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Use of Normal Pulse Voltammetry in Diagnosing Electrode Kinetics of Octacyanomolybdate(IV/V) Complexes Bound Electrostatically to Graphite Electrodes Coated with Polyelectrolytes

Keiichi Sato, Shuichiro Yamaguchi, Hiroaki Matsuda,
Takeo Ohsaka,† and Noboru Oyama*,†
Department of Electronic Chemistry, Graduate School at Nagatsuta, Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227
†*Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184*

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An electron transfer process of $[Mo(CN)_8]^{4-/3-}$ redox couple at the graphite electrode/protonated poly(4-vinylpyridine) (PVP) interfaces was examined by the normal pulse voltammetry. It became apparent that electrode reaction of the electroactive species confined in the polymer film on electrode surface obeys the conventional Butler-Volmer equation which characterizes the ordinary electrode reaction at electrode/solution interface. From the analysis of the dependences of the current-potential curves upon the sampling time the relevant kinetic parameters (*i.e.*, the standard rate constant, k° and the transfer coefficient, α) of the electrode reaction were evaluated. The value of k° decreased from 9.7×10^{-4} to 1.7×10^{-4} cm s^{-1} and the value of α was almost constant (0.50), when the molar ratio of the incorporated $[Mo(CN)_8]^{4-}$ to pyridine group of the PVP film, Γ_M/Γ_{PVP}, was increased from 0.0025 to 0.22. The apparent diffusion coefficient, D_{app}, for the process of charge transport within the film was also determined from the dependence of the limiting current upon the sampling time. The value of D_{app} decreased from 4.4×10^{-8} to 2.5×10^{-9} cm^2 s^{-1}, when the ratio Γ_M/Γ_{PVP} was increased from 0.0025 to 0.22.

Electrochemical reaction of solution species mediated by "redox polymer" films bound to the electrode surfaces, where the polymer itself is electroactive or the electroactive species are confined in the electroinactive polymer film, has recently received considerable attention.[1–4)] It is now well recognized that the kinetics of electrochemical reactions mediated by "redox polymer" films is controlled by the interplay of the three rate-limiting factors, *i.e.*, (1) the diffusion-like propagation of the electrons through the film from the electrode surface toward the film/solution interface, (2) the diffusion of the substrate from the film/solution interface toward the electrode surface and (3) the electron cross-exchange reaction between the substrate and the active form of the redox mediator.[1,2,5–13)] The theoretical approaches that take into account the interplay of these three factors, together with the diffusion of substrate in the solution, have been developed with regard to rotating disk electrode voltammetry.[4,9,14)] Experimental studies also have actively been carried out in line with much success of such theoretical approaches.[1,2,6–8,11–15)] However, no attempt to study in detail the kinetics on the electron transfer process at the electrode/film interface has yet been reported to our knowledge.

In order to conduct such a kinetic study, it seems to be at first indispensable to examine whether the Butler-Volmer theory[16)] being proposed for the conventional electrode reaction at the electrode/solution interface is applicable to the electrode reaction of electroactive species confined in the polymer domains on electrode surface or not. For this purpose, it seems to be convenient to examine the behavior of the electrode coated with polymer film, in which electroactive species are confined by some interaction (*e.g.*, electrostatic interaction,[1,2,6,15,17–22)] hydrophobic interaction,[23,24)] and coordination bond[20–22,25)] between the electroactive species and the polymer domain), in a solution containing only the supporting electrolyte. In this case, the overall electrode reaction consists of the electron transfer process at the electrode/film interface and the process of charge transport within the film. The latter process has been considered as the diffusion process of electroactive species to the electrode surface within the film and/or the hopping process of a series of electrons between adjacent pairs of oxidized and reduced reactants that serves to shuttle electrons from the electrode to reactants which are located away from the electrode surface.[1,2,15,17–19,23,24,26–35)] So far, it has become apparent that in either case (or with combinations of the two) the process of charge transport within the film can be described in terms of apparent diffusional motion.[36,37)]

