

Adsorption of self-assembling sulfur compounds through electrochemical reactions: Effects of potential, acid and oxidizing agents

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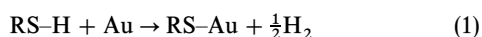
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Received 30th January 2001, Accepted 18th April 2001
First published as an Advance Article on the web 30th May 2001

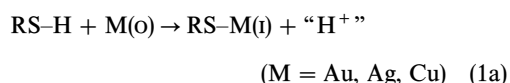
Adsorption of organosulfur compounds forming self-assembled monolayers (SAM) on gold was studied to examine the effects of the electrical potential, added redox couple and acidity of the solution on the rate and extent of adsorption. Also, by comparing behavior of the open-circuit potentials of platinum to those of gold and silver substrates, it was confirmed that no electrochemical reaction takes place for chemisorption of the organic sulfur compounds on a Pt surface whereas anodic (in the case of thiols) or cathodic (in the case of dialkyl disulfides) reactions occur during adsorption on gold and silver. From an acid solution, the oxidative adsorption of a thiol was retarded, whereas the reductive-dissociative adsorption of a disulfide was facilitated. Added ferrocene-ferrocenium redox couple enhanced adsorption of the thiol by maintaining the potential of the substrate high, thus providing a convenient way to help the formation of adsorbed layers.

Introduction

Adsorption of organosulfur compounds on gold and silver has been found to be an easy route to forming self-assembled monolayers (SAM). Despite the wide interest in recent years in the structure and applications of SAMs,^{1–6} and despite the fact that a SAM can be prepared relatively easily by simply dipping the substrate in solutions containing the adsorbate, the detailed reactions involved in the adsorption have not been well understood. From numerous studies, by X-ray photoelectron spectroscopy (XPS),⁷ Raman spectroscopy^{8–10} and FT-mass spectrometry coupled with laser desorption,¹¹ on SAMs formed from thiols, the adsorbed species were revealed to be thiolates without the hydrogen atom originally attached to the sulfur atom. However, the fate of the hydrogen atom and the process of loss of the hydrogen atom were not clear. The prevalently presumed adsorption reactions of thiols (RSH) and disulfides (RSSR') have been chemical bond-breaking and bond-making without electron transfer at the interface.^{2,3,6,7,12}



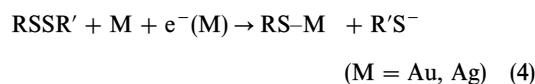
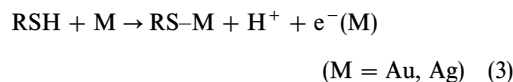
The following reaction was also hinted at as an alternative mechanism of adsorption of thiols on a metal (M):⁷



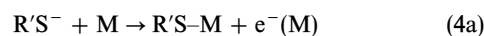
However, there have been reports indicating possible electron transport involved in the adsorption step. Reversible cathodic desorption of the thiolates and sulfur-containing amino acids at extremely negative potentials were reported by

many groups.^{12–17} Formation of SAMs from thiols on a gold substrate held at positive potentials was found to be fast and to yield SAMs of better structure.^{18–20}

In our previous studies^{21–23} we demonstrated that the adsorption steps for thiols and organic disulfides on gold and silver involve electrochemical electron transfer steps: Thiol molecules adsorb on Au and Ag through an anodic reaction, whereas dialkyl disulfides adsorb by a reaction that gives a net cathodic current.



followed by



We also demonstrated that the adsorption rates of thiols and disulfides are strongly influenced by the electrical potential of the metals with respect to the solution containing the adsorbate species, as would be expected from the above electrochemical reaction schemes. The adsorption of thiols was facilitated by maintaining the potential of the substrate metal near or above the usual open-circuit potential, or by the presence of dissolved oxygen in the solution when there was no potential control. Formation of the thiolate layer from adsorption of a dialkyl disulfide was found to be favored at lower potentials. Due to the lack of realization of the importance of potential of the substrate metal during the adsorption stage, control of potential has often been neglected in the preparation of SAMs and in the kinetic studies of SAM formation, thus making consistent results difficult to obtain.

