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ELECTRODE REACTION OF METHYL VIOLOGEN COUPLED WITH POLYSTYRENE SULFONATE

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The addition of polystyrene sulfonate (PSS) to methyl viologen (MV^{2+}) leads to a reversible one-electron transfer reaction of MV^{2+} without the complication due to the adsorption of both $MV^{2+}$and $MV^{\cdot +}$. MV^{2+} molecules coupled with a PSS molecule act as equivalent and weakly -interacting sites. The interaction between active sites is allosteric.

Recently in the studies of polymer coated electrodes$^{1-3)}$ and conductive polymers,$^{4)}$ polyelectrolytes have often been used with molecules having functional groups. Many polyelectrolytes which are present *in vivo* act as mediators in the electron transfer reactions.$^{5)}$ The study of electrochemical reaction of polystyrene sulfonate coupled with electron mediators will be useful in the simulation of redox reactions of redox polymers.

1,1'-Dimethyl-4,4'-bipyridinium dichloride (methyl viologen) was a reagent grade obtained from BDH, and ammonium polystyrene sulfonate ($\overline{MW}$ 25 000 and 51.6 % sulfonated) was supplied by the Central Research Laboratory, Mitsubishi Chemical Industries Limited.. The ratio of MV^{2+} to PSS was varied by adding MV^{2+} to 0.17 mM (1 M = 10^{-3} mol m^{-3}) PSS in 0.1 M phosphate buffer solution at pH 7.0. The solutions used in the present experiments were deaerated by bubbling purified argon. Dropping mercury electrode and hanging mercury drop electrode were used as working electrodes for polarographic and cyclic voltammetric experiments, respectively. All potentials were referred to the saturated calomel electrode (SCE) and all measurements were carried out at (25.0 ± 0.5)°C.

MV^{2+} is reduced in two steps and the first step is a reversible one-electron transfer with a half-wave potential of (-0.68 – -0.69) V.$^{6,7)}$ MV^{2+} shows complicated electrochemical behavior caused by the strong adsorption of both MV^{2+} and $MV^{\cdot +}$ to mercury electrode.$^{8,9)}$ Figures 1a and 1b are cyclic voltammograms and pulse polarograms of MV^{2+}. Both the prewave in the cyclic voltammogram and the polarographic maximum caused by the strong adsorption of both MV^{2+} and $MV^{\cdot +}$ become apparent with the decrease in the concentration of MV^{2+}. The ratio of cathodic to anodic polarographic limiting current is not unity at lower concentrations of MV^{2+}.

The addition of PSS to MV^{2+}, however, leads to a reversible electrochemical behavior of MV^{2+} without the complication due to the adsorption of both MV^{2+} and $MV^{\cdot +}$, as shown in Figs. 2a and 2b. The current function $i_p v^{-1/2}$ in cyclic voltammetry is independent of the rate of potential scan over a wide range, and i_p vs. $v^{1/2}$ plot passes through the origin, where i_p is the peak current and v the rate of potential scan. The ratio of cathodic to anodic peak current is almost unity. The peak-to-peak

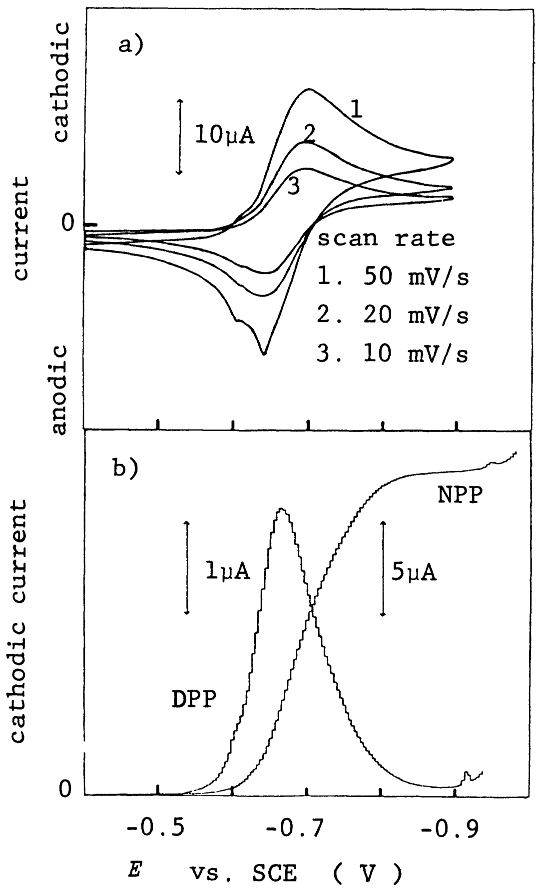

Fig. 1. Voltammograms of MV^{2+}. a) Cyclic voltammograms, b) normal (NPP) and differential (DPP) pulse polarograms of 5.1 mM MV^{2+} in 0.1 M phosphate buffer solution at pH 7.0.