This paper represents a first example on the kinetic study of the electron transfer process at the electrode/film interface. The main purpose of this work is to examine if the current-potential relationship[16)] of the Butler-Volmer type usually employed for the electrode reactions at electrode/solution interface is applicable to the electron transfer process of electroactive species confined in the polymer films on electrode surface. The $[Mo(CN)_8]^{4-/3-}$ redox couple which is electrostatically bound to the protonated poly(4-vinylpyridine) (PVP) film on a pyrolytic graphite electrode is chosen as a suitable system for this purpose, because the process of charge transport of this system within the film has been previously studied in detail by means of chrono-amperometry, -coulometry and -potentiometry and has been recognized to be treated as a diffusion process which obeys Fick's second law.[19)] The normal pulse voltammetric technique (NPV) is employed as a means of the measurement. Among the numerous pulse techniques, NPV has proved to be most suitable for the examination of electrode kinetics in polarographically quasi-reversible electrode processes and the current-potential curves of NPV are similar to that of d.c. polarography, so that the analysis of the current-potential curves in NPV can be easily carried out by using a similar procedure to that of d.c. polarography.[38–42] The apparent diffusion coefficients for the process of charge transport within the film are also determined by using NPV.

Experimental

Materials. The pyrolytic graphite (Union Carbide Corp.) disk electrodes were prepared and mounted in a glass holder as previously described.[21] The exposed area of each electrode was 0.17 cm^2. The average molecular weight of PVP reprecipitated from methanol-diethyl ether was 7.4×10^5. $K_4[Mo(CN)_8]\cdot2H_2O$ was synthesized according to the standard procedure.[43]

Apparatus and Procedures. Adherent coatings of PVP were produced by transferring aliquots of a 0.5 weight percent methanolic solution of the polymer to the surface of a freshly cleaved graphite electrode and then evaporating the solvent at room temperature. The resulting coatings were swelled in an aqueous solution but remained insoluble.

The $[Mo(CN)_8]^{4-}$ complex was firmly held within the domain of the protonated PVP film.[2] The quantities of $[Mo(CN)_8]^{4-}$ incorporated into the protonated PVP coatings were determined by the following procedure: After incorporation of the $[Mo(CN)_8]^{4-}$ complex, the electrodes were washed and transferred to solutions containing only supporting electrolyte (0.2 M $CF_3COONa+CF_3COOH$, pH 1.5) ($1 M=1 mol dm^{-3}$). Then, the electrode potential was scanned from a value before the oxidation of the incorporated $[Mo(CN)_8]^{4-}$ ion to a value well beyond the voltammetric peak potential for oxidation and thereafter maintained until the current falls to background levels. The quantity of incorporated reactant was calculated from the integration of the current with correction for background contributions.

Normal pulse voltammograms and cyclic voltammograms were obtained with instruments which were constructed in our laboratory and were recorded with a X-Y recorder (Watanabe Corp.). Positive feed-back circuitry was employed to compensate the resistances associated with the PVP coatings as much as possible. In normal pulse voltammetric experiments, the pulse width of 50 ms and the interval of 20 to 50 s between successive pulses were employed. Thus it can be safely considered that the depletion layer of reactants produced during the precedent pulse completely disappears before the following pulse starts. Solutions were deaerated with pre-purified argon 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