In view of the above reaction mechanisms involved in the adsorption, it is expected that the adsorption of organosulfur compounds might be influenced by the pH of the solution and

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also by the presence of a redox couple in the solution. Examinations of such influence will not only provide further insight into the adsorption process, but will also provide better means of preparing SAMs. In this paper we report results of experimental studies on the influences of added oxidant and acid on the adsorption of the SAM-forming organosulfur compounds on metals. This study also revealed, through examination of the potential behavior of Pt as compared to Au and Ag, that platinum is markedly different from gold and silver as a substrate.

Experimental

Electrochemical and quartz crystal microgravimetric (QCM) measurements were made for the adsorption of thiols and dialkyl disulfides on metals. The electrochemical measurements included recording of the open-circuit potential of the substrate metals while the organosulfur molecules were injected into solutions in contact with the substrate, and recording of the current when the potential was fixed. Au was the substrate metal studied primarily, platinum was also included in the study for comparison.

Dilute LiClO_4 , or HClO_4 solutions in organic solvents, mostly acetonitrile and water-ethanol mixture, were used. The cells were equipped with a Pt counter electrode and a reference electrode. The reference electrode was Ag/AgCl in 3 M NaCl, separated from the rest of the cell by a tube with a capillary ending. The potential values presented throughout this paper refer to this reference electrode. A digitally controlled potentiostat was used for potential control or for recording of the open-circuit potential. Acetonitrile used as solvent was purified before use by distillation. Absolute ethanol was used without further purification. Reagent grade lithium perchlorate (99.99%) from Aldrich and perchloric acid (99.9%) from Duksan Chemical were used as the electrolyte without purification. Thiols and dialkyl disulfides of the highest purity grade from Aldrich were dispensed from a micropipette to attain the desired concentration of the resulting solution, mostly 1 mM.

Gold-coated quartz crystal oscillator electrodes supplied by International Crystal Manufacturing or by Elchema were used for the electrochemical quartz crystal microbalance (EQCM) experiments. In EQCM, one of the exciting oscillator electrodes of the quartz crystal was plated with gold and served also as the working electrode of the electrochemical cell. The increase in the mass on the Au substrate due to adsorption was monitored by detecting the decrease in the resonant oscillating frequency of the quartz crystal, which is related to the mass change according to the Sauerbrey equation.^{24,25} The electrochemical quartz crystal microbalance from Elchema in combination with an Au-plated 10-MHz quartz crystal oscillator electrode had 1 Hz resolution and gave $4.42 \text{ ng cm}^{-2} \text{ Hz}^{-1}$ sensitivity. Thus the measurement limit in the mass change was a few ng.

Besides the QCM crystal electrodes, pieces of platinum and gold wire or a gold flag (all of 99.99% purity) were used as the substrate electrodes. The electrode surfaces were pre-cleaned by immersing in "piranha solution" (H_2O_2 - H_2SO_4 1:3 mixture) and by repeatedly scanning the potential between the hydrogen evolution and the oxygen evolution regions in dilute sulfuric acid. For most of the experiments the solutions were deaerated with purified (99.999%) nitrogen to avoid interference from oxygen. Bubbling nitrogen through the solution and forcing a jet stream of nitrogen along the surface of the solution also helped to homogenize the solution when the adsorbate was injected. Ferrocene from Aldrich (98%) was found to contain enough oxidized component (ferrocenium ion) to register an equilibrium potential of 0.21 V, and was used as such, as a redox couple.

Results and discussion

Comparison of Pt with Au and Ag

Sudden shifts of the electrical potential of the gold substrate on contact with organosulfur compounds in solutions were the first direct indication of electrochemical reactions involved in the adsorption of the compounds observed in the previous studies.²¹ In the present study we compared the potential behavior of platinum, to those of gold and silver under open-circuit condition in 0.1 M LiClO_4 acetonitrile solution into which a small amount of decanethiol or dipropyl disulfide was injected. Fig. 1 shows the results obtained with Pt electrodes. In the same figure the potential shift of a gold electrode with injection of thiol is also shown for comparison. Whereas there were clearly large sudden negative shifts in the potentials of gold (shown) and silver²³ (not shown) on injection of thiol, the potential change of the platinum electrode was only meagre and slow.

