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Unidirectional Electron Transfer at Self-Assembled Monolayers of 11-Ferrocenyl-1-undecanethiol on Gold

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The electron-exchange reaction between the ferrocenyl group of self-assembled monolayers of 11-ferrocenyl-1-undecanethiol on gold electrodes and Fe(III) species in solution is studied. The monolayer acts as an effective electron-transfer mediator for the reduction of $Fe(ClO_4)_3$ but inhibits the oxidation of $Fe(ClO_4)_2$ in $HClO_4$ and $NaClO_4$ solution. This behavior is also observed in $HClO_4$ solutions containing Fe^{III}(edta) but only when the concentration of $HClO_4$ is higher than 0.5 M. Absorption spectra and spectroelectrochemical and electrochemical measurements show that Fe^{III}(edta) dissociates in highly acidic solutions and generates Fe^{3+}aq, which acts as an electron-accepting species.

Recently much attention has been paid to the development of molecular electronic devices. To realize molecular devices, it is essential to have a technique to arrange specific molecules on solid substrates. In this regard, construction of well-ordered molecular layers have been studied significantly. The most popular technique to form monolayer and multilayer of assembled molecules on solid surfaces is Langmuir–Blodgett (LB) method.[2—6] Unfortunately, molecular layers formed by the LB method are not always stable because these layers adsorb only physically on solid substrate. To overcome this difficulty self-assembling method has been employed by many groups as an alternative way to the LB method.[7—13] In the self-assembling method, molecules which have long hydrocarbon chains chemisorb on solid surface by making covalent bonds with atoms of the solid and self-assemble due to attractive interactions between alkyl chains. One of the most studied self-assembled monolayer system is alkanethiols on gold.

Significant efforts have been made to form and characterize self-assembled monolayers of alkanethiols with various terminal groups such as $-CH_3$, $-OH$, $-COOH$ and ester on gold and the effects of the chain length, hydrophilicity and hydrophobicity of the terminal groups on the quality and properties of the self-assembled monolayers have been studied quantitatively for the last 10 years. It is, however, only quite recently that attempts have been made to give specific functionality to metal and semiconductor surfaces by forming self-assembled monolayers.[14]

Many research groups have investigated self-assembled monolayers of ω-ferrocenylalkanethiols on gold because the ferrocenyl group in the monolayer is expected to exchange electrons readily with gold and this system can be considered as a model system for the formation of molecular electronic devices by self-assembly.[15—22] This system was studied first by Chidsey et al. They have reported that stable monolayers of ferrocene terminated alkanethiols are formed on gold by coadsorption of ω-ferrocenylalkanethiols and unsubstituted alkanethiols and that the electron transfer between the ferrocenyl groups fixed on the surface and gold is facile in spite of the existence of long hydrocarbon chains.[15] We studied the formation process and electrochemical properties of ω-ferrocenylalkanethiols modified gold electrodes and confirmed the formation of self-assembled monolayer from the charge for redox reaction.[16] We found that the electrochemical response of the monolayer is strongly affected by anions present in the solution, and that very well-organized self-assembled monolayers which give very sharp current spikes can be obtained under certain preparation conditions.[16] We also showed that this system shows a diode property, one of the essential functions of molecular devices, in 1 M $HClO_4$ solution (1 M=1 mol dm^{-3}) containing Fe^{III}(edta).[17]

In this paper we studied in detail the electron-exchange reaction between the ferrocenyl group of a self-assembled monolayer of 11-ferrocenyl-1-undecanethiol on gold and Fe(II)/(III) species in solution and confirmed that the monolayer acts as a mediator for Fe (III) reduction but inhibits the oxidation of Fe(II). The reacting species in solutions containing Fe^{III}(edta) is determined to be Fe^{+3}aq not Fe^{III}(edta).

Experimental

Materials: 11-Ferrocenyl-1-undecanethiol ($FcC_{11}SH$) was synthesized by the method reported before.[16] A smooth gold substrate was obtained by vacuum deposition on cleaned glass. Iron (III) perchlorate and Iron (II) perchlorate were purchased from Nacalai Tesque, Inc. Sodium ethylenediaminetetraacetatoferrate(III) trihydrate $Na[Fe^{III}(edta)]\cdot 3H_2O$ was purchased from Dojin Chemicals Lab. (Dotite Reagent). They were used without further purification.