It has been well known that multiply-charged transition metal complexes can be incorporated into and confined in various polyelectrolytes coated on electrode surfaces by electrostatic interaction between the polyelectrolyte layer and metal complexes carrying the opposite charge.[1,2,6,15,17–22] The $[Mo(CN)_8]^{4-}$ complex can also be electrostatically attached to the protonated PVP coating on electrode.[2] When the PVP film is sufficiently thin, the cyclic voltammogram for the oxidation and reduction of the $[Mo(CN)_8]^{4-/3-}$ couple bound to the protonated PVP coatings yields symmetrical, identically shaped, anodic and cathodic waves and peak currents vary linearly with scan rates. These results are characteristic of the surface redox-reaction.[37,44] With thickening the polymer film, the shape of the cyclic voltammograms becomes less symmetric and the peak currents exhibit the proportionality to the square root of scan rate.[22] The separation between anodic and cathodic peak potentials becomes large even at the ordinary scan rate such as 50 mV s^{-1} and at fast scan rate (*e.g.*, 0.5 V s^{-1} with IR compensation) the separation is larger than ≈59 mV, typical of a Nernstian solution process. This suggests that the overall rate of the electrode reaction is limited by the charge transport within the film and the electron transfer at the electrode/film interface.[22,34,37]

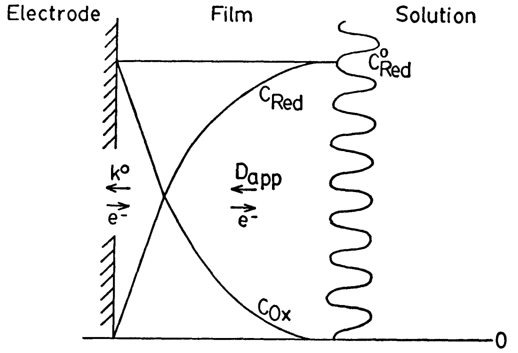

Fig. 1. Concentration profile of redox couple within polymer film at limiting current.

From the results obtained previously[19] by means of potential-step chronoamperometry, potential-step chronocoulometry and chronopotentiometry, the process of charge transport within the film can be treated as a semi-infinite diffusion process (Fig. 1), when the electrolysis time is below *ca.* 30 ms. In the present work, normal pulse voltammograms were taken at the sampling times between 2 and 16 ms. Therefore, the present experimental condition satisfies the condition of such a semi-infinite diffusion.

According to the usual kinetic theory[16] of a simple electrode reaction, $Red\rightleftharpoons Ox+ne$, the faradaic current, i, can be expressed by

$$i = nFA\{\overrightarrow{k}(E)C^s_{Red} - \overleftarrow{k}(E)C^s_{Ox}\}, \tag{1}$$

where $\overrightarrow{k}(E)$ and $\overleftarrow{k}(E)$ are the forward and backward rate constants, respectively, C^s_{Ox} and C^s_{Red} are concentrations of Ox and Red at the electrode surface, respectively, A is the electrode area, n is the number of electrons involved in the electron-transfer process and F is the Faraday constant.

By assuming that the Nernst equation can be applicable to an equilibrium situation of Ox and Red, Eq. 1 can be transformed into

$$i = nFA\overrightarrow{k}(E)\left\{C^s_{Red}-C^s_{Ox}\exp\left[-\frac{nF}{RT}(E-E^\circ)\right]\right\}, \tag{2}$$

where E is the electrode potential, E° is the formal standard potential of the reaction: $Red\rightleftharpoons Ox+ne$, and R and T have their usual significance. In the case of normal pulse voltammetry, the forward rate constant, $\overrightarrow{k}(E)$, can be given by[41]

$$\ln\{\vec{k}(E)\} = -\ln\left(\frac{4}{\sqrt{3}}\frac{\sqrt{\tau}}{\sqrt{D_{\mathrm{Red}}}}\right) + \ln\left\{x\left[\frac{1.75+x^2(1+\exp(-\zeta))^2}{1-x(1+\exp(-\zeta))}\right]^{1/2}\right\}, \quad (3)$$

with

$$\zeta = (nF/RT)(E-E^{\mathrm{r}}_{1/2}), \quad (4)$$

$$x = i/(i_{\mathrm{d}})_{\mathrm{Cott}}, \quad (5)$$

$$E^{\mathrm{r}}_{1/2} = E^{\circ} - (RT/nF)\ln\sqrt{D_{\mathrm{Ox}}/D_{\mathrm{Red}}}, \quad (6)$$

