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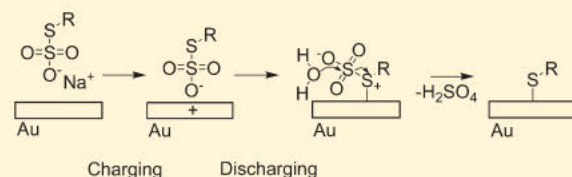
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Self-Assembly of Alkylthiosulfates on Gold: Role of Electrolyte and Trace Water in the Solvent

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ABSTRACT: Spontaneous self assembly of alkylthiosulfates on gold produce monolayers similar to the corresponding alkanethiols. Alkylthiosulfate self assembly from THF solutions is inhibited in the presence of tetrabutylammonium tetrafluoroborate electrolyte. The mechanism of alkylthiosulfate self assembly and the role of electrolyte and trace water in the solvent are investigated using open circuit potential measurements, contact angle goniometry and redox electron transfer blocking experiments to explore the hypothesis that trace water present in the solvent facilitates monolayer formation on gold. Furthermore, the unique behavior of tetrabutylammonium tetrafluoroborate, compared to other tetrabutylammonium electrolytes, on the inhibition of alkylthiosulfate self assembly has been explained.



INTRODUCTION

Self assembled monolayers (SAMs) provide a simple method to form highly ordered two dimensional organic assemblies.^{1–4} These monolayers have been used as prototypes for fundamental studies in the areas of tribology,⁵ surface patterning,⁶ bio and analytical sensors,^{7–9} and molecular electronics.^{10,11} Among the various self assembling systems, alkanethiolate monolayers on gold surfaces have received the greatest level of attention.⁴ Spontaneous self assembly of alkylthiosulfates (Bunte salts) on gold have been reported to form SAMs similar to that of alkanethiols and alkyldisulfides.¹² A novel method for the selective formation of SAMs on gold electrodes was reported using electrochemical oxidation of alkylthiosulfates under solution conditions where spontaneous self assembly is inhibited.¹³ In this particular system the monolayer formation depends on many factors including the applied potential, solvent, substrate, and electrolyte.^{14,15} Spontaneous chemisorption of alkylthiosulfates on gold was found to be inhibited by the presence of an electrolyte, tetrabutylammonium tetrafluoroborate (TBATFB), enabling electrochemically directed self assembly.¹³ This behavior was attributed to the tetrafluoroborate anion and was not observed with other tetrabutylammonium salts including tetrabutylammonium hexafluorophosphate and tetrabutylammonium perchlorate (TBAP).^{13,14}

The mechanism of alkylthiosulfate chemisorption on gold is not well understood. Lukkari and co workers reported that a heterolytic cleavage of the alkylthiosulfate molecule on gold surface, under anaerobic conditions, results in a sulfite ion and the corresponding alkylthiolate.¹² The XPS spectra for the SAMs of dodecylthiosulfate and dodecanethiol on gold were practically identical suggesting S–O₃ bond cleavage.¹² Shon and Murray reported that the monolayer protected clusters of gold prepared from dodecanethiol and dodecylthiosulfate, characterized by NMR, FTIR, and XPS techniques, were nearly indistinguishable.¹⁶ Alkylthiosulfates have also been used to form

passivating monolayers on copper surfaces.¹⁷ Impedance analysis on the alkylthiosulfate monolayers formed in toluene or water showed poorer passivation of the copper surface than those formed in THF or ethanol.¹⁷ The poor monolayer quality may be due to lower solubility of dodecylthiosulfate in water and toluene, compared to other solvents used. Recently, Ferguson and co workers have proposed that the spontaneous adsorption of monolayers on gold from solutions containing alkyl thiosulfates in organic solvents occurs via hydrolysis by trace water and that this process is inhibited in the presence of tetrafluoroborate ion by sequestration of that water in clusters with the ion.^{18,19} They have used contact angle measurements to study the kinetics of monolayer formation under various experimental conditions, further exploring the alkylthiosulfate adsorption process. It was concluded that alkylthiosulfate self assembly on gold involves alkanethiol or disulfide intermediates formed from the hydrolysis of alkylthiosulfates.¹⁸ However, contact angle measurements are limited in the amount of information regarding the mechanism of alkylthiosulfate self assembly, particularly with regard to charge transfer steps involved with the adsorption process.

