v_2 transition is normally very weak and is rarely unequivocally observed. For most octahedral cobalt(II) complexes, a band around 8,000-10,000 cm^{-1} is usually assigned to the $^4T_{1g}(F) \to {}^4T_{2g}(F)$ transition while a multiple structured band observed near 20,000 cm^{-1} is assigned to $^4T_{1g}(F) \to {}^4T_{2g}(P)$. The $^4A_{2g}$ transition appears as a very weak band around 12,000-14,000 cm^{-1}. The optical absorption spectrum of Co $(C_{15}H_{26}N_2)(NO_2)_2$ exhibit two bands at 9,615 cm^{-1} and 18,330 cm^{-1}, and the electronic spectral assignments of Co $(C_{15}H_{26}N_2)(NO_2)_2$ are made tentatively as follow; 9,615 cm^{-1} (v_1; $^4T_{1g}(F) \to {}^4T_{2g}(F)$) and 18,330 cm^{-1} ($v_3$; $^4T_{1g}(F) \to {}^4T_{1g}$ (P)). The optical absorption spectrum of $Ni(C_{15}H_{26}N_2)(NO_2)_2$ exhibits the characteristic spectral features of octahedral nickel(II) complexes. For octahedral nickel(II) complexes, three spin-allowed transitions are expected from the energy level diagram of d^8 ions[18] and three observed bands may thus be assigned; 9,852 cm^{-1} (v_1; $^3A_{2g} \to {}^3T_{2g}$), 15,220 cm^{-1} (v_2; $^3A_{2g} \to {}^3T_{1g}(F)$), 25,550 cm^{-1} ($v_3$; $^3A_{2g} \to {}^3T_{1g}(P)$).

The infrared spectrum of $Ni(C_{15}H_{26}N_2)(NO_2)_2$ shows strong NO_2 stretching bands ($v_{a\,NO2}$ and $v_{s\,NO2}$) at 1307 cm^{-1} and 1196 cm^{-1}, and a weak deformation band (δ_{NO2}) at 872 cm^{-1}. These data are in good agreement with the crystallographically determined molecular structure in which the NO_2^- groups[19] are almost symmetrically bidentated with nickel(II) center utilizing two oxygen donor atoms. The infrared spectra of $Co(C_{15}H_{26}N_2)(NO_2)_2$ shows strong stretching bands ($v_{a\,NO2}$ and $v_{s\,NO2}$) at 1273 cm^{-1} and 1177 cm^{-1}, and a weak deformation band (δ_{NO2}) at 857 cm^{-1}. The infrared spectral data of $Co(C_{15}H_{26}N_2)(NO_2)_2$ are also in agreement with the crystallographic results.

Supplementary Data

Tables of (1) H-atom coordinates and isotropic thermal parameters, (2) anisotropic thermal parameters for non-hydrogen atoms, and (3) observed and calculated structure factors with estimated standard deviations are available from IHS.

References

1. Choi, S.-N.; Bereman, R. D.; Wasson, J. R. *J. Inorg.*

Nucl. Chem. **1975**, *37*, 1087.

2. Mason, S. F.; Peacock, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, *226*; and references therein.

3. Boschmann, E.; Weinstock, L. M.; Carmack, M. *Inorg. Chem.* **1974**, *13*, 1297; and references therein.

4. Fraenkel, G.; Appleman, B.; Ray, J. G. *J. Am. Chem. Soc.* **1974**, *96*, 5113; and references therein.

5. Kuroda, R.; Mason, S. F. *J. Chem. Soc., Dalton Trans.* **1977**, 371.

6. Boschmann, E.; Nypaver, G. A.; Majors, J. P.; Ealy, S. M.; van Horn, M. *J. Coord. Chem.* **1978**, *7*, 141.

7. Togni, A.; Rihs, G.; Pregosin, P. S.; Ammann, C. *Helv. Chim. Acta* **1990**, *73*, 723.

8. Childers, L. S.; Folting, K.; Merritt, L., Jr.; Streib, W. *Acta Cryst.* **1975**, *B31*, 924.

9. Kuroda, R.; Mason, S. *J. Chem. Soc., Dalton Trans.* **1979**, 727.

10. Choi, S.-N.; Kwon, M.-A.; Kim, Y.; Bereman, R. D.; Singh, P.; Knight, B.; Seff, K. *J. Coord. Chem.* **1995**, *34*, 241

