'Interfacial Buffer Effect' of Self-assembled Monolayers of a Carboxylic Acid Terminated Alkanethiol on a Gold Electrode

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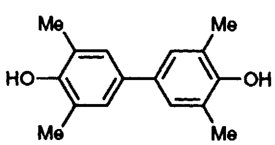
Assembled monolayers of a carboxylic acid terminated alkanethiol on a gold electrode have been found to show an 'interfacial buffer effect' on the redox reaction of a pH-dependent electroactive compound embedded in the monolayers.

Increasing attention is being given to the study of assembled monolayers of alkanethiols on gold electrodes,[1] because so-formed ultrathin organic films provide biomembrane–mimetic organised hydrophobic microenvironments with an ultimate thickness which are useful to regulate the flow of molecules and electrons.[2–6] Here, we describe hydrophobic microenvironments, which are formed by self-assembled monolayers on gold. In order to achieve this project, we incorporated a hydrophobic proton-dependent redox compound, 3,5,3′,5′-tetramethyl-4,4′-dihydrobiphenyl **1** into self-assembled monolayers on gold and examined their electrochemistry which would be expected to reflect proton concentration in the microhydrophobic monolayer environment. We found that the assembled monolayers of a carboxylic acid-terminated alkanethiol on a gold electrode behaved as an 'interfacial buffer' on the redox reaction of **1** in the monoloayer.

Compound **1** was synthesized by the oxidation of 2,6-dimethylphenol with $K_3[Fe(CN)_6]$,[7] followed by the reduction with hydrazine/active carbon. 11-Mercaptoundecan-1-oic acid **2** was synthesized from the substitution reaction of 11-bromoundecan-1-ol with thiobenzoic acid followed by the reduction with hydrazine. Satisfactory elemental analyses were obtained for the compounds **1** and **2**. 1-Mercaptododecane **3** was used as the reference compound.



1

$HS\text{-}(CH_2)_{10}\text{-}CO_2H$

2

$HS\text{-}(CH_2)_{11}\text{-}Me$

3

Modified electrodes were prepared by the following procedure. A well-polished gold disk electrode (Bioanalytical Systems, diameter: 1.6 mm) was immersed in the thiol compound (**2** or **3**) (10 mmol dm^{-3}) in ethanol for 200 min and then rinsed with ethanol. The obtained monolayer-modified electrodes were immersed in a 10 mmol dm^{-3} ethanolic solution of **1** for 10 min, followed by rinsing in ethanol (*ca.* 2 s) and were then air-dried (**1** + **2**/Au, **1** + **3**/Au). Cyclic voltammograms [(CVs) Electrochemical Analyzer, BAS-100B, Bioanalytical Systems] were measured in deoxygenated aqueous Na_2SO_4 (1.0 mol dm^{-3}) solution at 25 °C; pHs were adjusted with HCl and NaOH aqueous solutions.

Fig. 1 shows typical CVs (multiscans) of a **1** + **2**/Au electrode and a **1** + **3**/Au electrode at given pHs. Both electrodes exhibit clear *i–E* curves corresponding to quinone/hydroquinone-type redox couples. The broadness in the CVs indicates that dispersion of **1** in the monolayer membranes is not uniform and that strong physical adsorption of **1** onto the electrode does not occur. The amount of **1** calculated from the peak area of the CVs was 2 ± 1 × 10^{-11} mol cm^{-2}, compound

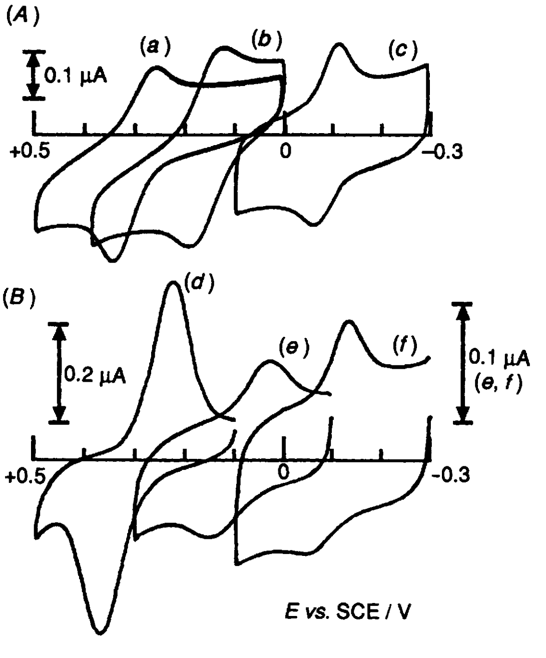


Fig. 1 Typical CVs for (*A*) a **1** + **2**/Au electrode (*a*) at pH 3.53, (*b*) pH 6.90 and (*c*) pH 10.45 and for (*B*) a **1** + **3**/Au electrode (*d*) at pH 3.46, (*e*) pH 7.02, and (*f*) pH 10.46 in 1.0 mol dm^{-3} Na_2SO_4 aqueous solution at 25 °C. Scan rate, 100 mV s^{-1}.