The work presented herein further investigates the role of solvent and electrolyte on alkylthiosulfate self assembly and the charge transfer process associated with the monolayer formation. Open circuit potential (OCP) measurements are used to study charge transfer steps associated with the alkylthiosulfate adsorption on gold. The quality of SAMs was determined by contact angle measurements and redox electron transfer blocking experiments. Contact angle goniometry provides valuable information regarding the wetting properties of the monolayers. For example, a well ordered monolayer of alkanethiols or alkylthiosulfates on

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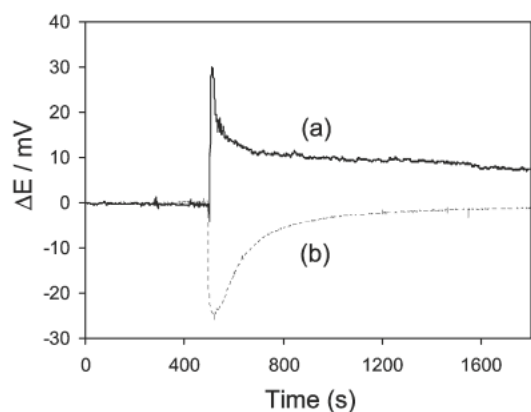


Figure 1. OCP vs time response of a gold electrode in THF (no electrolyte) upon the addition of (a) dodecylthiosulfate and (b) dodecanethiol.

gold gives hexadecane advancing contact angles (θ_a) close to $44\text{--}46^\circ$ and the θ_a values will be less than 10° when no monolayer is formed.^{12,14} Electron transfer blocking experiments using redox probes (e.g., ferricyanide/ferrocyanide couple) are an indirect means for monitoring adsorption and surface passivation.^{20,21} In cases where adsorption results in a passivating layer, electron transfer between the electrode surface and the redox species in solution will be attenuated. This is a common technique used for characterizing monolayer formation and their quality since the presence of disorder or pinholes will result in a measurable redox current from solution species.²⁰ The results are compared to SAMs formed from the corresponding alkanethiol. The role of electrolyte on the inhibition of alkylthiosulfate self assembly has also been discussed. Determining the role of TBATFB on the inhibition of alkylthiosulfate monolayer formation is important for extending this selective self assembly technique to other systems. Furthermore, a better understanding of the self assembly of alkylthiosulfate on gold surface is necessary for their applications in molecular electronics and sensors.

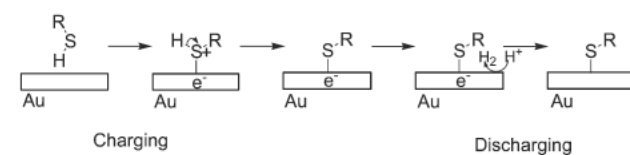
EXPERIMENTAL SECTION

Materials. High purity grade solvents and electrolytes were used for electrochemical and surface characterization studies. Tetrabutylammonium tetrafluoroborate (Aldrich, $\geq 99\%$), tetrabutylammonium perchlorate (Fluka, $\geq 99\%$), tetrahydrofuran (THF, Aldrich or Fisher Scientific, $\geq 99.9\%$), potassium ferrocyanide (Aldrich, $\geq 99.5\%$), 1 hexadecanethiol (Aldrich, $\geq 92\%$), 1 dodecanethiol (Aldrich, $\geq 98\%$), hexadecane (Aldrich, $\geq 99\%$), 1 bromohexadecane (Aldrich, $\geq 97\%$), and 1 bromododecane (Aldrich, $\geq 96\%$) were used as received. All of the water (resistivity $\geq 18.2\text{ M}\Omega\text{ cm}^{-1}$) used in this work was purified with a Millipore Milli Q water purifier system.

Synthesis of Alkylthiosulfates. Sodium salts of alkylthiosulfates (Bunte Salts), $\text{CH}_3(\text{CH}_2)_n\text{S}_2\text{O}_3\text{Na}$ ($n = 11, 13, 15$) were synthesized by the previously reported procedure.¹⁴ For example, 1 bromododecane (5 mmol) dissolved in 20 mL of ethanol was added to a solution of sodium thiosulfate (5 mmol) in 20 mL of water, and the mixture was brought to reflux until the solution become homogeneous. The solution was then cooled and filtered. The precipitated Bunte salt was recrystallized twice from absolute alcohol. The white crystals of Bunte salts were dried and stored at -20°C .