Electrochemical Measurement: A three electrode, three compartment cell was used for electrochemical measurements. A potentiostat/galvanostat (Hokuto Denko Co., Ltd., HA-301) was used to control the potential of the working electrode with respect to a sodium saturated calomel electrode (SSCE). All potentials are presented with respect to this electrode in this paper. A Pt foil was used as a counter electrode. External potential was provided by a function generator (Hokuto Denko Co., Ltd., HB-105). Current–potential relations were recorded on an X–Y recorder

(Rika Denki Co., Ltd., RW-11T). All electrochemical measurements were carried out at room temperature after solution was deaerated by flowing high purity N_2 gas (Teisan, 99.999%) for at least 15 min. Milli-Q water was used to prepare electrolyte solutions.

Spectroelectrochemistry: A thin-layer quartz cell (optical path length=1 mm) was used for spectroelectrochemical measurements. A Pt mesh (0.7 cm×3.5 cm) was used as a working electrode and a Pt foil was used as a counter electrode. The working electrode was in the thin-layer portion and the counter and the reference electrode were placed in an upper portion of the cell so that they do not interfere the optical path (see the inset of Fig. 6 for the arrangement). Absorption spectra were measured with a UV-vis spectrophotometer (Japan Spectroscopic Co., Ltd., Model Ubest-30 and Hitachi, Model U-3200).

Results and Discussion

Electrochemical Behavior in 1 mM $Fe(ClO_4)_3$–$HClO_4$ Solution: Figure 1 shows the cyclic voltammogram (CV) of a $FcC_{11}SH$-modified gold electrode in 1 M $HClO_4$ solution (a) and in 1 M $HClO_4$ solution containing 1 mM $Fe(ClO_4)_3$ at various sweep rate ((b)—(e)). As a comparison, CV at a bare gold electrode in 1M $HClO_4$–1 mM $Fe(ClO_4)_3$ solution is also presented in Fig. 1 (f). Although reversible redox peaks are observed in 1 mM $Fe(ClO_4)_3$–1 mM $HClO_4$ solution at the bare gold electrode around +450 mV, reduction of Fe^{+3} is totally blocked at the $FcC_{11}SH$-modified gold electrode in this potential region. However, the cathodic peak current around +150 mV grows if $Fe(ClO_4)_3$ is present in solution. On the other hand the anodic peak current at the same potential decreases by the addition of $Fe(ClO_4)_3$. The degree of increase of the cathodic peak current is larger when the sweep rate is lower. Figure 2 shows the relation between the cathodic peak current and the sweep rate both with and without $Fe(ClO_4)_3$ in solution. The sweep rate dependence of the ratio of the current with and without $Fe(ClO_4)_3$ in solution is shown in the inset of Fig. 2. The cathodic peak current approaches to the value without $Fe(ClO_4)_3$ at higher sweep rate.

The electrochemical characteristics of the electrode is strongly affected by the concentration of $Fe(ClO_4)_3$ in solution. Figure 3 shows CVs of the modified electrode in 1 M $HClO_4$ solution containing various concentrations of $Fe(ClO_4)_3$. The cathodic peak current increases as the concentration becomes higher and is proportional to the concentration of $Fe(ClO_4)_3$ in solution (Fig. 4).

These results were similar to those obtained in Fe^{III}(edta)/1 M $HClO_4$ solution reported previously.[17] There are two possibilities for the increase of the cathodic current peak at +150 mV. As mentioned before (Fig. 1(f)), the electrochemical reaction of Fe^{2+}/Fe^{3+} in 1 M $HClO_4$ is reversible at bare gold electrode and the redox potential of the couple in the present condition is +450 mV (vs. SSCE). Thus, one possibility is that

