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Electrode Kinetics of the $Fe(CN)_6{}^{4-/3-}$ and $Fe(CN)_5{}^{3-/2-}$ Complexes Confined to Polymer Film on Graphite Surfaces

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Abstract: An electron-transfer process of $Fe(CN)_6{}^{4-/3-}$ and $Fe(CN)_5{}^{3-/2-}$ redox couples, which were incorporated into the protonated poly(4-vinylpyridine) (PVP) film and coordinated to the unprotonated PVP film, respectively, at the graphite electrode/PVP film interfaces was examined by normal pulse voltammetry. From the analysis of the dependence of the current-potential curves upon the sampling times, the relevant kinetic parameters (i.e., the standard rate constant, $k°$, and the cathodic transfer coefficient, α) of electrode reaction were evaluated. For the $Fe(CN)_6{}^{4-/3-}$ complex confined electrostatically into the PVP film on the electrode surfaces, the values of $k°$ and α decreased from 3.2×10^{-3} to 1.6×10^{-4} cm s^{-1} and from 0.50 to 0.30, respectively, when the molar ratio of the incorporated metal complex to pyridine group of the PVP film, Γ_M/Γ_{PVP}, was increased from 0.005 to 0.18. For the $Fe(CN)_5{}^{3-/2-}$ coordinated to the PVP film, the value of $k°$ decreased from 1.5×10^{-3} to 1.5×10^{-4} cm^{-1}, and the value of α was almost constant (0.52) when the ratio Γ_M/Γ_{PVP} was increased from 0.005 to 0.075. In addition, the apparent diffusion coefficient, D_{app}, for the electron-transfer process within the film was determined from the dependence of the limiting currents upon the sampling times. In both redox systems, the value of D_{app} depended on Γ_M/Γ_{PVP} and decreased from 4.2×10^{-7} to $\sim 1 \times 10^{-9}$ cm^2 s^{-1}, when the ratio Γ_M/Γ_{PVP} was changed from 0.005 to 0.18.

A first attempt of the kinetic study on the electron-transfer reaction between the electrode and the metal complexes confined to the polymer film on the electrode surface by means of normal pulse voltammetry (NPV) has been performed in our previous paper,[1] where the electrode reaction of $Mo(CN)_8{}^{4-/3-}$ complexes incorporated into the protonated poly(4-vinylpyridine) (PVP) film on a pyrolytic graphite electrode and the diffusion-like electron-transfer reaction within the PVP film incorporating $Mo(CN)_8{}^{4-/3-}$ complexes have been examined. It has been shown therein that 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, and the electrode reaction of $Mo(CN)_8{}^{4-/3-}$ complexes confined in the protonated PVP film on electrode surface obeys the conventional Butler-Volmer equation which characterizes the electrode reaction at an uncoated, ordinary electrode in a solution. Further, it has become apparent that when the electrolysis time of NPV is below ca. 30 ms and the thickness of swollen polymer films is thicker than $\sim 1 \times 10^{-4}$ cm, the electron-transfer reaction can be treated as a semiinfinite diffusion process, and thus the analytical procedure of normal pulse voltammograms for the electrode reaction of the redox species in the bulk solution is straightforwardly applicable to the analysis of normal pulse voltammograms obtained at the polymer-coated electrode. We also have found that the value of standard rate constant ($k°$) at the electrode/film interface and the value of apparent diffusion coefficient (D_{app}) for the diffusion-like electron-transfer process within the film decrease with increasing the molar ratio of the incorporated metal complex to pyridine group of the protonated PVP, Γ_M/Γ_{PVP}. But, the present experimental data concerning the electron-transfer reaction of this type are scarce and thus insufficient to give a successful explanation for such a dependence of $k°$ and D_{app} upon Γ_M/Γ_{PVP}. Thus, as a continuation of the previous paper,[1] the present work is done by NPV to obtain the kinetic data of electrode reaction of $Fe(CN)_6{}^{4-/3-}$ redox couple at the graphite/protonated PVP film interface and the D_{app} within this polymer. The D_{app} of the $Fe(CN)_6{}^{4-/3-}$ redox couple incorporated electrostatically into the cationic films has been already examined by Oyama et al.[2,3] and Facci and Murray[4] according to potential-step chronoamperometry and other methods. But, no kinetic data of the electrode reaction at the electrode/coating film interface have been reported yet. Kinetic examination of the electron-transfer reactions of the $Fe(CN)_5{}^{3-/2-}$ complexes coordinated to the PVP film (abbreviated as $PVP[Fe(CN)_5]_n$) is also performed.