11. Lopez, S.; Muravyov, I.; Pulley, S. R.; Keller, S. W. *Acta Cryst.* **1998**, *C54*, 355.

12. Lee, Y.-M.; Choi, S.-N.; Suh, I.-H.; Bereman, R. D. *Acta Cryst.* **1998**, *C54*, 1582.

13. Enraf-Nonius, Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1985.

14. Sheldrick, G. M. *'SHELX86'*, Program for Crystal Structure Determination, Univ. of Cambridge, England, 1986.

15. Sheldrick, G. M. *'SHELX76'*, Program for Crystal Structure Determination, Univ. of Cambridge, England, 1976.

16. Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Vol. IV; Table 2.2A, Table 2.3.1., The Kynoch Press, Birmingham, England, 1974.

17. Shin, W. *'GEOM'*, Seoul National University, Korea, 1978.

18. Lever, A. B. P. *Inorganic Electronic Spectroscopy*; 2nd' Elsevier, 1984.

19. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 4ed., John Wiley & Sons: 1986, pp. 221-227; and references therein.

Adsorbate Substitution and Electrochemical Behavior in Self-Assembled Monolayer of 2-Mercaptomethylhydroquinone (MH2Q) on Gold

Hyunsoo Kim and Hun-Gi Hong*

Department of Chemistry, Sejong University, Seoul 143-747, Korea
Received July 31, 1998

Quinone/hydroquinone derivatives[1] take part in several biologically important oxidation-reduction processes. These redox-active molecules play key roles in electron/energy transfer occuring onto biological membrane which they are bound. This type of electron transfer in membrane systems can be mimicked by self-assembled monolayers[2] containing

redox-active species which act as a channel or gate site in membrane. Majda[3] recently reported formation of mixed monolayer assemblies consisting of octadecanethiol and ubiquinone on electrode surface in which ubiquinone is a gate molecule in electron transfer. Hubbard and co-authors[4] have extensively investigated on the structure, orientation, and electrochemical behavior of various quinone derivatives adsorbed on well-defined metal surfaces. In recent years, the *in situ* FT-IR[5] and quartz crystal microgravimetric methods[6] have been used to probe potential-dependent orientation and structure of 2,5-dihydroxythiophenol (DHT) derivatives monolayer attached on electrode in electrolyte solution. Especially, Soriaga and co-workers[7] studied for substrate-mediated adsorbate-adsorbate interaction within an adsorbed layer of DHT molecule on Au and Pt electrode and they reported the effects of submonolayer coverage and coadsorbed iodine on the interaction between adsorbate and substituent using thin-layer electrochemical techniques. It is important to investigate how the electroactive surface-bound species behaves when another surface-active reagent is introduced. The adsobate substitution always takes place on solid surface exposed to the solution containing other species and it provides means of fabrication of stable mixed monolayer, which has many applications for sensoring material. In view of these aspects, it is necessary to estimate factors determining surface substitution of adsorbate for preparation of coadsorbed monolayer on electrode surface.

In this paper, we have constructed a self-assembled monolayer of a 2-mercaptomethylhydroquinone (MH_2Q) as an adsorbate on smooth gold electrode and reported pH defendence of redox peak potential and adsorbate displacement reaction between MH_2Q and n-alkyl or benzylmercaptan(as a substituent). These adsorbates have been chosen because they have surface-active thiol group. In addition, MH_2Q shows reversible electrochemical activity in adsorbed state. Thus, it is easy to monitor the surface coverage of adsorbate which remains on the surface in coadsorbed surface states.

