



# The effect of supporting electrolyte on the electron transfer at mixed self-assembled monolayers containing ferrocene moieties



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## ABSTRACT

The effect of supporting electrolyte on the apparent redox potential ( $E_{app}$ ) of ferrocene (Fc) moieties in mixed self-assembled monolayers (SAMs) has been studied by means of cyclic and ac voltammetry. When the Fc moieties are exposed on the surface of the SAM (i.e., for the mixed SAM of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and 1-hexylmercaptan), the  $E_{app}$  is little dependent on the supporting electrolytes used, i.e., sodium salts of 4-hydroxybenzenesulfonate (HBS), *p*-toluenesulfonate (TS), and 2-naphtalenesulfonate (NS). On the other hand, when the Fc moieties are buried in the SAM (i.e., for the mixed SAM of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and 1-octadecylmercaptan), the  $E_{app}$  is significantly shifted to more positive potentials and is further affected by the nature of the electrolyte anions. The more hydrophobic the anion becomes in the order  $\text{HBS} < \text{TS} < \text{NS}$ , the less positive the  $E_{app}$  value. This effect has been successfully explained by the theory proposed by Smith and White (Anal. Chem., 64 (1992) 2398–2405), with an additional consideration on the anions' ability to neutralize the positive charge of oxidized Fc moieties.

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## 1. Introduction

The self-assembled monolayer (SAM) is an oriented monolayer film formed by spontaneous chemisorption of organic molecules such as thiols on a solid surface (typically, a gold electrode surface [1–3]). The SAM modified electrode is promising for a biomembrane model, since the SAM/solution interface provides a reaction field for biological redox species, which is analogous to the biomembrane surface. Recently, we studied the redox reaction of a quinone derivative XQ (= ubiquinone-10 or vitamin  $\text{K}_1$ ) incorporated in alkanethiol SAMs, and then found that a strongly hydrophobic supporting-electrolyte cation such as tetrabutyl- or tetrapentyl-ammonium ion was adsorbed on the SAM/solution interface and the resultant structural disorder of the monolayer facilitated the proton transfer coupled with the electron transfer of XQ [4]. In this system, however, the electric charge was carried by protons across the SAM/solution interface, so that the apparent redox potential ( $E_{app}$ ) of XQ was not considerably changed at a constant pH. Mainly a kinetic effect was observed therein.

In this study, we have investigated a “thermodynamic” effect of the SAM/solution interface by using a mixed SAM containing 6-ferrocenyl-1-hexanethiol ( $\text{Fc}(\text{CH}_2)_6\text{SH}$ ; with Fc = ferrocene) and 1-octadecylmercaptan (OM). Such Fc-terminated SAM modified electrodes show a one-electron redox reaction:  $\text{Fc} \rightleftharpoons \text{Fc}^+ + \text{e}^-$ . So far, many reports have been published on electron-transfer kinetics [5–8], electric double-layer effects [9,10], application as an electron mediator [11] and also biosensing [12–14]. In these studies,

however, Fc moieties were usually exposed on the surface of SAM. There are few reports about the measurement system in which Fc moieties are buried within the monolayer interior [8].

In the present mixed SAM as well, Fc moieties are buried in the long alkyl chains of the OM monolayer. Accordingly, the electrochemical oxidation of Fc moieties would induce the transfer of anions (not protons) from the solution to the SAM. In this study, we have used three different supporting electrolytes, i.e. sodium salts of 4-hydroxybenzenesulfonate (HBS), *p*-toluenesulfonate (TS), and 2-naphtalenesulfonate (NS), and have examined the influence on the electron transfer of Fc moieties. Previously, the effect of electrolyte anions was studied for the SAM with Fc moieties exposed on the surface [15]. However, as far as the authors know, there is no paper on such effect for the SAM with Fc moieties completely buried in the monolayer. In this study, we have chosen the above three electrolyte anions with different hydrophobicities or membrane permeability, and then have found, as expected, that the  $E_{app}$  value depends on the nature of the anions. The observed dependence has been successfully explained by the theory of Smith and White (S&W) [16] with an additional consideration on the anions' ability to neutralize the positive charge of oxidized Fc moieties.

