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Organic Thiosulfates (Bunte Salts): Novel Surface-Active Sulfur Compounds for the Preparation of Self-Assembled Monolayers on Gold

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In this paper, we demonstrate that organic thiosulfates (Bunte salts) with the general formula R–SSO₃M, where R is either an aliphatic or aromatic group and M a monovalent cation, constitute a novel class of surface-active compounds with a sulfur-containing headgroup. Bunte salts form self-assembled monolayers (SAMs) on gold under anaerobic conditions and chemisorb forming a Au–S bond, in which the chemical nature of sulfur is indistinguishable by X-ray photoelectron spectroscopy (XPS) from gold thiolate formed upon chemisorption of thiols and disulfides. The S–SO₃ bond in the thiosulfate is cleaved during adsorption on the gold surface and the sulfite moiety is released. We have prepared one alkyl thiosulfate (sodium *S*-dodecylthiosulfate, C₁₂SSO₃Na) and two aromatic redox-active thiosulfates (potassium *S*-(2,5-dihydroxyphenyl)thiosulfate, QSSO₃K, and dipotassium *S,S'*-(3,6-dihydroxy-1,2-phenylene)bisthiosulfate, Q(SSO₃K)₂) and compared the formation and properties of the SAMs prepared from these Bunte salts and the corresponding thiols (1-dodecylmercaptan, C₁₂SH, and 1,4-dihydroxy-2-mercaptobenzene, QSH) using XPS, cyclic voltammetry, and ac impedance spectroscopy. The chemisorption of Bunte salts takes place 1–2 orders of magnitude slower than the adsorption of thiols. The SAMs formed from aromatic Bunte salts QSSO₃K or Q(SSO₃K)₂ have lower surface coverage than those prepared using QSH. With aliphatic compounds, the films prepared from Bunte salts are either slightly or relatively well-blocking, although they do not reach the quality achieved with thiol-based SAMs. The differences in the adsorption time scale and surface coverage are attributed to the bulky thiosulfate headgroup. A major advantage of using Bunte salts derives from the general synthetic pathway to organic thiosulfates, generally involving a one-pot synthesis starting from the corresponding halides and yielding the products as odorless crystalline compounds. This offers a synthetically feasible way of introducing a sulfur-containing surface-active headgroup into several redox-active or other functional molecules, allowing their incorporation in SAMs. This facilitates the preparation of functional monolayers for applications in sensor technology and molecular electronics.

Introduction

Self-assembled monolayers (SAMs) have become important in many studies of surface-related phenomena.¹ On the basis of the chemical nature of the surface-active headgroup in the molecules used in self-assembly (SA), different types of SAMs can be envisaged. In particular, compounds with a sulfur-containing headgroup constitute the source of an important class of self-assembled films on transition-metal substrates (e.g., gold).² After the initial report by Nuzzo and Allara several sulfur-containing molecules have been used for the preparation of SAMs on gold and other transition-metal surfaces.^{2,3} The compounds include aliphatic and aromatic thiols and disulfides,

sulfides, thiophene,⁴ xanthates,⁵ thiocarbamates,⁶ thioureas,⁷ and thiocarboxylic acids.⁸ Very little is known about the structure and stability of the SAMs formed from xanthates, thiocarbaminates, thiocarbamates, and thiourea. Thiocarboxylic acid SAMs undergo facile hydrolysis on the surface. On the other hand, thiols and disulfides form stable SAMs, in which the organic film is attached to the gold substrate via a polar covalent bond. With thiols, the reaction is assumed to take place as an oxidative addition to gold with the concomitant release of hydrogen whereas, in the case of disulfides, the cleavage of the S–S bond occurs.^{9,10} For alkanethiols and disulfides, hydrophobic interactions between the aliphatic chains increase the stability of the film.¹¹ The SAMs formed from corresponding thiols and disulfides are identical in all properties and it is generally accepted that they form a ($\sqrt{3} \times \sqrt{3}$)-*R30°* adlayer on Au(111) with the sulfur atoms occupying

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the 3-fold hollow sites on the surface. Dimerization of the adjacent surface thiolates has been suggested, but the experimental data on the nature of the surface-bound sulfur atoms are somewhat controversial.^{12–17}

Measurements of the film formation kinetics have shown that the adsorption of thiols from solution proceeds in several steps.^{18–22} The initial steps are fast and have been attributed to the adsorption of the molecules and to the formation of a disordered phase. The generation of an ordered, two-dimensional film takes place with a much longer time scale. This multistep adsorption mechanism has also been observed in scanning tunneling microscopy (STM) studies, both in ultrahigh vacuum (UHV) and in situ.^{15,23,24} Second harmonic generation (SHG) measurements, which probe the formation of the gold–sulfur bond, have demonstrated that disulfides adsorb approximately 40% slower than thiols.²² In addition to thiols and disulfides, only sulfides have been examined more closely in order to assess their applicability for SAM preparation.^{9,25–27} The SAMs formed using sulfides are different from films prepared from thiols or disulfides and their adsorption kinetics is several orders of magnitude slower.^{22,27} In addition, a recent study suggested that dialkylsulfides most probably only physisorb on gold.²⁸

Simple thiols can be used only as passive films on the substrate. To form active functional SAMs, redox and photoactive molecules that can respond to external stimuli have to be incorporated into the film.²⁹ These molecules, which generally contain aromatic subunits, can be used in molecular electronics applications as immobilized molecular sensors, switches, or other components.³⁰ However, aromatic moieties introduced into the molecular body generally increase disorder within the film.³¹ This effect is dependent on the position of the aromatic moiety

