Electrode Kinetics of Viologen Polymers Attached on Graphite Surfaces

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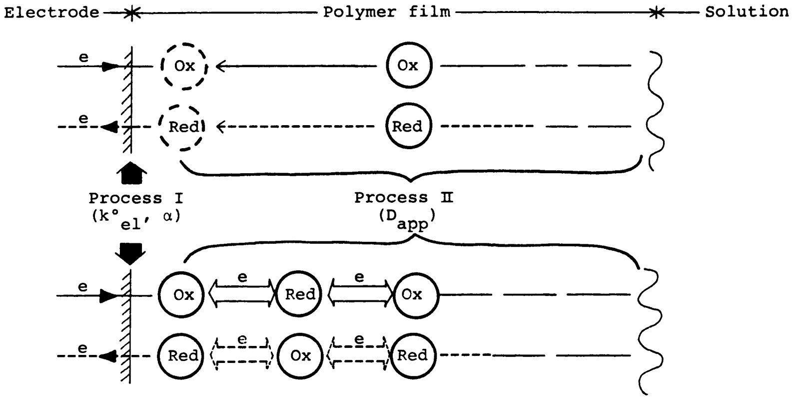
A "heterogeneous" electron-transfer process of three kinds of viologen polymers, *i.e.*, *N,N'*-dimethyl-4,4'-bipyridinium (methylviologen, MV)–Nafion^R, poly(xylylviologen) (PXV)-poly(*p*-styrenesulfonate) (PSS) and poly(methylviologen) (PMV), in which MV and PXV were electrostatically trapped in Nafion and PSS, respectively, on a basal-plane pyrolytic graphite (BPG) electrode and PMV was directly attached to the BPG electrode surface, was examined by normal pulse voltammetry. The relevant kinetic parameters (*i.e.*, the standard rate constant, k°_{el} and the cathodic transfer coefficient, α) of the electrode reaction and the apparent diffusion coefficients, D_{app}, for the "homogeneous" charge transport within these polymer films were determined at the various surface concentrations ($\Gamma_{MV^{2+}}$ in units of mol cm^{-2}) of viologen dication site. With the PMV and PXV–PSS systems, both k°_{el} and D_{app} were independent of $\Gamma_{MV^{2+}}$, while with the MV–Nafion system both k°_{el} and D_{app} decreased with an increase in $\Gamma_{MV^{2+}}$ under the constant concentration of Nafion. The values of α were independent of $\Gamma_{MV^{2+}}$ and constant (*i.e.*, 0.56, 0.58, and 0.20 for the PMV, MV–Nafion and PXV–PSS systems, respectively).

In a series of papers concerning the "polymer-coated electrodes,"[1–4] we have examined the "heterogeneous" electron-transfer reactions between the electrode and the electroactive species confined to the polymer films on the electrode surfaces as well as the "homogeneous" charge transport process within the polymer films incorporating the electroactive species by means of the normal pulse voltammetry (Scheme 1). It has become apparent that the "heterogeneous" electron-transfer reaction (process I) at the electrode/film interface obeys the conventional Butler-Volmer equation[5] which characterizes the electrode reaction at an uncoated, ordinary electrode in a solution and that the "homogeneous" charge transport process (process II) within the films obeys the Fick's law relations which are the same as those in thin layer electrochemistry[6] except that the polymer film is *ca.* 10^3 thinner than the usual thin layer electrochemical cell. The process II can be treated as a semi-infinite diffusion process when the distance of charge transport δ ($\approx 2(D_{app}\cdot t)^{1/2}$) is smaller than the thickness of the film (ϕ) (D_{app}: the apparent diffusion coefficient for the diffusion-like charge transport process within the film, t: time). Furthermore, from the previous data with respect to the $[Mo(CN)_8]^{4-/3-}$,[1,2] $[Fe(CN)_6]^{4-/3-}$,[3] $[W(CN)_8]^{4-/3-}$ and $[IrCl_6]^{3-/2-}$[4] incorporated electrostatically into the protonated poly(4-vinylpyridine) (PVP) films and the $[Fe(CN)_5]^{3-/2-}$[3] coordinated to the unprotonated PVP films, we have also found that the kinetic parameters (*i.e.*, the standard rate constant, k°_{el}, and the transfer coefficient, α) of "heterogeneous" electron transfer reaction and D_{app} depend upon the molar ratio of the incorporated



