

Interpretation of the Mass Change Behavior in the Binary Monolayer of Hydroquinone-tethered Alkylthiol and Aminoalkylthiol

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The hydroquinone/quinone redox couple has drawn much interests for a long time because of their importance in biological activities.¹ The electrochemistry of hydroquinone-tethered alkylthiol self-assembled monolayers (SAMs) has been studied previously and many characteristics including structural and vibrational properties,^{2,3} electron transfer kinetics,^{4,5} and mass change properties⁶ were reported. By the way the monolayers with a large tail group are usually packed with disorders depending on the bulkiness of the tail group. Disordered monolayers have many defects that allow penetration of electrolytes and solvent molecules into the monolayer. For this reason, a monolayer with a large tail group shows mass changing behaviors originated from the redox reaction of the monolayer and extra mass changes due to counterions adsorbed onto the SAM surface. Mixed monolayers formed from simple alkylthiol molecules and the surfactant bearing large tail groups are known to show an enhanced packing and ordering.⁷⁻⁹ Well-prepared mixed monolayers usually show that the penetration of the electrolytes and solvents is excluded.

The mass change property of the mixed SAMs of 2-(*n*-mercaptodecyl)hydroquinone ($H_2Q(CH_2)_{10}SH$; abbr. $H_2QC10SH$) and 1-Aminoundecylthiol ($NH_2(CH_2)_{11}SH$; abbr. NH_2C11SH) has been examined by electromicrogravimetry in the sulfuric acid solution. It shows a mass increase upon oxidation of hydroquinone moiety while the mass decreased in case of the $H_2QC10SH$ monolayer or the mixed monolayer of $H_2QC10SH$ and dodecylthiol ($CH_3(CH_2)_{11}SH$; abbr. $C12SH$). In this article, the reason for this unusual behavior is mainly due to an intake of bisulfate ions bound to a carbonyl group of quinone and two amine groups of NH_2C11SH molecules as a diluent in the mixed SAM.

Experimental Section

Materials. 2-(*n*-mercaptodecyl)hydroquinone was synthesized according to the procedure described in the literature^{3,5} and stored in a cool and dark place under an atmosphere of dry Argon. Absolute EtOH (HPLC grade, Fisher) and 1-dodecylthiol (98%, Aldrich) were used as received. 1-Aminoundecylthiol ($NH_2(CH_2)_{11}SH$)¹⁰ was donated from Prof. Dongjin Yoo (Seonam Univ.). Electrolyte solutions of

H_2SO_4 (97%, Showa) and KOH (95+%, Aldrich) were prepared with de-ionized water (resistivity > 18 M Ω cm). All the electrochemical measurements were carried out at room temperature after the electrolyte solution was deaerated by purging Argon gas for at least 10 min.

Apparatus. A commercial EQCM (SHIn EQCN 1000, Korea) was used for all electrochemical measurements. The electrochemical cell consisted of a quartz crystal gold electrode as the working electrode, a Pt wire as the counter electrode, and an Ag|AgCl(sat'd) electrode as the reference electrode. The gold film electrode coated on 10 MHz quartz crystal (ICM Co., OK, USA or Morion Inc., Petersburg, Russia) was chemically cleaned in a piranha solution (98% H_2SO_4 and 30% H_2O_2 , 2 : 1 by volume; Use with caution!) or electrochemically polished in 0.1 M H_2SO_4 . The mass sensitivity of 10 MHz quartz crystals is calculated to be 4.42 ng cm⁻² Hz⁻¹. It was rinsed with deionized water, ethanol, and then dried with a stream of nitrogen gas. The monolayers were formed on the Au electrode by soaking the electrode in an ethanol solution containing 1 mM surfactant for 2 h, followed by rinsing thoroughly with ethanol and drying with a stream of nitrogen gas, and then used in electrochemical measurements. For the formation of a mixed monolayer, a mixture solution of $H_2QC10SH/C12SH$ or NH_2C11SH as a diluent (1 : 1 in molar ratio) was used while the total concentration of thiols was kept to be 1 mM. The surface coverage of hydroquinone was calculated from the charge obtained by integration of voltammetric peaks.