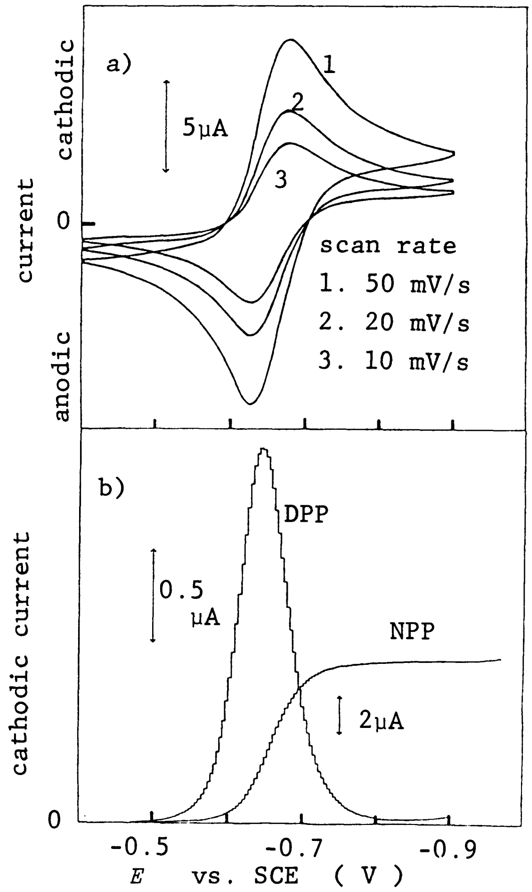

Fig. 2. Voltammograms of MV^{2+} coupled with PSS. a) Cyclic voltammograms, b) NPP and DPP of 5.1 mM MV^{2+} and 0.35 mM PSS in 0.1 M phosphate buffer solution at pH 7.0.

separation is (55 ± 2) mV and independent of the scan rate. With the increase in the number of MV^{2+} molecules in PSS, the polarographic limiting current increases linearly and the half-wave potential shifts toward positive potential as shown in Figs. 3 and 4 up to the mole ratio of MV^{2+} to PSS, that is 21, which corresponds to the ratio of $[MV^{2+}] / [SO_3^-]_{pss} = 0.25$, where $[MV^{2+}]$ and $[SO_3^-]_{pss}$ are the numbers of MV^{2+} molecules immobilized and sulfonate groups in a PSS molecule, respectively. With further increase in the amount of MV^{2+}, the slope of the line in Fig. 3 becomes steeper and the change in the $E_{1/2}$ in Fig. 4 becomes smaller. Moreover, the polarographic maxima and the prewave caused by the adsorption of both MV^{2+} and $MV^{\cdot +}$ become observable because of the presence of free MV^{2+} in the solution.

The diffusion coefficients of PSS coupled with MV^{2+} were calculated by using Cottrell equation,

$$I_{NPP} = \frac{n_p F A C_{ox} D_{ox}^{1/2}}{\pi^{1/2} t^{1/2}} , \qquad (1)$$

and the results are shown in Table 1 , where I_{NPP} is the limiting current of normal pulse polarography, n_p the average number of MV^{2+} molecules coupled with a PSS mole-

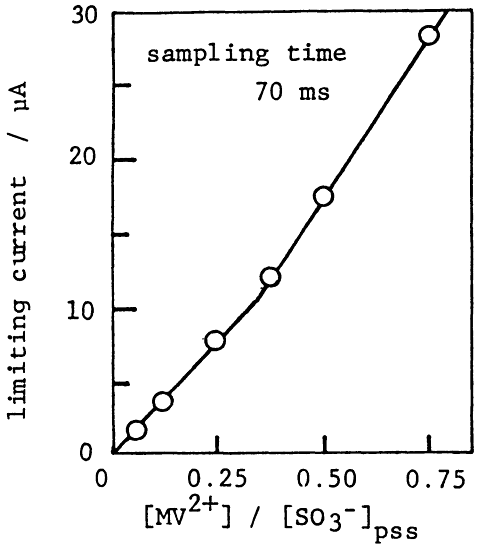

Fig. 3. Relationship between $[MV^{2+}]$ / $[SO_3^-]_{pss}$ and the limiting current of NPP, 0.17 mM PSS in 0.1 M phosphate buffer solution at pH 7.0.