Experimental

The electrochemical measurements were carried out in one-compartment cell with Au thin film (purchased from EMF Corp., Ithaca, N.Y.) or disk electrode (BAS, West Lafayette, IN) as working electrode, platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Voltammetric experiments were performed with the use of a EG&G/PAR 273A Potentiostat coupled to a HP 7475A x-y plottor. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 $M\Omega/cm$ with UHQ II system (Elga) and deaerated by purging with nitrogen. The pH of electrolyte solution was adjusted with adding of 0.1 M NaOH to 0.1 M $HClO_4$ solution. Propanethiol, hexanethiol, decanethiol, benzylmercaptan, toluhydroquinone and all other chemicals were used as received. MH_2Q was synthesized according to published procedures.[5a]

The Au electrode was cleaned by sonication in chloroform followed by immersion for 10 s in a hot "piranha" solution (3 : 1 mixture of concentrated H_2SO_4 and 30% H_2O_2) prior to use. Gold disk electrode (geometric area, 0.02 cm^2) was polished to a mirror finish with aqueous slurries of 1.0, 0.3,

and 0.05 μm alumina before adsorption of MH_2Q. After rinsing with deionized water and drying with nitrogen gas blowing, gold electrode was immersed in 10 mM ethanol solution of MH_2Q for 1 h. The electrode was then rinsed with fresh ethanol and deionized water and then used for voltammetric studies.

Results and Discussion

Figure 1 shows typical cyclic voltammograms for 2-mercaptomethylhydroquinone (MH_2Q) chemisorbed with maximum coverage at smooth polycrystalline gold electrode in 0.1 M $HClO_4$ solution. These cyclic current-potential curves present well-developed surface wave characteristics in which peak current is linearly proportional to scan rate and peak potential separation (ΔE_p) is *ca.* 5-10 mV independent of hired scan rates in the range of 50 to 500 mV/s. With the anodic/cathodic peak current ratio of unity, these facts indicate that the electron transfer of MH_2Q molecule is highly reversible in its adsorption state, unlike hydroquinone which is known as slow redox couple in solution phase. The Faradaic charge under the cathodic or anodic peak for chemisorbed MH_2Q in this study generally yields surface coverage of $5.9(\pm0.4)\times10^{-10}$ mole·cm^{-2}. This value almost corresponds to a coverage of full monolayer of MH_2Q when compared to coverage $(5.7\times10^{-10}$ mole·cm$^{-2})$ of 2,5-dihydroxythiophenol adsorbed on gold previously reported.[4] This implies that MH_2Q molecule is vertically chemisorbed through the SH group and that self-assembled monolayer of MH_2Q is structurally close-packed on gold surface.[7b]

Figure 2 shows cyclic voltammetric curves for chemisorbed MH_2Q obtained in the electrolyte solutions of different pH value. It is remarkable to note that the geometric shape of each cyclic voltammogram was maintained to have the same i-E features at different pH solutions. The observed surface formal potential of MH_2Q is 0.37 V *vs.* SCE in 0.1
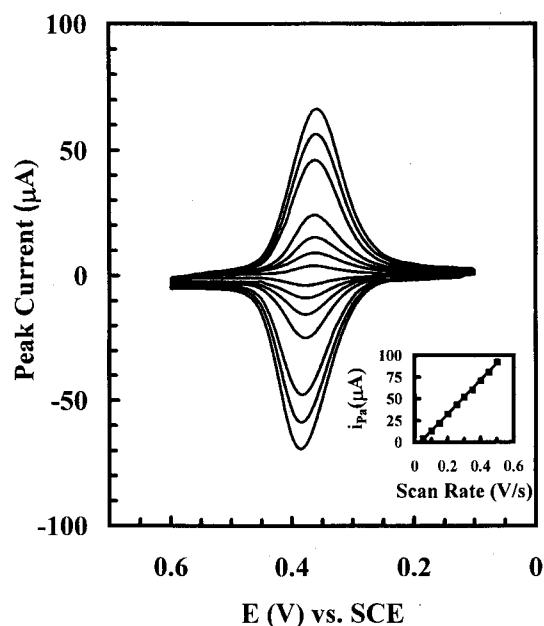

