

pH-dependent binding interaction between thiol monolayers having terminal amino group and indigo ion

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Molecular recognition based on interfacial electron transfer has attracted a growing interest because of possible applications to chemical sensors, electroanalysis, electrocatalysis, and molecular electronic devices. Molecularly structured interfaces such as self-assembled monolayers and Langmuir-Blodgett multilayers on metals serve as ideal model systems suited for controlling the environment of redox sites and examining the signal conversion on guest binding. These highly ordered electrode surfaces thus enable us to understand the mechanisms of intermolecular interaction and electron transfer at electrode-solution interfaces¹. Most of the molecular recognition systems often presented rely on the binding interaction of target analytes with the ionizable terminal groups of thiols². Limited data on the molecular interaction on/in monolayers have however hampered a thorough understanding of the charge-transfer kinetics at monolayer-modified electrodes. So far, selective and sensitive voltammetric sensing remains unsuccessful except for metal ions. To develop the promising electrode-modification strategies for detecting a target species selectively, it is necessary to examine the effect of the monolayer-analyte interaction on interfacial electron-transfer kinetics.

This study inquires how to control the interfacial electron transfer rate by variable interactions between the amino terminal groups and ionic redox-active species in solution. The effects of the following factors on electron transfer rates were examined by potential scan voltammetry and electrochemical impedance spectroscopy. In addition, a change in the solution pH (i.e. the protonation/diprotonation of terminal amino groups) allowed us to discuss the degree of contribution from non-coulombic interactions. Fig. 1 shows the cyclic voltammograms of indigotetrasulfonate at a bare gold and 4-aminothiophenol monolayer electrode in a 0.2 M KCl solution of pH 2 and 6. Since the redox reaction of indigotetrasulfonate includes protons as shown by scheme 1, its rate may decrease with increasing pH. While the electron-transfer rate constant (k^0) of indigotetrasulfonate for bare gold was decreased from $2.5 \times 10^{-3} \text{ cm s}^{-1}$ at pH 2 to $4.7 \times 10^{-5} \text{ cm s}^{-1}$ at pH 6, that for 4-aminothiophenol monolayer-modified electrode was increased from $3.2 \times 10^{-5} \text{ cm s}^{-1}$ to $1.6 \times 10^{-2} \text{ cm s}^{-1}$. This increase in k^0 is consistent with the corresponding decrease in the peak-to-peak potential separation obtained from cyclic voltammogram. Reversible redox reactions of indigotetrasulfonate were also observed at cystamine and 4-mercaptopyridine modified electrodes at pH 6, but were not observed at 3-mercaptopropanesulfonic acid, 1-butanethiol and 4-hydroxythiophenol at pH 6. Fig. 2 shows peak-to-peak separations of indigodi-, tri-, and tetrasulfonate at a 4-aminothiophenol modified electrode at $\nu = 100 \text{ mV s}^{-1}$. Our results suggest that the electron transfer rate of indigo ion is controlled by a specific chemical interaction between the carbonyl group of

indigo ion and the unprotonated terminal amino groups of thiol.

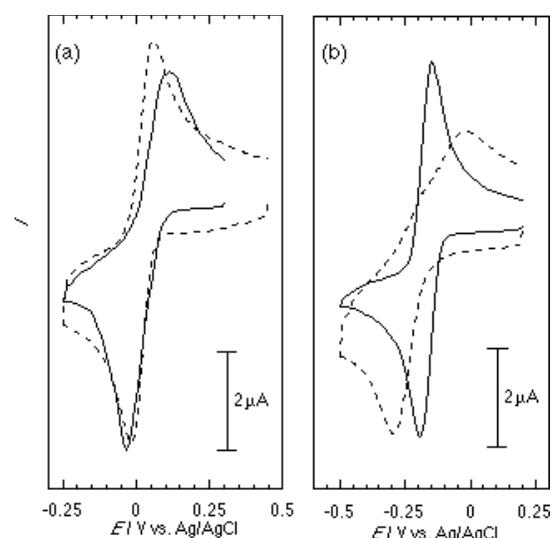
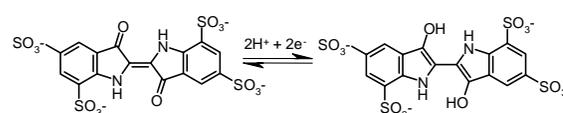


Fig. 1 Cyclic voltammograms of indigo ion at bare gold (----) and 4-aminothiophenol monolayer-modified (—) electrodes. The solution pH was (a) pH 2 and (b) pH 6.



Scheme 1

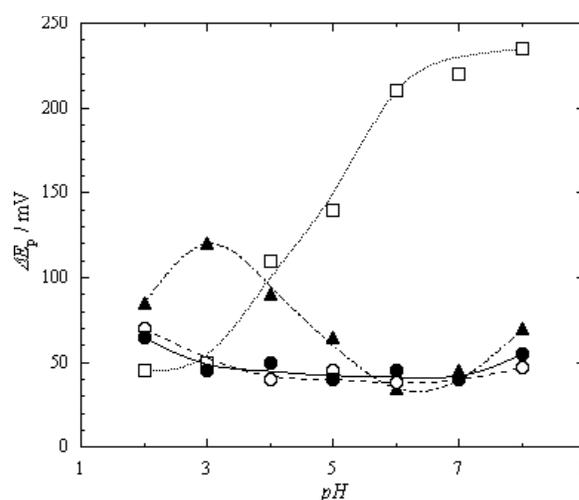


Fig. 2 Peak-to-peak potential separation of indigodi- (▲), tri- (○), tetrasulfonate (●) at 4-aminothiophenol monolayer, and bare Au electrode (□) as a function of pH solution.

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