Experimental Section

Materials. Poly(4-vinylpyridine) (PVP) was recrystallized twice from methanol-diethyl ether; its average molecular weight was 7.4×10^5. The basal plane pyrolytic graphite (BPG) (Union Carbide Corp.) disk electrodes were prepared and mounted into Teflon tube as previously described.[2] The exposed area of each electrode was 0.17 cm^2. Solutions containing PVP to which various quantities of $Fe(CN)_5{}^{3-}$ groups were coordinated were prepared, as described previously,[5] by mixing methanolic solutions of PVP having appropriate concentrations and aqueous solutions of $Fe(CN)_5OH_2{}^{3-}$ which were prepared by dissolving $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ (Tokyo Kasei Kogyo Co., Ltd.) in aqueous solutions under conditions where substitution of the NH_3 group by H_2O proceeds rapidly. The sodium trifluoroacetate was used as an indifferent salt in sample solution, the pH of which was adjusted to the desired value by using NaOH and CF_3COOH solutions. Other chemicals were reagent grade and were used as received.

Apparatus and Procedures. Adherent coatings of PVP were produced by transferring aliquots of a 0.5 wt % 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.

During the normal pulse voltammetric experiments, it was observed that the $Fe(CN)_6{}^{3-}$ or $Fe(CN)_6{}^{4-}$ ion incorporated into the protonated PVP film slowly comes out from the domain of the polymer into the bulk solution. In order to prevent the incorporated Fe complexes from leaching out, a very low concentration ($\sim$0.1-0.2 mM) of the corresponding species was added in the bulk solution, and thus the constant concentration of the Fe complexes within the film was attained.

The quantities of $Fe(CN)_6{}^{3-}$ (or $Fe(CN)_6{}^{4-}$) incorporated into the protonated PVP coatings were determined by the following procedure. After incorporation of the $Fe(CN)_6{}^{3-}$ (or $Fe(CN)_6{}^{4-}$) complex, the electrodes were transferred to solution containing only supporting electrolyte (0.2 M CF_3COONa + CF_3COOH, pH 1.5). Then the electrode potential was scanned from a value before the reduction (or the oxidation) of the incorporated $Fe(CN)_6{}^{3-}$ (or $Fe(CN)_6{}^{4-}$) ion to a value well beyond the voltammetric peak potential for reduction (or oxidation) and thereafter maintained until the current fell to background levels (20-180

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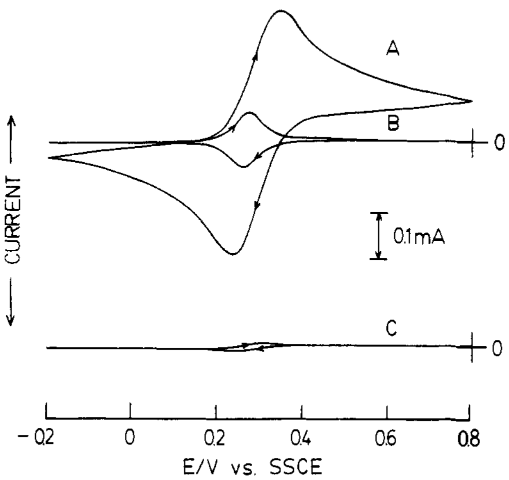

Figure 1. Cyclic voltammograms for the $Fe(CN)_6^{4-/3-}$ couple. (A) A pyrolytic graphite electrode coated with 4.6×10^{-7} mol cm^{-2} of pyridine as PVP was soaked for 10 min in a 5 mM solution of $Fe(CN)_6^{3-}$, washed, and transferred to pure supporting electrolyte which was 0.2 M CF_3COONa + CF_3COOH (pH 1.5): quantity of $Fe(CN)_6^{3-}$ incorporated into PVP film; 3.9×10^{-8} mol cm^{-2}. (B) A pyrolytic graphite electrode coated with 4.6×10^{-7} mol cm^{-2} of pyridine as PVP was soaked for 10 min in a 0.2 mM solution of $Fe(CN)_6^{3-}$, washed, and transferred to pure supporting electrolyte used in (A): quantity of $Fe(CN)_6^{3-}$ incorporated into PVP film; 7.5×10^{-9} mol cm^{-2}. (C) At a bare graphite electrode in 0.2 mM solution of $Fe(CN)_6^{3-}$ containing 0.2 M CF_3COONa + CF_3COOH (pH 1.5). Scan rate: 100 mV s^{-1}.

s). The quantity of incorporated reactant was calculated from the integration of the current with correction for background contributions.