Results and Discussion

Figure 1 exhibits the cyclic voltammogram and the mass change response of the hydroquinone-tethered decylthiol ($H_2QC10SH$) monolayer in 0.05 M sulfuric acid with the surface coverage of 5.65×10^{-10} mol cm⁻². It shows a couple of symmetric redox peaks of hydroquinone moiety with a mass decrease during oxidation of the redox center and returning to the original mass value in the reduction scan. Since there is no change in charge for the redox reaction of hydroquinone moiety, there is no reason to expect for counterions to move into or out of the monolayer. Thus the mass decrease in the oxidation process is obviously due to the ejection of protons hydrated with water molecules regarding the redox mechanism of the hydroquinone-

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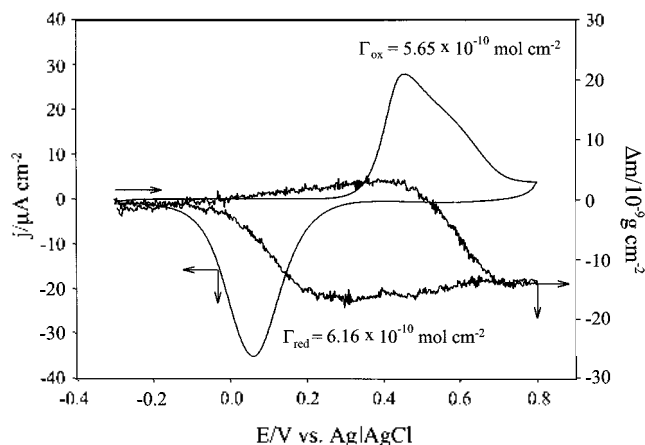


Figure 1. CV and mass change of H₂QC10SH monolayer modified gold electrode. Coverage: $\Gamma_{\text{ox}} = 5.65 \times 10^{-10} \text{ mol cm}^{-2}$; Electrolyte: 0.05 M H₂SO₄; Scan rate: 50 mV s⁻¹.

quinone system.⁶

In the oxidation process, however, a close examination reveals the baseline in the mass change response slightly arises as the electrode potential shifts in the positive direction. As described in our previous report, it is explained by the adsorption of counteranions onto the gold surface,

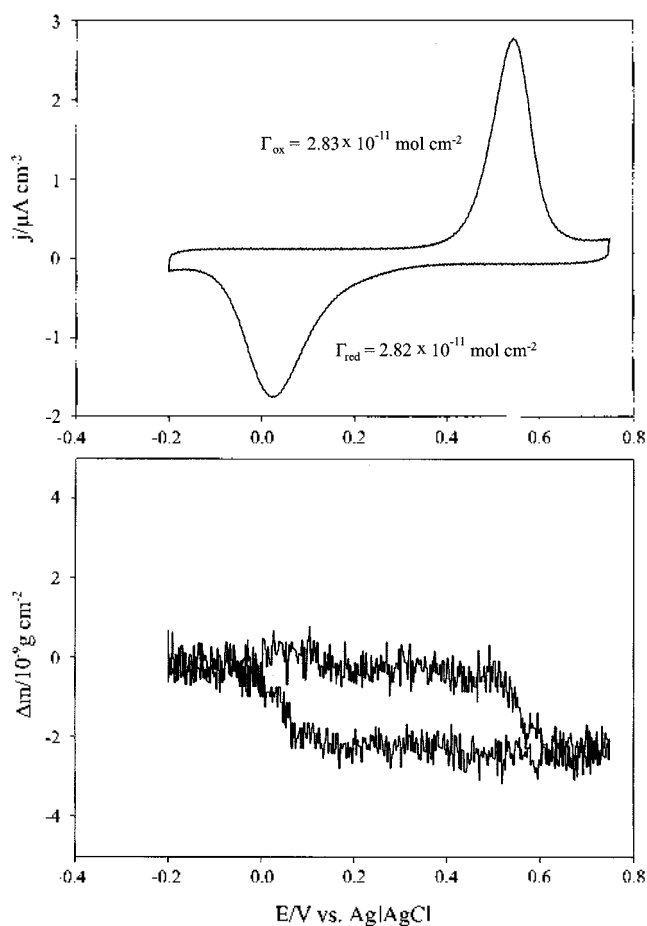


Figure 2. CV and mass change of the binary monolayer of H₂QC10SH and C12SH. Coverage: $\Gamma_{\text{red/ox}} = 2.8 \times 10^{-11} \text{ mol cm}^{-2}$; Electrolyte: 0.05 M H₂SO₄; Scan rate: 50 mV s⁻¹.