^1H NMR (300 MHz, $\text{MeOH-}d_4$, δ , ppm): $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{CH}_2\text{S}_2\text{O}_3\text{Na}$, 0.86 (t, 3H, $3J = 6.9\text{ Hz}$, CH_3), 1.26–1.46 (m, 18H, $(\text{CH}_2)_9$), 1.70 (m, 2H, CH_2), 3.02 (t, 2H, $3J = 7.5\text{ Hz}$, $\text{CH}_2\text{S}_2\text{O}_3\text{Na}$);

Scheme 1. Proposed Mechanism for Alkanethiol²² Adsorption on Gold Surface



$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{CH}_2\text{S}_2\text{O}_3\text{Na}$, 0.86 (t, 3H, $3J = 7.0\text{ Hz}$, CH_3), 1.26–1.46 (m, 18H, $(\text{CH}_2)_9$), 1.69 (m, 2H, CH_2), 3.02 (t, 2H, $3J = 7.4\text{ Hz}$, $\text{CH}_2\text{S}_2\text{O}_3\text{Na}$); $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{CH}_2\text{S}_2\text{O}_3\text{Na}$, 0.86 (t, 3H, $3J = 6.9\text{ Hz}$, CH_3), 1.26–1.46 (m, 26H, $(\text{CH}_2)_9$), 1.70 (m, 2H, CH_2); 3.03 (t, 2H, $3J = 7.4\text{ Hz}$, $\text{CH}_2\text{S}_2\text{O}_3\text{Na}$).

Electrochemistry. Electrochemical experiments were carried out using a Bioanalytical Systems BAS 100B potentiostat or CH Instrument electrochemical workstation (CHI 760C) with a conventional three electrode configuration. Working electrodes were gold disk electrodes (CH Instruments, CHI 101) or gold ($\sim 200\text{ nm}$ thick) sputtered on glass having a thin adhesion layer of titanium ($\sim 20\text{ nm}$ thick). A platinum wire is used as the counter electrode. The potentials for all the experiments in nonaqueous solvents are referred to Ag/Ag^+ reference electrode (3 mM Ag/AgNO_3 , 0.1 M TBATFB in acetonitrile), unless otherwise specified.

The gold disk electrodes were polished with alumina suspensions (MicroPolish, Buehler) of different particle size in the order 1.0, 0.3, and $0.05\text{ }\mu\text{m}$ and rinsed with water. The polished gold disk electrodes were then exposed to "piranha" solution (3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2) [CAUTION: Piranha solution reacts violently with most organic materials and should be handled with extreme care] for less than a minute, washed with Millipore water, and dried in nitrogen.

Redox electron transfer blocking experiments were carried out using aqueous potassium hexacyanoferrate solution (3 mM) with 0.1 M potassium chloride. The solutions were purged for at least 15 min with high purity nitrogen prior to their use in voltammetry experiments. The potentials were referred to an aqueous reference electrode (Ag/AgCl with saturated KCl).

Open circuit potential (OCP) measurements were performed at 1 s intervals with Agilent 34970A Data Acquisition unit controlled by a PC using BenchLink data logger software or CH Instrument electrochemical workstation (CHI 760c). Prior to OCP measurements, the solutions were filtered thorough an inorganic membrane filter (Whatman Anotop 25, $0.02\text{ }\mu\text{m}$) to remove any fine particles. The nitrogen purged solutions were kept in a closed glass vial and gently stirred with a micro stirrer bar throughout the experiment. For all OCP measurements, the concentration of the organosulfur compound in the final solutions was approximately 10 mM.

Contact Angle Measurements. Advancing hexadecane contact angles were measured with Rame Hart NRL model 100 goniometer. The measurements were performed on sputter deposited gold electrodes ($\sim 200\text{ nm}$ thick) on glass with titanium adhesion layer (20 nm thick) having a dimension of $1\text{ cm} \times 2.5\text{ cm}$ each. A minimum of five measurements on three independent drops were made for each sample.