Gold and silver are well known to adsorb thiols strongly and they produced anodic current peaks when the potential was fixed at the time of injection of the adsorbate molecules whereas platinum did not produce a significant current peak, as reported in our previous papers.²¹⁻²³ Platinum does not seem to interact so readily as gold and silver with the sulfur compound through an electrochemical reaction such as reaction scheme (3) for chemisorption. A small change in the potential of a metal in the open-circuit condition can occur without a reaction with the adsorbate because the potential in the open-circuit condition is determined by minute reactions at the interface of various minor components such as trace oxygen, hydronium ions, *etc.* Such spurious reactions are influenced by surface contamination by sulfur compounds. Thus, we can conclude that either thiols do not chemisorb on platinum or any chemisorption that may occur is extremely slow.

In Fig. 1 the potential behavior of Pt on injection of dipropyl disulfide is also shown. The potentials of gold and silver were shown in the previous study to shift rapidly to the positive direction with adsorption from disulfide solution, indicating a cathodic reaction according to scheme (4). The subsequent anodic reaction (4a) will contribute less to the potential changes of Au and Ag because it is only a minor reaction, part of the R^+S^- ions being removed from the interface region into the bulk of solution.

Although the large positive potential jumps of gold and silver under the same condition are not shown here, it can be

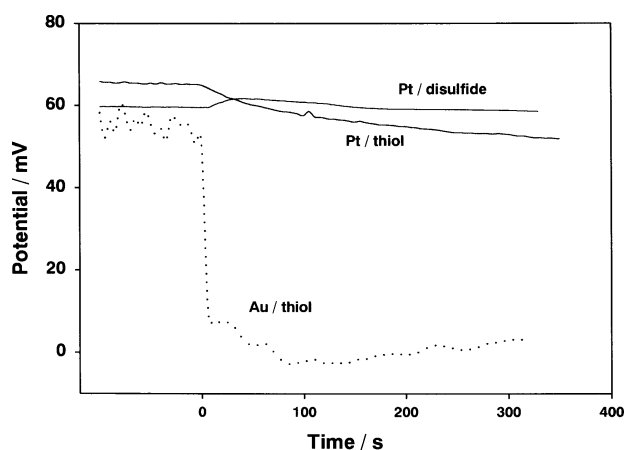


Fig. 1 Changes in open-circuit potential of platinum after introduction of decanethiol or dipropyl disulfide to 1 mM concentration into an acetonitrile solution of 0.1 M LiClO_4 . The change in open-circuit potential of gold with injected decanethiol is also shown for comparison.

clearly seen that the change in Pt potential here is almost indiscernible, in marked difference to gold and silver. Platinum has been shown to produce no current peak at a fixed potential with either thiol or disulfide, in contrast to gold and silver.^{21–23} Platinum evidently does not undergo electrochemical reactions resulting in chemisorption at an appreciable rate with either thiols or disulfides. Although thiol molecules are known to adsorb on a platinum surface, the adsorption was reported to be slow (5 h for 11-ferrocenyl-1-undecanethiol) and the resulting SAM was loosely packed and unstable.²⁶ The difficulty of adsorption of sulfur compounds on Pt can be viewed as a consequence of the electrochemical reaction mechanism, because Pt is a difficult metal to oxidize. It should be noted that in either reaction (3) or (4) the surface metal M(0) is oxidized to M(I) to bond with the sulfur atom. In the case of thiols (reaction (3)) the oxidation state of sulfur does not change whereas in the case of disulfides (reaction (4)) the two sulfur atoms undergo 2-electron reduction.

Potential scan and potential jump

To test further the potential dependence of adsorption of thiols on gold, the potential of a QCM-gold electrode was linearly swept from about -1100 to $+1200$ mV at a scan rate of 10 mV s^{-1} . The result is shown in Fig. 2, which shows the increase in mass on the gold surface calculated from the frequency decrease of the quartz crystal as the potential was scanned. From the very negative potential, where no adsorption is expected, up to about -800 mV no significant increase in mass was found. The mass increased rapidly as the potential was swept above -700 mV until about 0 V, after which the mass showed saturation. The total mass increase up to the saturation level was 132 ng cm^{-2} of the real gold surface area after correction for the roughness of the gold surface. The theoretical monolayer coverage is 135 ng cm^{-2} ($7.8 \times 10^{-10} \text{ mol cm}^{-2}$) when the adsorption overlayer structure is assumed to be $(\sqrt{3} \times \sqrt{3})R30^\circ$ for Au(111) surface.^{12,27,28} Although the gold electrode used was polycrystalline, the average coverage may be assumed to be approximately represented by the coverage on the (111) face since this face is usually abundant on the surface. Therefore, the close agreement between the measured and theoretical mass increase on Au(111) reveals that an approximate monolayer coverage was attained by the time the potential reached 0 V, which took about 70 s from the time when the potential was at -700 mV. As the potential rose above 1000 mV, an abrupt mass decrease was observed. Thiol adsorbed on the metal surface is considered to be desorbed at high potentials by oxidation to sulfate or sulfonate moieties.^{7,11,12,29,30}

