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Gate Function of Viologen Monolayer Adsorbed on Mercury Electrode for Some Redox-Electrode Reactions

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The progress of electron exchange between 4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPOL) and a hanging mercury drop electrode can be controlled by changing the oxidation state of monolayer of 1,1'-diheptyl-4,4'-bipyridinium dication (heptyl viologen) adsorbed on the electrode; the monolayer is "open" in the oxidized state and "closed" in the reduced state.

Electrochemical behavior of viologens has been widely studied in connection with their possible use as electrochromic materials and as electron relays in photochemical energy conversion systems.1) It is well known that cyclic voltammograms (CV's) of viologens usually exhibit two pairs of redox-waves corresponding to two one-electron steps:

$$V^{2+} + e^- = V^+ \qquad (1)$$

$$V^+ + e^- = V^0 \qquad (2)$$

where V^{2+}, V^+ and V^0 denote three main oxidation states of viologens. On a hanging mercury drop electrode (HMDE), however, we found that a pair of waves like spikes appear as shown in Fig. 1 for heptyl viologen (HV^{2+}). The peak potentials are much more positive (about 0.25 V) than those corresponding to step (1) and these waves are ascribed to the redox-electrode reaction of the viologen adsorbed in a monolayer to the HMDE:

$$(HV^{2+})_{ads} + e^- = (HV^+)_{ads} \qquad (3)$$

The adsorption of the oxidized form HV^{2+} on the HMDE at -0.2 V has been confirmed by the dependence of the spike height on the duration time between the birth of the HMDE and the start of the potential sweep.

In the course of our work on the redox-electrode reactions of such viologens as a prototype of electroactive strong adsorbates, we found that the adsorbed viologen monolayer behaves like a gate or a switch for the electroreduction of TEMPOL and reoxidation according to the oxidation state of the viologen. Furthermore we found such an effect of the adsorbed viologen monolayer on the kinetics of electrode reactions of species present in the solution depends not only on the oxidation state of the adsorbed viologen but also on the kind of redox species. In this paper we report these interesting phenomena and discuss them in view of mechanisms of charge transfer at the electrode.

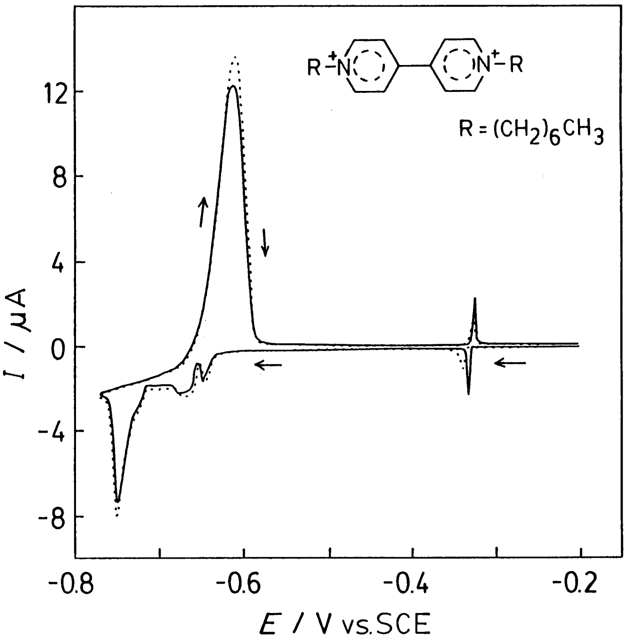

Fig. 1. Cyclic voltammograms for 1 mM heptyl viologen at HMDE in 0.1 M K_2SO_4 (——) and in 10 mM KOH + 0.1 M K_2SO_4 (····). Sweep rate was 50 mV/s.

A static mercury drop electrode (PAR303, EG&G Princeton Applied Research) was used as the HMDE, area of which was determined as $A=(1.10\pm0.05)\times10^{-2}$ cm^2. Electrochemical measurements were performed using an HECS311B potentiostat, an HECS1104 potential sweeper, and an HECS332B lock-in amplifier (Huso Electrochemical System). A saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrodes, respectively. Heptyl viologen dibromide (Eastman Kodak) and TEMPOL (Aldrich) were used as received. Water was purified by a Millipore Milli-Q system. All the measurements were performed at a room temperature.