Scheme 1. Schematic depiction of charge transfer process on electrodes coated with polymers containing electroactive species.
Processes I and II represent heterogeneous electron transfer process and homogeneous charge transfer process, respectively. k°_{el} and α are the standard rate constant and the transfer coefficient respectively, of process I. D_{app} is the apparent diffusion coefficient for process II. Overall electrode reaction: (——) reduction, (----) oxidation. Charge can be transported through polymer films *via* (A) physical diffusion of electroactive species itself and (B) electron self-exchange between the redox couples. Note that process II (A and B) is associated with charge-compensating counter ion motion.

electroactive species to pyridine group of PVP. Such a concentration dependence of k°_{el}, α and D_{app} is worthy of remark, since this behavior has been rarely observed in the case of ordinary electrode reaction with an uncoated electrode and the physical diffusion in the solution phase except for special cases.[7—9]

In this paper, we will extend the normal pulse voltammetric study concerning "heterogeneous" electron-transfer reaction and "homogeneous" charge transport process on polymer-coated electrodes for the *N,N'*-dimethyl-4,4'-bipyridinium (methylviologen, MV)–Nafion (perfluorinated ion exchange polymer), poly(xylylviologen) (PXV)–poly(*p*-styrenesulfonate) (PSS) and poly(methylviologen) (PMV) systems. The MV and PXV are electrostatically trapped in the anionic polymer coatings, *i.e.*, Nafion and PSS, respectively, on a basal-plane pyrolytic graphite (BPG) electrode and PMV is directly attached to the BPG electrode surfaces owing to the water insolubility of PMV itself (Fig. 1). In these three systems, the viologen dication group is the common electroactive site. In each system, the dependence of k°_{el}, α and D_{app} upon the concentration of viologen dication site in polymer coatings will be examined and compared with the previous results[1—4] obtained with the highly charged anionic redox species confined in cationic polymer films on electrodes.

Experimental

Materials. *N,N'*-Dimethyl-4,4'-bipyridinium dichloride (methylviologen, $\mathrm{MVCl_2}$) (Wako Chemical Co.) was recrystallized twice from methanol–acetone. The polymer pendant methylviologen (PMV) and poly(xylylviologen) (PXV) with average molecular weight 9.8×10^3 and 8×10^3, respectively, were prepared as described elsewhere.[10—13] Nafion membrane 125$^{\mathrm{R}}$ which was obtained from Du Pont de Nemours and Company (Wilmington, DE) was used as an electrode-coating film of polyelectrolyte. The stock solution of Nafion was prepared as described previously[10—13] and the concentration was 2.55 mg ml^{-1}. The preparation of sodium poly(*p*-styrenesulfonate) (PSS) was carried out according to the same procedure as described previously.[13] The average molecular weight of the PSS was 5×10^4. The concentration of styrenesulfonate as PSS was 2.4 mM (1M=1 mol dm^{-3}). The basal-plane pyrolytic graphite (BPG) (Union Carbide Co.) disk electrodes (area: 0.17 cm^2) were prepared and mounted into glass tube with heat-shrinkable polyolefin tube.[14,15] Sodium perchlorate was used as a supporting electrolyte in sample solution (pH 3.4). All other chemicals were reagent grade and were used without further purification.