where $E^{\mathrm{r}}_{1/2}$ is the reversible half-wave potential, τ is the sampling time, D_{Red} and D_{Ox} are the diffusion coefficients of Red and Ox, respectively, $(i_{\mathrm{d}})_{\mathrm{Cott}}$ denotes the diffusion current expressed by the Cottrell equation in the following manner:[45]

$$(i_{\mathrm{d}})_{\mathrm{Cott}} = nFAC^{\circ}\sqrt{D_{\mathrm{app}}/\pi\tau}, \quad (7)$$

with

$$D_{\mathrm{app}} = (D_{\mathrm{Ox}})^{\alpha}(D_{\mathrm{Red}})^{1-\alpha}, \quad (8)$$

where C° is the bulk concentration of Ox or Red in the film, and α is the anodic transfer coefficient.

Figure 2 shows the typical normal pulse voltammograms for the oxidation of $[\mathrm{Mo(CN)_8}]^{4-}$ incorporated into the PVP film at various sampling times. The S-shaped waves shown in Fig. 2 are similar to those observed for redox species present in a solution at an uncoated electrode. The half-wave potential of the normal pulse voltammograms shifted to anodic direction with decreasing sampling times.

As shown in Fig. 3, plots of the anodic limiting currents of these normal pulse voltammograms against the inverse square root of the sampling times were found to be linear. This means that the limiting current is diffusion-controlled and the values of diffusion coefficients, D_{app}, for the process of charge transport within the film can be obtained from the anodic limiting currents by using Eq. 7.

Figure 4 shows the logarithmic plot of D_{app} *vs.* the molar ratio of the incorporated $[\mathrm{Mo(CN)_8}]^{4-}$ ion to pyridine group of the protonated PVP, $\Gamma_{\mathrm{M}}/\Gamma_{\mathrm{PVP}}$, together with D_{app} for the reduction of $[\mathrm{Mo(CN)_8}]^{3-}$.[38] This plot shows clearly the dependence of D_{app} on the concentration of the incorporated $[\mathrm{Mo(CN)_8}]^{4-}$. As the ratio $\Gamma_{\mathrm{M}}/\Gamma_{\mathrm{PVP}}$ decreases, the apparent diffusion coefficient increases. Similar results have also been obtained in a previous work[19] where anionic reactants, $[\mathrm{Mo(CN)_8}]^{4-/3-}$, $[\mathrm{Fe(CN)_6}]^{4-/3-}$, and $[\mathrm{W(CN)_8}]^{4-/3-}$, were incorporated into the PVP coating and the diffusion coefficients of the incorporated anions were evaluated by chronoamperometric, chronocoulometric and chronopotentiometric measurements.[46] The results shown in Fig. 4 and the previous data[19] suggest that the physical motion of $[\mathrm{Mo(CN)_8}]^{4-}$ through the polymer film dominates its diffusional rate at the lower concentrations. One factor that contributes to the larger values of D_{app} may be the smaller extent of electrostatic cross-linking[6,15,17–19,30] of the $[\mathrm{Mo(CN)_8}]^{4-}$ ion with the surrounding cation sites, as the concentration of the $[\mathrm{Mo(CN)_8}]^{4-}$ ion decreases. At higher concentrations of $[\mathrm{Mo(CN)_8}]^{4-}$, *i.e.* $\Gamma_{\mathrm{M}}/\Gamma_{\mathrm{PVP}} > 15\%$, the value of D_{app} becomes smaller but constant. In this

