$C_{14}TS$, THF	116 ± 1	91 ± 4	42 ± 2	17 ± 3

^a The \pm values indicate one standard deviation from the sample mean. Samples were formed in aqueous solution at 40°C ; all others at 23°C .

shifted to a higher wavenumber ($\sim 2921\text{ cm}^{-1}$) than the value of 2918 cm^{-1} assigned to a highly crystalline monolayer with no gauche defects. These changes in the spectrum are consistent with a higher concentration of gauche defects in the SAM formed from $C_{12}TS$.

The spectrum for a SAM formed from $C_{12}TS$ in water at 40°C shows deviations similar to those observed for the $C_{12}TS$ SAM formed in ethanol, but these deviations are much more pronounced. The decrease in intensity for the methyl modes and increased intensity of the methylene modes suggest a chain density significantly lower than that for SAMs formed from $C_{12}TS$ or $C_{12}SH$ in ethanol. The shift in wavenumber for the methylene stretching modes ($\nu_s(CH_2) = 2855\text{ cm}^{-1}$, $\nu_a(CH_2) = 2926\text{ cm}^{-1}$), along with the broadness of these peaks, indicates a higher density of gauche defects and a more random orientation of the alkyl chains on the surface. In addition, the enhanced broadness of the $\nu_a(CH_3)$ peak is consistent with a heterogeneous conformation of methyl groups at the surface of the film. These results are supported by contact angle measurements taken on these SAMs (Table 2). In general, advancing contact angles of water and hexadecane are 110 – 115° and 44 – 50° , respectively, on well-ordered methyl surfaces.²⁰ Disorder or defects in the monolayer

can expose methylene groups to the contacting liquid, which effectively reduces the hexadecane contact angles.² Advancing and receding contact angles for water and hexadecane on the $C_{12}SH$ -based SAM are comparable to those previously reported²¹ and are consistent with a well-ordered methyl surface. For thiosulfate SAMs, the contact angles for water are consistent with a low-energy surface containing methyl and/or methylene²² groups, but the larger hystereses of these angles indicate an increased surface roughness of the SAM, consistent with the more disorganized nature of the films. For the $C_{12}TS$ SAM formed from ethanol, the large hysteresis for water and the advancing angle of $\sim 25^\circ$ for hexadecane suggest a more chemically heterogeneous surface with exposed methylene groups at the surface. For the water-borne $C_{12}TS$ SAM, the surface was completely wet by hexadecane, suggesting a high methylene content near the surface. On the basis of these results, the $C_{12}TS$ SAMs contain greater amounts of disorder within the outermost angstroms of the film in comparison to that for the $C_{12}SH$ SAM that has the structural characteristics and wetting properties of a well-ordered monolayer.

Resistance and capacitance values for these three films (Table 1) show variations in barrier properties consistent with those observed in their structural properties. In general, SAMs with more crystalline structures exhibit enhanced barrier properties.²³ Remarkably, SAMs formed from $C_{12}TS$ in ethanol exhibit comparable resistance values to those of $C_{12}SH$ -based SAMs. These results suggest that the gauche defects within the $C_{12}TS$ SAM as correlated from IR spectra (Figure 2) do not appreciably impact its barrier properties. In contrast, films formed from aqueous solutions of $C_{12}TS$ have much lower resistance and higher capacitance than SAMs formed from $C_{12}SH$, consistent with a greater density of larger defects that are more easily penetrated by electrolyte. Because of the more disordered structure of the water-borne $C_{12}TS$ SAM, it is not expected to produce a corrosion barrier as strong as that of a $C_{12}SH$ SAM; nonetheless, it does provide an increase in resistance of ~ 2 orders of magnitude compared to that for uncoated copper.

We recorded XPS spectra for a water-borne $C_{12}TS$ SAM on copper to determine if its inferior structural and barrier properties are a result of a different mode of binding to the copper surface (Figure 3). Lukkari et al.⁹ have shown that thiosulfate SAMs on gold yield XPS signals consistent with the presence of thiolates. Figure 3 suggests that $C_{12}TS$ forms SAMs onto copper from water consisting primarily of thiolates, as indicated by the spin-orbit doublet for S(2p) at 162 – 164 eV .²⁴ The presence of a weaker peak at higher binding energy (~ 168 – 169 eV) is consistent with a small fraction of oxidized sulfur species such as sulfonates or sulfates. The position of this smaller peak is inconsistent with sulfites or intact thiosulfates that have binding energies at 167 eV .^{9,25} One possible scenario for the presence of this peak is that adsorbed sulfites could be converted to sulfates upon exposure to oxygen.²⁵ However, we expect that an adsorbed sulfate would bond weakly to the copper surface and would likely