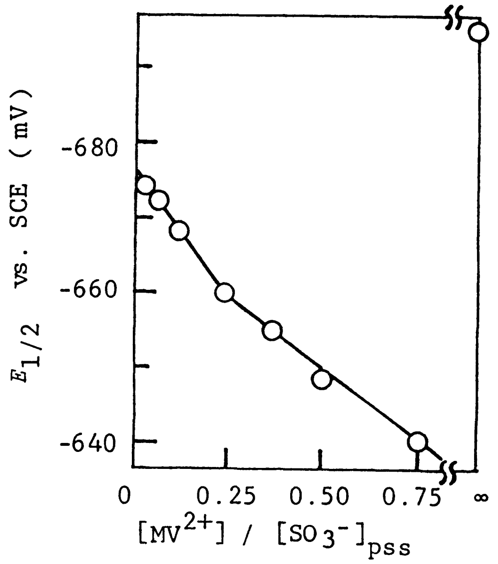

Fig. 4. Relationship between $[MV^{2+}]$ / $[SO_3^-]_{pss}$ and the half-wave potential ($E_{1/2}$). Conditions are given in Fig. 3.

cule,10) C_{ox} and D_{ox} the concentration and the diffusion coefficient of PSS, respectively, t the sampling time, F Faraday constant, and A the area of electrodes.

It is interesting to note that the diffusion coefficient of PSS coupled with MV^{2+} becomes larger with the increase in the amount of MV^{2+} in PSS. The increase in D_{ox} is too large to be explained only by the decrease in the viscosity. This is probably due to the formation of the rigid polymer complex bridged by the divalent MV^{2+}.

The apparent number of electrons (n_{ap}) transferred in the electrochemical reduction of PSS–MV^{2+} complex calculated from the slope of the logarithmic plot of the pulse polarographic wave is 1.1, when $[MV^{2+}]$ / $[SO_3^-]_{pss}$ is smaller than 0.25. With further increase in the concentration of MV^{2+}, the n_{ap} becomes larger and the logarithmic plot of the polarogram deviates from the linear relation.

Table 1. Electrochemical behavior of MV^{2+} coupled with PSS.a)

MV^{2+} / mM	n_p	$[MV^{2+}]$ / $[SO_3^-]_{pss}$	I_{NPP} / μA	D_{ox} / $10^{-6}cm^2/s$	$-E_{1/2}$ / mV(SCE)	slopeb) / mV/decade	n_{ap}
0.44	2.6	0.031	0.82	1.3	674	58	1.0
0.89	5.2	0.063	1.7	1.4	672	53	1.1
1.8	10	0.13	3.7	1.7	668	53	1.1
3.5	21	0.25	7.7	1.8	660	52	1.1
5.3	31	0.38	11.9	1.9	665	47	1.3
7.1	42	0.50	17.3	2.3	648	50	1.2
10.6	62	0.75	28.3	2.7	641	66	0.89
5.1c)	–	–	17.5	4.4	695	64	0.92

a) Conditions are given in Fig. 3. b) Slope of the logarithmic plot of the pulse polarographic wave. c) Conditions are given in Fig. 1.

The peak current of the cyclic voltammogram is given by

$$i_p = 0.446\, A n_{ap}^{1/2} (F/RT)^{1/2} n_p F C_{ox} D_{ox}^{1/2} v^{1/2} \quad . \qquad (2)$$

The peak current calculated from the equation (2) agrees very well with the measured value as shown in Table 2.

Table 2. Calculated and measured peak currents in cyclic voltammograms

$[MV^{2+}]$ / $[SO_3^-]_{pss}$ [a]	$(i_p)_{cal}$ [b] / μA	$(i_p)_{mes}$ [b] / μA	$(i_p)_{mes}$ / $(i_p)_{cal}$
0.057	3.8	3.7	0.97
0.086	4.6	5.0	1.1
0.17	6.0	6.5	1.1
0.35	8.6	9.5	1.1
0.69	8.4	10.1	1.2

a) PSS is coupled with 5.1 mM MV^{2+} in 0.1 M phosphate buffer solution at pH 7.0.
b) The rate of potential scan is 20 mV/s.

Because I_{NPP} is proportional to n_p and n_{ap} is not equal to n_p but 1.1, MV^{2+} molecules immobilized on a PSS molecule act as equivalent and very weakly-interacting sites,[11,12] and their interactions are allosteric, up to $[MV^{2+}]$ / $[SO_3^-]_{pss}$ of 0.25. The shift of the $E_{1/2}$ indicates that the interaction between MV^{2+} and sulfonate in PSS is not only electrostatic but also chemical in nature. The interaction between them is so strong that it is difficult to replace MV^{2+} by simple cations. This complex may be useful for the simulation of not only the heme-heme interaction but also electron transfer chains in biological systems.

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