in the molecule, the strength of the intermolecular interactions, and the flexibility of the molecular structure close to the surface-active headgroup.^{31–33} This emphasizes the importance of synthetic work in the design of surface-active compounds with desired structure and properties. In particular, a facile method for incorporating a surface-active headgroup in a functional molecule is desirable. General synthetic strategies for preparing thiols or disulfides include an addition of hydrogen sulfide to alkenes or substitution of alkyl halides and haloaromatic compounds carrying a strong electron-withdrawing substituent with sulfide.³⁴ To circumvent the formation of significant amounts of side products, mostly sulfides, a variety of synthetic methods have been devised. All these necessarily include additional hydrolysis, reduction, or bond cleavage steps. The products, thiols, are characterized by their strong, unpleasant smell. It is, therefore, desirable to find novel surface-active compounds for monolayer preparation on metal electrodes. In this paper, we demonstrate the applicability of organic thiosulfates for the preparation of SAMs. Organic thiosulfates have the general formula RSSO_3M , where R is an aliphatic or aryl group and M a monovalent cation, and they can be regarded as *S*-alkyl or *S*-aryl esters of thiosulfuric acid. These compounds are also commonly known as Bunte salts after the German chemist Hans Bunte who first studied them in the 1870s.³⁵ We have prepared one alkyl thiosulfate, sodium *S*-dodecylthiosulfate ($\text{C}_{12}\text{SSO}_3\text{Na}$), and two aromatic redox-active benzoquinone derivatives, potassium *S*-(2,5-dihydroxyphenyl)thiosulfate (QSSO_3K) and dipotassium *S,S'*-(3,6-dihydroxy-1,2-phenylene)bisthiosulfate ($\text{Q}(\text{SSO}_3\text{K})_2$). We report the formation and characterization of SAMs formed from these Bunte salts using X-ray photoelectron spectroscopy (XPS), cyclic voltammetry, and impedance spectroscopy and compare the results with SAMs prepared from the corresponding thiols, 1-dodecylmercaptan (C_{12}SH) and 1,4-dihydroxy-2-mercaptobenzene (QSH). We show that chemically identical SAMs can be formed from thiols and the corresponding thiosulfates. A major advantage in using thiosulfates is the facility of their preparation compared to that of the corresponding thiols and disulfides. Bunte salts can be conveniently obtained by the action of thiosulfate on the corresponding halide (or, in the case of quinones, on 1,4-benzoquinone) in aqueous or mixed organic–aqueous media (eq 1) and, in many instances, the preparation of a surface-



active Bunte salt can be achieved in a one-pot synthesis and the product obtained as a crystalline, odorless salt that is easily separated from the reaction mixture. In addition, Bunte salts offer a convenient synthetic route

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to thiols as they can be converted to the corresponding thiols in good yields without prior isolation.

Experimental Section

Synthesis and Chemicals. 1-Dodecylmercaptan (98%) was obtained from Aldrich and used without further purification. All the other chemicals were of reagent grade and were used as received.

Sodium *S*-Dodecylthiosulfate ($C_{12}SSO_3Na$). $C_{12}SSO_3Na$ was prepared according to the method described by Peak and Watkins.³⁶ Shortly, 24.9 g (0.1 mol) of 1-bromododecane was dissolved in 50 mL of ethanol and 25.0 g (0.1 mol) of $Na_2S_2O_3 \cdot 5H_2O$ in ca. 500 mL of water was added. The mixture was refluxed for 3 h and the white precipitate (a monohydrate) was filtered and recrystallized from ethanol.

Potassium *S*-(2,5-Dihydroxyphenyl)thiosulfate ($QSSO_3K$). $QSSO_3K$ was prepared by the reaction of sodium thiosulfate with 1,4-benzoquinone.³⁷ $Na_2S_2O_3 \cdot 5H_2O$ (35.0 g, 0.13 mol) was dissolved in 30 mL of water and the solution cooled to 10–15 °C. To the stirred solution, 10.8 g (0.1 mol) of 1,4-benzoquinone in 80 mL of glacial acetic acid was added dropwise. After being stirred for 30 min, the mixture was saturated with KCl and put to +4 °C for 2 h. The white precipitate was collected, washed with cold water, and recrystallized from water.

Dipotassium *S,S'*-(3,6-dihydroxy-1,2-phenylene)bisthiosulfate ($Q(SSO_3K)_2$).³⁷ 1,4-Benzoquinone (10.8 g, 0.1 mol) was dissolved in 80 mL of glacial acetic acid and a solution containing 27.5 g (0.11 mol) of $Na_2S_2O_3 \cdot 5H_2O$ in 35 mL of water was added dropwise at room temperature. After the color had disappeared, 12.0 g of KCl in 12 mL of water was added and the mixture was allowed to stand several hours at +4 °C. The white precipitate was collected and recrystallized from water.

1,4-Dihydroxy-2-mercaptobenzene (*QSH*). *QSH* was prepared by reduction from the corresponding Bunte salt.³⁸ In short, 20 mL of concentrated hydrochloric acid was added to 2.6 g (10 mmol) of $QSSO_3K$ in 25 mL of water. Zn powder (5 g) was added under vigorous stirring at 40–50 °C. After completion of the reaction, the mixture was extracted three times with 50 mL portions of ether and the combined ethereal extracts evaporated to dryness. The product was recrystallized from toluene.

Substrates and Monolayer Formation. Polycrystalline gold disk electrodes (Cypress Systems, Kansas City, MO; disk diameter 1 mm) were pretreated and their real surface area determined as described earlier.³⁹ Electrodes were then placed in 1 mM solutions of the surface-active compounds either in ethanol (aliphatic compounds $C_{12}SSO_3Na$ and $C_{12}SH$) or in a pH 7.0 phosphate buffer (total buffer concentration 0.1 M; quinone derivatives $QSSO_3K$, $Q(SSO_3K)_2$ and *QSH*). All thiosulfate solutions were deaerated with argon and adsorption was carried out under an argon atmosphere. After an appropriate time the electrodes were removed from the solution and rinsed thoroughly with the solvent. Before measurements all electrodes were finally rinsed with Millipore water. The thin film Au electrodes were prepared by thermal evaporation on Si(100) wafers. The wafers were cleaned in hot piranha solution (3:1 concentrated H_2SO_4 /30% H_2O_2) (WARNING! Piranha solution is very corrosive and must be treated with extreme caution; it reacts violently with organic material and must not be stored in tightly closed vessels) for 2 h, rinsed thoroughly with Millipore water, and dried overnight at 80 °C. The wafers were then treated in the vapor phase above the refluxing (3-mercaptopropyl)trimethoxy silane solution (10% v/v in dry toluene) for 6 h under dry nitrogen and rinsed thoroughly with toluene.⁴⁰ The thin gold films (approximately 70 nm) were formed using resistive thermal evaporation at a rate of approximately 2 nm/s and the film thickness was monitored by a quartz crystal oscillator. The crystal orientation of gold films evaporated on mercaptopropyl silanized

silicon is not known but the cyclic voltammograms (in 0.5 M H_2SO_4) were typical of polycrystalline gold. Repetitive cycling, however, lead to an increase in the apparent (111) character in the voltammograms.⁴¹ An average roughness factor of 2.3 was observed after reductive removal of the SAMs in 0.5 M KOH.