The various quantities of $Fe(CN)_5^{3-}$ groups which were coordinated to the unprotonated PVP coating were previously controlled by mixing aqueous solutions of $Fe(CN)_5OH_2^{3-}$ and methanolic solutions of PVP having appropriate concentrations to produce a final mixture with the desired stoichiometric ratio of PVP to $Fe(CN)_5OH_2^{3-}$ in a 50/50 vol % methanol–water mixture. The accurate estimate of the concentration of $Fe(CN)_5^{3-}$ group in the resulting $PVP[Fe(CN)_5^{3-}]_n$ polymer was made by the same procedure as described above.

Normal pulse voltammograms and cyclic voltammograms were obtained with instruments which were constructed in our laboratory[1] and were recorded with a X–Y recorder (Watanabe Corp.). Positive feedback circuitry was employed to compensate the resistances of polymer film and the cell (these were typically ca. 20–80 Ω). In normal pulse voltammetric experiments, the pulse width of 50 ms and the intervals 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 prepurified 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

Electron-Transfer Reactions of $Fe(CN)_6^{4-/3-}$ Redox Couple at the BPG/Protonated PVP Film Interface and within the PVP Film. It has been well known that multiply charged transition metal complexes remain attached to various polyelectrolyte films on electrode surfaces by electrostatic interaction between the polyelectrolyte layer and metal complexes carrying the opposite charge.[1-12] Figure 1 shows the equilibrium cyclic voltammograms for the oxidation and reduction of the $Fe(CN)_6^{4-/3-}$ couple partitioned into the protonated PVP coatings in 0.2 M CF_3COONa (pH 1.5) solution of $Fe(CN)_6^{3-}$. A typical cyclic voltammogram for $Fe(CN)_6^{3-}$ at an uncoated graphite electrode is also shown in Figure 1. The peak currents at a coated electrode are ten times larger than those at a bare electrode in the same loading solution because the concentration of the complex within the PVP coating is much higher than its concentration in the loading solution (see Figures 1B and 1C). Thus, it is apparent that $Fe(CN)_6^{3-}$ can be electrostatically attached to the protonated PVP coating on electrodes. Further, the shape of the cyclic voltammograms and their peak separation were found to vary with the concentration (Γ_M) of the incorporated $Fe(CN)_6^{3-}$ ion. When Γ_M is relatively low ($\Gamma_M \sim 10^{-11}$–10^{-9} mol cm^{-2}, e.g., Figure 1B), the shape of the cyclic voltammetric waves is similar to that expected for a surface-confined species;[13-15] i.e., the waves are nearly symmetrical and anodic and cathodic peak separation, ΔE_p, is near zero (ca. 15 mV). As Γ_M is increased, the waves become to be more diffusion-like, with broad peaks, a nonzero ΔE_p, and a diffusional tail. For example, the ΔE_p of Figure 1A ($\Gamma_M = 3.9 \times 10^{-8}$ mol cm^{-2}) was about 120 mV at the scan rate of 100 mV s^{-1} (with *iR* compensation) which is significantly larger than the near Nernstian value of 62 mV found for the reduction of $Fe(CN)_6^{3-}$ present in solutions (see Figure 1C). It can be considered that such a large ΔE_p is attributed to slow heterogeneous electron transfer between the electrode and the redox centers in the polymer film and film (or solution) resistance effects.[15-20]

According to the previous results,[1,3] the electron-transfer process within the film can be treated as a semiinfinite diffusion process, when the electrolysis time is below about 30 ms. In the present work, normal pulse voltammograms are obtained with the sampling times between 2 and 16 ms. Therefore, the present measurement condition satisfies the condition of such a semiinfinite diffusion. Furthermore, it has been previously confirmed[1] that the electrode reaction of the electroactive species confined in the polymer film on electrode surface obeys the conventional Butler–Volmer equation.[21] Thus, the analysis procedure of normal pulse voltammograms for the electrode reaction of the redox species present in the solution can be applicable to that for the electrode reaction of the redox species confined in the polymer film.