Figure 1. Cyclic voltammograms of 2-mercaptomethylhydroquinone (MH_2Q) modified Au electrode in 0.1 M $HClO_4$. Inset is the plot of anodic peak current *vs.* scan rate (mV/s).
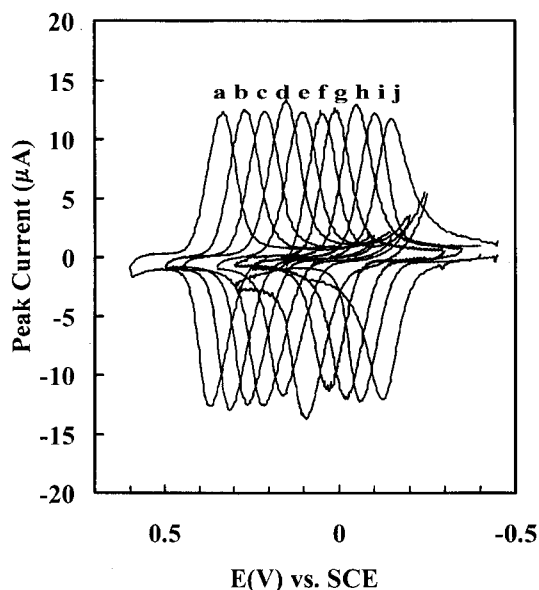
Figure 2. Cyclic voltammograms of gold electrode modified with MH_2Q molecule in the electrolyte solutions of different pH. Voltammetric curves of (a) to (j) were respectively obtained in the solution pH of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0. All scan rates were 100 mV/s.

M $HClO_4$. However, the redox peak potential of pendant hydroquinone moiety in MH_2Q shifts toward negative potential direction as pH of the electrolyte solution increases. Figure 3 shows that the pH-sensitive gold electrode modified with MH_2Q monolayer exhibits a near-Nernstian response with a slope of 54 mV/ pH in the wide range from 1 to 10 of pH. This remarkable pH dependence of $E_{1/2}$ shift is definitely due to the fact that the adsorbed MH_2Q in self-assembled monolayer undergoes reversible two-electron, two-proton electrochemical oxidation-reduction reaction to adsorbed quinone molecule $(Q(ads))$(eq 1).[4]

$$MH_2Q(ads) \rightleftarrows Q(ads) + 2H^+ + 2e^- \qquad (1)$$
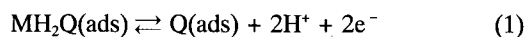
The surface coverage of MH_2Q monolayer on gold is

typically decreased by only one tenth of its original value $(5.9 \times 10^{-10}$ mole·$cm^{-2})$ even after extensive potential cycling for 4 h in 0.1 M $HClO_4$ solution. This demonstrates that the irreversible chemisorption of MH_2Q is thermodynamically quite stable in acidic condition. However, the adsorbed MH_2Q molecule is easily displaced by other adsorbate molecule like alkylthiol or benzylthiol on gold surface. Figure 4 shows time-courses of surface displacement behavior in which the coverage of MH_2Q is quickly decreased with immersion into solution containing mercaptan molecules. In this experiment, gold disk electrodes pretreated with a full monolayer of MH_2Q were exposed to 5 mM ethanol solu- tion of electroinactive organomercaptans. During the substitution of adsorbed thiol, surface coverage of MH_2Q remained on Au surface was monitored by cyclic voltammetry at regular interval. This surface displacement reaction (eq. 2) on gold may be written

$$H_2Q\text{-}CH_2S\text{-}Au(ads) + RSH(solution) \rightleftarrows RS\text{-}Au(ads)$$
$$+ H_2Q\text{-}CH_2SH(solution) \qquad (2)$$
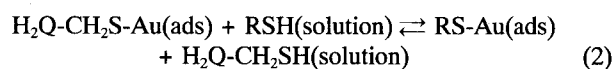
where the $H_2Q\text{-}CH_2SH$ represents MH_2Q molecule.