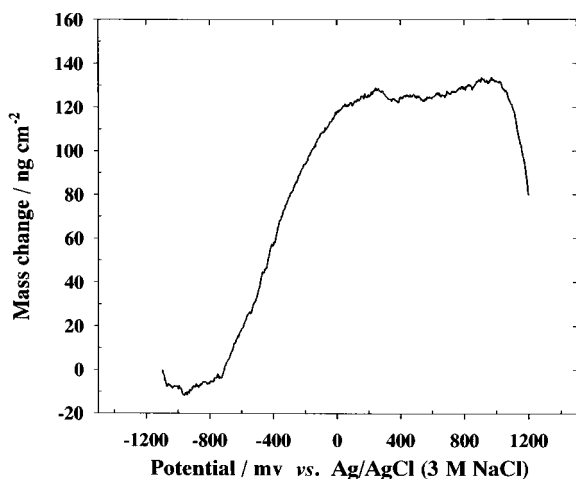


Fig. 2 Mass change on QCM-Au electrode as the potential was swept in 1 mM decanethiol, 0.1 M LiClO_4 solution in acetonitrile. Scan rate: 10 mV s^{-1} .

In the potential-jump experiment previously reported,²³ the EQCM frequency showed a sudden drop, indicating sudden adsorption, at the moment when the electrode potential was stepped from -0.9 V to 0 V in 1 mM decanethiol solution. The current response was a sharp anodic peak flanked by a long tail. When this current curve is expanded in the time-scale, the curve can be deconvoluted into a sharp initial current peak coinciding with the potential jump and a second slowly decaying current. The initial sharp current peak represents charging of the double layer with the potential step, and the second component represents the anodic current of the adsorption reaction. The present result obtained with the potential scan and the previous result from the potential-jump, taken together, clearly demonstrate that the adsorption can be suppressed by a lower potential and can be conveniently switched on by a change in potential.

Added redox couple

We studied influence of an added redox couple that can elevate the substrate potential. The electrical potential of gold was monitored in a solution of ferrocene-ferrocenium couple (2 mM overall) and 1 mM LiClO_4 as decanethiol was added to the solution. The degree of adsorption (relative coverage) was also monitored by the frequency shift of the gold-plated QCM electrode (Fig. 3). As before, the gold electrode potential (initial open-circuit potential) shifted abruptly in the negative direction as the thiol adsorbate was injected into an oxidant-