RESULTS AND DISCUSSION

Mechanism of Alkylthiosulfate Self-Assembly on Gold. The mechanism of charge transfer processes accompanying alkanethiol adsorption on gold surface has been explored through *in situ* OCP measurements.^{22–25} The results suggest an electrochemical charge transfer step associated with the adsorption of alkanethiols and dialkyl disulfides on gold.²⁵ A negative shift in the OCP upon the addition of alkanethiol

Scheme 2. Proposed Mechanism for Alkylthiosulfate Adsorption on Gold Surface

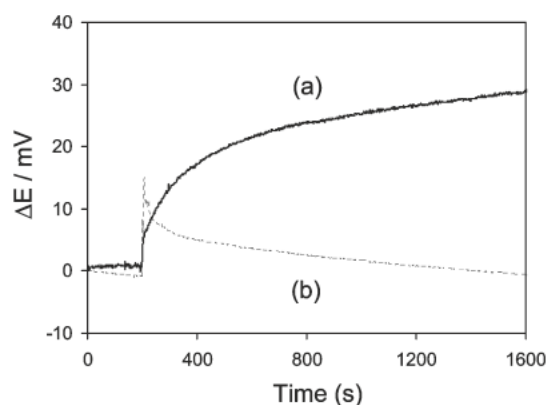


Figure 2. OCP vs time response of a gold electrode in THF containing 0.1 M (a) TBATFB and (b) TBAP after the addition of dodecylthiosulfate.

(Figure 1) is consistent with the charge transfer from thiol to gold, leading to Au–S bond formation.^{22,25} In presence of a protic solvent or oxygen, the negative shift in the OCP is followed by a gradual positive shift due to discharging of the negative charge on gold (Scheme 1).²²

The change in OCP of a bare gold electrode in THF upon the addition of sodium dodecylthiosulfate and dodecanethiol is shown in Figure 1. The initial negative shift in the OCP with the addition of dodecanethiol is in agreement with previous studies.^{22,25} The residual negative charge on the gold electrode can be discharged in the presence of any oxidizing agents (e.g., oxygen or proton) present in the solution.^{22,23} Here we propose a similar mechanism for alkylthiosulfates adsorption on gold (Scheme 2) since they form monolayers similar to the corresponding alkanethiols. According to this mechanism a positive shift in OCP is expected due to the polarization of gold electrode by alkylthiosulfate anion. A negative shift in OCP is expected when discharging of the electrode takes place after alkylthiosulfate adsorption. A sudden positive shift in the OCP of the gold electrode followed by a gradual return of the potential in the negative direction is observed after the addition of dodecylthiosulfate. The positive shift in OCP is consistent with changes observed upon the addition of sodium dodecylsulfate (SDS) surfactant on gold.²⁶ In the case of dodecylthiosulfate or dodecylsulfate, the anion generates a positive image charge on the gold surface that results in a positive shift in the OCP. The gradual return of the OCP in the negative direction is consistent with the discharging mechanism, shown in Scheme 2.

In presence of TBATFB and TBAP electrolytes, the change in OCP of a gold electrode after the addition of alkylthiosulfates show significant differences (Figure 2). The OCP change in presence of TBAP is similar to that in Figure 1 where a sudden