## 2. Experimental

### 2.1. Reagents

$\text{Fc}(\text{CH}_2)_6\text{SH}$  was purchased from Dojindo Laboratories, Japan and used without further purification. OM, 1-hexylmercaptan (HXM), sodium TS (>90%), sodium NS (>98%), and sodium HBS (>98%) were

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purchased from Tokyo Chemical Industry, Japan and used without further purification.

## 2.2. Electrode Preparation

The formation of a mixed SAM on a gold electrode was performed as follows: A gold disk electrode (purchased from BAS Inc., Japan; 1.6 mm diameter; polycrystalline) was polished with 0.25  $\mu\text{m}$  diamond slurry and rinsed under ultrasonic irradiation in ethanol and deionized water. The mixed SAM of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and OM was formed on the gold-electrode surface by soaking in a mixed ethanol solution of 0.1 mM  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and 0.1 mM OM (1:5 v/v) for 1 h. For the preparation of the mixed SAM of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and HXM, a mixed ethanol solution of 0.1 mM  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and 0.1 mM HXM (1:20 v/v) was used. The prepared mixed SAM modified electrode was rinsed successively with ethanol and purified water.

## 2.3. Electrochemical Measurements

Cyclic voltammetry (CV) and alternating-current voltammetry (ACV) were performed with a conventional three-electrode system and the Hokuto Denko HA1010mM1A potentiostat. A mixed SAM modified gold electrode, a platinum wire electrode, and a Ag/AgCl (saturated KCl) electrode were used as the working, counter, and reference electrodes, respectively. These electrodes were immersed in an aqueous solution containing only 0.1 M supporting electrolyte. No deaeration of the electrolyte solution was provided, because there was no effect of dissolved oxygen on the voltammetric behaviors of the SAM modified electrodes studied. Unless noted otherwise, the electrode potential ( $E$ ) was referred to the Ag/AgCl electrode. A laboratory-constructed computer assisted system was used to perform voltammetric measurements and the data acquisition.

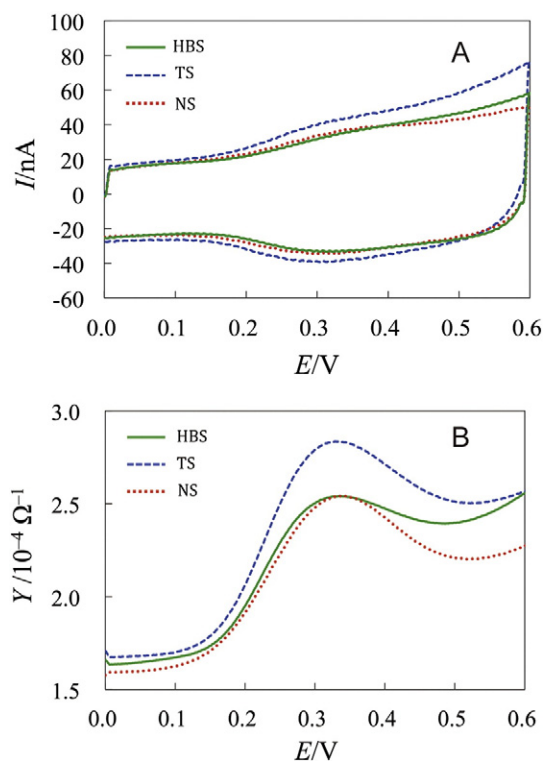
In AVC measurements, a small ac voltage (frequency,  $f = 10$  Hz–50 kHz; 0.010 V rms) was superimposed on a dc voltage sweep at  $0.05 \text{ V s}^{-1}$ . A lock-in amplifier (NF Co., Japan; LI5640) was used to detect the absolute admittance ( $Y$ ). The performance of the measurement system was checked with a dummy cell.

All the electrochemical measurements were performed in an air-conditioned room and the temperature of the electrolytic cell was kept at  $25 \pm 2$  °C.