The current–potential relationship[1,22-25] for normal pulse voltammograms for the simple electrode process, Red ⇄ Ox + *n*e, is given by

$$E = E^* \mp \frac{RT}{\alpha nF} \ln \left\{ X \left[\frac{1.75 + x^2(1 + \exp(\pm\zeta))^2}{1 - x(1 + \exp(\pm\zeta))} \right]^{1/2} \right\} \quad (1)$$

with

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

$$x = i/(i_d)_{Cott} \quad (3)$$

$$\zeta = (nF/RT)\left(E - E^r_{1/2}\right) \quad (4)$$

$$D_{app} = (D_{Ox})^{\alpha_a} (D_{Red})^{\alpha_c} \quad (5)$$

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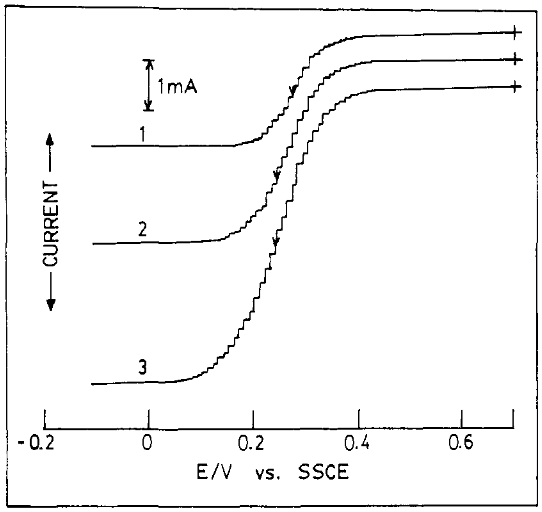

Figure 2. Normal pulse voltammograms for the reduction of $Fe(CN)_6^{3-}$ incorporated in a coating of the protonated PVP film (4.6×10^{-7} mol cm^{-2}) on a graphite electrode in 0.2 M CF_3COONa solution (pH 1.5): concentration of $Fe(CN)_6^{3-}$ incorporated into PVP, Γ_M; 7.9×10^{-9} mol cm^{-2}. Sampling time: (1) τ = 16 ms, (2) 8 ms, (3) 4 ms.

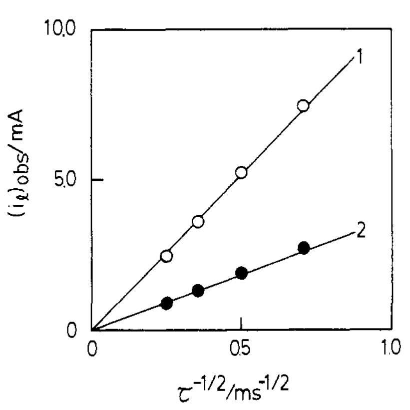

Figure 3. Plots of limiting current, $(i_l)_{obsd}$ vs. (sampling time)$^{-1/2}$ for the reduction of $Fe(CN)_6^{3-}$ incorporated into the protonated PVP film on BPG electrode. Quantities of $Fe(CN)_6^{3-}$ incorporated into PVP film: (1) $\Gamma_M = 2.8 \times 10^{-8}$ and (2) 3.9×10^{-9} mol cm^{-2}. Quantity of pyridine as PVP, Γ_{PVP}, 4.6×10^{-7} mol cm^{-2} in both cases.

where the upper and lower signs in double signs (± or ∓ of eq 1 and 2 are employed to analyze the reaction processes corresponding to the reduction and oxidation, respectively; E is the electrode potential, i the normal pulse voltammetric current, and $E^r_{1/2}$ the voltammetric reversible half-wave potential; α denotes cathodic or anodic transfer coefficient (α_c and α_a for the cathodic and anodic reactions, respectively), $k°$ the standard rate constant, and τ the sampling time. D_{Ox} and D_{Red} are the diffusion coefficients of Ox and Red, respectively, and F, R, and T have their usual meanings. $(i_d)_{Cott}$ denotes the diffusion current expressed by the Cottrell equation[26] in the following manner:

$$(i_d)_{Cott} = nFAC°\sqrt{D_{app}/\pi\tau} \qquad (6)$$

where A is the electrode area and $C°$ the bulk concentration of Red or Ox.