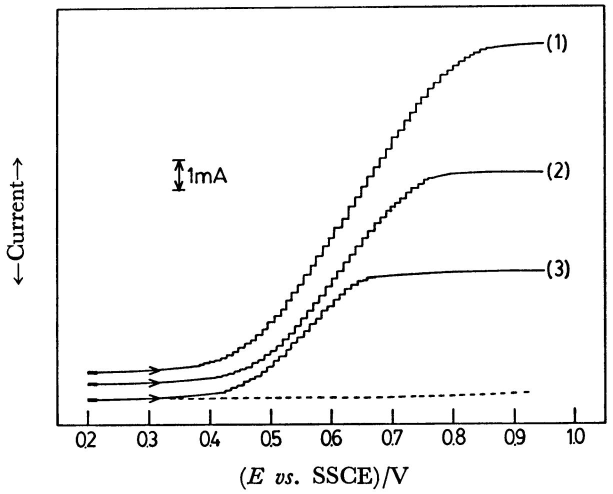

Fig. 2. Typical normal pulse voltammograms for the oxidation of $[\mathrm{Mo(CN)_8}]^{4-}$ incorporated into the protonated PVP film on BPG electrode in 0.2 M $\mathrm{CF_3COONa}$-$\mathrm{CF_3COOH}$ (pH 1.5) solution. Sampling time; (1) $\tau = 2$ ms, (2) 4 ms, and (3) 8 ms. Concentration of $[\mathrm{Mo(CN)_8}]^{4-}$ incorporated into PVP, Γ_{M}: 7.0×10^{-8} mol cm^{-2}; Concentration of PVP coated on electrode, Γ_{PVP}: 4.6×10^{-7} mol cm^{-2} of pyridine as PVP. Dotted line shows a residual current.

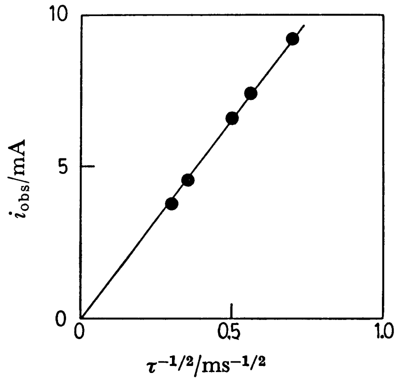

Fig. 3. Plots of observed limiting current (i_{obs}) *vs.* (sampling time)$^{-1/2}$ for the oxidation of $[\mathrm{Mo(CN)_8}]^{4-}$ incorporated into the protonated PVP film on BPG electrode. Other conditions are the same as in Fig. 2.

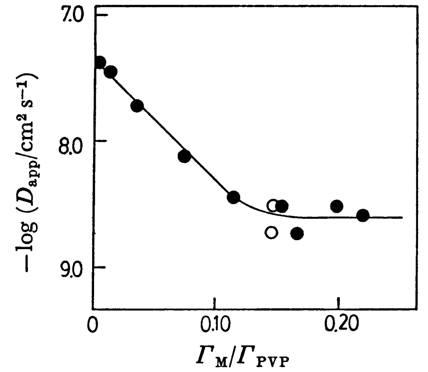

Fig. 4. Logarithmic plot of D_{app} *vs.* the molar ratio of incorporated $[\mathrm{Mo(CN)_8}]^{4-}$ ions to protonated pyridine groups of PVP, $\Gamma_{\mathrm{M}}/\Gamma_{\mathrm{PVP}}$. Anion incorporated: (●) $[\mathrm{Mo(CN)_8}]^{4-}$; (○) $[\mathrm{Mo(CN)_8}]^{3-}$. Supporting electrolyte: 0.2 M $\mathrm{CF_3COONa}$-$\mathrm{CF_3COOH}$ (pH 1.5).