Figure 1 shows a typical CV for 1 mM HV^{2+} obtained with the HMDE in 0.1 M K_2SO_4 aqueous solution ($M=mol/dm^3$). In addition to the main waves which appear at potentials more negative than about -0.55 V, a pair of peaks like spikes appear at -0.33 V and -0.31 V in the scan to negative and positive direction, respectively. These sharp spikes corresponding to reaction (3) indicate strong interaction among adsorbed redox species, and we will call these peaks as adsorption spikes. Though spikes become somewhat blunt when KOH (0.01 M) is added to the solu-

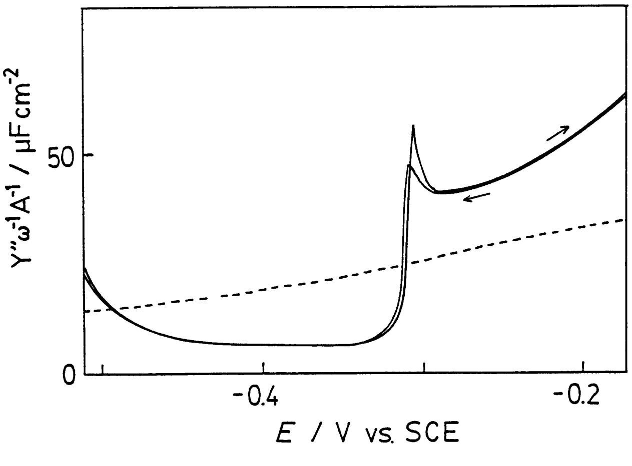

Fig. 2. Potential dependence of capacitance for 1 mM heptyl viologen at HMDE in 0.1 M K_2SO_4 (——) and the background (----). Y" is the imaginary component of admittance. $\omega=2\pi\times177$ Hz, and sweep rate was 5 mV/s.

tion, there occur no significant changes in main features in the CV. Graphical integration of these spikes allows us to evaluate the amount of HV^{2+} adsorbed and we found the maximum amount to be 1.86×10^{-10} mol/cm^2. This value gives a mean surface area per molecule of 89 Å^2 which almost corresponds to adsorption of HV^{2+} with pyridine rings flat on the HMDE and heptyl groups perpendicular to the electrode surface.[2] The presence of adsorbed layer of HV^{2+} in the potential region more positive than the spike is obvious from the large difference in capacitance compared to the background (Fig. 2).

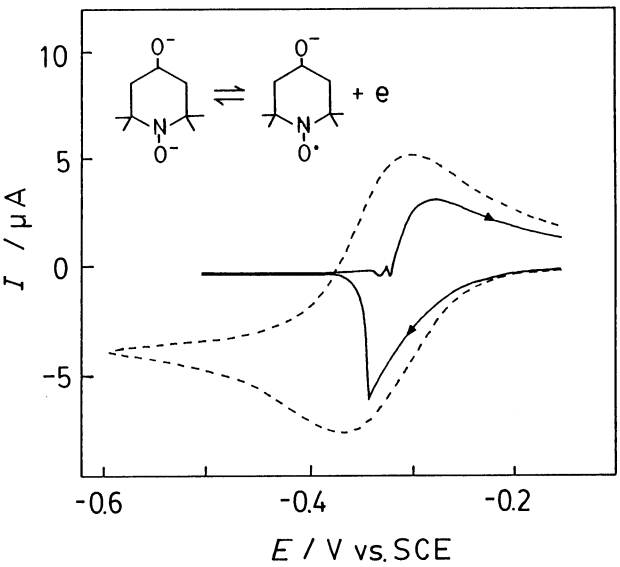

Fig. 3. Cyclic voltammograms for 5 mM TEMPOL in 10 mM KOH + 0.1 M K_2SO_4, in the absence (----) and presence (——) of 1 mM heptyl viologen. Sweep rate was 50 mV/s.