X-ray Photoelectron Spectra. The XPS spectra were recorded with a Perkin-Elmer PHI 5400 spectrometer using an electron takeoff angle of 45° and an analyzer pass energy of 35.75 or 89.45 eV for narrow scan spectra or wide scan survey spectra, respectively. All samples were measured using monochromatized Al K α radiation except the solid sample of $Q(SSO_3K)_2$, with which unmonochromatized Mg K α radiation was used in order to decrease sample charging. The energy scale was calibrated using the Au 4f_{7/2} and Cu 2p_{3/2} lines (84.0 and 932.7 eV, respectively) in order to ensure linearity over a wide energy range.⁴² With the solid sample of compound $Q(SSO_3K)_2$, the C 1s component with the lowest binding energy (assigned to unsubstituted ring carbons and carbons bound to sulfur, 283.9 eV)³⁹ was used as an internal standard to correct for the sample charging shift. An adventitious hydrocarbon contamination signal could not be used because of the intense carbon signal from the samples.

Part of the samples were measured first at 130 K and then at room temperature to investigate a possible layer volatility or decomposition. A special sample introduction chamber equipped with a coldfinger, N₂ inlet and vacuum gauge was used to cool the samples under controlled conditions before evacuation in order to minimize possible sample evaporation in the ultrahigh vacuum (UHV) of the analyzing chamber (approximately 10^{−7} Pa).⁴³ No differences could be observed between any of the spectra measured at the two temperatures, indicating good resistance of the studied films against UHV conditions and irradiation. The measured spectra were submitted to a Shirley-type background correction and were fitted using symmetrical, mixed Gaussian–Lorentzian peaks of the same width. The S 2p spectra were fitted to a 1:2 doublet with a splitting of approximately 1.2 eV. The atomic concentrations reported were obtained by using spectral intensities divided by the experimental sensitivity factors provided by the manufacturer.

Electrochemistry. Voltammetric and chronocoulometric measurements were carried out using a EG&G 283 potentiostat and a conventional one-compartment three-electrode cell. The reference electrode was a sodium-saturated calomel electrode (SSCE), to which all potentials reported are referred. A Pt wire served as an auxiliary electrode. For measurements of adsorption kinetics of the quinone derivatives $QSSO_3K$, $Q(SSO_3K)_2$, and *QSH*, the electrodes were removed from the plating solution at suitable intervals, rinsed thoroughly with the solvent and Millipore water, and immersed in the measurement solution (typically a 0.1 M phosphate buffer, pH = 6.0, containing 1.0 M NaClO₄). Chronocoulometric measurements of the adsorption of the aliphatic compounds were carried out in situ at 0.000 V versus SSCE in an ethanol solution containing NaClO₄ (20 mM) and either $C_{12}SSO_3Na$ or $C_{12}SH$ (both 1 mM). The potential was stepped from 0.000 to +0.050 V versus SSCE and back for 5 ms. The interfacial capacitance was determined by extrapolating the linear portion of the charge-time curve to zero time and dividing the charge by the potential step. Impedance spectroscopic measurements of the SAMs formed from 1-dodecylmercaptan or *S*-dodecylthiosulfate were carried out with a VoltaLab PGZ301 potentiogalvanostat electrochemical impedance meter (Radiometer, Copenhagen) and the data analyzed by the Boukamp's fitting software.⁴⁴ The analysis results are calculated per geometrical area of the electrode. SAMs for impedance measurements were prepared by immersing evaporated Au thin film electrodes in deaerated 1 mM solutions of $C_{12}SSO_3Na$ or $C_{12}SH$ in ethanol for 24 h under an argon atmosphere. The emphasis was in the comparison of SAMs prepared from thiols and thiosulfates under identical conditions and, therefore, no attempts were made to optimize the self-assembly process in either case. The impedance spectra were measured in aqueous solutions that

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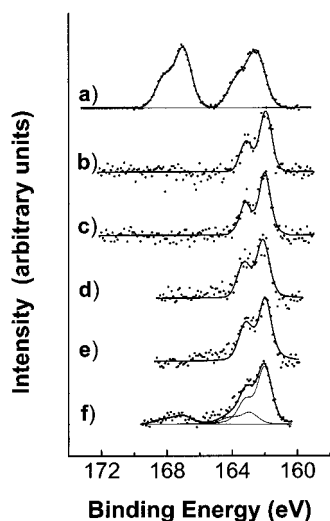


Figure 1. S 2p XPS spectra of (a) solid $\text{Q}(\text{SSO}_3\text{K})_2$ and SAMs of (b) $\text{C}_{12}\text{SSO}_3\text{Na}$ on Au, (c) C_{12}SH on Au, (d) QSSO_3K on Au, (e) QSH on Au, and (f) $\text{Q}(\text{SSO}_3\text{K})_2$ on Au. Deconvoluted peaks and their sums (thick line) are shown. The spectrum in (a) has been corrected for sample charging (see text).

were 2.5 mM with respect to $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 1.0 M with respect to KCl. All solutions used were deaerated with argon and all measurements were carried out at room temperature.

Results and Discussion

XPS. The Bunte salts contain sulfur in two different chemical environments and, therefore, with solid $\text{Q}(\text{SSO}_3\text{K})_2$, two states of sulfur with different binding energies (BE) but equal intensities were observed in the S 2p XPS spectrum (Figure 1a and Table 1). The doublet at lower BE (162.5 eV) can be assigned to sulfur bound to carbon. Similar values have been obtained for this sulfur atom in inorganic thiosulfates (e.g., 162.2 and 161.7–162.5 eV for PbS_2O_3 and $\text{Na}_2\text{S}_2\text{O}_3$, respectively).⁴⁵ Therefore, the doublet at 167.0 eV originates from sulfur bound to the oxygen atoms of the thiosulfate group. The BE of this peak is somewhat lower than the values reported for sulfur in inorganic thiosulfates (167.7 eV).^{45a,b} The C 1s spectrum of solid $\text{Q}(\text{SSO}_3\text{K})_2$ showed two components at 283.9 and 285.1 eV, assigned to unsubstituted ring carbons (C^4 and C^5) and carbons bound to sulfur (lower BE) and to hydroxyl-substituted carbons (higher BE).³⁹ The two O 1s peaks can be attributed to the two oxygen species in the molecule.⁴⁶ The relative atomic concentration ratios K:S:C:O determined from the XPS spectra were 1.0:2.0:4.8:4.3, which is in good agreement with the expected ratio 1:2:3:4.