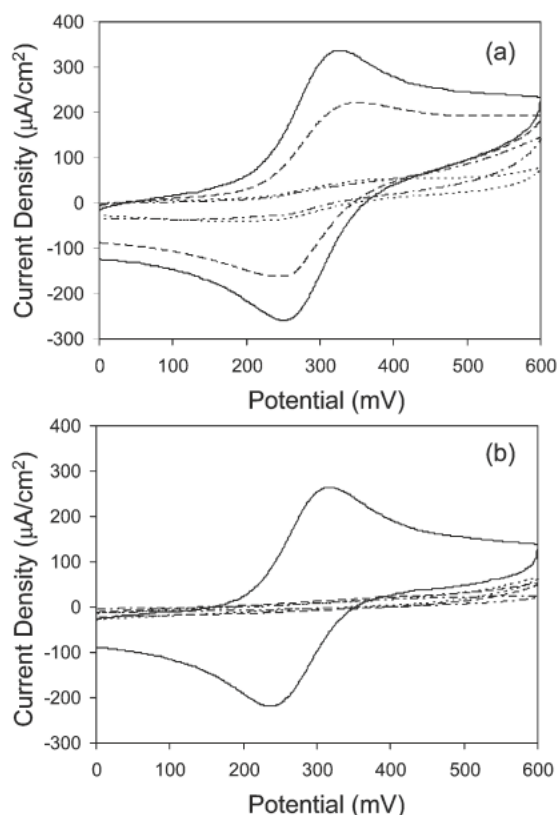


Figure 3. Cyclic voltammograms (1.0 mM $K_4Fe(CN)_6$, 0.1 M KCl, scan rate 100 mV s^{-1} ; saturated Ag/AgCl reference electrode) of gold electrode before and after modification (30 min) with 10 mM (a) sodium dodecylthiosulfate and (b) dodecanethiol in THF in the absence and presence of electrolytes: (—) bare electrode, (---) TBATFB, (···) TBAP, and (· ·) no electrolyte.

positive shift in the potential is observed followed by a gradual negative shift, presumably due to Au–S bond formation (Scheme 2). However, in the presence of TBATFB, the discharging of the electrode is not observed after the addition of thiosulfate. The absence of a negative shift in OCP shows that the Au–S bond formation process is either not occurring or is very slow.

Role of Electrolyte. Inhibition of alkylthiosulfate self assembly by the electrolyte, TBATFB, has been previously reported.^{13–15,18} However, other tetrabutylammonium salts including tetrabutylammonium hexafluorophosphate and TBAP do not exhibit this behavior.^{13,14} For example, a comparison of the effect of TBATFB and TBAP electrolyte on alkylthiosulfate self assembly has been explored by electron transfer blocking experiments using ferricyanide/ferrocyanide redox couple, as shown in Figure 3. Spontaneous adsorption of dodecylthiosulfate on gold electrode from THF in the presence of TBATFB for 30 min yields only partial monolayer formation (Figure 3a). Dodecylthiosulfate adsorption shows less passivation than that of dodecanethiol on gold, possibly due to the slow rate of monolayer formation of alkylthiosulfate compared to thiol.¹² Consistent with the previous reports,^{13,14} adsorption of dodecanethiol on gold was found to be unaffected by the presence of electrolytes (Figure 3b).

Since alkylthiosulfates, not thiols, adsorption is preferentially inhibited; the electrolyte may be interfering with any of the adsorption steps mentioned in Scheme 2. Therefore, it has been hypothesized that the inhibition of alkylthiosulfate self assembly

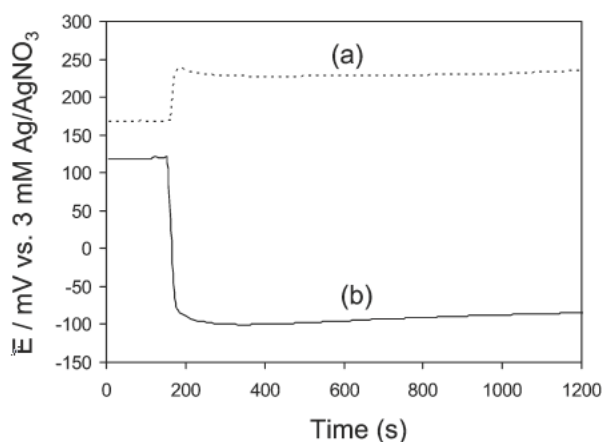


Figure 4. OCP vs time response of a gold electrode in THF upon the addition of (a) TBAP and (b) TBATFB electrolytes.

by TBATFB may be due to one or more of the following; (a) physical blocking, (b) electrostatic repulsions, and (c) trace water in the solvent. Considering the surface passivation of gold in the presence of alkylthiosulfates and TBAP, the physical blocking of the electrode by electrolyte adsorption can be ruled out. Figure 4 shows the OCP shift of a gold electrode in THF upon the addition of two tetrabutylammonium electrolytes having different anionic species. The gold electrode becomes positively polarized after the addition of TBAP whereas a negative polarization of the electrode observed with the addition of TBATFB. This excess negative charge on the electrode may electrostatically repel the incoming alkylthiosulfate anion and prevent monolayer formation. Inhibition of monolayer formation is also expected on gold electrodes kept in THF and TBAP at negative potentials equivalent to the OCP of gold electrode in presence of TBATFB. To test this hypothesis, a clean gold electrode was kept in THF with 10 mM dodecylthiosulfate and 0.1 M TBAP for 30 min at -0.3 V. After 30 min, the electrode was taken out, washed with THF and water. The electron transfer blocking experiment in ferricyanide/ferrocyanide solution shows passivation of the electrode due to monolayer formation. Therefore, electrostatic interactions may not play a significant role in preventing alkylthiosulfate monolayer formation on gold in presence of TBATFB.