Among organomercaptans used in this study, decanethiol was shown to be the most effective substituent in comparison with short chain-length alkylthiols. In case of decanethiol, the coverage of MH_2Q was dramatically decreased to *ca.* 3% of full monolayer coverage within 5 min and was converted to zero value after 20 min of immersion. This fact indicates that the equilibrium of the RSH-MH_2Q displacement reaction (eq 2) lies far to the right. The equilibrium position is further supported by experiment in which a gold electrode was first treated with a full monolayer of decanethiol and later exposed to 5 mM ethanol solution of MH_2Q. No electrochemical response resulting from the adsorption of MH_2Q was measured in this experiment. This observation implies that MH_2Q in solution is unable to displace the initially chemisorbed decanethiol. The driving force for surface substitution of chemisorbed MH_2Q might be ascribed to the hydrophobic interaction between alkylchain of adsorbate thiol and readiness in packing of
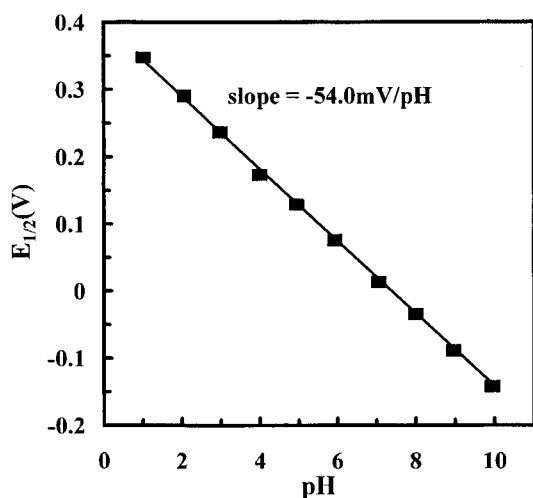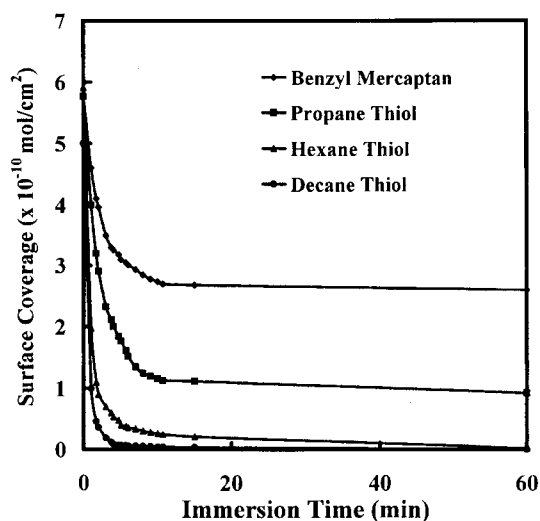

Figure 3. Plot of redox peak potential $(E_{1/2})$ of MH_2Q adsorbed on Au electrode *vs.* Electrolyte solution pH. Data in Figure 2 were used in this plot.

Figure 4. Plot of surface coverage $(\times 10^{-10}$ mole·$cm^{-2})$ of MH_2Q *vs.* Immersion time (min) of MH_2Q-modified Au electrode into the ethanol solution (5 mM) of organomercaptans.

alkylthiol. As known, the van der Waals interaction between alkylchain becomes larger as alkyl chain-length of organomercaptan increases. Therefore, the longer alkylthiol as adsorbate makes desorption more MH_2Q molecules on electrode surface. However, unlike alkylthiols, benzylthiol made displacement only one half of a total amount of the adsorbed MH_2Q even in longer immersion time. This demonstrates that there is no preference in chemisorption of benzylthiol and MH_2Q on gold surface. In fact, MH_2Q molecule has the same chemical structure and size as benzylthiol except two hydroxy groups on benzene ring and their nonpreferential chemisorption is a result from the structural similarity between adsorbate and substituent molecules. However, as shown in Figure 4, the fact that long alkylthiol readily displaces MH_2Q from Au surface states that alkylthiol is preferentially or selectively chemisorbed into MH_2Q layer. In this substitution, the adsorbate and the substituent are not only structurally dissimilar to each other but also different in size. The theoretical calculation[4d] of molecular cross-sectional area (σ) determined from van der Waals radii by Pauling[8] gives insight on size effect of substituent molecule. According to literature,[4d] the σ value (22.5 Å^2/molecule) of alkylthiol is only one half of that of benzylthiol (47.4 Å^2/molecule). Therefore, it seems to be much easier for alkylthiol to be displaced on gold surface than benzylthiol over the SH functional group of MH_2Q. It is nontrivial question whether the two different components in the surface mixture are present homogeneously or heterogeneously. Although this question cannot be answered unambiguously at this moment, hiring of redox-active substituent and adsorbate molecules can provide indications of the heterogeneity of the mixed adsorbed layer from the comparison in the apparent cross sectional areas of substituent and adsorbate.