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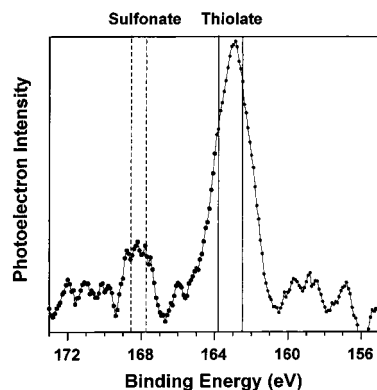


Figure 3. XPS spectra of the S(2p) region of a copper sample exposed to a 1 mM solution of $C_{12}TS$ in water at 40 °C for 15 min. The solid lines denote the approximate positions of the S(2p) peaks due to a thiolate; the dashed lines denote the approximate positions of the S(2p) peaks due to a sulfonate.²⁴ Binding energies are referenced to C(1s) at 284.8 eV.

be removed during the rinsing of the surface. A more likely scenario involves the conversion of surface-bound thiolates to sulfonates after rinsing and prior to transfer of the sample to high vacuum for the XPS measurements.²⁶ Alkanethiolates on copper and gold are converted to sulfonates upon exposure to air and UV light.^{1,27}

The differences in structure for thiol- and thiosulfate-based SAMs on copper are consistent with the proposed mechanism of thiosulfate SAM formation onto gold, as described by Lukkari et al.,⁹ in which the S–S bond is cleaved upon adsorption of the thiosulfate to yield adsorbed thiolate and sulfite species. Desorption of the loosely bound sulfite would then leave an adsorbed thiolate and an adjacent site that is empty. At high coverage, the desorption of sulfite ions would result in molecule-sized vacancies or pinholes that are not as likely to be filled by the bulky thiosulfate molecules. As schematically shown in Figure 4, these pinholes effectively reduce the packing density of the thiosulfate-based SAMs and should negatively impact their barrier properties. Nonetheless, the $C_{12}TS$ -based SAMs from ethanol and THF still provide large resistances against the diffusion of ions and represent a possible alternative to the use of alkanethiols, which are less soluble in polar solvents, are more difficult to synthesize, and have a much stronger odor.

Comparisons of $C_{12}TS$ SAMs formed from various solvents suggest that water plays a prominent role in lowering the quality of these SAMs. This phenomenon may be attributed to a combination of related factors, including the enlargement of the thiosulfate headgroup in water due to hydration, low surface mobility of the adsorbed thiolates, and steric effects that prevent the diffusion of the bulky, hydrated thiosulfate into small pinholes. Figure 5 schematically illustrates the hydrated thiosulfates and the pinhole defects mentioned above. The larger size of the headgroup in water hinders the diffusion of the thiosulfate into small pinholes. If the alkyl chains are oriented so as to prevent access to these pinhole defects, the sites would remain open, resulting in lower overall coverage and inferior barrier properties in comparison to those observed for thiosulfate SAMs in ethanol. This hypothesis is supported by the fact that increasing the temperature improves the quality of the film (Table 1),

(26) After removal from solution, the SAM-coated copper samples were exposed to ambient conditions for ~3 h before being transferred into the XPS chamber.

(27) Hunt, D. A.; Leggett, G. J. *J. Phys. Chem.* **1996**, *100*, 6657–6662.

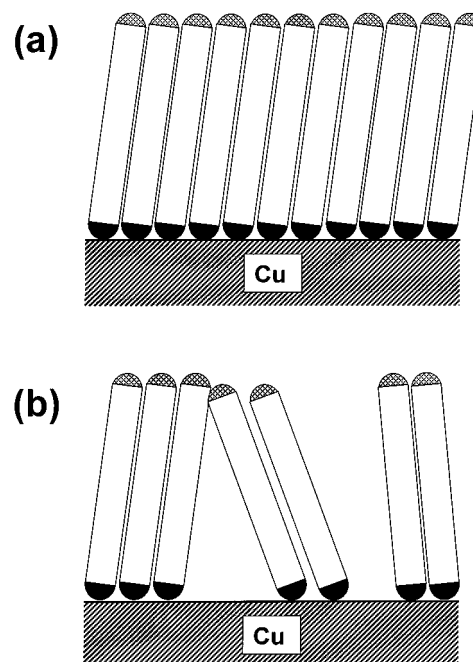


Figure 4. Schematic of a structural model for SAMs formed from (a) $C_{12}SH$ and (b) $C_{12}TS$ on copper. The vacancies in the thiosulfate SAM may be attributed to steric effects that prevent the thiosulfate molecule from diffusing to the copper surface and filling in vacancies.