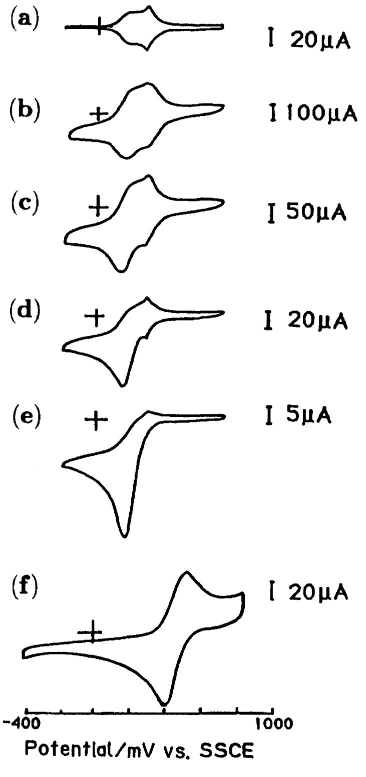


Fig. 1. Cyclic voltammogram of a gold electrode, which was dip-treated in 1 mM $FcC_{11}SH$ hexane solution for 96 h (a) measured in 1 M $HClO_4$ with sweep rate of 100 mV s^{-1} and (b)—(e) measured in a solution containing 1 M $HClO_4$ and 1 mM $Fe(ClO_4)_3$ with sweep rate of (b) 1000 mV s^{-1}, (c) 500 mV s^{-1}, (d) 100 mV s^{-1}, and (e) 10 mV s^{-1}. Cyclic voltammogram of an untreated gold electrode measured in a solution containing 1 M $HClO_4$ and 1 mM $Fe(ClO_4)_3$ with a sweep rate of 100 mV s^{-1} is presented as a comparison (f).

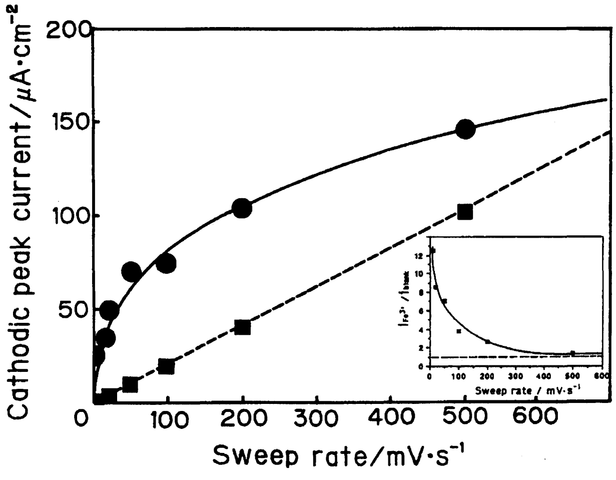


Fig. 2. Sweep rate dependence of cathodic peak current observed in a solution containing 1 M $HClO_4$ with (●) and without (■) 1 mM $Fe(ClO_4)_3$. Other conditions are of Fig. 1. Inset: Sweep rate dependence of ratio of peak currents with and without 1 mM $Fe(ClO_4)_3$ in solution.

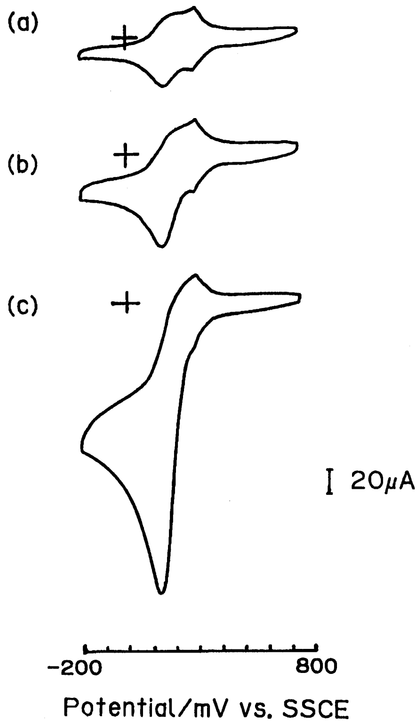


Fig. 3. Cyclic voltammograms of the gold electrode, which was modified under the same condition employed to prepare the electrode used in Figs. 1 and 2, measured in solutions containing 1 M $HClO_4$ and (a) 0.2 mM, (b) 0.5 mM, and (c) 2 mM of $Fe(ClO_4)_3$. Sweep rate: 100 mV s^{-1}.