Figure 2 shows the typical normal pulse voltammograms for the reduction of $Fe(CN)_6^{3-}$ incorporated into the PVP film with various sampling times. These S-shaped waves are similar to those obtained for redox species present in a solution at an uncoated electrode.[22,23] The half-wave potential of the normal pulse voltammograms shifted to more negative values with decreasing sampling times. As shown in Figure 3, plots of the cathodic 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 was diffusion controlled and the behavior of diffusion process appears to be semiinfinite. Thus, the apparent diffusion coefficients, D_{app}, for the electron-transfer process within the film were obtained from the cathodic limiting currents by using the Cottrell equation. When the concentration of the $Fe(CN)_6^{3-}$ ion incorporated into the PVP film was changed under constant concentration of PVP, the straight lines shown in Figure 3 had different slopes. This shows that the apparent diffusion coefficients for the electron-transfer process within the film vary with the concentration of the incorporated $Fe(CN)_6^{3-}$ ion.

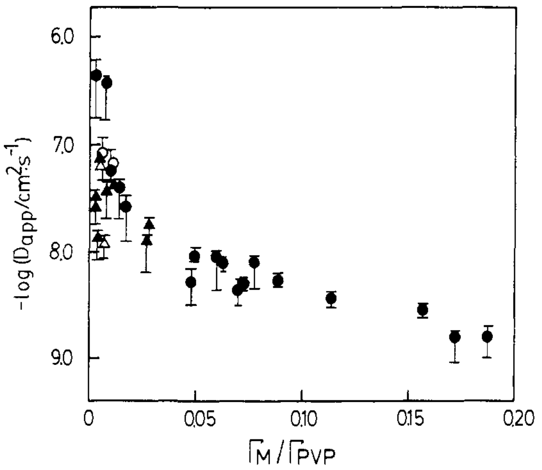

Figure 4. Logarithmic plot of D_{app} vs. the molar ratio of incorporated electroactive species to the protonated or unprotonated pyridine group of PVP, Γ_M/Γ_{PVP}. Electroactive species incorporated: (●) $Fe(CN)_6^{3-}$, (○) $Fe(CN)_6^{4-}$, (▲) $Fe(CN)_5^{2-}$ group, (△) $Fe(CN)_5^{3-}$ group. Supporting electrolyte: 0.2 M CF_3COONa–CF_3COOH (pH 1.5 for $Fe(CN)_6^{4-/3-}$ system and pH 3.0 for $PVP[Fe(CN)_5]_n$ system). Quantity of pyridine group as PVP is the same as in Figure 3.

Figure 4 shows the logarithmic plot of D_{app} vs. the molar ratio of the incorporated $Fe(CN)_6^{3-}$ ion to pyridine group of the protonated PVP, Γ_M/Γ_{PVP}, together with D_{app} for the oxidation of $Fe(CN)_6^{4-}$ and $PVP[Fe^{II}(CN)_5]_n$ and the reduction of $PVP[Fe^{III}(CN)_5]_n$. It is apparent from this plot that D_{app} is dependent on the concentration of the incorporated $Fe(CN)_6^{3-}$ ion. As the ratio Γ_M/Γ_{PVP} decreases, the apparent diffusion coefficient increases. D_{app} for $Fe(CN)_6^{4-}$, $PVP[Fe^{II}(CN)_5]_n$ and $PVP[Fe^{III}(CN)_5]_n$ also has similar dependence upon Γ_M/Γ_{PVP}. Such a result has also been obtained in a previous work,[3] where anionic reactants, $Fe(CN)_6^{4-/3-}$, $Mo(CN)_8^{4-/3-}$, and $W(CN)_8^{4-/3-}$ were incorporated into the PVP coating and the diffusion coefficients of the incorporated anions were evaluated by chrono-amperometric, -coulometric, and -potentiometric measurements[3] and further by the NPV technique with respect to $Mo(CN)_8^{4-}$.[1,25] From the results shown in the Figure 4 and the previous data,[3] it may thus be concluded that the physical motion of the redox anions through the polymer film dominates their diffusional rates in the range of lower value of Γ_M/Γ_{PVP} (≤ 0.1). One factor contributing to the larger values of D_{app} probably exists in the smaller extent of electrostatic cross-linking of the anions with the surrounding polymer cation sites, as the concentrations of the anions decrease. Further, as decreasing the value of Γ_M/Γ_{PVP} for the $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions, the value of D_{app} tends to approach those (5×10^{-6} cm^2 s^{-1}) of the diffusion coefficients of these anions in the bulk solutions. This seems to support the above conclusion. As the concentrations of the anions increase, the values of D_{app} become gradually smaller. Under these circumstances, physical motion of the anions through the film becomes more difficult because of the higher extent of electrostatic cross-linking.[3,4,9] This probably suggests that the motion of diffusing counterions accompanying the electron transfer within the coating film dominates the rate of the electron transfer.[3,4] For D_{app} of $PVP[Fe^{II}(CN)_5]_n$ and $[Fe^{III}(CN)_5]_n$ in Figure 3, we notice that a drop in D_{app} occurs when the number of redox sites was decreased sufficiently. In the case of these redox films the redox center is immobilized to the PVP by the coordination, and charge can be transferred through the film by electron exchange between the pair of redox