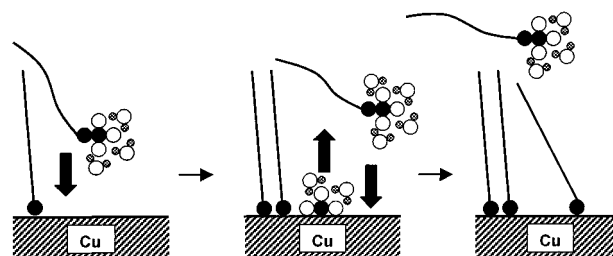


Figure 5. Schematic illustration of the adsorption of hydrated alkyl thiosulfates onto copper and the pinhole defects that are likely created during the assembly.

since a higher temperature would enhance the diffusion of the thiosulfate while dehydrating its headgroup to some extent. A higher temperature should also increase the surface mobility of the thiolate species and enhance the desorption of sulfites from the surface.

Effects of Chain Length on Thiosulfate SAM Properties. Previous studies have indicated that SAMs formed from alkanethiols (C_nSH) on copper provide improved barrier properties for increasing values of chain length (n), due to both the increased thickness of the barrier film and the improved crystalline character of the thicker films.^{1,5} To investigate similar trends in SAMs formed from alkyl thiosulfates, we synthesized C_nTS ($CH_3(CH_2)_{n-1}S_2O_3^-Na^+$) with chain lengths (n) of 8, 10, 12, and 14 total carbons. No chains longer than 14 carbons were examined because of limitations on the solubility of these salts in water (the solubility of $C_{14}TS$ is <1 mM at 23 °C but ~1 mM at 40 °C). Samples were immersed for 15 min in 1 mM aqueous solutions of C_nTS ($n = 8, 10, 12, 14$) at 40 °C.

Infrared spectra for thiosulfate SAMs of each chain length, shown in Figure 6, confirm that C_8TS and $C_{10}TS$ achieved poor coverage on the surface, particularly evident on the basis of the low intensities for the methyl stretching modes at ~2880 and ~2957 cm^{-1} . These surfaces were

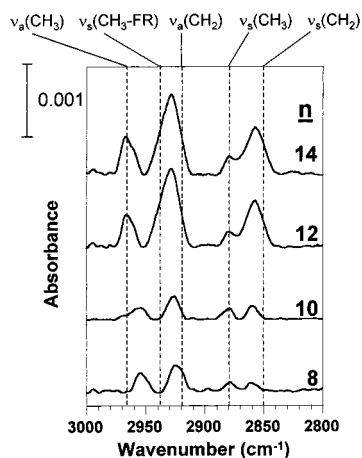


Figure 6. Infrared spectra of the C–H stretching region for SAMs of C_n TS on copper. Films were formed by 15-min exposure to 1 mM aqueous solutions of C_n TS at 40 °C. The dashed lines indicate the positions of the methyl and methylene modes for a trans-extended monolayer with no gauche defects: $\nu_a(\text{CH}_3) = 2965 \text{ cm}^{-1}$, $\nu_s(\text{CH}_3\text{--FR}) = 2938 \text{ cm}^{-1}$, $\nu_a(\text{CH}_2) = 2918 \text{ cm}^{-1}$, $\nu_s(\text{CH}_3) = 2879 \text{ cm}^{-1}$, and $\nu_s(\text{CH}_2) = 2851 \text{ cm}^{-1}$. The spectra have been offset for clarity.

wet by water immediately after removal from solution, further indicating that the surface had a low coverage of hydrophobic species. Copper surfaces exposed to solutions of C_8 TS and C_{10} TS for prolonged periods of time (> 30 min) were visibly corroded, even after deaeration of the solutions. This phenomenon may be attributed to the low driving force for adsorption, as both C_8 TS and C_{10} TS are much more soluble in water than longer-chained thiosulfates, and to the fact that thiosulfates tend to etch copper in the presence of oxidants. In contrast, IR spectra for films formed from C_{12} TS and C_{14} TS indicate a much greater chain density but a high degree of noncrystalline content, as inferred from the broadness of the methyl and methylene peaks and the shift of the methylene peaks to higher wavenumbers.

We did not observe corrosion of the copper surface upon prolonged exposure to 1 mM aqueous solutions of C_{12} TS and C_{14} TS. However, multilayers did form onto copper from these solutions for exposure times greater than 45 min, as evidenced by a white film on the surface and dramatic increases in the C–H stretching intensities of IR spectra. These multilayers are consistent with those observed by Keller et al.²⁸ upon exposure of alkanethiols to oxidized copper. The inability of C_8 TS and C_{10} TS to form these multilayers and their enhanced tendency to corrode the surface are likely related to the higher solubility of these salts and their copper complexes.

