Unusual Electron Tunneling Constant for Long Range Electron Transfer in Hydroquinone (H₂Q)-terminated Self-Assembled Monolayers on Gold in Alkaline Solution

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In order to study the interfacial electron transfer, self-assembled monolayers (SAMs)[1] on electrode surface have been attractive as a model system because they provide a stable and structurally well-defined monolayer with an adjustable thickness and desirable function. This characteristic of SAMs affords an opportunity to study fundamental issues such as the effects of distance and interfacial structure on the long-range electron transfer kinetics between a redox active species and an electrode. Weaver and Li[2] obtained the first evidence of the distance-dependence of heterogeneous electron transfer rate constant for reduction of pentaaminecobalt(III) complexes anchored to gold and mercury surface. After Chidsey and co-workers[3] reported heterogeneous electron transfer rate and electron tunneling constant (β) for the ferrocene-terminated alkanethiol monolayers with different alkyl chain length, a number of groups have reported β values for SAMs containing redox couples such as pentaamine (pyridine) Ru(II) complex,[4a] Os(II) bipyridyl complex,[5] viologen,[6] naphtoquinone,[7] azobenzene,[8] and hydroquinone.[9] All of these reports demonstrated that the logarithmic heterogeneous apparent rate constant (k_{app}) linearly decreases as the distance between the electroactive center and the electrode surface increases as expected by Marcus theory.[10] Those investigations on the distance dependence of electron transfer gave β values which are roughly ranging from 0.7 to 1.3 per methylene unit in the alkyl chain spacer. It is interesting to note that these β values are quite similar each other in their magnitude even though the electroactive SAMs contain different redox molecules and they follow significantly different electron transfer mechanism each other. For example, the electron transfer of ruthenium complex[4] containing pentaamine and pyridine tether is highly reversible due to one-electron outer-sphere redox couple. However, redox center such as azobenzene undergoes substantially slow heterogeneous electron transfer because of its protonation reaction and structural change during its 2e⁻, 2H⁺ redox process. Among these redox centers studied, the electron transfer kinetics of a hydroquinone (H₂Q) is also quite complicated due to its 2e⁻, 2H⁺ transfer reaction though Laviron[11] presented a theoretical treatment of proton-coupled electron transfer reaction based on the nine-member square scheme. The electrochemical

properties of hydroquinone/benzoquinone derivatives have been extensively studied in solutions because of their important biological activities.[12] Especially, Hubbard and Soriaga[13,14] have studied on the orientation of various quinones and mercaptohydroquinone derivatives adsorbed on metal surfaces using thin-layer electrochemistry. And Uosaki and coworkers[15] have investigated the pH dependent redox behaviors of mercaptohydroquinone adsorbed on gold surface. We have reported the distance dependence of heterogeneous proton-coupled electron transfer rate constant of H₂Q redox center in ω-mercaptoalkylhydroquinone SAMs[9] on gold in 0.1 M HClO₄ solution a few years ago. The β value reported for the H₂Q-SAMs was 1.04 ± 0.06 and it was in good agreement with the values for the electroactive SAM systems reported up to now. However, the electron transfer kinetics of the H₂Q-SAMs on gold shows remarkably different kinetic behavior in 0.1 M NaOH solution.

In this note, we report an unusual observation for long range electron transfer in the ω-mercaptoalkylhydroquinone SAMs on gold electrode in a strong basic media. At this moment, the distance dependence of electron transfer of H₂Q group is not observed in basic solution unlike that in acidic condition. Almost zero value of β determined from this phenomenon, to the best of our knowledge, is the first one in investigation of electron tunneling constant for long range electron transfer in the electroactive SAMs so far. The present work provides some understandings on the controlling factors related to proton-coupled electron transfer reaction nature.