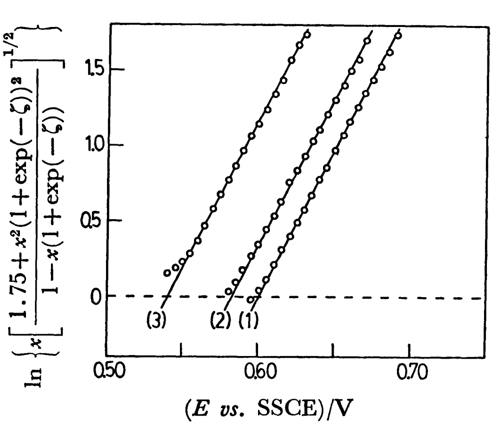

Fig. 5. Modified log-plots of normal pulse voltammograms for the oxidation of $[Mo(CN)_8]^{4-}$ incorporated into the protonated PVP film. Sampling time; (1) $\tau=2$ ms, (2) 4 ms, and (3) 8 ms. Other experimental conditions are the same as in Fig. 2.

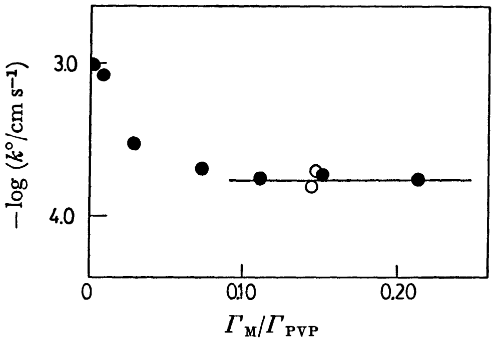

Fig. 6. Logarithmic plot of the standard rate constant, k°, against the molar ratio of incorporated $[Mo(CN)_8]^{4-}$ ions to protonated pyridine groups of PVP. Anion incorporated: (●) $[Mo(CN)_8]^{4-}$; (○) $[Mo(CN)_8]^{3-}$. Other experimental conditions are the same as in Fig. 5.

case, physical motion of the $[Mo(CN)_8]^{4-}$ ions through the film may be more difficult because of the higher extent of electrostatic cross-linking.[6,15,17–19,30] The fact that the D_{app} values are independent of the concentration of the incorporated $[Mo(CN)_8]^{4-}$ ion probably suggests that the structural changes caused by cross-linking may have reached their limit so that this factor no longer affects the measured values of D_{app}.[19]

Equation 3 indicates that the plot of $\ln(x[\{1.75+x^2(1+\exp(-\zeta))^2\}/\{1-x(1+\exp(-\zeta))\}]^{1/2})$ *vs.* E manifests the potential dependence of the forward rate constant. Figure 5 shows the typical examples of such log-plots of the normal pulse voltammograms, in which the logarithm of the second term on r.h.s. of Eq. 3 is plotted against E for the oxidation of $[Mo(CN)_8]^{4-}$ incorporated into the protonated PVP coatings. These plots gave the straight lines the slopes of which were constant at the different sampling times within experimental errors. This fact concludes that the electrode reaction of the electroactive species confined in the polymer film on electrode surfaces obeys the conventional Butler-Volmer equation[16] which characterizes the electrode reaction at electrode/solution interface. Thus, the forward rate constant, $\vec{k}(E)$, can be expressed as follows:

$$\vec{k}(E) = k^\circ \exp[(\alpha nF/RT)(E-E^\circ)], \tag{9}$$

where k° is the standard rate constant.

As can readily be seen from the comparison of Eqs. 3 and 9, the slope of the straight lines shown in Fig. 5 is equal to $(\alpha nF/RT)$ and the value, E^*, of the intersect of these lines with the zero-line can be expressed by

$$E^* = E^r_{1/2} - \frac{RT}{\alpha nF}\ln\left(\frac{4}{\sqrt{3}}\frac{k^\circ\sqrt{\tau}}{\sqrt{D_{app}}}\right), \tag{10}$$

under the assumption that $D_{Red}=D_{Ox}$, so that $E^\circ=E^r_{1/2}$. Thus, the anodic transfer coefficient was evaluated from the slopes of the straight lines shown in Fig. 5 and its value was 0.50 ± 0.05. The values of α were independent of Γ_M/Γ_{PVP}. The standard rate constants of electron transfer process at electrode/film interface were evaluated by introducing the experimental values of D_{app}, α and $E^r_{1/2}$ into Eq. 10, where the value of $E^r_{1/2}$ was estimated as the average of the anodic and cathodic peak potentials of the cyclic voltammogram for the oxidation-reduction of $[Mo(CN)_8]^{4-/3-}$ couple.