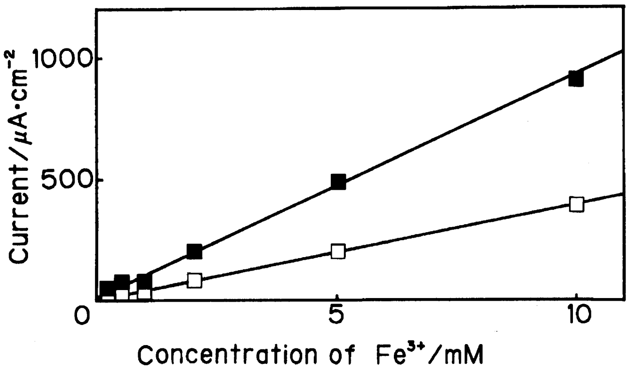


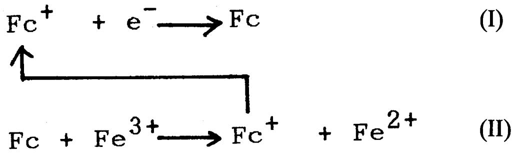
Fig. 4. Relation between cathodic peak current and concentration of $Fe(ClO_4)_3$. Sweep rate :10 mV s^{-1} (□) and 100 mV s^{-1} (■).

the reduction of Fe^{3+} become irreversible by the surface modification and the cathodic peak at +450 mV at the bare gold shifts to +150 mV. This possibility is quite low because the peak appears at the same potential when sweep rate is changed and the decrease of anodic peak current around +150 mV cannot be explained by this model. Furthermore, when $Fe(ClO_4)_2$ was added in 1 M $HClO_4$, the CV was exactly the same as that obtained in 1 M $HClO_4$ without $Fe(ClO_4)_2$, suggesting the surface monolayer totally inhibit the direct electron transfer to and from Fe(II)/Fe(III) in solution.

More probable mechanism is the one we already proposed for Fe^{III}(edta) system.[17] Since the redox potential of Fe^{2+}/Fe^{3+} couple in solution is more positive than that of the surface-attached ferrocenyl group, the ferrocenyl group donates an electron to Fe^{3+}aq forming Fe^{2+}aq and becoming a ferricinium cation. If the potential is more negative than the redox potential of the ferrocenyl group, the ferricinium ion accepts an electron from the electrode and the surface ferrocene is regenerated. These steps are repeated and a large cathodic current flows, as summarized in Scheme 1. In other words, surface ferrocenyl groups act as electron mediators for the reduction of Fe^{3+}aq. The cathodic current peak is the result of diffusion of Fe^{3+}aq from the solution bulk to the surface. When the potential of the modified electrode is scanned to more positive values, ferrocene moiety is oxidized to ferricinium cation, but some of the surface ferrocenyl groups are already oxidized to ferricinium cations by the Fe^{3+} in solution, the anodic current due to this process is smaller than that without Fe^{3+} in solution. Since the redox potential of Fe^{2+}/Fe^{3+} is more positive than that of surface ferrocene/ferricinium cation, ferricinium cation cannot accept electrons from Fe^{2+} in solution. Moreover, the compact surface monolayer inhibits the direct electron transfer from Fe^{2+}. Thus, the ω-ferrocenylalkanethiols modified electrode acts as a rectifier or a diode. This is a quite important property for constructing molecular electronic devices.

Reactive Species in Fe^{III}(edta)–$HClO_4$ Solutions : As mentioned before, we reported similar results for Fe^{III}(edta)/1 M $HClO_4$ solutions in our previous paper[17] but the actual species involved was not clear. To clarify this, the pH dependence of the electrochemical characteristics were investigated.

Figure 5 shows CVs of a gold electrode, which was dip-treated in 1 mM $FcC_{11}SH$ hexane solution for 50 h, measured in 1 M $HClO_4$ solution (Fig. 5 (a)) and in solutions containing 1 mM Fe^{III}(edta) and various concentration of $HClO_4$. Only when the concentration of $HClO_4$ is high (1 M: Fig. 5 (e), 0.5 M: Fig. 5 (d)), the growth of the cathodic peak current at +150mV is observed. In 1 M $NaClO_4$ solution, almost the same CVs are observed with and without 1 mM Fe^{III}(edta). These results may be due to the pH dependence of the redox potential of Fe^{II}(edta)/Fe^{III}(edta), which was reported by Koltoff et al.[23] According to the Scheme 1, the cathodic current peak should grow only when the redox potential of solution species is more positive than



Scheme 1.