In conclusion, it is important to take into account the chemical/geometrical structure of substituent molecule in surface-adsorbate displacement reaction which is analogous to ligand exchange on metal substrate. Especially, when the substituent molecule has the same functional group as adsorbate, structural similarities in those molecules play a

key role on preferential and nonpreferential coadsorptions of surface ligands on substrate.

References

1. (a) Chambers, J. Q. In *The chemistry of the quinonoid compounds*, Ed. Patai, S., Wiley: New York, 1974; pp 737-792 (b) Finley, K. T. In *The chemistry of the quinonoid compounds*, Ed, Patai, S. Wiley: New York, 1974; pp 877-1144.
2. Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: Boston, 1991.
3. Bilewicz, R.; Majda, M. *J. Am. Chem. Soc.* **1991**, *113*, 5464
4. (a) Soriaga, M.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3937. (b) Stern, D. A.; Wellner, E.; Salaita, G. N.; Davidson, L. L.; Lu, F.; Frank, D. G.; Zapien, D. C.; Walton, N.; Hubbard, A. T. *J. Am. Chem. Soc.* **1988**, *110*, 4885. (c) Hubbard, A. T. *Chem. Rev.* **1988**, *88*, 633. (d) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 2735
5. (a) Bae, I. T.; Sandifer, M.; Lee, Y. W.; Tryk, D. A.; Sukenik, C. N.; Scherson, D. A. *Anal. Chem.* **1995**, *67*, 4508. (b) Sato, Y.; Ye, S.; Haba, T.; Uosaki, K. *Langmuir* **1996**, *12*, 2726. (c) Ye, S.; Yashiro, A.; Sato, Y.; Uosaki, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3813
6. Mo, Y.; Sandifer, M.; Sukenik, C.; Barriga, R. J.; Soriaga, M.; Scherson, D. *Langmuir* **1995**, *11*, 4626
7. (a) Bravo, B. G.; Mebrahtu, T.; Soriaga, M. P.; Zapien, D. C.; Hubbard, A. T.; Sticckney, J. L. *Langmuir* **1987**, *3*, 595. (b) Mebrahtu, T.; Berry, G. M.; Bravo, B. G.; Michelhaugh, S. L.; Soriaga, M. P. *Langmuir* **1988**, *4*, 1147. (c) Bravo, B. G.; Michelhaugh, S. L.; Soriaga, M. P. *Langmuir* **1989**, *5*, 1092.
8. Pauling, L. C. *Nature of the Chemical Bond*; 3rd ed.; Cornell University Press: New York, 1960; pp 221-264.

Synthesis and Properties of Branched Polycarbonates

Sang-Pil Kim, Bong Hee Lee*, Sang Hern Kim**, Hee-Gweon Woo***, and Whan-Gi Kim[†]

Sam Yang Group Research Center,
*Department of Chemical Engineering, Chungbuk National University,
**Department of Chemical Technology, Taejeon National University of Technology,
***Department of Chemistry, Chonnam National University,
[†]Department of Applied Chemistry, College of Natural Science, Kon-Kuk University
Received August 13, 1998

Polycarbonates are one of the major thermoplastic engineering polymers and well known not only their excellent mechanical and electrical properties but also optical and self-

[†]To whom correspondence should be addressed.

extinguish characteristics.[1-4] Most polycarbonates are manufactured by an interfacial polymerization process which offers advantage to modify chemical structure and process. The linear polycarbonate has been severely restricted their use in the production of large hollow bodies by conventional