Figure 6 shows the dependence of k° upon the ratio of Γ_M to Γ_{PVP}. The value of k° decreased gradually with increasing the ratio Γ_M/Γ_{PVP} and in the region of $\Gamma_M/\Gamma_{PVP}=10$—20% the values of k° were constant and 2×10^{-4} cm s^{-1}. This value of the standard rate constant was in agreement with that obtained from the reduction of $[Mo(CN)_8]^{3-}$ confined in the protonated PVP on a graphite electrode (see open circles in Fig. 6) and the value of cathodic transfer coefficient was 0.50 ± 0.02. The standard rate constant of the electrode reaction of $[Mo(CN)_8]^{4-/3-}$ redox couple at an uncoated platinum electrode has been reported as 5×10^{-1} cm s^{-1}, which has been obtained with $[Mo(CN)_8]^{4-/3-}$ redox couple dissolved in an aqueous solution.[49] It is very interesting that the largely different values of k° were obtained, depending upon the experimental conditions where the electroactive species exist in the polymer film or the solution. In the former case, the electroactive species are firmly bound to the polymer films by electrostatic force. There is no such a special interaction in the latter case.

From the fact that there is a linear relation between $\ln(x[\{1.75+x^2(1+\exp(-\zeta))^2\}/\{1-x(1+\exp(-\zeta))\}]^{1/2})$ and electrode potential (E) (see Fig. 5), in the case of the electrode reaction at the polymer-coated electrode the formation of electrical double layer and the electron transfer process at the electrode/film interface can be considered to be essentially the same as those in an ordinary electrode reaction at electrode/solution interface. As can readily be seen from the essential ground (*i.e.*, electrostatic interaction) of the incorporation of $[Mo(CN)_8]^{4-/3-}$ redox couple into the protonated PVP film, $[Mo(CN)_8]^{4-/3-}$ couple is strongly interacting with its surroundings, *i.e.*, polymeric domains.[2,19] Under these circumstances, thus, the formation of "activated complex"[47,48] prior to the electron transfer seems to be more difficult than in the case of electron transfer reactions in a bulk solution.

The free energy required to reorganize the surrounding medium (outer shells) prior to the electron transfer becomes to be larger,[50–53] under the assumption that the free energy required to reorganize the inner coordination shells of the reactants can be almost the same for the electrode reactions of both the electroactive species present in a bulk solution and the electroactive species confined in the polymer film. Thus it seems to be likely that a large difference between the values of k° obtained in this study and the value obtained with $[Mo(CN)_8]^{4-/3-}$ redox couple dissolved in a bulk solution originates from the difference of the energy needed for the solvent reorganization occuring outside the inner coordination shells of $[Mo(CN)_8]^{4-/3-}$ couple prior to (and necessary for) electron transfer in the reaction media in which the rate constants were measured. Similarly, the dependence of k° on Γ_M/Γ_{PVP} shown in Fig. 5 appears to arise from the change of the solvent reorganization energy by Γ_M/Γ_{PVP}.

A kinetic study on the electrode reactions at polymer-coated electrodes has just been started[38,42] and the present experimental data concerning the electrode reactions of this type are scarce. Many experimental data should thus be accumulated in order to give a successful explanation for some interesting problems mentioned above. It is of great interest to examine the dependence of k° on temperature and to obtain the activation parameters of these electrode reactions. Study on the effect of ion strength and the kind of supporting electrolyte upon the kinetic parameters of electrode reactions would also give further information.

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