For the species adsorbed on gold, Figure 1 shows the S 2p spectra of *S*-dodecylthiosulfate and 1-dodecylmercaptan. The spectra are identical to a 1:2 doublet at 161.95 ± 0.05 eV, which is typical of thiolate on gold.^{47,48} No signal due to loosely bound or isolated sulfur was observed. An important observation is the lack of oxygen-containing

sulfur species in the SAM formed from *S*-dodecylthiosulfate. Sulfur at a higher oxidation state on the gold surface (e.g., surface sulfonate) has a BE of ca. 167 eV.⁴⁹ The result shows that sulfur is in the same chemical state in the self-assembled monolayers formed from aliphatic thiol and the corresponding Bunte salt. The same conclusion can be drawn from the comparison of the S 2p spectra of 1,4-dihydroxy-2-mercaptobenzene (QSH) and its Bunte salt derivative QSSO_3K (Figure 1d,e). Both spectra have a doublet at 162.0 eV and display no other sulfur species. This BE is lower than either of the values obtained for the solid sample of the Bunte salt $\text{Q}(\text{SSO}_3\text{K})_2$. Hence, the S 2p spectra clearly demonstrate that the S– SO_3 bond cleavage takes place upon adsorption of organic thiosulfates on gold and the chemisorption results in surface-bound sulfur in a chemical state indistinguishable from surface thiolate. It is also of interest to compare the S 2p spectrum of a gold surface treated analogously with a 1 mM $\text{Na}_2\text{S}_2\text{O}_3$ solution (Table 1, figure not shown). No indication for thiosulfate could be found in the spectrum. Instead, two doublets were observed at 161.3 and 161.5 eV. The former constituted the main component of the spectrum and can be assigned to gold sulfide whereas the other broad doublet probably originates from several polysulfide species on the surface.⁵⁰ Therefore, adsorption on gold leads to the cleavage of the S– SO_3 bond in inorganic thiosulfates, too.

Interestingly, somewhat different results were obtained with the bithiosulfate derivative $\text{Q}(\text{SSO}_3\text{K})_2$ (Figure 1f). In addition to a doublet assigned to surface thiolate at 162 eV two weaker doublets were observed at higher BE. These two doublets are of the same size and their BEs are close to those in the solid $\text{Q}(\text{SSO}_3\text{K})_2$ sample. Hence, it seems probable that they originate from intact thiosulfate groups on the surface. As no loosely bound sulfur was observed in any of the samples the presence of a physisorbed Bunte salt is unlikely. We attribute, therefore, these additional signals to bithiosulfates chemisorbed only through the other thiosulfate substituent. Using the relative intensities in the spectrum, the percentage of this kind of singly bound bithiosulfate can be estimated to be ca. 46%. With an intact thiosulfate group on the surface the lack of the potassium signal is somewhat surprising. This may be due to ion exchange by protons during the extensive rinsing of the monolayer prior to XPS measurements.

XPS spectra of the other elements contemplate the conclusions obtained. The C 1s spectra of $\text{C}_{12}\text{SSO}_3\text{Na}$ and C_{12}SH on gold were practically identical, displaying the binding energy typical for carbons in the hydrocarbon chain (Table 1).⁵¹ With the surface-active quinones, the peaks in the C 1s spectra can be assigned to unsubstituted and hydroxyl-substituted ring carbons at ca. 283.8 and 285.2 eV, respectively.³⁹ In addition, peaks at ca. 284.1 and 287.1 eV were attributed to C–S and C=O carbons, respectively.^{39,52} The O 1s spectra showed a peak assigned to hydroquinone oxygen (532.4 eV) and additional peaks due to carbonyl oxygen (531.7 eV) and, possibly, some oxidized carbon species (530.6 eV). The latter peaks were observed in the SAMs prepared using the Bunte salts. Therefore, the surface-attached hydroquinone derivatives

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Table 1. Binding Energies (eV) and the Relative Intensities of the Fitted Components in the XPS Spectra^a

sample	S 2p _{3/2}	C 1s	O 1s	K 2p _{3/2}	Au 4f _{7/2}
solid Q(SSO ₃ K) ₂	162.5 (50%) 167.0 (50%)	283.9 (66%) ^b 285.1 (34%)	531.1 (81 %) 532.5 (19%)	292.2	^c
C ₁₂ SH/Au	162.0	284.9		^c	84.0
C ₁₂ SSO ₃ Na/Au	161.9	284.8		^c	^d
QSH/Au	162.0	283.7 (37%) 284.1 (15%) 285.1 (37%) 287.1 (6%)	532.4	^c	^d
QSSO ₃ K/Au	162.1	283.8 (28%) 284.4 (19%) 285.2 (35%) 287.2 (18%)	530.6 (19%) 531.7 (36%) 532.4 (45%)	^c	^d
Q(SSO ₃ K) ₂ /Au	162.0 (69%) 162.9 (18%) 167.0 (13%)	284.1 (40%) 285.3 (31%) 286.7 (20%) 288.4 (9%)	531.0 (42%) 532.3 (58%)	^c	^d
Na ₂ S ₂ O ₃ /Au	161.3 (67%) 161.5 (33%)	^c	^c	^c	^d

^a See text for assignments. ^b Used for internal calibration; actual measured value was 286.7 eV. ^c Not detected/measured (applies to Na in the case of C₁₂SSO₃Na/Au). ^d Same as above.

of Bunte salts seem to be oxidized to quinones to a larger extent than the corresponding mercaptohydroquinone. The C 1s spectrum of Q(SSO₃K)₂ on gold is slightly different from those of adsorbed QSSO₃K and QSH, with the signal due to unsubstituted ring carbons shifted upward. Additional signals appeared at higher BEs, which may tentatively be attributed to some oxidized carbon species. This shows that the SAM prepared from Q(SSO₃K)₂ is more complicated than the other films studied in this work.