Impedance spectra for the films formed from C_n TS are shown in Figure 7. In addition to spectra for the four salts examined, a spectrum for untreated copper is shown as a reference. As expected, the spectra for $n = 8$ and $n = 10$ indicate relatively poor barrier properties and little if any capacitive effect. These two spectra were best fit by a Warburg impedance model, indicating that mass-transfer effects are providing the resistance rather than the SAM. In contrast, the spectra for the C_{12} TS and C_{14} TS SAMs show relatively well blocking films, indicating a substantial enhancement in performance, and the C_{14} TS SAM produced the higher resistance. Calculated resistance and capacitance values for these SAMs (Table 3) illustrate the Warburg behavior of the C_8 and C_{10} films and the dramatic increase in performance observed for C_{12} and C_{14} films. Hexadecane contact angle measurements for C_{14} TS SAMs formed from both water and THF

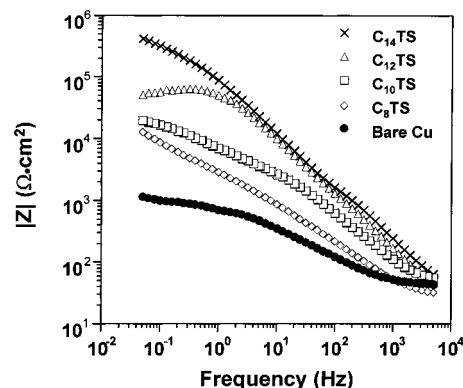


Figure 7. Electrochemical impedance spectra obtained in 0.1 M $\text{Na}_2\text{SO}_4(\text{aq})$ for SAMs formed from C_n TS on copper. Films were formed from 15-min exposure to 1 mM aqueous solutions of C_n TS at 40 °C. The spectrum for untreated copper is shown as a reference.

Table 3. Resistance and Capacitance Values for SAMs Formed from C_n TS ($n = 8, 10, 12, 14$) and a Film Formed from BTAH on Copper^a

precursor	solvent ^b	$\log R_{ct}$ ($\Omega \cdot \text{cm}^2$)	C_t ($\mu\text{F}/\text{cm}^2$)	$\log Z_W^c$ ($\Omega \cdot \text{cm}^2$)
C_8 TS	H_2O	1.60	3.4	3.69
C_{10} TS	H_2O	3.25	2.3	3.94
C_{12} TS	H_2O	4.43	1.9	
C_{14} TS	H_2O	5.19	1.8	
	THF	6.25	1.7	
BTAH	H_2O	5.22	2.1	

^a All films were formed from 15-min exposure to 1 mM solutions.

^b All aqueous self-assembly was performed at 40 °C, while self-assembly in THF was performed at 23 °C. ^c The SAMs of C_8 TS and C_{10} TS exhibited active oxidation in the EIS cell, resulting in a fit to a Warburg circuit model.

(Table 2) suggest a more ordered methyl surface than that formed by C_{12} TS. When formed in THF, the C_{14} TS SAM exhibits advancing contact angles for hexadecane (42°) that are comparable to those for a thiol-based SAM.

Table 3 also contains resistance and capacitance values for a film formed by exposure of copper to a 1 mM aqueous solution of benzotriazole (BTAH) at 40 °C for 15 min. BTAH is a commonly used, commercially available corrosion inhibitor for copper.^{29–32} As shown in Table 3, a SAM formed from C_{14} TS in water exhibits comparable barrier properties to those of a film of BTAH formed under analogous conditions. In comparison, the C_{14} TS SAM formed from THF greatly outperforms both water-borne films. Based on EIS measurements of these SAMs, C_{14} TS may provide a feasible alternative to BTAH as a corrosion inhibitor, particularly if the copper surfaces can be pretreated with C_{14} TS from organic solution. After initial adsorption, the process stream could be treated with low concentrations of C_{14} TS in water to replenish the SAM as it deteriorates over time.

Conclusions

Alkanethiols and alkyl thiosulfates form SAMs on copper with different levels of packing density. For thiol-

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based SAMs, our results are consistent with previous studies^{5,13} and suggest that the SAMs are densely packed and highly crystalline. Results from thiosulfate-based SAMs formed in ethanol and THF also indicate monolayers with well-ordered structures, but these films exhibit more gauche defects and lower overall chain density. In comparison, water-borne thiosulfate SAMs have a more disordered structure with a greater number of defects and a lower surface coverage, as supported by complementary characterization methods. Our results with thiosulfate-based SAMs formed in water imply that a critical chain length is required in order to form SAMs that provide a protective barrier for the underlying metal (Figure 7). While C₈TS and C₁₀TS do not form protective SAMs in water and facilitate corrosion of the copper surface, C₁₂TS

and C₁₄TS formed films with resistances that were orders of magnitude greater than that for the uncoated metal. A comparison of C₁₄TS, the best-performing thiosulfate studied, to benzotriazole showed comparable effectiveness as a corrosion barrier when assembled onto copper in aqueous solution.

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