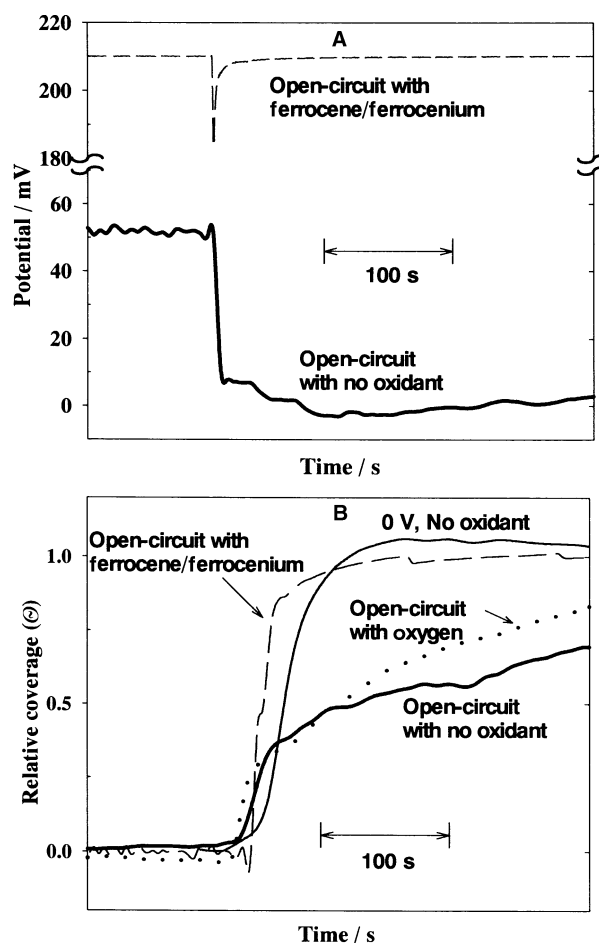


Fig. 3 Comparison of shifts of potential of Au substrate with addition of decanethiol in the presence and absence of ferrocene-ferrocenium couple (A), and comparison of the relative coverage increase in the presence and absence of ferrocene-ferrocenium couple under various conditions (fixed potential, presence of dissolved oxygen) are shown.

free solution as shown in Fig. 3A because of the anodic reaction of adsorption, scheme (3). Fig. 3A also shows that if ferrocene–ferrocenium couple is present in the solution the abrupt negative shift of potential reversed quickly and the potential rose back to approach the initial value. This is in sharp contrast with the case when there is no added redox couple in the solution.

The values of the relative surface coverage by thiol molecules were estimated by dividing the magnitudes of the frequency shift by the saturation value of the shift reached after several minutes, and are shown in Fig. 3B. When there was no oxidizing agent present and the potential of the electrode was not controlled, the adsorption proceeded rather slowly after the brief initial fast adsorption to a low coverage that started with the contact of the adsorbate with the metal surface. However, when the ferrocene–ferrocenium couple was added to the solution, the adsorption was rapid, to near full coverage (Fig. 3B). As can be seen the rate of adsorption in the presence of the redox couple is as fast as in the case of controlled potential at 0 V where the adsorption is faster than at more negative potentials.

As discussed in the previous paper,²³ the ubiquitous presence of oxygen is responsible for the relatively easy adsorption of thiols on gold and silver in the usual manner of SAM preparation. The effect of the ferrocene–ferrocenium couple is analogous to the effect of dissolved oxygen, but is much more effective in bringing full coverage in a shorter time. This effectiveness stems from the fact that the redox reactions of ferrocene and ferrocenium ion are fast on a gold surface, and consequently the equilibrium potential of the gold surface is established quickly. The drastic effect of the redox couple indicates that addition of such a redox couple or an oxidant might be beneficially employed to facilitate adsorption and consequently obtain better-defined SAMs in the absence of potential control.

Adsorption from acid solutions

Adsorption rates and the extent of adsorption of thiols from solutions with two different pHs, 0.5 M HClO₄ and 0.5 M LiClO₄ in ethanol–water 1 : 1 mixture, were compared. The ethanol–water mixed solvent was chosen to give better solubility of both the acid and the thiol. Potential shifts of the Au electrode, the mass change registered by the EQCM–Au electrode, and the current peaks with addition of the adsorbates were recorded. Fig. 4 shows that in the perchloric acid solution the potential shift after injection of decanethiol is much smaller than with neutral lithium perchlorate solution. The

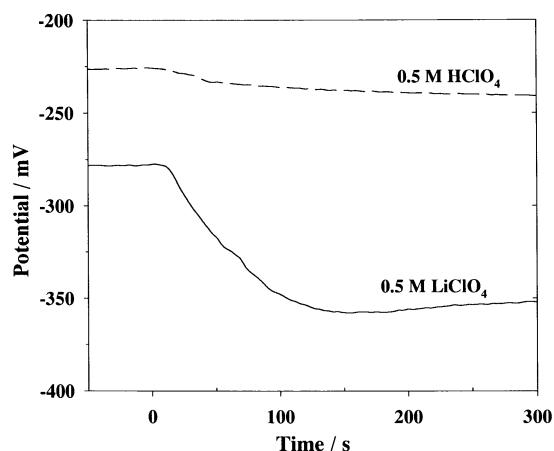


Fig. 4 Changes of gold potential in open-circuit after injection of decanethiol into solutions of LiClO₄ and HClO₄ in ethanol–water 1 : 1 mixture.