Adsorption of Thiols and S-Thiosulfates on Gold. Adsorption of thiols on gold has been probed using a multitude of experimental techniques, including contact angle measurements, surface plasmon resonance spectroscopy, surface IR spectroscopy, second harmonic generation, quartz crystal microbalance, and interfacial capacitance.^{18,19,21,22,53–55} We have chosen the measurement of the interfacial capacitance for comparing the kinetics of adsorption of aliphatic thiol C₁₂SH and the corresponding Bunte salt C₁₂SSO₃Na.⁵⁵ This technique relies on the description of the Au/SAM/solution interface with a simple resistor-capacitor equivalent circuit, which is usually a good approximation in the absence of redox species. The capacitances of the modified and bare gold surface fractions are assumed to be additive. Figure 2a shows the changes in the capacitance of the polycrystalline gold electrode after immersion in 1 mM ethanolic solutions of the aliphatic compounds C₁₂SSO₃Na or C₁₂SH. It is evident from the figure that thiol and thiosulfate clearly differ in their adsorption behavior. As discussed in the Introduction, the adsorption of thiols takes place in several phases, the first of which occurs in a very short time scale (i.e., in seconds from solutions of millimolar concentrations). Therefore, the capacitance of the interface rapidly achieves a constant value as the gold surface becomes modified with thiol and very little initial change is seen in the time scale of the experiment. In contrary, the adsorption of the corresponding Bunte salt proceeds at a markedly slower rate and the initial sharp drop of the capacitance is clearly observed. With aliphatic thiol, the steady-state capacitance

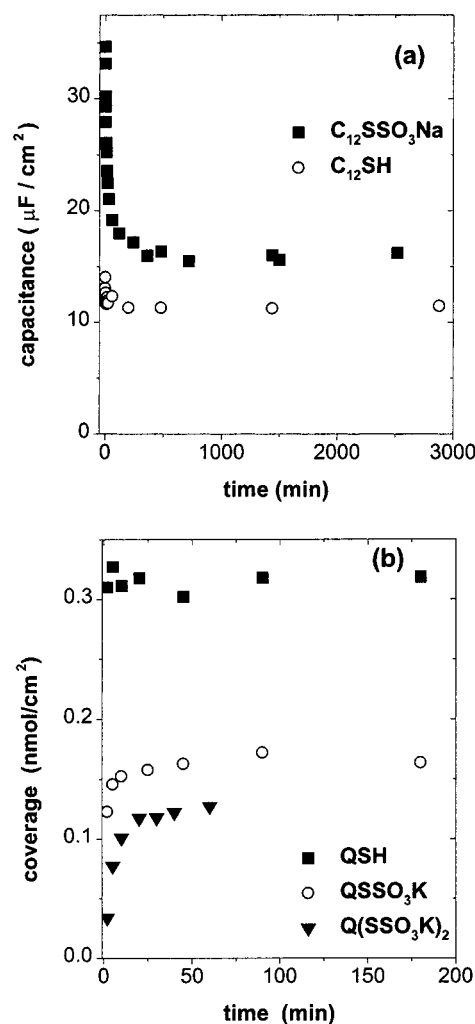


Figure 2. (a) Change in the interfacial capacitance after immersing a polycrystalline gold electrode in a 1 mM solution of C₁₂SSO₃Na (solid symbols) or C₁₂SH (open symbols) in ethanol/20 mM NaClO₄. (b) Quinone surface coverage as a function of immersion time in a 1 mM solution of 2-mercapto-1,4-dihydroxybenzene (QSH), potassium *S*-(2,5-dihydroxyphenyl)thiosulfate (QSSO₃K), or dipotassium *S,S'*-(3,6-dihydroxyphenylene-1,2)bis(thiosulfate) (Q(SSO₃K)₂) in a pH 7.0 phosphate buffer.

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is achieved in approximately 10–20 min whereas it takes about 6 h with the corresponding thiosulfate (i.e., 1–2 orders of magnitude longer). In addition, the final capacitance value is higher than that obtained with thiol, which indicates lower coverage and/or a lower degree of order within the SAM obtained from the Bunte salt. The capacitance remains relatively high in both cases which is attributed to the nonideal nature of the polished gold electrodes with many scratches, giving rise to a large number of defects in the SAMs.

The same conclusions can be drawn from the comparison of the adsorption measurements of mercaptoquinone (QSH) and the corresponding mono- and bithiosulfates QSSO_3K and $\text{Q}(\text{SSO}_3\text{K})_2$ (Figure 2b). In this case, the time dependence of the coverage of these redox-active compounds was determined by the charge under the redox waves of the surface-bound quinone. The coverage of mercaptoquinone reaches a constant value very rapidly after immersion in the adsorption solution. The saturation coverage of QSH on Au(111) has previously been reported to be achieved within 5 min from 1 mM aqueous solutions.⁵⁶ The obtained coverage (per real surface area) is 0.32 nmol/cm², in accordance with most of the coverages reported for this compound on single crystal or polycrystalline Au and Pt electrodes.^{56,57} On the other hand, the surface coverage of the corresponding monothiosulfate derivative $\text{Q}(\text{SSO}_3\text{K})$ displays a clear initial rise and levels off after ca. 100 min. It remains, however, at a markedly lower level compared to the coverage of mercaptoquinone (0.22 nmol/cm²). The same trend is even clearer with the bithiosulfate derivative. The coverage at short adsorption times (below 10 min) is very low, which implies a slower rate of adsorption already in the beginning. As with monothiosulfate, the adsorption rate levels off after ca. 20 min but a slow increase in surface concentration is observed at longer adsorption times.

Characterization of the Thiosulfate SAMs with Cyclic Voltammetry and Impedance Spectroscopy. The blocking efficiency of electrochemically inactive SAMs depends critically on the existence of defects (e.g., pinholes). Cyclic voltammetry of a reversible redox couple in solution is a convenient method to obtain information about the quality of the blocking monolayer.^{2d,58,59} Figure 3 shows the voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on bare, $\text{C}_{12}\text{-SH}$ -modified and $\text{C}_{12}\text{SSO}_3\text{Na}$ -modified gold electrodes. In view of the relatively high double-layer capacitances observed with the polished gold electrodes, these measurements were carried out using thermally evaporated gold electrodes. A reversible redox behavior with $E^0 = +0.235$ V versus SSCE was observed on a bare gold electrode whereas modification with 1-dodecylmercaptan lead to effective blocking of the faradaic process. Some variation was observed between the samples but all showed only a small increase of the current at high overpotentials, which indicates good, almost defect-free

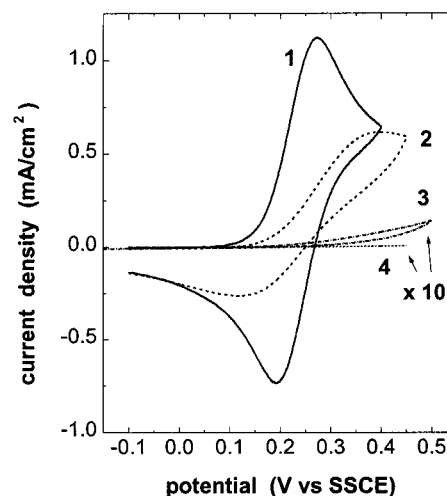


Figure 3. Cyclic voltammogram (100 mV/s) of a 5.0 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution in 1 M KCl. Bare Au-electrode (curve 1), Au-electrode modified with $\text{C}_{12}\text{SSO}_3\text{Na}$ (curve 2, slightly blocking SAM; curve 3, relatively well-blocking SAM), and Au-electrode modified with C_{12}SH (curve 4). Curves 3 and 4 multiplied by a factor of 10.