Role of Trace Water in the Solvent. The reactions involving alkylthiosulfate and water have been previously reported.²⁷ For example, hydrolysis of alkylthiosulfates give their corresponding thiols and the reaction is catalyzed by dilute acids, bases or heat.^{27,28} The SAM formation in anhydrous conditions was performed inside a nitrogen filled glovebox where water and oxygen concentrations were less than 20 ppm (0.002%). Table 1 shows the advancing hexadecane contact angle on hexadecylthiosulfate SAMs formed under ambient and anhydrous solvent (THF) conditions. Self assembly was not observed for alkylthiosulfates in THF except in the case where a trace amount of water was present and TBATFB was absent. In contrast, a good monolayer (hexadecane, $\theta_a = \sim 44^\circ$) was observed in the spontaneous self assembly of alkanethiols under the conditions mentioned in Table 1. These results indicate that water plays a critical role in the spontaneous self assembly process. The addition of hygroscopic TBATFB apparently mitigates the presence of trace water in the solvent (THF), otherwise available for alkylthiosulfate

Table 1. Advancing Hexadecane Contact Angle (θ_a)^a on a Gold Electrode Treated with 10 mM Hexadecylthiosulfate in THF for 30 min under Different Conditions

	ordinary THF ($>0.02\%$ water)	anhydrous THF ($<0.002\%$ water)
without TBATFB	44.2 ± 0.6	17.4 ± 1.8
with TBATFB	14.8 ± 1.9	<10

^a Contact angles are mean values \pm standard deviations based on three measurements.

self assembly, possibly due to the formation of stable tetrafluoroborate water clusters.^{19,29}

Tetraalkylammonium salts are reported to form stable water clusters that contain at least three molecules of water.²⁹ These clusters can be neutral or double ionic and are stabilized by hydrogen bonding. The clusters of tetrabutylammonium salts and water can be represented as $(C_4H_9)_3N \cdots (C_4H_9)A \cdots (H_2O)_3$ (neutral) and $(C_4H_9)_4N^+ \cdots (H_2O)_3 \cdots A^-$ (double ionic), where A^- represents the counterion.²⁹ The stability of these clusters largely depends on the nature of the counterion. For example, the double ionic cluster of tetrabutylammonium tetrafluoroborate is more stable than tetrabutylammonium perchlorate.²⁹ Also, the presence of a polar aprotic solvent like THF may stabilize these double ionic clusters. This additional stability of the tetrafluoroborate water clusters may explain inhibition of alkylthiosulfate self assembly in presence of tetrafluoroborate and not in the presence of perchlorate.

The role of trace water in the solvent on alkylthiosulfate self assembly is further explored using electron transfer blocking experiments with ferricyanide/ferrocyanide redox couple. SAMs were formed on clean gold electrodes kept in solutions containing 10 mM dodecylthiosulfate and 0.1 M TBATFB in anhydrous grade THF with varying water content. After 30 min, electrodes were taken out, washed with THF and water. Then electron transfer blocking experiments were performed in a deaerated solution of 3 mM $K_4[Fe(CN)_6]$ aqueous solution with 0.1 M KCl. Figure 5 shows the variation of oxidation peak current is plotted as a function of added water to THF. The surface passivation of the electrode found to increase with the amount of water present in the solution and shows a maximum at 0.3 M water added to THF. At this concentration (0.3 M), the TBATFB (0.1 M) present in the solvent may be saturated with water due to the formation of clusters with three water molecules per TBATFB, and the water already present in the anhydrous solvent (0.001 M) becomes available for the monolayer formation of alkylthiosulfate on gold. Solutions having more than 0.3 M water show a decrease in surface passivation due to poor solubility of alkylthiosulfates in presence of excess water. These results are also in agreement with the previous reports that inhibition of alkylthiosulfate self assembly shows TBATFB concentration dependence.¹⁴

Figure 6 shows the effect of added water on the OCP change for gold electrode in THF solution with 10 mM dodecylthiosulfate and 0.1 M TBATFB. In the presence of 0.3 M water, the discharging of the electrode is observed after dodecylthiosulfate addition. Similar discharging of the electrode was observed after dodecylthiosulfate addition either in the absence of electrolyte (Figure 1) or in presence of TBAP (Figure 2), where a good monolayer is formed. The excess water available for alkylthiosulfate self assembly may facilitate the dissociation of S—S bond and hence the discharging of the electrode as shown in Scheme 3.