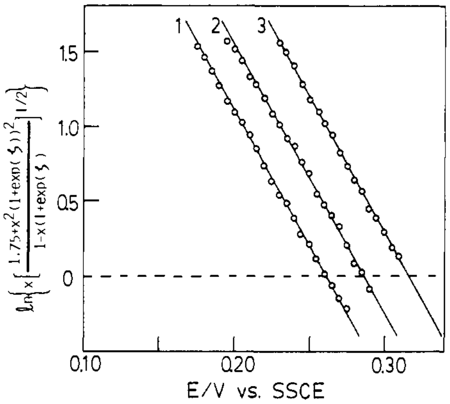

Figure 5. Modified log plots of normal pulse voltammograms for the reduction of $Fe(CN)_6^{3-}$ incorporated into the protonated PVP film. Sampling time: (1) τ = 4 ms, (2) 8 ms, and (3) 16 ms. Other experimental conditions are the same as in Figure 2.

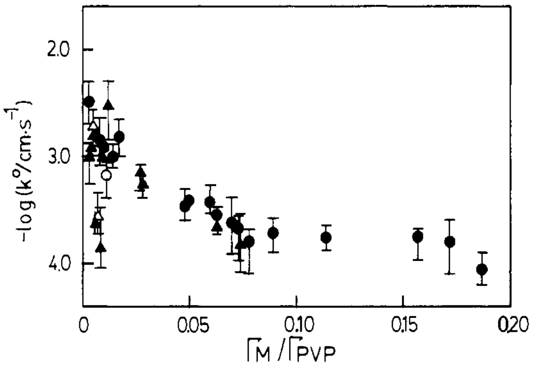

Figure 6. Logarithmic plot of the standard rate constant, k°, against the molar ratio of incorporated electroactive species to protonated or unprotonated pyridine group of PVP. Electroactive species incorporated: (●) $Fe(CN)_6^{3-}$, (○) $Fe(CN)_6^{4-}$, (▲) $Fe(CN)_5^{2-}$ group, (△) $Fe(CN)_5^{3-}$ group. Other experimental conditions are the same as in Figure 2.

centers. Therefore, it can be considered that the drop in D_{app} reflects an increase in the encounter distances required for efficient electron transfer, as mentioned previously.[5] When Γ_M/Γ_{PVP} is decreased sufficiently, the distance becomes longer and thus begins to limit the rate of charge transfer through the film.