SAMs.⁶⁰ Interestingly, the electrodes modified with thiosulfate displayed greater variation in the blocking properties. In general, the data falls into two categories, representing slightly or relatively well-blocking SAMs (curves 2 and 3 in Figure 3, respectively). The latter showed only a small increase of the current at high overpotentials, indicating a low level of defects in these monolayers, too. The former, on the other hand, displayed a sigmoidal voltammogram typical of an ensemble of microelectrodes consisting of pinholes with partially overlapping diffusion profiles.⁶¹ The marked distortion of the voltammograms at a relatively slow sweep rate and the suppression of the maximum current imply that the pinholes are small and their separation large.⁶²

The best nondestructive electrochemical technique for the characterization of electroinactive SAMs is impedance spectroscopy.^{2d,32a,58,59} For the case with equal concentrations of the oxidized and reduced forms of a reversible redox couple in the solution, a simple Randles equivalent circuit has been shown to be generally applicable for aliphatic SAMs.^{58,59} It consists of a charge-transfer resistance, R_{ct} , in series with a Warburg impedance (Z_W) and parallel to a total interfacial capacitance C_{surface} . These are assumed to be in series with the uncompensated solution resistance R_s . The contribution from the diffuse layer capacitance to C_{surface} can be neglected in the concentrated electrolyte solutions used.⁶⁵ The advantage of using this simple description of the interface is that the circuit elements have a clear physical interpretation.⁶⁵ However, the behavior of the bare metal/solution interface is known to deviate from a pure capacitance and to be best described by a constant phase element (CPE).⁶⁶ The Nyquist plot obtained on the bare gold electrode displays mainly the Warburg impedance (Figure 4a). The data can

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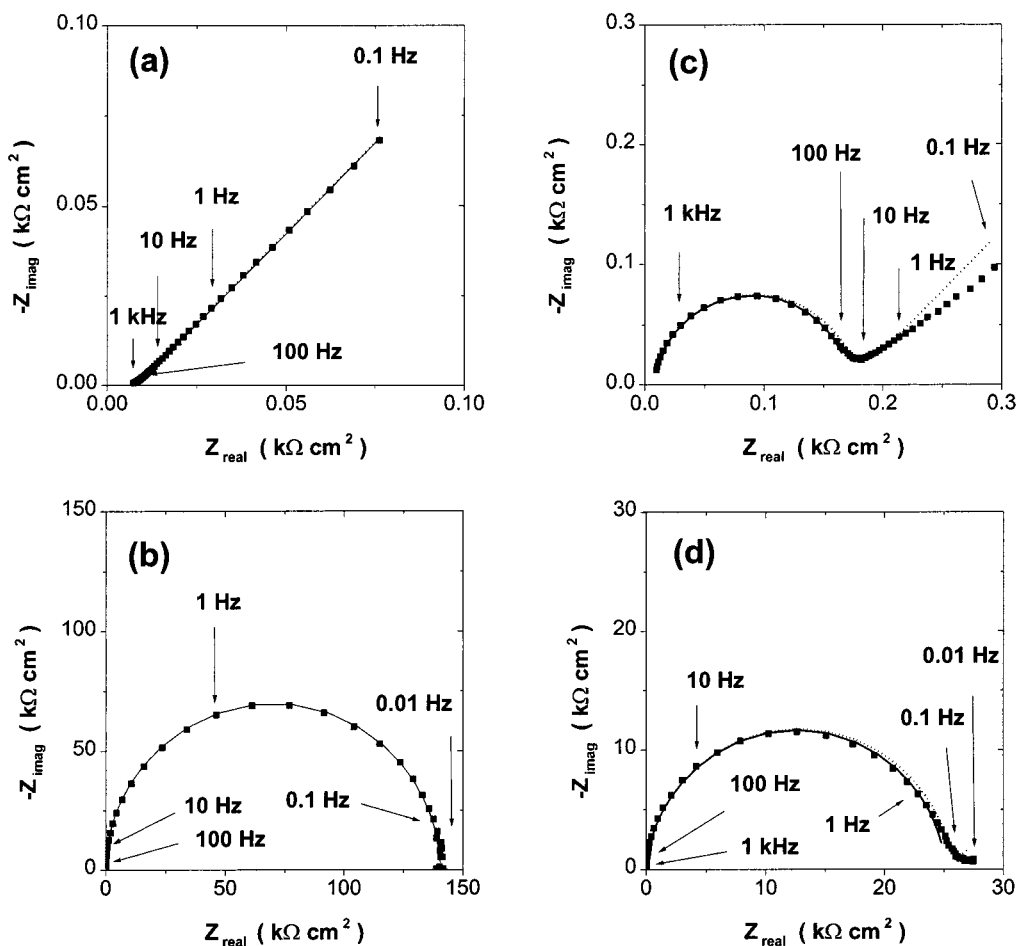


Figure 4. Impedance spectra measured in a 1 M KCl solution containing 2.5 mM $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ (10 mV amplitude). (a) Bare Au-electrode (solid line, modified Randles circuit; dotted line, R_s in series with Z_W), (b) $Au/C_{12}SH$ (Randles circuit), (c) slightly blocking $Au/C_{12}SSO_3Na$ (dotted line, modified Randles; solid line, medium-to-high-frequency fit without Z_W), and (d) relatively well-blocking $Au/C_{12}SSO_3Na$ (dotted and solid lines as those in Figure 4c).