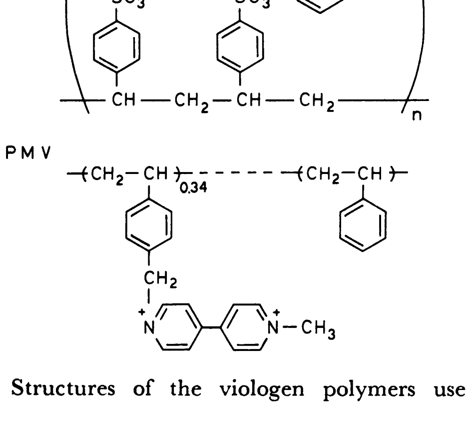


Fig. 1. Structures of the viologen polymers used.

Apparatus and Procedures. Aliquots of the stock solution of Nafion were spread by a microsyringe on the freshly cleaved electrode surface of BPG and then the solvent was evaporated at room temperature. The resulting electrode was soaked in a 0.2 to 10 mM solution of MV for 1 to 60 min in order to achieve the incorporation of desired quantities of MV in Nafion coatings. Adherent coatings of intermolecular complex of PXV and PSS (PXV–PSS) were produced by transferring aliquots (1—6 μl) of an aqueous stock solution containing 1.2 mM of viologen as PXV and of an aqueous stock solution containing 2.4 mM styrenesulfonate as PSS to the surface of a freshly cleaved BPG electrode, mixing them on it, and then evaporating the solvent at room temperature. With PMV film coating, aliquots of methanolic solution containing 3 mM methylviologen as PMV were spread by a microsyringe on the freshly cleaved BPG surface and air-dried to remove methanol. The quantity of the electroactive reactants (*i.e.*, viologen dication) existing in polymer coatings on electrodes was determined by measuring the charge required in a potential-step experiment[15] to quantitatively reduce the dications ($\mathrm{MV^{2+}}$) of MV, PXV of PMV to the corresponding radical monocations ($\mathrm{MV^{\dot{+}}}$) and/or measuring the area of cyclic voltammograms (for the oxidation-reduction reaction of the $\mathrm{MV^{2+/\dot{+}}}$ redox couple) obtained at slow potential scan rates. The quantity of incorporated reactant estimated by two procedures was the same within an experimental error.

Normal pulse voltammograms were obtained with instruments which were constructed in our laboratory and were recorded with an X-Y recorder (Watanabe Corp.). Positive feedback circuitry was employed to provide as much compensation as possible of the additional resistance (20—80Ω) associated with the polymer coatings. Measurements were confined to times sufficiently short to ensure that semi-infinite linear diffusion prevailed.[1—4,16] Solutions were deaerated with prepurified nitrogen and experiments were conducted at 25 °C. Potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode (SSCE).

Results and Discussion

Homogeneous Charge Transport Process within the Coatings Incorporating Electroactive Species. A set of normal pulse voltammograms for the reduction of $\mathrm{MV^{2+}}$ (to $\mathrm{MV^{\dot{+}}}$) as PXV–PSS complex or PMV coated on BPG or as MV incorporated into Nafion film on BPG at various sampling times is shown in Fig. 2. The electrode was scanned only over the first of the two reduction waves (*i.e.*, $\mathrm{MV^{2+}}$ to $\mathrm{MV^{\dot{+}}}$ and $\mathrm{MV^{\dot{+}}}$ to $\mathrm{MV^0}$), because the salt of the PXV–PSS, MV in Nafion and PMV become water soluble when the charge of the viologen is reduced to zero.[13] Thus, the responses observed arise from reduction of the viologen dication