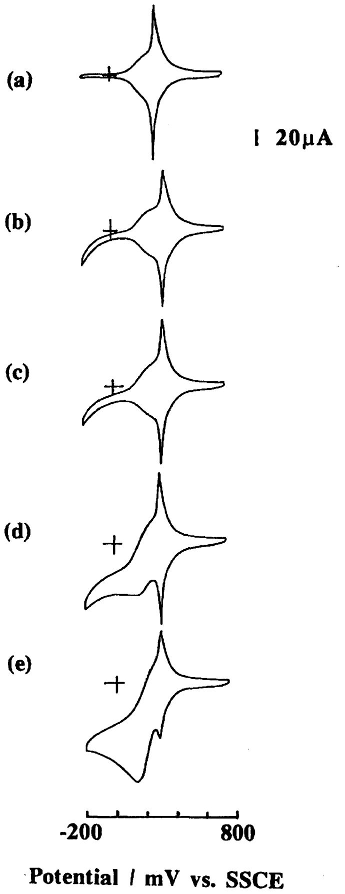


Fig. 5. Cyclic voltammograms of the gold electrode modified with $FcC_{11}SH$ by dipping treatment in 1 mM $FcC_{11}SH$ hexane solution for 50 h. Solution: (a) 1 M $HClO_4$, (b) 1 mM Fe^{III}(edta)/0.1 M $HClO_4$, (c) 1 mM Fe^{III}(edta)/0.2 M $HClO_4$, (d) 1 mM Fe^{III}(edta)/0.5 M $HClO_4$, and (e) 1 mM Fe^{III}(edta)/1 M $HClO_4$. Sweep rate: 100 mV s^{-1}.

that of the surface ferrocene/ferricinium cation couple. It is very difficult to determine the redox potential of Fe^{III}(edta) by electrochemical measurements because the reversibility of the reaction is low. Thus, we determined the redox potential of Fe^{II}(edta)/Fe^{III}(edta) in solutions containing $HClO_4$ and $NaClO_4$ with the total concentration of ClO_4^- was kept at 1 M, by a spectroelectrochemical method. Figure 6 shows the ratio of Fe^{III}(edta) to Fe^{II}(edta) in 1 M $HClO_4$ solution as a function of potential. The inset of the figure shows the arrangement of electrodes in the spectroelectrochemical cell. In this particular case, the redox potential of Fe^{II}(edta)/Fe^{III}(edta) in solution is determined to be +520 mV. The redox potentials of Fe^{III}(edta) in solutions containing 1 M [ClO_4^-] at various pH values are summarized in Fig. 7. The results are in good agreement with those reported by Koltoff et al. for pH values above 1.[23] The larger the pH is, the more negative the redox potential is. When the pH is lower than 1, the redox potential of Fe^{II}(edta)/Fe^{III}(edta) is very positive.

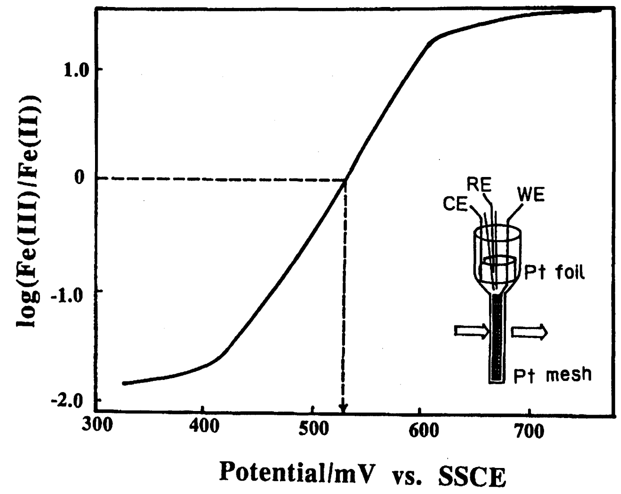


Fig. 6. Potential dependence of the concentration ratio of Fe^{III}(edta)/Fe^{II}(edta) in 1 M $HClO_4$ determined spectroelectrochemically. Inset: Arrangement of the quartz cell for spectroelectrochemical measurements.