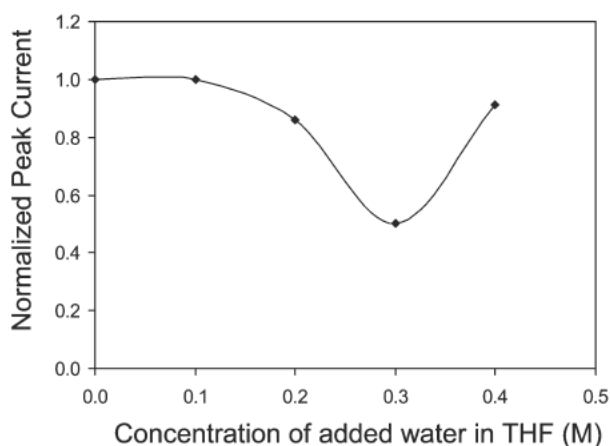


Figure 5. Variation of ferrocyanide/ferricyanide oxidation peak current for gold electrodes kept in anhydrous THF solution (30 min) containing 10 mM dodecylthiosulfate and 0.1 M TBATFB with varying water content. The peak currents are normalized with that of bare gold electrode.

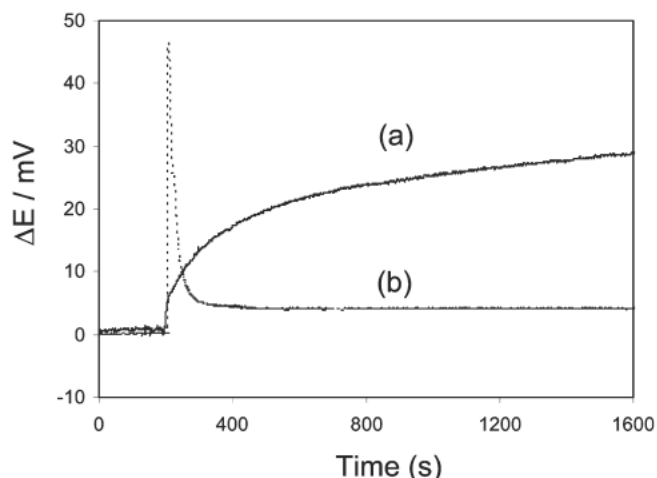
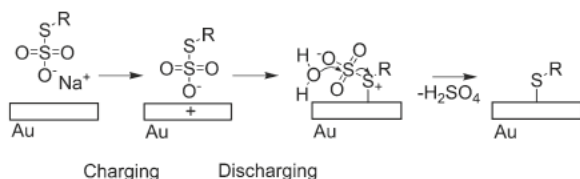


Figure 6. OCP vs time response of a gold electrode after the addition of dodecylthiosulfate to a solution of 0.1 M TBATFB and (a) THF and (b) THF with 0.3 M water.

Scheme 3. Proposed Mechanism for Alkylthiosulfate Adsorption on a Gold Surface in the Presence of Trace Water Present in the Solvent



CONCLUSIONS

Spontaneous self assembly of alkylthiosulfates on gold surfaces is influenced by electrolyte and solvent. The redox electron transfer blocking, OCP and contact angle experiments show that alkylthiosulfate self assembly on gold from THF is inhibited by

TBATFB, however alkanethiol adsorption is independent of the presence of electrolytes. Alkylthiosulfate adsorption on gold is facilitated by trace water present in the solvent. In the presence of TBATFB, alkylthiosulfate self assembly is inhibited since the electrolyte sequesters trace water in the solvent, otherwise available for alkylthiosulfate monolayer formation, by forming stable TBATFB–water clusters. A mechanism for alkylthiosulfate self assembly under these conditions has been proposed. The results of our studies are consistent with Ferguson's proposed mechanism for the spontaneous adsorption of monolayers from solutions of alkyl thiosulfates and inhibition of that process by BF_4^- . These results are particularly important since they conclude that solvent must be sufficiently dry to get good selectivity in monolayer formation by electrochemically directed self assembly.

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