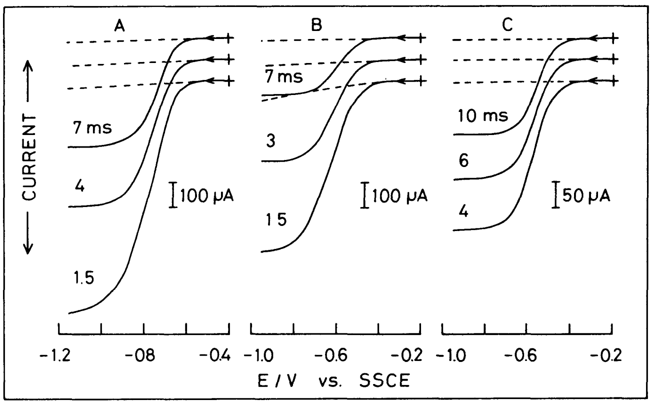


Fig. 2. Typical normal pulse voltammograms for the reduction of viologen dication as (A) MV incorporated into Nafion film on BPG electrodes and (B) PXV–PSS and (C) PMV coated on BPG electrodes at various sampling times in a 0.2 M $NaClO_4$ solution (pH=3.4). (A): $\Gamma_{MV^{2+}}=9.2\times10^{-9}$ mol cm^{-2}, $\Gamma_{Nafion}=1.5\times10^{-7}$ mol cm^{-2}, (B): $\Gamma_{MV^{2+}}=5.6\times10^{-8}$ mol cm^{-2}, $\Gamma_{PSS}=1.1\times10^{-7}$ mol cm^{-2}, (C): $\Gamma_{MV^{2+}}=7.3\times10^{-9}$ mol cm^{-2}. Sampling times (ms) are given on each voltammogram. Dotted lines show residual current.

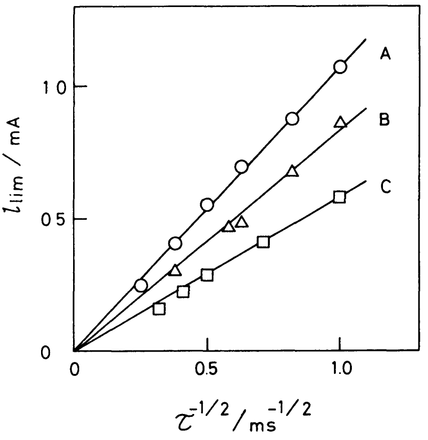


Fig. 3. Plots of limiting current, i_{lim}, *vs.* (sampling time)$^{-1/2}$ for the reduction of viologen dication as (A) MV–Nafion, (B) PXV–PSS, and (C) PMV on BPG electrodes. Other experimental conditions are the same as in Fig. 2.

to the radical cation.

The wave shapes are similar to those observed for solution-phase redox species at an uncoated electrode.[17–19] The half-wave potentials of the first waves obtained with MV–Nafion, PXV–PSS and PMV coated BPG electrodes are observed at −0.74, −0.52, and −0.57 V *vs.* SSCE, respectively at sampling time of 6 ms. This indicates differences in the spatial distribution and the electrostatic interaction of the redox centers and differences in the degree of porosity and hydrophobic nature of the coating film (*i.e.*, changes in the chemical environment of the coating film).[13,20,21] At any rate, the half-wave potential of the normal pulse voltammograms shifted to more positive values with increasing sampling times. Plots of the cathodic limiting current (i_{lim}) of these normal pulse voltammograms against the inverse square root of the sampling time (τ) were found to be linear as expected for the diffusion-controlled limiting current (Fig. 3).[1–4,17–19] Thus, the values of the apparent diffusion coefficients, D_{app}, for the process of the charge transport within the films were obtained from the slopes of the i_{lim} *vs.* $\tau^{-1/2}$ plots by using the Cottrell equation:[22)]

$$(i_d)^{C}_{Cott} = nFAC^{\circ}\sqrt{D_{app}/\pi\tau} \qquad (1)$$

where $(i_d)^{C}_{Cott}$ denotes the cathodic limiting diffusion current, n the number of electrons involved in the "heterogeneous" electron transfer reaction, F the Faraday constant, A the electrode area and C° the bulk concentration of the redox sites confined in polymeric coatings.