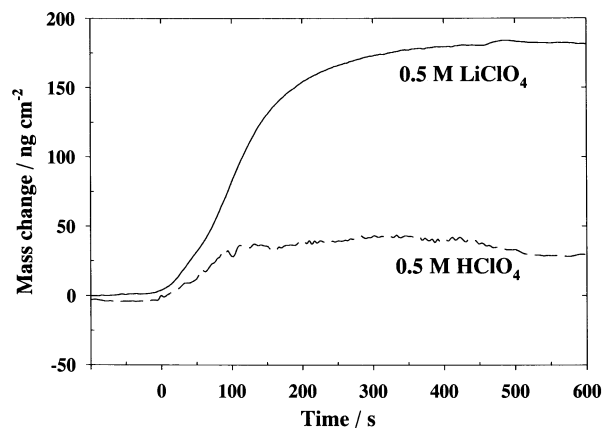


Fig. 5 Increase of surface mass after injection of decanethiol into solutions of LiClO₄ and HClO₄ in ethanol–water 1 : 1 mixture. The gold substrate was in the open-circuit condition.

mass changes are shown in Fig. 5. The mass increase was also much less from the acid solution than from the neutral solution.‡

Fig. 6 shows the current peaks obtained in acid and neutral solutions. While there was a large current peak with the neutral solution, the current with the acid solution was much smaller. The small background currents appearing before the injection of the adsorbate were probably residual currents originating from reduction of impurities such as oxygen, present in spite of the purging of the solution by nitrogen bubbling. The above results, as summarized in Fig. 4–6 indicate that the adsorption reaction of thiol is retarded by a high concentration of hydronium ion. The reverse reaction of scheme (3) seems to be in equilibrium with the forward reaction when the hydronium ion concentration is high, and hence adsorption of a thiol from an acidic solution is not favored. The above effect of acid on adsorption of a thiol cannot be

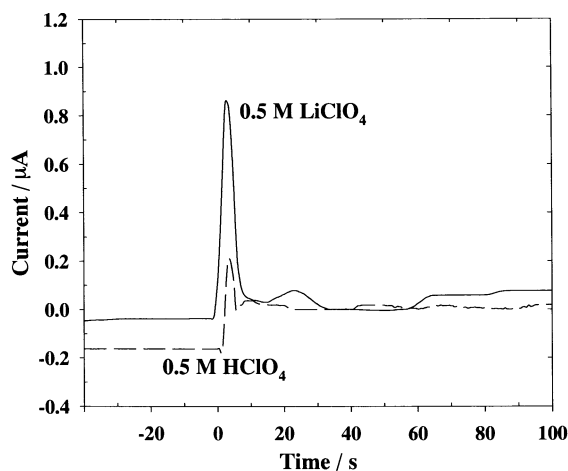


Fig. 6 Current after injection of decanethiol into solutions of LiClO₄ and HClO₄ in ethanol–water 1 : 1 mixture. The gold substrate was held at 0 V.

‡ The mass increase from the LiClO₄ in ethanol–water solution shown in Fig. 5 is about 30% larger than that shown in Fig. 2, which was considered to be close to a monolayer value. The discrepancy is not fully understood, but may be due to partial multilayer formation from a poor solvent mixture. Fig. 2 was obtained in acetonitrile solution and Fig. 5 was obtained in ethanol–water solution. Multilayer formation was indicated in ref. 7 when deposition of a thiol was made from a solvent in which the thiol is only slightly soluble.

explained by the chemical reaction mechanism leading to molecular hydrogen ($\text{RSH} + \text{Au} \rightarrow \text{RS-Au} + \frac{1}{2}\text{H}_2$) that has been prevalently accepted previously.