be fitted with a modified Randles circuit, in which a CPE replaces the pure capacitance. However, practically equally good fit was obtained by a simpler equivalent circuit consisting of only Z_W and R_s in series. This indicates that the kinetics of the redox reaction are too fast on the metal surface to allow reliable extraction of kinetic data (i.e., R_{ct}). An estimated value of $70 \mu F/cm^2$ for the interfacial capacitance of bare gold electrode in a 1.0 M KCl solution (at +0.235 V vs SSCE) was determined by cyclic voltammetry. On the other hand, electrodes modified with 1-dodecylmercaptan show only a well-defined semicircle, in accordance with the voltammetric measurements which indicated that these electrodes are well-blocking (Figure 4b). Fitting the data to the Randles equivalent circuit yields a value of $1.5 \pm 0.2 \mu F/cm^2$ for the interfacial capacitance, in accordance with values reported for similar SAMs.^{55,67,68} The charge-transfer resistance, however, exhibits much greater variance between the samples, ranging from ca. $9 k\Omega cm^2$ for low-quality SAMs to ca. $280 k\Omega cm^2$ for practically defect-free monolayers. This shows that the interfacial capacitance is a much less sensitive probe for monolayer quality than the charge-transfer resistance. The latter is a measure of the accessibility of the redox-active molecules to the gold surface, and in a layer with few pinholes the closing of some of them results in a large proportional change in the accessibility. On the

other hand, capacitance probes the dielectric constant of the interfacial region, which depends on the permeability of water into the hydrocarbon layer with a low dielectric constant. Altering the number of pinholes results in negligible changes in the relative amount of water in the SAM and the capacitance remains practically constant.

As previously discussed, the monolayers prepared using *S*-dodecylthiosulfate exhibited greater variation in the blocking properties than the thiol-based SAMs. The two categories of the Bunte salt SAMs display quite different impedance behavior (Figure 4c,d). The layers that exhibited sigmoidal voltammograms showed both a semicircle and a linear part in the Nyquist plot. Data in the Warburg region showed a deviation from the theoretical slope of unity, a behavior that has been attributed to the nonuniform radii and spacing of the pinholes.^{2d,58} The semicircle part could be described better by the modified Randles circuit, which may be attributed to a more irregular film and a larger area of bare electrode surface exposed to the solution in these low-quality SAMs. With the relatively well-blocking films prepared from Bunte salt, the Warburg region was barely observed and the spectrum was dominated by a semicircle. In this case, also, the modified Randles circuit provided a better description of the spectrum. With both SAMs the circuit parameters adhering to the monolayer properties were determined in the medium-to-high-frequency range (i.e., in the range where the diffusion controlled Warburg behavior was not seen (solid lines in Figures 4c,d)). Using a CPE in the equivalent circuit, we loose, however, the

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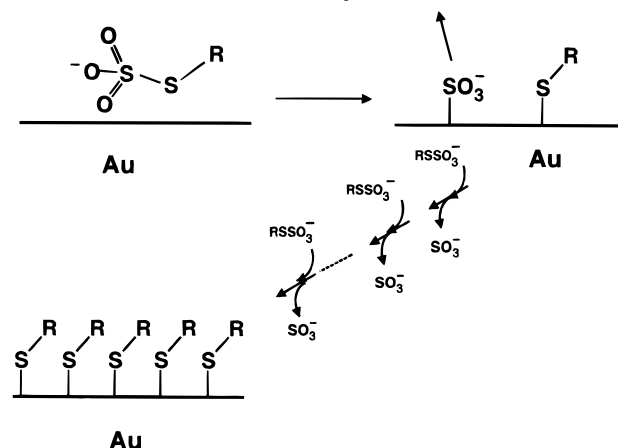
straightforward physical interpretation of the model parameters related to the "capacitive" behavior of the interface, although the CPE exponents are close to unity. The values for R_{ct} do not depend much on the model used, being ca. 150–160 $\Omega\text{ cm}^2$ and 20–30 $\text{k}\Omega\text{ cm}^2$ for the two types of Bunte salt SAMs (Figure 4, parts c and d, respectively). The former value is close to the charge-transfer resistance observed with some aromatic SAMs.^{32a}

The charge-transfer resistance of the relatively well-blocking SAMs prepared from Bunte salt is smaller than that obtained with the best quality monolayers prepared using dodecyl thiol, implying higher fractional pinhole coverage. The fractional area of pinholes in the SAMs, their radii, and their spacing can be estimated from the high-frequency behavior of the faradaic impedance data, obtained after subtraction of the components due to the solution uncompensated resistance and the interfacial capacitance (or CPE) from the total impedance.^{2d,32a,58,59} Additional information (average pinhole radius) can be obtained from the "knee" frequency in the real faradaic impedance. For the relatively well-blocking SAMs prepared from Bunte salts, the faradaic impedance yielded a fractional pinhole coverage of ca. $(1 - \Theta) = 0.00005$. The knee frequency gave the approximate pinhole diameter of ca. 3.0 μm . For well-blocking thiol SAMs the corresponding figures were ca. 0.00002 and 6.5 μm . These values allow us to estimate the average pinhole separation distances 200 and 1350 μm for these Bunte salt and thiol SAMs, respectively.^{2d} The pinhole diameters agree with the values observed on thiol-modified gold electrodes but the fractional pinhole coverages seem very small.^{58,59} However, the values obtained by the same method for different SAMs can reveal tendencies in the parameters, even though the actual values were not correct. Therefore, the results show that the pinhole density of the relatively well-blocking monolayers prepared from Bunte salts does not differ much from that of the thiol-based SAMs.

Mechanism of SAM Formation from Thiosulfates.

A central factor in the chemistry of organic thiosulfates is the elimination of the sulfite moiety in the molecule and this S–SO₃ bond cleavage can be effected by several factors.⁶⁹ The result of the heterolytic cleavage is a sulfite ion and the corresponding thiolate. XPS data show that sulfur–sulfur bond breakage takes place also upon adsorption of Bunte salts on the gold surface. Analogous bond cleavage and metal thiolate formation has been observed in the reaction between organic thiosulfates and mercuric salts. Therefore, the formation of a self-assembled monolayer from organic thiosulfates can be tentatively presented as a successive dissociative chemisorption of thiosulfate molecules and desorption of the sulfite moieties (Scheme 1). Both theoretical and experimental evidence indicate that oxidized sulfur species on a gold surface are only weakly bound and are easily displaced.⁷⁰ Sulfite at the surface will, therefore, desorb to the solution. A hypothetical follow-up reaction could be dimerization to form a soluble dithionate ion, S₂O₆²⁻. The detailed mechanism of chemisorption remains, however, somewhat unclear and, in general, the chemistry involved in the adsorption of organic thiosulfates on gold is more complex than in the chemisorption of thiols and disulfides. Our initial efforts to form monolayers from nondeaerated