## 3. Results and Discussion

### 3.1. The Mixed SAM of $\text{Fc}(\text{CH}_2)_6\text{SH}$ and HXM

A Fc moiety in a mixed SAM becomes positively charged upon oxidation ( $\text{Fc} \rightarrow \text{Fc}^+ + \text{e}^-$ ), and then shows an electrostatic interaction with anions [15,18]. In the SAM, where Fc moieties are exposed on the surface, inorganic anions ( $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_2\text{SO}_3^-$ , and  $\text{F}^-$ ) strongly influenced not only the electron transfer rate but also the apparent redox potential [15]. These effects, which are related to the ion-pairing ability of  $\text{Fc}^+$  with anions, vary greatly according to the nature of the anion. In this study, we focused on the membrane permeability of anions, and chose three organic sulfonate anions (HBS, TS, and NS). Since the sulfonate group forms an ion pair with  $\text{Fc}^+$ , the ion-pair abilities of the anions would be similar to each other. This may be supported by a DFT calculation at B3LYP/6-311++G(2d,p) level; the averaged partial atomic charge on the oxygen atoms of the sulfonate groups has been obtained using the natural population analysis (NPA) method as  $\bar{Q}_\text{O} = -1.64$ ,  $-1.64$ , and  $-1.63 \times 10^{-19}$  C for HBS, TS, and NS, respectively. On the other hand, judging from the chemical structures, it is supposed that the hydrophobicity of the anions increases in the order of  $\text{HBS} < \text{TS} < \text{NS}$ . This is also supported by an estimation of the Gibbs energy of ion transfer across the nitrobenzene/water interface [17]:  $\Delta G_{\text{tr}}^{\text{W} \rightarrow \text{O}} = 21.7$ ,  $19.0$ ,  $13.6 \text{ kJ mol}^{-1}$  for HBS, TS, and NS,



**Fig. 1.** (A) Cyclic voltammograms (scan rate,  $0.1 \text{ V s}^{-1}$ ) and (B) AC voltammograms (50 Hz; DC scan rate,  $0.05 \text{ V s}^{-1}$ ) of the mixed SAM of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and HXM. Supporting electrolyte: 0.1 M sodium salts of HBS, TS, and NS.

respectively (note that the less positive the  $\Delta G_{\text{tr}}^{\text{W} \rightarrow \text{O}}$  value, the more hydrophobic the ion).

Fig. 1A shows cyclic voltammograms of the mixed SAM of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  and HXM, which were recorded with 0.1 M sodium salts of HBS, TS, and NS as the supporting electrolyte. To avoid the intermolecular interaction between Fc moieties and its unfavorable effect on the electron transfer, the adsorption amount of  $\text{Fc}(\text{CH}_2)_6\text{SH}$  was kept low (i.e.,  $\sim 9 \times 10^{-8} \text{ mol m}^{-2}$  as estimated from the anodic peak; cf. the surface concentration of HXM being estimated to be  $\sim 3.4 \times 10^{-6} \text{ mol m}^{-2}$  by reductive desorption [19–21]). This resulted in the redox wave of Fc being very small compared with the charging current. Then, in order to determine the  $E_{\text{app}}$  values accurately, AC voltammograms ( $Y$  vs.  $E$  curves) were recorded as shown in Fig. 1B. As seen in the figure, well-defined voltammetric peaks were obtained, so that the  $E_{\text{app}}$  values could be determined from the peak potentials:  $E_{\text{app}} = 0.352 \pm 0.014 \text{ V}$  (HBS),  $0.369 \pm 0.031 \text{ V}$  (TS), and  $0.360 \pm 0.025 \text{ V}$  (NS) for triplicate measurements.<sup>1</sup> Thus, no considerable effect of the electrolyte anions was observed on the  $E_{\text{app}}$  value.

The kinetic effect of the electrolyte anions was also studied by determining the electron transfer rate constant ( $k_{\text{et}}$ ) by means of ACV. We employed the method reported by Creager and Wooster [6] to determine the values of  $k_{\text{et}}$ :  $5000 \text{ s}^{-1}$  (HBS),  $5500 \text{ s}^{-1}$  (TS), and  $5000 \text{ s}^{-1}$  (NS) at the respective  $E_{\text{app}}$ . The same method was successfully employed to determine the rate constants ranging from 200 to  $40\,000 \text{ s}^{-1}$  for Fc thiols under various conditions [8].

It has thus been shown that the presently used three sulfonate anions make neither thermodynamic nor kinetic effects on the electron transfer of the Fc moieties exposed on the surface of SAM.

<sup>1</sup> The  $E_{\text{app}}$  values usually showed experimental errors of 10–30 mV. This is probably because in this study, the polycrystalline gold electrode was used to form the SAMs, in which a considerable amount of pinholes or defects may form and affect the redox activity of Fc moieties to some extent.

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