On the other hand, TEMPOL is reduced to the anion in alkaline solution and exhibits a well-defined reversible CV as shown in Fig. 3. Adding 1 mM of HV^{2+} to the solution, however, causes a drastic modification of the CV as revealed in Fig. 3. Though TEMPOL is reduced easily at the potential less negative than that of the adsorption spikes, the cathodic current abruptly falls down when the potential becomes more negative than that of the adsorption spikes and cathodic current starts to increase at the potential where HV^{2+} in the bulk of solution is reduced. When the potential sweep is reversed, the anodic current is also depressed and then suddenly starts to flow when the potential becomes more positive than that of the spike. This finding indicates that the adsorbed viologen monolayer plays a role of a gate, depending on its oxida-

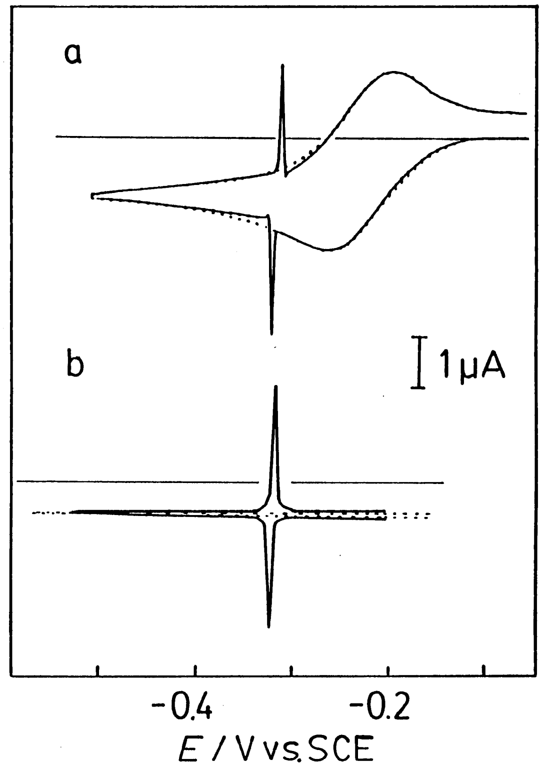

Fig. 4. Cyclic voltammograms of (a) 2 mM $[Ru(NH_3)_6]^{3+}$ and of (b) 1 mM $[Fe(CN)_6]^{3-}$ in 0.1 M K_2SO_4 in the absence (····) and presence of 1 mM heptyl viologen (——). Sweep rate was 50 mV/s.

tion state, with respect to the electron transfer reaction of TEMPOL; $(HV^{2+})_{ads}$ allows the electron exchange between TEMPOL and the electrode to proceed ("open") whereas $(HV^{+})_{ads}$ prohibits it ("closed"). We found a similar gate function for the reduction of O_2.

We tried similar measurements for the reduction of $[Fe(CN)_6]^{3-}$ or redox reaction of $[Ru(NH_3)_6]^{3+}$, but the results revealed no influence of adsorbed HV^{+} layer with respect to these reactions (see Fig. 4).

The observations reported here will be interpreted as follows: metal complex ions like $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$ are known as typical examples which undergo electron exchange in the outer-sphere pathway.3) They can exchange electron with the electrode even if it is covered with adsorbed viologen. On the other hand, though TEMPOL shows a reversible wave in the absence of the adsorbed layer, the electron transfer to other molecules or to the electrode may not be fast enough as compared with such outer-sphere electron transfer because of the presence of four methyl groups (otherwise TEMPOL would be unstable). This gate function of the adsorbed viologen monolayer will be ascribed to its structure change accompanied by the redox reaction of the monolayer.

The adsorbed viologen monolayer may release counter anions when it is reduced and has more compact structure in the reduced state than in the oxidized state. This is also supported from the potential dependence of differential capacitance measured by AC voltammetry (Fig. 2). On traversing the spike, the capacitance abruptly changes between 40 and 8 μFcm^{-2}. The adsorbed monolayer in the oxidized state will be more disordered in structure than the reduced state so that TEMPOL may penetrate into the layer or can access to the electrode surface to exchange electron with the electrode, while the reduced layer, which may be more compact than oxidized layer, hinders the reduction of TEMPOL. The fact that the electrode reactions of $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{3+/2+}$ are not hindered by the adsorbed layer will offer an important key to a question about the distance of possible electron transfer between the electrode and the reactant via the outer-sphere mechanisms.

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