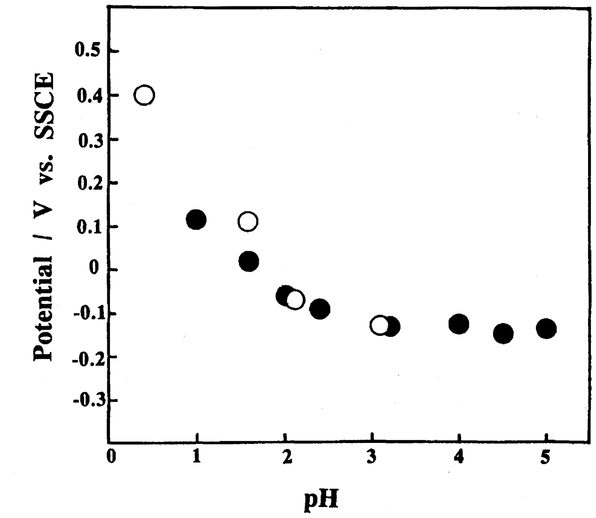


Fig. 7. Redox potentials of Fe^{III}(edta) as a function of pH. The open circles show the results obtained in the present study by spectroelectrochemical measurement and close circles show the results reported by Kolthoff et al.

If one compares the results in Fig. 5 and those in Fig. 7, it is clear that the cathodic current peak grows only when the redox potential of Fe^{II}(edta)/Fe^{III}(edta) in solution is more positive than that of the surface attached ferrocene/ferricinium ion. On the other hand, when $Fe(ClO_4)_3$ is present in solution, the cathodic peak (+150 mV) increases even when the $HClO_4$ concentration is as low as 0.01 M. Furthermore, the growth of the cathodic current peak is also observed in $NaClO_4$ solution containing $Fe(ClO_4)_3$. In all solutions investigated the redox potential of $Fe(ClO_4)_3$ solutions are always more positive than that of the ferrocene/ferricinium ion couple.

Table 1. Absorption Maximum and Electrochemical Response of Fe(III) Species in Various Solutions of Various Concentration of $HClO_4$

Fe(III)-species	Concentration of $HClO_4$/mol dm^{-3}	pH	Absorption maximum / nm	Growth of cathodic peak around+150 mV
Fe^{III}(edta)	1	<0	238	○
	0.5	0.12	240	○
	0.2	0.55	250	×
	0.1	0.88	259	×
	0.01	1.96	259	×
	0.001	3.00	260	×
$Fe(ClO_4)_3$	1	<0	238	○
	0.1	0.92	238	○
	0.01	1.91	240	○

These results confirm that the increase of the cathodic peak current is observed only when the redox potential of the solution species is more positive than that of the ferrocene/ferricinium cation, as is expected from Scheme 1.

As mentioned before, when the pH is lower than 1, the redox potential of Fe^{II}(edta)/Fe^{III}(edta) becomes very positive and approaches the value of the Fe^{2+}/Fe^{3+} couple. Thus, there may be a possibility that the chemical species accepting the electron from the surface ferrocenyl group is Fe^{3+}aq ion in both cases. To identify the solution species, absorption spectra of Fe^{III}(edta) and $Fe(ClO_4)_3$ in various concentrations of $HClO_4$ were measured. The results are summarized in Table 1 with the results of the electrochemical response. While the absorption maxima appear around 238 nm in solutions containing $Fe(ClO_4)_3$, those in solutions containing Fe^{III}(edta) are around 260 nm when the pH is high but are around 238 nm at lower pH, suggesting that the Fe^{3+} species in the latter case is Fe^{3+}aq not Fe^{III}(edta). It is clear that the cathodic current peak grows only when the absorption maximum is around 238 nm, suggesting that the electron-accepting species is indeed Fe^{3+}aq in both cases.