Figure 5 shows the examples of the modified log plots of normal pulse voltammograms at $\Gamma_M/\Gamma_{PVP} = 0.017$, in which the ln term or right-hand side of eq 1 is plotted against E for the reduction of $Fe(CN)_6^{3-}$ incorporated into the protonated PVP coatings. These straight lines have constant slopes within experimental errors. The cathodic transfer coefficient, α_c, was evaluated from their reciprocal slopes and its value was 0.50 ± 0.03. The anodic transfer coefficient, α_a, which was obtained from the similar modified log plots for the oxidation reaction of the incorporated $Fe(CN)_6^{4-}$ ion, was also 0.50 ± 0.03. Both values of α_a and α_c were independent of Γ_M/Γ_{PVP} under the condition of $\Gamma_M/\Gamma_{PVP} \leq 0.05$. The value of α_c was nearly equal to that (0.48) obtained for the reduction of $Fe(CN)_6^{3-}$ ion present in solution at an uncoated electrode. In the range of the ratio Γ_M/Γ_{PVP} between 0.05 and 0.15, however, the value of α_c decreased from 0.45 ± 0.03 to 0.30 ± 0.03 with increasing Γ_M/Γ_{PVP}. When Γ_M/Γ_{PVP} was above ca. 0.15, α_c was nearly independent of Γ_M/Γ_{PVP} and its value was 0.30 ± 0.03. The value of E^* expressed by eq 2 was obtained from the intersects of these lines with the zero line, as shown in Figure 5. The standard rate constants of electrode reaction at the electrode/film interface were thus evaluated by introducing the experimentally obtained values of D_{app}, α_c or α_a, and $E^r_{1/2}$ into eq 2, where the values of $E^r_{1/2}$ were obtained from the cyclic voltammograms for the oxidation and reduction reactions of the incorporated anions.

Figure 6 shows the dependence of k° upon the ratio of Γ_M to Γ_{PVP}. As the ratio Γ_M/Γ_{PVP} increases, the values of k° decrease.

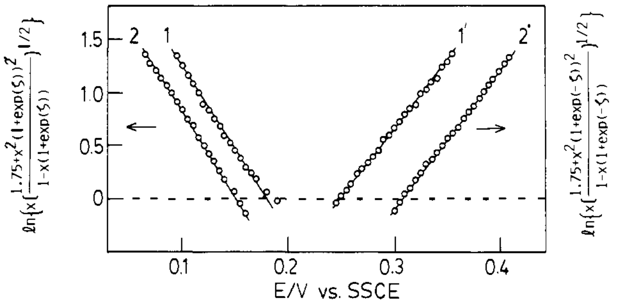

Figure 7. Modified log plots of normal pulse voltammograms for the oxidation of $Fe(CN)_5^{3-}$ group and the reduction of $Fe(CN)_5^{2-}$ group coordinated to the unprotonated PVP film. Sampling time: (1, 1′) τ = 4 ms; (2, 2′) τ = 2 ms. (1, 2) reduction; (1′, 2′) oxidation. Supporting electrolyte: 0.2 M $CF_3COONa + CF_3COOH$ (pH 3.0).

In the Γ_M/Γ_{PVP} region beyond 0.1, the values of k° became nearly constant and were 1.6×10^{-4} cm s^{-1}.

Electron-Transfer Reactions of the $Fe(CN)_5^{3-/2-}$ Groups Coordinated to Unprotonated PVP Film. The electron-transfer reaction within the polymer films prepared by coordinating $Fe(CN)_5^{3-/2-}$ redox groups to unprotonated PVP films has been studied previously.[5] It has been shown therein that the electron transfer between adjacent pairs of redox groups limits the rate of charge transfer through the polymer. Normal pulse voltammograms for the oxidation and reduction of $Fe(CN)_5^{3-/2-}$ groups coordinated to the unprotonated PVP film were measured at different sampling times. The voltammograms similar to those for $Fe(CN)_6^{4-/3-}$ couple incorporated into the protonated PVP film by electrostatic binding[1-12] were obtained. The apparent diffusion coefficients, D_{app}, for the electron-transfer process within the film were determined in a similar manner as in the previous section from the limiting currents of normal pulse voltammograms by using the Cottrell equation. The values obtained are plotted against Γ_M/Γ_{PVP} in Figure 4. It is likely that the dependence of D_{app} on Γ_M/Γ_{PVP} is slightly different from that for the $Fe(CN)_6^{4-/3-}$ system. In the region of $\Gamma_M/\Gamma_{PVP} \leq 0.05$, the value of D_{app} seems to decrease with decreasing ratio Γ_M/Γ_{PVP}. This result seems most likely to reflect a real increase in the distances required for electron transfer between redox centers in polymer films. The factor controlling the charge transfer through the film is the rates of electron self-exchange reaction between adjacent pairs of oxidized and reduced species,[16,17,20,27-32] since no rupture of the Fe–C bond occurs in the solution employed here (pH 3),[33,34] so that the $Fe(CN)_5^{3-}$ or $Fe(CN)_5^{2-}$ group itself cannot move independently in the domain of the PVP polymer.