which is penetrated into the loosely packed SAM.¹¹ In case of a lower coverage, the baseline is much steeper than that in more compact SAM.

In the binary SAM of C12SH and H₂QC10SH, the mass change is mainly due to an ejection of protons hydrated with water as shown in Figure 2. The coverage of H₂QC10SH is *ca.* $2.8 \times 10^{-11} \text{ mol cm}^{-2}$ and the mass change is about 2 ng cm⁻² which is equivalent to *ca.* 71 g mol⁻¹. It is similar to the responses from the H₂QC1SH or H₂QSH SAMs.⁶

However, the mass change behavior in the binary monolayer of NH₂C11SH and H₂QC10SH in 0.05 M sulfuric acid are exhibited in Figure 3. In this figure the voltammogram and the mass change for the NH₂C11SH SAM are also represented, which look like background signals. As expected there is no remarkable mass change in the NH₂C11SH SAM.

In the mixed monolayer, however, the mass change increases with the potential increase. The mass change per unit charge is found to be about $40 \pm 4 \text{ g mol}^{-1}$. It is

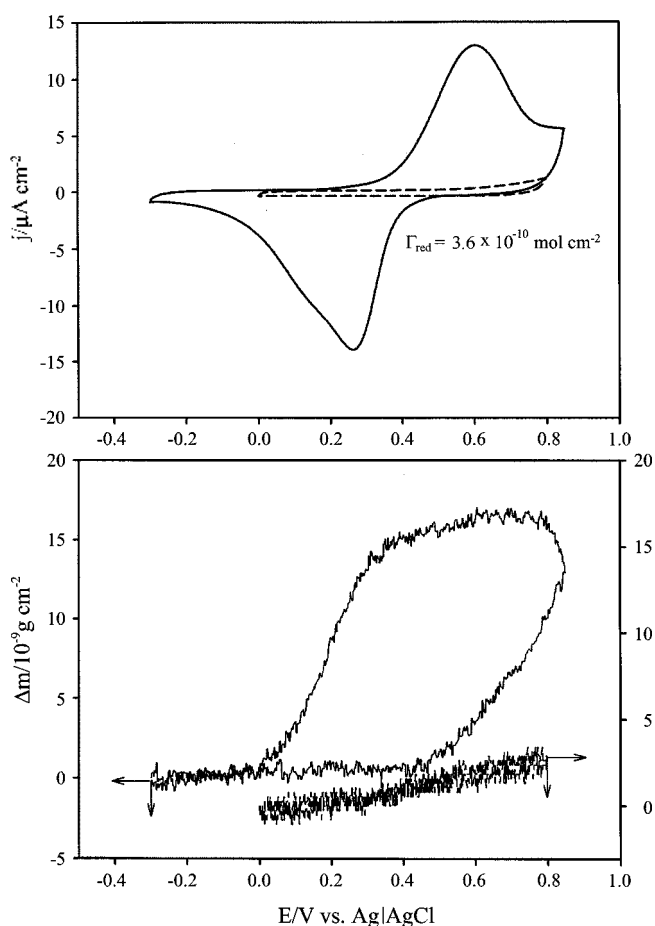


Figure 3. CV and mass change response of NH₂C11SH monolayer (broken line for CV and lower skewed response for mass change) and the binary monolayer of H₂QC10SH and NH₂C11SH. Coverage: $\Gamma_{\text{red}} = 3.6 \times 10^{-10} \text{ mol cm}^{-2}$; Electrolyte: 0.05 M H₂SO₄; Scan rate: 50 mV s⁻¹.