Experimental Section

The electrochemical measurements were carried out in a single compartment cell with home-made Au bead electrode 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 BAS 100B/W Potentiostat controlled by a software package. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 MΩ/cm with UHQ II system (Elga) and deaerated by purging with argon (99.99%

purity). All measurements were carried out at room temperature. Five ω-mercaptoalkylhydroquinone derivatives of $H_2Q(CH_2)_nSH$ (n = 4, 6, 8, 10, and 12) were synthesized by the published procedure[9] and identified with ^1H NMR. The Au bead electrodes (*ca.* 2.1-2.4 mm diameter) were made by annealing the tip of a gold wire (99.999%, 0.5 mm diameter) and were cleaned by immersion for 10 min in a "piranha" solution (3 : 1 mixture of concentrated H_2SO_4 and 30% H_2O_2. Caution: Extreme care must be taken to avoid contact with organic materials in use of piranha solution.) prior to use. After rinsing with deionized water, the Au electrode was cycled electrochemically in 0.5 M H_2SO_4 between −0.30 and 1.20 V *vs.* SCE until the typical cyclic voltammogram of clean gold was obtained.[4b] After rinsing with deionized water, ethanol and drying with nitrogen gas blowing, the gold electrode was immersed in 1 mM ethanol solution of $H_2Q(CH_2)_nSH$ for 2-5 h. The electrode was rinsed with fresh ethanol and deionized water and then used for voltammetric studies.

Results and Discussion

The cyclic voltammetric behaviors of the spontaneously adsorbed ω-mercaptoalkylhydroquinone derivatives on gold were studied in Ar saturated 0.1 M NaOH. Figure 1 shows the typical cyclic voltammograms (CVs) for $H_2Q(CH_2)_4SH$-SAM on gold electrode at different scan rates. The CV shapes are stable to successive potential scans, indicating the electrochemical stability of the H_2Q-terminated monolayer in basic solution. A pair of symmetric redox peaks for the surface-confined H_2Q species can be seen. The inset in
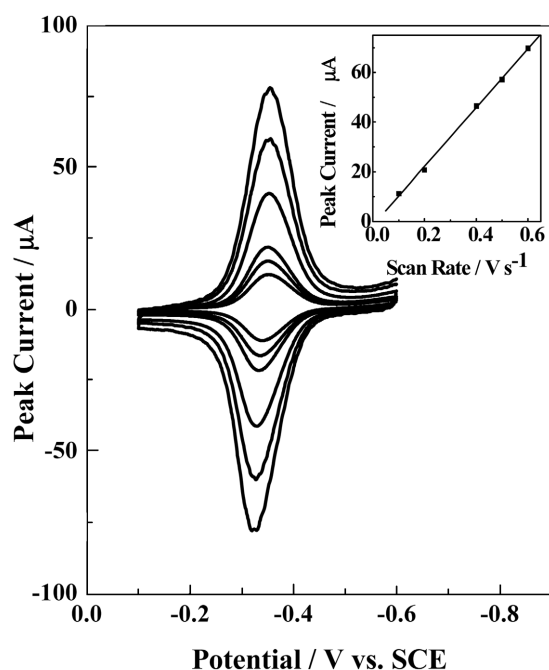

Figure 1. Typical cyclic voltammograms of $H_2Q(CH_2)_4SH$ SAMs on gold in 0.1 M NaOH. Scan rate: 0.1, 0.15, 0.2, 0.4, 0.5, 0.6 V/s. The inset shows scan rate dependence of the cathodic peak current for the hydroquinone-terminated SAMs.

Table 1. CV characteristics of $H_2Q(CH_2)_nSH$ SAMs (n = 4, 6, 8, 10, and 12) on gold in 0.1 M NaOH. All scan rates were 0.1 V/s[a]

n	ΔE_p / V	$-E°'$ / V	i_{pc} / i_{pa}
4	0.014	0.346	1.03
6	0.016	0.344	0.96
8	0.014	0.335	1.01
10	0.011	0.340	1.07
12	0.013	0.339	1.05

[a]The values of $E°'$ and i_{pc}/i_{pa} are surface formal potential and ratio of cathodic peak current to anodic peak current, respectively.