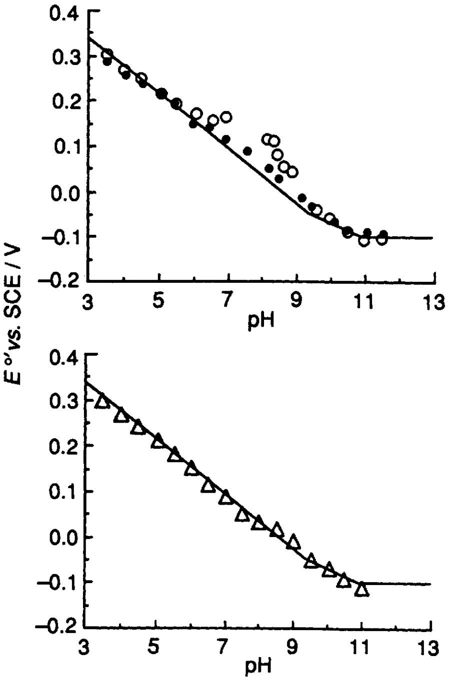


Fig. 2 pH Profiles for the oxidation/reduction potentials of **1** + **2**/Au (○) and **1** + **3**/Au (△) electrodes in the absence of Me_3CO_2H and a **1** + **2**/Au electrode (●) in the presence of 0.1 mol dm^{-3} $MeCO_2H$ in 1.0 mol dm^{-3} Na_2SO_4 aqueous solution at 25 °C. Solid lines represent the theoretical lines drawn based on the data of CVs of **1** (10^{-6} mol dm^{-3}) with a bare electrode in 1.0 mol dm^{-3} Na_2SO_4 aqueous solution. Scan rate, 100 mV s^{-1}.

1 was incorporated, in this study, by a simple adsorption method, therefore, precise control of adsorption amount was impossible.

Fig. 2 shows the formal potential ($E^{o\prime}$) of **1** as a function of pH. From the Nernst eqn., $E^{o\prime}$ of **1** is given by the eqn. (1),

$$E^{o\prime} = E^{o} - 0.0296\, m\mathrm{pH} \qquad (1)$$

where E^{o} is the standard redox potential of an electrode and m is the proton number involved in the electron-transfer reaction. The solid lines in Fig. 2 are drawn theoretically based on the data from the CVs of **1** [1.0×10^{-6} mol dm^{-3} (aq)] with a bare electrode. Three slopes (solid line) are −0.059, −0.030 and 0 V/pH which explain the 2−, 1− and 0 protons involved in the redox reaction, respectively. Two break points correspond to pK_{a1} and pK_{a2} of **1** are observed.

$E^{o\prime}$ values of **1** in the monolayer on the electrode obtained from the CVs of **1** + **2**/Au and **1** + **3**/Au electrodes were plotted against pHs of the bulk electrolyte solution (Fig. 2). Evidently, electrode **1** + **2**/Au gave positive deviation of $E^{o\prime}$ from the theoretical slope at neutral pHs. No such deviation was observed for a **1** + **3**/Au electrode. Addition of 0.1 mmol dm^{-3} acetic acid to the **1** + **2**/Au electrode system was found to diminish the deviation. These results suggest that the concentration of protons in the monolayer membrane of **1** + **2** on gold at neutral pHs are not the same as those in the bulk solution, instead the monolayer phase could maintain a higher proton concentration in this region because at neutral pH, where the concentrations of H^+ (or H_3O^+) and OH^- are very low, the carboxylic acid moiety of the monolayer could act as an 'interfacial buffer' as shown schematically in Fig. 3. Ward *et al.*[8] described that the pK_a of a self-assembled monolayer of 15-mercaptohexadecanoic acid determined by the quartz crystal microbalance is *ca.* 8, which is greater than the values observed for carboxylic acids in aqueous solution (pK_a 4.5). The 'buffer effect' in the **1** + **2**/Au system at neutral pH region therefore is understandable. Acetic acid can easily penetrate into the monolayer and behave as a proton source which leads to the disappearance of the deviation. The results mentioned above mean that despite the ultimate thickness, the monolayer of **1** + **2** on gold forms a rather strong hydrophobic microenvironment that can prevent the penetration of protons from the bulk solution.

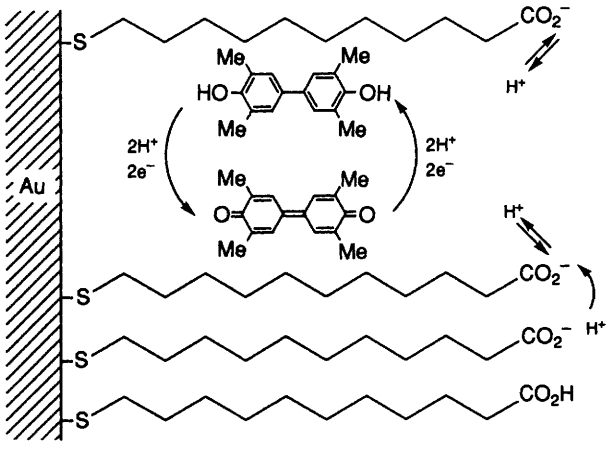


Fig. 3 Schematic representation for 'interfacial buffer effect' at a monolayer of 11-mercaptoundecan-1-oic acid on a gold electrode

Further evidence on the interfacial buffer effect was obtained from the peak separation of the CVs of the monolayer electrodes; *i.e.* **1** + **2**/Au electrodes gave smaller peak separation (*ca.* 80 mV) in comparison with those (*ca.* 120 mV) for **1** + **3**/Au electrodes. This indicates that the electron transfer of **1** in the monolayer of **2** is faster than that for the monolayer **3** system because protons could be supplied from the carboxylic acid of the monolayer.

In conclusion we have found that the assembled monolayer of the carboxylic acid-terminated alkanethiol on gold can act as interfacial buffer at neutral pHs where the concentration of protons is very low. The finding should be useful for the design of surfaces with specific functions based on the structures of ultrathin organized molecular membranes.

Received, 12th November 1993; Com. 3/06785H

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