It has been generally recognized that the values of the apparent diffusion coefficients for the charge transport process within the polymeric films depend upon the kind and the concentration of the incorporated redox species, the kind of the film confining the redox species, the kind of the soaking solution, *etc.*[1–4,16,23–32] So far, the three types of dependences of D_{app} on the volume concentration (C°_{M} in units of mol cm^{-3}) of the incorporated electroactive species in polymeric films, that is, (1) D_{app} decreases with an increase in C°_{M},[1–4,16,26–29] (2) D_{app} increases with an increase in C°_{M},[29] and (3) D_{app} is independent of C°_{M}[28,30–32] have been reported and some possible models of the physical meaning of the D_{app} obtained have been ever proposed for the individual cases. In this study, the dependence of D_{app} upon the surface concentration of electroactive sites in polymer films (*i.e.*, $\Gamma_{MV^{2+}}$ in units of mol cm^{-2}) was examined. The results obtained are shown in Fig. 5, together with the dependence of k°_{el} and α upon $\Gamma_{MV^{2+}}$. With PMV and PXV–PSS systems, D_{app} is independent of $\Gamma_{MV^{2+}}$, while with MV–Nafion system D_{app} decreases with increasing $\Gamma_{MV^{2+}}$.

When the "homogeneous" charge transport process within the coatings follows the electron-exchange mechanism which was originally proposed by Kaufman and Engler,[33,34] electrons are removed from MV^{2+} sites that are remote from the BPG electrode by successive electron transfers between neighbor MV^{2+} and MV^{+} sites in the coating. D_{app} will be determined by the process limiting charge transport, which may be the intrinsic electron-transfer rate between adjacent sites, the rate of charge compensating counter ion motion which is necessarily coupled to electron transfer, or the rate of segmental motions of the polymer backbone. Translation of D_{app} into an electron transfer rate constant is of interest. If every "collision" in fact results in electron self-exchange, then the reaction is truly diffusion-controlled, D_{app} represents the diffusion rate, and D_{app} can be converted to an effective electron-transfer rate constant, k^{diff}_{ex}, by using a conventional formula for collision-controlled reaction rates:[4,29,35]

$$k^{diff}_{ex} = \frac{4\pi NRD}{10^3} \qquad (2)$$

where N is Avogadro's number, R and D are the sum of the radii and of the diffusion coefficients, respectively, of the reactants. For $D_{app}=1\times10^{-9}$ cm^2

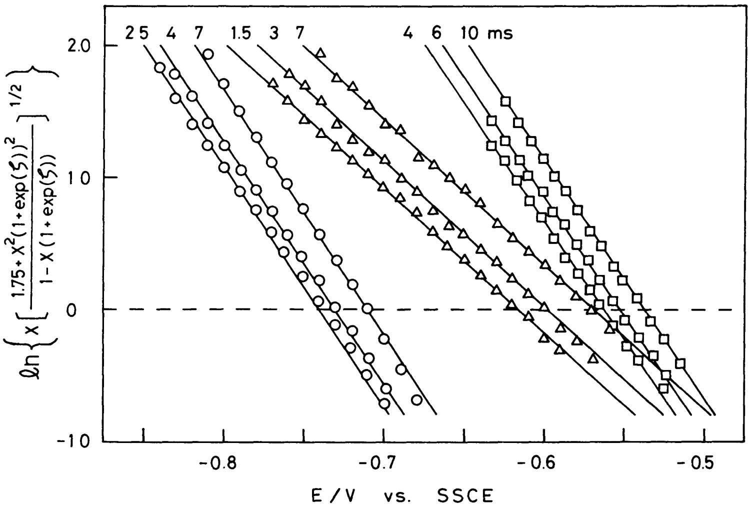


Fig. 4. Modified log plots of normal pulse voltammograms for the reduction of viologen dication as MV–Nafion, PXV–PSS and PMV on BPG electrodes. (○): MV–Nafion, (△): PXV–PSS, (□): PMV. Sampling times (ms) are indicated on each straight line. Other experimental conditions are the same as in Fig. 2.