Figure 1 shows the redox peak currents for the $H_2Q(CH_2)_4SH$ monolayer are linearly proportional to scan rate. These redox wave characteristics were generally observed for all $H_2Q(CH_2)_nSH$-SAMs (n = 4, 6, 8, 10, and 12) on gold electrode in 0.1 M NaOH and were summarized in Table 1. As expected for the voltammetric behavior of the surface-confined redox molecule,[16] each pair of reversible redox peaks produce very small peak-to-peak separation (ΔE_p) values of 11-16 mV and the ratios of peak current are quite close to unity as shown in Table 1. As an thermodynamic indicator, the $E°'$ of H_2Q moiety does not vary within an experimental error of *ca.* 10 mV. This presents that there is no change in the solvation environment around the redox center without respect to the different alkyl chain length in SAM. The small ΔE_p values almost remain invariant in spite of an increase in the alkyl chain length. This indicates that the reversibility in the electron transfer kinetics of H_2Q moiety in SAMs is maintained even at a much longer distance. The maintenance of reversibility observed in 0.1 M NaOH solution shows a keen contrast with the results in our previous report[9] that the electron transfer kinetics of $H_2Q(CH_2)_nSH$ SAMs on gold in 0.1 M $HClO_4$ is transformed from reversibility to irreversibility due to an increase in spacer length. For example, the ΔE_p value observed for the $H_2Q(CH_2)_{12}SH$ SAM on gold was *ca.* 630 mV at 100 mV/s.[9] This value is substantially large in comparison with only 13 mV of ΔE_p obtained for the SAM at the same scan rate as shown in Table 1. The remarkable change in reversibility of $H_2Q(CH_2)_{12}SH$ SAM possessing the same electron transfer distance, as represented with large difference in ΔE_p, only suggests that a solution pH also plays an important role in the electron transfer kinetics of H_2Q-terminated SAM. H_2Q follows a two-electron two-proton transfer reaction mechanism in its redox reaction. The mechanism and rate constant depending on pH, based on the nine-member square scheme, was theoretically treated by Laviron[11] under the assumption that protonation reactions are at equilibrium in the absence of disproportionation and dimerization. However, there are many practical limits in using the theoretical treatment to analyze the proton-coupled electron transfer reaction pathway for many quinone derivatives. Those limits usually come from the fact that the informations such as pK_a values, redox potentials, reaction sequence for the elemental electron or proton transfer reaction step, and transition potential related to the thermo-

Notes

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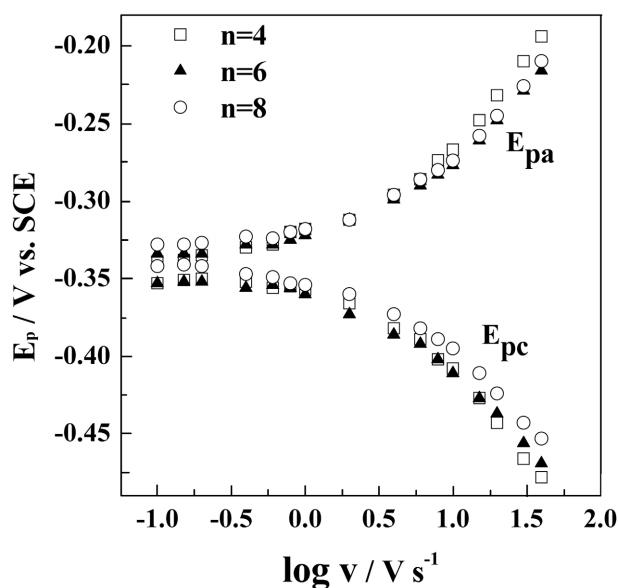
Figure 2. Plot of E_p *vs.* log V for $H_2Q(CH_2)_nSH$ SAMs (n = 4, 6, and 8) on gold. The cases of n = 10 and 12 were omitted for clarity.

Table 2. Electrochemical kinetic parameters of $H_2Q(CH_2)_nSH$ SAMs (n = 4, 6, 8, 10, 12) on gold electrode[a]

| n	$(1-\alpha)n$	αn	$\log k_{app}/\,s^{-1}$
4	0.96	0.91	1.49
6	1.05	0.98	1.42
8	0.99	1.04	1.49
10	1.01	1.03	1.39
12	1.00	1.06	1.41

[a]The values of αn and $(1-\alpha)n$ are transfer coefficients due to reduction and oxidation of hydroquinone group for overall reaction. The value of k_{app} is the average value of anodic and cathodic apparent rate constants for overall redox reaction.