Scheme 1. Chemisorption of Organic Thiosulfates on Gold and the Formation of a Self-Assembled Monolayer



solutions of Bunte salts were unsuccessful. This is not surprising because thiosulfate solutions containing an oxidant are known to effectively etch gold.⁷¹

The adsorption studies showed that the rate of adsorption of Bunte salts on gold is lower than that with the corresponding thiols, both in the beginning and close to the maximum coverage. The maximum coverage is smaller than that achieved with thiols, although the difference is very small with alkyl *S*-thiosulfates. These effects can be attributed to the chemical and steric properties of the thiosulfate headgroup. A recent study has shown that the chemisorption rate of disulfide, referenced to the number of thiolate units, is about 57% of the rate for a corresponding thiol.²² Steric effects due to the size of the molecule were excluded and the displacement of solvent molecules from the surface was suggested as the rate-determining step. This is easier for thiol than for disulfide because the latter requires two chemisorption sites on the surface. The thiosulfate headgroup is somewhat larger than the S–S moiety in disulfides. The chemical attack that leads to the elimination of the sulfite moiety generally takes place at the backside of the inner, dicoordinate sulfur.^{69a,72,73} Reaction of a surface gold atom with this sulfur, however, brings the SO₃⁻ group also in the close vicinity of the electrode surface and requires desorption of solvent molecules. If the solvent displacement is rate-determining, the adsorption of Bunte salts should take place ca. 70% (i.e., approximately 1 order of magnitude) slower than the corresponding thiols because only one thiolate unit per thiosulfate group is immobilized. As the exact mechanism of the S–SO₃ bond cleavage upon adsorption on gold is unknown, we do not know for certain whether the bond-breaking reaction itself can be rate-determining and slow the chemisorption process. However, bulky groups adjacent to the dicoordinate sulfur seem to decrease the reactivity of the thiosulfate moiety, which may contribute to the slow rate of adsorption of the aromatic thiosulfates studied.⁷²

Other factors also contribute to the lower surface coverage and the slow rate of adsorption, especially close to the maximum coverage. Adsorption of one molecule of thiosulfate creates one surface thiolate and leaves the adjacent site empty after desorption of the sulfite moiety. The steric effects play a minor role in the beginning of the

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adsorption when the film is in a disordered state, but close to the maximum coverage the adjacent surface-bound molecules present restrictions for the approach trajectory of the incoming thiosulfate molecule. Pinholes of molecular size cannot accommodate the *S*-dodecylthiosulfate molecule in such an orientation which would place the backside of the inner sulfur atom in close contact with the surface. Therefore, we believe that the attachment of new thiosulfate molecules takes place mainly within larger pinholes and at the edges of the densely packed domains. However, the surface mobility of the thiolate molecules, either at the domain edges or the diffusion of individual molecular vacancies within ordered domains, is probably rather slow at ambient temperature.^{2e,23,74} Desorption of the chemisorbed thiolates, on the other hand, takes place during self-assembly and this provides a mechanism for the film annealing.^{9,75} Interestingly, impedance data suggests that the thiol-based SAMs contained few large pinholes with a large spacing whereas the relatively well-blocking Bunte salt SAMs had more but smaller pinholes with a closer spacing. The mechanism of the chemisorption of the Bunte salts, in which one vacant site is produced for each thiolate formed, may explain this difference. In general, the as-formed SAMs tend to have relatively large pinholes distributed far from each other.⁵⁸ On the other hand, SAMs prepared from small aromatic molecules are considerably less densely packed because of the lack of intermolecular interactions.^{32a,56} The small free volume within the monolayer, taking into account the rotational freedom of the immobilized molecules, hampers the approach of the bulky thiosulfate group to the surface in the right orientation and restricts the maximum achievable surface coverage to a value lower than that with the smaller thiol derivative.

The SAMs prepared from $\text{Q}(\text{SSO}_3\text{K})_2$ differed from other monolayers derived from Bunte salts in that the XPS spectra showed the presence of mono- and bithiolates on the surface. Molecular mechanics modeling of both 3,6-dihydroxy-1,2-dimercaptobenzene and the corresponding bithiosulfate suggests that the sulfur atoms bonded to the ring are rigidly spaced approximately 3.2 Å apart, which is much less than the observed S–S spacing in alkanethiol SAMs on Au(111) or Au(100).⁷⁶ However, recent studies on the adsorption of two rigid dithiols on

Au(111) suggest that they attach to the surface via two thiolate bonds, although the exact bonding scheme is not known for certain.^{77,78} Therefore, the fraction of mono-thiolates (ca. 46%) is actually rather high. A tentative explanation may be that it becomes increasingly more difficult for both thiosulfate groups in $\text{Q}(\text{SSO}_3\text{K})_2$ to approach the surface close enough at the right angle as the surface coverage increases.

Conclusions

Organic thiosulfates, or Bunte salts, can easily be prepared as crystalline, odorless salts. Bunte salts constitute a new group of surface-active sulfur compounds, which can be used to prepare self-assembled monolayers on gold under anaerobic conditions. Upon adsorption from solution the S–SO₃ bond is broken and the molecule is chemisorbed on gold via a thiolate bond indistinguishable by XPS from the Au–S bond formed from thiols or disulfides. The rate of adsorption of organic thiosulfates is lower than that with thiols. However, it is possible to prepare relatively well-blocking SAMs from *S*-dodecylthiosulfate, although their quality is still inferior to that of the films prepared from 1-dodecylmercaptan and the adsorption of the Bunte salt is more irreproducible. With small aromatic molecules the attainable coverage remains lower than that with the corresponding thiols.

However, organic thiosulfates present a novel method to prepare self-assembled monolayers with a variety of chemical structures. Especially in cases where the coverage is not of prime importance (e.g., surface-attached redox- or photoactive molecules) the generally simple synthesis of Bunte salts offers a feasible method to introduce a sulfur-containing surface-active headgroup into these kinds of functional compounds, allowing their immobilization in SAMs for applications in the fields of sensor technology and molecular electronics. In addition, the easy cleavage of the sulfur–sulfur bond in organic thiosulfates by various agents may present a method for the in situ generation of the corresponding thiols or disulfides in cases where the maximum coverage is needed.

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