s^{-1} and R=10Å,[29] with the assumption of $D=2\ D_{app}$, $k_{ex}^{diff}=1.5\times10^6\ M^{-1}\ s^{-1}$ which is ~5 times smaller than the self-exchange rate constant of the $MV^{2+/+\cdot}$ redox couple ($k_{ex}=8\times10^6\ M^{-1}\ s^{-1}$).[36] If we assume that the electron transfer is itself the slow step, then $D_{app}\approx\pi k_{ex}^{act}\ \delta^2C/4$ (δ: the distance between the centers of the reactants when the electron transfer occurs, C: the sum of the volume concentrations of the oxidized and reduced forms of the redox couple, k_{ex}^{act}: the second-order self-exchange rate constant for the redox couple).[7,8,28–30,32] In this case, for $D_{app}=1\times10^{-9}\ cm^2\ s^{-1}$, δ=10Å[29,32] and $C_{MV^{2+}}=\Gamma_{MV^{2+}}/\phi$ (film thickness)$=1.1\times10^{-4}\ mol\ cm^{-3}$, $k_{ex}^{act}=1.1\times10^6\ M^{-1}\ s^{-1}$. This is also smaller than the self-exchange rate constant of the $MV^{2+/+\cdot}$ couple.[36] From these calculations, it is likely that the process limiting charge transport may be the rate of charge compensating counter ion motion and/or the rate of segmental motions of the polymer film.[1–4,15,16,23–26,33,34]

Heterogeneous Electron-transfer Reactions between the Electrodes and Electroactive Sites Confined in the Polymer Coatings on Electrode Surfaces. An analysis of the rising part of the current-potential curves shown in Fig. 2 allows us to estimate the kinetic parameters (*i.e.*, the standard rate constant and the cathodic transfer coefficient) of the heterogeneous electron-transfer reaction. The relevant current-potential relationship[1–4,17–19] for normal pulse voltammograms for the simple electrode process, Red⇆Ox+ne, has already been derived and is given for the reduction by

$$E = E_{1/2}^{r} + \frac{RT}{\alpha nF}\ln\left\{\frac{4}{\sqrt{3}}\frac{k^\circ_{el}\sqrt{\tau}}{\sqrt{D}}\right\} - \frac{RT}{\alpha nF}\ln\left\{x\left[\frac{1.75+x^2(1+\exp(\zeta))^2}{1-x(1+\exp(\zeta))}\right]^{1/2}\right\} \tag{3}$$

where E is the electrode potential, $E_{1/2}^{r}$ the reversible half-wave potential, α the cathodic transfer coefficient, k°_{el} the standard rate constant, τ the sampling time, R the gas constant, T the absolute temperature, ζ the dimensionless parameter expressed as $\{(nF/RT)(E-E_{1/2}^{r})\}$, and D the diffusion coefficient expressed as $\{(D_{app}$(for cathodic process)$)^{\alpha}(D_{app}$(for anodic process)$)^{1-\alpha}\}$.*1 The x is the ratio of the current at potential E to the cathodic limiting diffusion current, $(i_d)_{Cott}^{C}$, expressed by the Cottrell equation (Eq. 1).

Figure 4 shows the typical examples of the modified log plots of normal pulse voltammograms in which the logarithm of the third term on r.h.s. of Eq. 3 is plotted against E for the reduction of viologen dications to the corresponding radical monocations in polymer coatings. These plots gave the straight lines the slopes of which were constant at the different sampling times ranging from 1 to 10 ms in each system. From the slope of the straight lines shown in Fig. 4 and the intersect of these lines with the zero-line the values of k°_{el} and α were estimated by using the known values of $E_{1/2}^{r}$, D*1, and τ. For doing this, the values of $E_{1/2}^{r}$ were estimated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms for the oxidation-reduction of the $MV^{2+/+\cdot}$ redox couple in coatings on BPG electrodes in a solution containing only supporting electrolyte.