dynamic and kinetic characteristics are not completely covered for the $2e^-$, $2H^+$ surface electrochemical processes. In fact, it is not possible experimentally to determine a correct rate constant for the elemental electron transfer step without the informations as listed above. However, under the condition of highly deficient proton ion such as 0.1 M NaOH solution, H_2Q in the monolayer seems to follow a much simpler redox mechanism like two successive electron transfer reaction because two protons of the surface-confined H_2Q would be deprotonated. In the highly basic condition, totally deprotonated H_2Q moiety (Q^{2-}) behaves as a major species in SAMs because the second pK_a[17] (known to be 11.4) of H_2Q is smaller than a pH value of 0.1 M NaOH. And the dianion mainly undergoes a bielectronic transfer reaction consisting of two monoelectronic steps in which proton is rarely coupled in the electron transfer reaction. The direct pseudo-bielectronic transfer reaction is expected to be very fast in basic solution because the elemental protonation reaction deterring the overall electron transfer would be suppressed. Under this simplification, k_{app} for the overall bielectronic process can be extracted by Laviron's procedure.[18] Figure 2 shows typical redox peak splitting by E_{pc} and E_{pa} observed for $H_2Q(CH_2)_nSH$-SAMs on gold electrode as a function of log scan rate (Vs^{-1}). Using this procedure, the kinetic parameters such as k_{app} and symmetry factor may be obtained in a straightforward manner from Eqs (1) and (2),

$$E_{pc} = E_c^{o'} - (RT/\alpha nF)\ln[\alpha nFv_c/RTk_{app}] \qquad (1)$$

$$E_{pa} = E_a^{o'} - (RT/(1-\alpha)nF)\ln[(1-\alpha)nFv_a/RTk_{app}] \qquad (2)$$

where v_c and v_a are the critical scan rates obtained by extrapolating the linear portion of the E_p versus $\ln(v)$ plot to the formal cathodic and anodic potentials $E_c^{o'}$ and $E_a^{o'}$. The slopes of the linear portion of the E_p *vs.* $\ln(v)$ curve are $RT/$

αnF for the cathodic branch and $RT/(1-\alpha)nF$ for the anodic branch. The values of αn and $(1-\alpha)n$ were obtained from the values of each slope and substituted back in eqs 1 and 2 to solve for k_{app}. The electrochemical kinetic parameters for $H_2Q(CH_2)_nSH$-SAMs on gold electrode were summarized in Table 2. All of the anodic and cathodic transfer coefficient values for each H_2Q-terminated SAM, *i.e.* $(1-\alpha)n$ and αn, are in fact unity respectively. This indicates that the oxidation and reduction process of H_2Q moiety in SAM take place through a very symmetric energy barrier which is independent of a length of alkyl chain spacer. In addition, the sum of cathodic and anodic transfer coefficient values is quite close to 2, indicating the total number of transferred electron in the redox reaction of a H_2Q group. It is worth noting the fact that the logarithmic value of k_{app} almost does not vary with the number of methylene group of $H_2Q(CH_2)_nSH$ SAM. This observation seems to imply the independence of the heterogeneous electron transfer rate of H_2Q moiety on the distance between the redox center and the electrode surface. This strongly contradicts the distance dependence of electron transfer rate constant known from several reports[3-5,7-9,19,20] published up to now. According to Marcus theory,[10] the dependence of the electron transfer rate constant (k) on the distance (d) can be evaluated by eq (3),