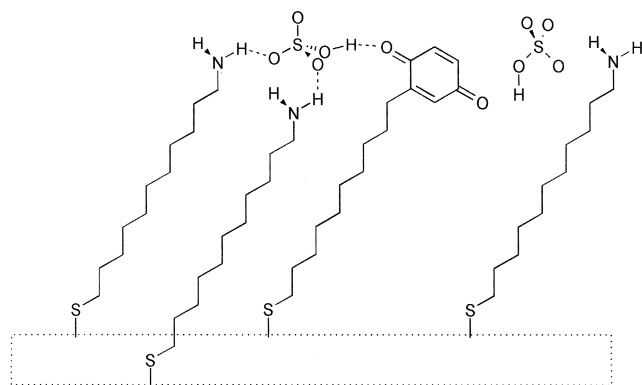


Figure 4. Schematic diagram suggesting an intake of bisulfate anions bound to a carbonyl group through hydrogen bonding and two neighboring amine groups by coordination bonding.

obviously contrary to the response of the SAM of $\text{H}_2\text{QC10SH}$ or the mixed SAM of $\text{H}_2\text{QC10SH}$ and C12SH SAM. Considering the mass change responses of SAMs described above, the mass increase arises only from the mixed SAM composed of $\text{H}_2\text{QC10SH}$ and $\text{NH}_2\text{C11SH}$. In the presence of bisulfate, the most plausible explanation for the mass increase is that a bisulfate anion binds to the carbonyl group. It can be interpreted as the binding of bisulfate ion through hydrogen bonding with carbonyl oxygen of quinone and intermolecular coordination with amine group near the quinone-tethered molecule. Since the alkyl chain length of $\text{H}_2\text{QC10SH}$ and $\text{NH}_2\text{C11SH}$ is quite close each other, the bisulfate ion does not experience difficulty in making a coordination bond with amine and carbonyl oxygen functionalities. The hydrogen binding scheme is given in Figure 4. It is expected that two neighboring amine groups and a carbonyl group coordinate a bisulfate ion. However, it may not be possible that the oxygen atom in opposite position participates in coordination of a bisulfate ion because a geometric disadvantage for coordination and repulsive interaction between a charged bisulfate ion and the hydrophobic layer are expected.

It is a very similar result to that observed in a study of ion selective electrode. According to Jeon *et al.*,¹² a bisulfate anion is caught by a calixcrown molecules connected with urea functional groups *via* the hydrogen bonding with oxygen of oxidized quinone moiety and the coordination bonding between oxygen atoms of bisulfate and amine groups in urea functional groups in the same molecule.

Regarding the mass change per unit charge, Scherson *et al.*⁶ suggested that three water molecules are bound to each hydroxyl group in hydroquinone and two water molecules are bound to each carbonyl group upon oxidation in a

solution of perchloric acid. As a result the mass decrease in the oxidation is confirmed experimentally to be 38 g mol^{-1} . This value is equivalent to the loss of two protons and two water molecules.

However, it is expected in the presence of bisulfate ions that a water molecule bound to a carbonyl group in quinone be replaced with a bisulfate ion resulting in the loss of a water molecule and the subsequent acquirement of a bisulfate ion. The additional contribution from the binding of a bisulfate ion is an increase in mass of 79 g mol^{-1} which is equivalent to the intake of a bisulfate ion (97 g mol^{-1}) and the simultaneous release of a water molecule (18 g mol^{-1}). Consequently it is possible to expect a net mass change of 41 g mol^{-1} when the hydroquinone moieties in a mixed SAM of $\text{H}_2\text{QC10SH}$ and $\text{NH}_2\text{C11SH}$ are oxidized in the presence of bisulfate anion. This value is well matched with the observed mass change per unit charge $40 \pm 4 \text{ g mol}^{-1}$.

Finally we expect that it would be possible to utilize the mixed monolayer of $\text{H}_2\text{QC10SH}$ and $\text{NH}_2\text{C11SH}$ as a very sensitive bisulfate ion sensor. Further experiments for determining sensitivity and detection limit are in progress.

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