Figure 5 shows the dependence of k°_{el} and α upon $\Gamma_{MV^{2+}}$. With the PMV and PXV–PSS systems, the values of k°_{el} were independent of $\Gamma_{MV^{2+}}$ and were $(3.9\pm0.4)\times10^{-5}$ and $(1.1\pm0.3)\times10^{-4}\ cm\ s^{-1}$, respectively. The difference in k°_{el} values may be primarily attributed to the difference in the molecular polymer-structure of PMV and PXV–PSS and their overall film-morphology. On the other hand, with the MV–Nafion system the values of k°_{el} decreased gradually with increasing $\Gamma_{MV^{2+}}$. The similar dependence of k°_{el} upon the concentration of electroactive species in coatings has been previously observed for several other systems (*e.g.*, the $[Mo(CN)_8]^{4-/3-}$, $[Fe(CN)_6]^{4-/3-}$, and $[IrCl_6]^{3-/2-}$ redox couples incorporated into the proto-

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*1 With the assumption that D_{app} (for cathodic process)$\approx D_{app}$ (for anodic process), the values of D were estimated as those of D_{app} (for cathodic process).

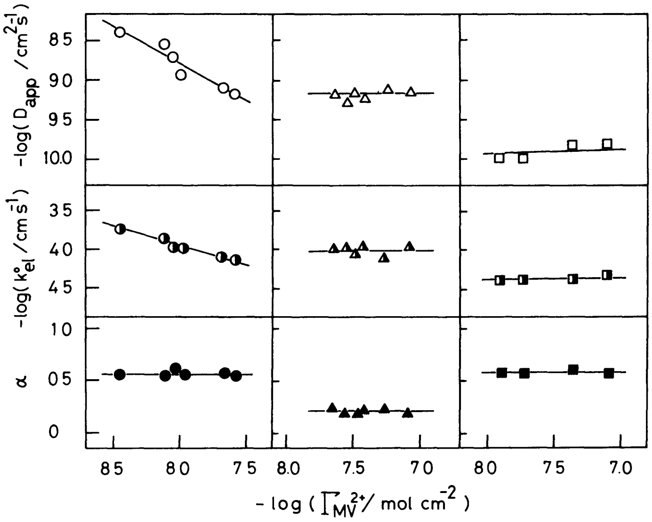

Fig. 5. Dependence of k°_{el}, α and D_{app} upon $\Gamma_{MV^{2+}}$. (○,◑,●): MV-Nafion ($\Gamma_{Nafion}=1.5\times10^{-7}$ mol cm^{-2}), (△,◭,▲,): PXV-PSS ($C_{MV^{2+}}=1.1\times10^{-4}$ mol cm^{-3} and $C_{pss}=2.2\times10^{-4}$ mol cm^{-3}), (□,◨,■): PMV ($C_{MV^{2+}}=1.1\times10^{-4}$ mol cm^{-3}). Other experimental conditions are the same as in Fig. 2.

nated poly(4-vinylpyridine) (PVP) film on BPG electrodes.[1–4]