$$k_2 = k_1 \exp[-\beta(d_2-d_1)] \qquad (3)$$

where β is the electron tunneling constant. As for different electroactive SAM systems, the reported β value is 1.06 for ferrocene-SAM,[3] 1.06 ± 0.04 for mixed SAM prepared with $Ru(NH_3)_5Py$/diluent alkanethiols,[4a] 1.34 ± 0.2 for the azobenzene-SAM,[8] and 1.04 ± 0.06 for H_2Q-terminated SAMs,[9] respectively. On the other hand, some β values were estimated for nonelectroactive SAM systems using redox probes in solution. For example, 1.08 ± 0.2 for aqueous $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, and $Fe^{3+/2+}$ with ω-hydroxy-alkylthiol films,[19] and 1.02 ± 0.2 for aqueous $Fe(CN)_6^{3-/4-}$ and $Fe^{3+/2+}$ with alkanethiol films[20] are reported in the unit of methylene number of alkyl spacer. All of these β values demonstrate that the heterogeneous electron transfer rate constant is strongly dependent upon the distance transferring electron. Unlike these values, the slope in Figure 3 gives the â value of $0.01(\pm 0.01)$, which is almost zero value from the least square method. First of all, this value obtained in 0.1 M NaOH is largely different from the β value (1.04 ± 0.06)[9]
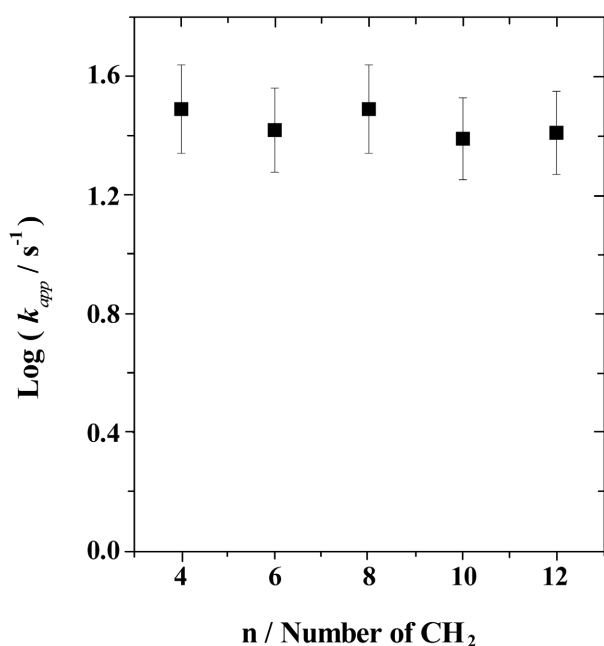
Figure 3. Dependence of log (k_{app}/s^{-1}) on the number of CH_2 group in the alkyl chain spacer of $H_2Q(CH_2)_nSH$ SAMs (n = 4, 6, 8, 10, and 12) on Au electrode. Data were taken from Table 2.

previously reported for the same H_2Q-terminated SAMs in 0.1 M $HClO_4$ solution. At this moment, the remarkable difference in β might be temporarily ascribed to the high reversibility of H_2Q molecule, which can not be discriminated at the current experimental condition. The physical meaning of β is an energy barrier height in electron transfer reaction. When the distance between the H_2Q group and an electrode surface is very short (n $\leq$ 1), the transfer rate is quite fast whether the redox center is exposed in strong acid or base condition. In this situation, the electron transfer reaction rate of H_2Q does not largely depend upon the solution pH. However, when the distance is long enough (n > 4), the transfer rate is controlled by the distance and solution pH. During the redox process, H_2Q fully protonated in acidic-neutral region follows multiple pathways of a $2e^-$, $2H^+$ transfer mechanism which is proton-coupled. Herein, the real electron transfer mechanism might be too complicated to be analyzed. However, the mechanism becomes much simpler into a $2e^-$ transfer reaction in very basic condition (0.1 M NaOH). At the moment, molecular structural change of a deprotonated hydroquinone dianion (Q^{2-}) does not happen during the electron transfer process. This factor might greatly speed up the electron transfer reaction to overcome distance-dominated H_2Q electron transfer in SAMs, as represented with highly reversible CV characteristics shown in Table 1. After all, the high reversibility results in the extremely small β value. In this situation, it might be difficult to observe distance-dependence of electron transfer because the longest alkyl chain length (n = 12) used in this work seems to be too short to make a difference in the electron transfer rate of Q^{2-} moiety

in SAMs. We think this is a good experimental example about how the proton-coupled heterogeneous electron transfer kinetics depends on the distance and solution pH at the interface of a solution and an electroactive SAM. However, it is noteworthy that electron transfer also depends on the orientation and structure of a SAM.[8] If electron transfers with a through-space tunneling and if the orientation angle changes largely, as compared with that in acidic solution, it might be possible to find clues of understanding fast electron transfer kinetics of H_2Q in very basic solution.

Currently, we are under investigation to identify the effects of spacer chain length on the high reversibility of redox couple and to check the orientation of the SAMs using spectroscopic technique. These trials will be tested with $H_2Q(CH_2)_nSH$-SAMs (n = 16, 20) on gold in 0.1 M NaOH solution to find out the orientation effect and the minimum alkyl chain length to observe distance dependence of electron transfer rate of H_2Q group. These results will give us insights on the parameters controlling long-range electron transfer at an extreme condition.

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