Potential shifts on addition of dibutyl disulfide, in acidic and neutral solutions, are compared in Fig. 7. The positive potential shift in the neutral solution was smaller than that in acetonitrile solutions. However, in acid solution the potential change was very large. Thus, in the case of the disulfide, the adsorption reaction seems to proceed to a greater extent from acidic solution than from neutral solution, in contrast to the case of the adsorption of thiol. This could be understood by reaction scheme (4). If the thiolate ions $\text{R}'\text{S}^-$ produced by the cathodic split-adsorption reaction of the disulfide are removed from the equilibrium by combination with H^+ forming thiol molecules, which is possible because thiols are extremely weak acids, the equilibrium in reaction scheme (4) will shift towards more adsorbed RS-Au . The above effect of acid on adsorption of a disulfide cannot be explained by the chemical splitting-adsorption mechanism ($\text{RSSR}' + \text{AuAu} \rightarrow \text{RS-AuAu-SR}'$) that has been prevalently accepted previously.

All the results presented in this paper are in accord with the electrochemical reaction mechanisms as summarized by schemes (3) and (4). The reported results from other laboratories on reversible desorption of thiolates at extremely negative potentials,^{13–17} faster adsorption of thiols, and the better-defined SAMs obtained with raised potentials^{18–20} are all in accord with the electrochemical reaction mechanism of adsorption.

It is also interesting in this regard to note that most carboxylic acids do not adsorb on gold to a high coverage except when high potentials near the region of gold oxide formation are applied,^{31,32} but a quinone carboxylic acid, which is itself an oxidant, adsorbs on gold to monolayer coverage without artificially applied potential.³² Although the adsorption of carboxylic acids on gold is weaker than that of thiols, the adsorption reactions of the two classes of compounds seem analogous in that the adsorption is helped by potentials maintained high or by the presence of an oxidizing agent.

Further investigations on the possible intermediate states or transition states are needed to fully understand the kinetic aspect of the influence of pH on adsorption. A different adsorption mechanism may be operative when adsorption of thiol takes place from the gas phase. It is known that adsorbed layers are formed on gold from the gas phase when thiol gas is introduced into a vacuum chamber. Fully close-packed coverage is obtained very slowly, however, only after gradual transformation from the loosely packed physisorbed state.³³ A different reaction path may be followed in this case

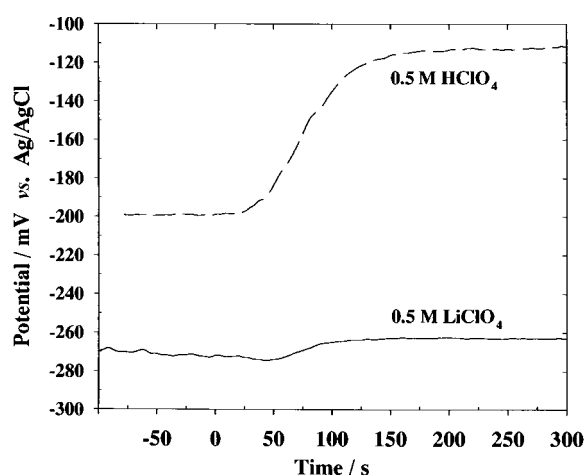


Fig. 7 Changes of gold potential in open-circuit after injection of dibutyl disulfide into solutions of LiClO_4 and HClO_4 in ethanol-water 1 : 1 mixture.

because an electrochemical reaction in the usual sense cannot take place at the metal/gas interface.

Summary

The purpose of this study was to obtain more insight into the electrochemical reactions involved in the adsorption of organosulfur compounds forming SAMs on gold and silver. The adsorption was studied in relation to electrical potential, added redox couple, and acidity of the solution from which adsorption takes place. Comparison of the potential behavior of platinum was made with those of gold and silver after organic sulfur compounds (thiols and disulfides) were added to the solution in contact with the substrate metals. From the comparison it was confirmed that no electrochemical reaction takes place for chemisorption of the organic sulfur compounds on a Pt surface whereas anodic (in the case of thiols) or cathodic (in the case of dialkyl disulfides) reactions occur during adsorption on gold and silver. From an acid solution, the oxidative adsorption of a thiol was found to be retarded whereas the reductive-dissociative adsorption of a disulfide was facilitated. Added ferrocene-ferrocenium redox couple enhanced adsorption of thiols by maintaining the potential of the substrate at a favorable level, thus providing a convenient way to aid adsorption and SAM formation.

Acknowledgements

This research was supported by a grant from Korea Science and Engineering Foundation (996-0300-001) and partially by a grant from Sogang University.

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