In the case of the PMV and PXV–PSS systems, the volume concentration ($C_{MV^{2+}}$) of MV^{2+} is constant ($C_{MV^{2+}}=1.5\times10^{-4}$ and 1.1×10^{-4} mol cm^{-3} for the PMV and PXV–PSS systems, respectively), because the thickness of the coating film can be assumed to be proportional to the amount of coating on the electrode surfaces. The independence of D_{app} against $\Gamma_{MV^{2+}}$ indicates that the degree of the solvent swelling and the porosity of the coating film, the spatial distribution of the viologen sites and the supporting electrolytic ions, the electrostatic interaction of the viologen sites, *etc.* do not change substantially with the thickness (ϕ) of coatings in the range examined of ϕ (1.9×10^{-4} to 7.5×10^{-4} cm). On the other hand, in the case of the MV–Nafion system, the values of $\Gamma_{MV^{2+}}$ were changed deliberately (see Experimental Section) under the constant amount coated of Nafion ($\Gamma_{Nafion}=1.5\times10^{-7}$ mol cm^{-2}), so that $C_{MV^{2+}}$ increases with an increase in $\Gamma_{MV^{2+}}$. As can readily be seen from the essential ground (*i.e.*, electrostatic interaction[1–4,16,26]) of the incorporation of methylviologen dication (MV) into anionic Nafion film, MV is strongly interacting with its surroundings. As the $\Gamma_{MV^{2+}}$ increases, the degree of electrostatic cross-linking of the film by the dication, *i.e.*, multiple ion pairing of dications with the sulfonyl groups of Nafion becomes to be large. It is thus thought that the free energy required to reorganize the surrounding medium prior to the electron transfer becomes to be large with an increase in $\Gamma_{MV^{2+}}$.[3,4] On the basis of such a consideration, the dependence of k°_{el} on $\Gamma_{MV^{2+}}$ shown in Fig. 5 appears to arise from the change of the solvent reorganization energy by changing $\Gamma_{MV^{2+}}$.

The values of cathodic transfer coefficient (α) were independent of $\Gamma_{MV^{2+}}$ in the systems studied. Note that the values (0.56 and 0.58) of α obtained with PMV and MV-Nafion coated BPG electrodes are almost the same and largely different from that (0.20) obtained with PXV–PSS coated BPG electrode. Such a significant small value of α has been obtained in the PMV system when the polyelectrolyte such as sodium poly(*p*-styrenesulfonate) was used as a supporting electrolyte.[37] Such different α-values may reflect the different reaction positions of the viologen dication sites (*e.g.*, with respect to the outer Helmholtz plane) in the transition state of the electron-transfer reaction and/or the existence of the potential-independent chemical reaction preceding the electron-transfer reaction proper.[4,38–41]

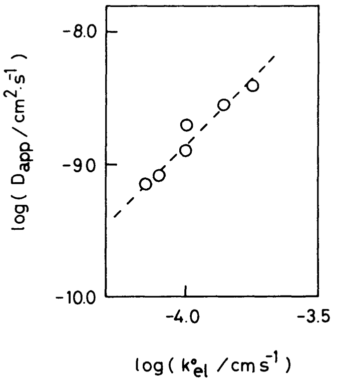

Fig. 6. Linear relationship between log k°_{el} and log D_{app} in the MV-Nafion system. The values of k°_{el} and D_{app} were taken from Fig. 5.

Comparison with Previous Results. As mentioned above, in the MV–Nafion system, the values of both D_{app} and k°_{el} decreased with increasing concentration of viologen dication in Nafion coatings. A similar dependence of both D_{app} and k°_{el} upon the concentration of the incorporated species has been previously observed with the $[Fe(CN)_6]^{4-/3-}$, $[Mo(CN)_8]^{4-/3-}$, and $[IrCl_6]^{3-/2-}$ incorporated into the protonated PVP film coated on BPG electrodes.[1–4] Furthermore, it has been found in these redox systems that there is a linear relationship between log k°_{el} and log D_{app}, even though the theoretical explanation for this relationship has not been given yet. For the MV–Nafion system also, we can see the establishment of this linear relationship (see Fig. 6). Such a linear relationship may suggest that the increase of the concentration of the redox sites (or species) confined in polymer coatings causes an increase in the degree of electrostatic cross-linking[1–4,16,26,42] and/or the electrostatic repulsions[4,43] between the highly charged redox sites (or species) and these result in the decrease in the rates of both heterogeneous electron transfer reaction at the electrode/film interfaces and homogeneous charge transfer process within the coatings. Additional work is required to make this point clearer.

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