These behaviors can be explained by considering the dissociation of Fe^{III}(edta), i.e., the formation of free Fe^{3+}. Although EDTA exists as five states in solution with different degree of proton dissociation, only ethylenediaminetetraacetate ion $edta^{4-}$ forms chelate with Fe^{3+}.[24] Thus, the formation of the EDTA chelate of Fe^{3+} can be represented by

$$Fe^{3+} + edta^{4-} \rightleftarrows Fe(edta)^{-}, \tag{1}$$

and the formation constant, K_f, is given by

$$K_f = \frac{[Fe(edta)^-]}{[Fe^{3+}][edta^{4-}]}. \tag{2}$$

The total concentration of EDTA ($[edta]_T$) is given by

$$[edta]_T = [edta^{4-}] + [Hedta^{3-}] + [H_2edta^{2-}] + [H_3edta^-] + [H_4edta], \tag{3}$$

where $Hedta^{3-}$, H_2edta^{2-}, H_3edta^-, and H_4edta are the EDTA species with one, two, three, and four protons, respectively. $[edta]_T$ is also represented by using $[edta^{4-}]$, proton concentration and four K_a values corresponding to stepwise dissociation of the four protons as

$$[edta]_T = [edta^{4-}]\left\{1 + \frac{[H^+]}{K_{a4}} + \frac{[H^+]^2}{K_{a4}K_{a3}} + \frac{[H^+]^3}{K_{a4}K_{a3}K_{a2}} + \frac{[H^+]^4}{K_{a4}K_{a3}K_{a2}K_{a1}}\right\}. \tag{4}$$

The fraction of $edta^{4-}$, only which participates the complex formation with Fe^{3+}, to the total concentration, α_H, is given by

$$\alpha_H = \frac{[edta^{4-}]}{[edta]_T}. \tag{5}$$

The conditional formation constant, K'_f, at different pH value is defined as :[24]

$$K'_f = K_f\alpha_H = \frac{[Fe(edta)^-]}{[Fe^{3+}][edta^-]}. \tag{6}$$

At lower pH, K'_f becomes smaller and the amount of free Fe^{3+} increases, since α_H is small. The values of α_H, K'_f and therefore, the amount of free Fe^{3+} are calculated for solutions of various pH with initial concentration of 1 mM Fe^{III}(edta) by using Eq. 6 with known values of K_{a1}, K_{a2}, K_{a3}, K_{a4}, and K_f which are all independent of pH and are 1.0×10^{-2}, 2.2×10^{-3}, 6.9×10^{-7}, 5.5×10^{-11}, and 1.3×10^{25}, respectively.[24] The results are summarized in Table 2.

It is clear that Fe(III) species in solution whose pH is higher than 1 exist almost as Fe^{III}(edta) complexes but at pH 0 or below the complexes dissociate and considerable amount of free Fe^{3+} exists in solution. Thus, we can conclude that the chemical species accepting electron from ferrocenyl group is not Fe^{III}(edta) but free Fe^{3+}

Conclusion

We have studied the electron-exchange reaction between the ferrocenyl group of self-assembled monolayers

Table 2. pH Dependence of the Fraction of edta^{4-} (α_H), the Conditional Formation Constant (K_f'), and the Concentration of Free Fe^{3+} of $\mathrm{Fe^{III}(edta)}$ System

pH	α_H	$K_{\mathrm{f}'}$	Free $[\mathrm{Fe}^{3+}]$/M
0	8.3×10^{-22}	1.1×10^{4}	3.0×10^{-4}
0.1	2.1×10^{-21}	2.7×10^{4}	1.9×10^{-4}
0.2	5.3×10^{-21}	6.9×10^{4}	1.2×10^{-4}
0.5	8.3×10^{-20}	1.1×10^{6}	3.0×10^{-5}
1.0	7.6×10^{-18}	9.9×10^{7}	3.2×10^{-6}
2.0	3.8×10^{-14}	4.9×10^{11}	4.5×10^{-8}

of 11-ferrocenyl-1-undecanethiol on gold electrodes and Fe(III) species in solution and have demonstrated that self-assembled monolayers of 11-ferrocenyl-1-undecanethiol act as effective electron-transfer mediators for the reduction of $\mathrm{Fe(ClO_4)_3}$ but inhibit the oxidation of $\mathrm{Fe(ClO_4)_3}$ in $\mathrm{HClO_4}$ and $\mathrm{NaClO_4}$ solution. This behavior has also been observed in $\mathrm{HClO_4}$ solution containing $\mathrm{Fe^{III}(edta)}$ but only when the concentration of $\mathrm{HClO_4}$ is higher than 0.5 M. In these cases, $\mathrm{Fe^{3+}aq}$ generated as a result of partial dissociation of $\mathrm{Fe^{III}(edta)}$ acts as an electron-accepting species, as confirmed by absorption spectra and spectroelectrochemical and electrochemical measurements.

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