Figure 7 shows the typical examples of the modified log plots of normal pulse voltammograms, in which the ln term on the right-hand side of eq 1 is plotted against E for the oxidation and reduction of the $Fe(CN)_5^{3-/2-}$ groups coordinated to the unprotonated PVP film. The log plots afford a set of straight lines at different sampling times. The cathodic and anodic transfer coefficients, α_c and α_a, were evaluated from the reciprocal slopes of these lines as follows: $\alpha_c = 0.52 \pm 0.05$ and $\alpha_a = 0.40 \pm 0.05$ under the condition $\Gamma_M/\Gamma_{PVP} \leq 0.1$. The dependence of the standard rate constants, being evaluated from the values of E^* by using eq 2, upon Γ_M/Γ_{PVP} is shown in Figure 6, together with that of the $Fe(CN)_6^{4-/3-}$ couple. Figure 6 shows clearly the similar dependence of k° upon the concentration of the incorporated

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electroactive species irrespective of the kind of the incorporated species and the type of the binding by which electroactive species are attached to the PVP films.

When the value of Γ_M/Γ_{PVP} is below 0.005, the value of $k°$ for the $Fe(CN)_6^{4-/3-}$ couple incorporated into the protonated PVP film is almost equal to or slightly larger than that (1.5×10^{-3} cm s^{-1}) for the same redox couple in the bulk of solution containing 0.2 M CF_3COONa (pH 1.5) at a BPG electrode by means of normal pulse voltammetry. As the value of Γ_M/Γ_{PVP} increases, the value of $k°$ decreases gradually and tends to approach a constant value (1.6×10^{-4} cm s^{-1}) above $\Gamma_M/\Gamma_{PVP} = 0.15$, where the sum of the concentrations of the supporting electrolyte and the protonated pyridine group of PVP is ca. 4 M. Peter et al.[35] have reported that the value of $k°$ for the dissolved $Fe(CN)_6^{4-/3-}$ couple at a gold electrode increases with the concentration of the supporting electrolyte; e.g., $k°$ is $\sim 10^{-2}$ and $\sim 10^{-1}$ cm s^{-1} in 0.2 and 4 M $NaClO_4$ solutions, respectively. They suggested that the electrode reaction of the $Fe(CN)_6^{4-/3-}$ couple is catalyzed by the cations of the supporting electrolyte which form the ion-paired species with the highly charged reactant anions and results in the increase of $k°$ with increasing concentration of the supporting electrolyte. However, the above results obtained with the electrode process of the redox species bound to the polymeric domains cannot be explained by the same idea as mentioned above. Under the condition of $\Gamma_M/\Gamma_{PVP} >$ ca. 0.15, $Fe(CN)_6^{4-/3-}$ anions are strongly confined by electrostatic force to the domain of the protonated PVP, so that physical motion of $Fe(CN)_6^{4-/3-}$ anions through the film may be more difficult because of the higher extent of electrostatic cross-linking.[1-12] Under these circumstances, the formation of "activated complexes"[36,37] before the electron-transfer process occurs seems to be more difficult than in the case of electron-transfer reactions in an ordinary solution, because the electroactive species is strongly interacting with the surroundings, i.e., the domains of the polymer films by the electrostatic force in the case of $Fe(CN)_6^{4-/3-}$ couple and the coordination in the case of $PVP[Fe(CN)_5^{3-/2-}]_n$, respectively. The free energy required to reorganize the surrounding medium (outer shells) prior to the electron transfer becomes larger,[38-42] 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 to the polymer films. Thus, it seems likely that the dependence of $k°$ on Γ_M/Γ_{PVP} shown in Figure 6 originates from the change of the energy needed for the solvent reorganization, which occurs outside the inner coordination shells of $Fe(CN)_6^{4-/3-}$ couple prior to (and necessary for) electron transfer, by Γ_M/Γ_{PVP}. We have also obtained similar results as shown in Figure 6 in the case of the reaction of $Mo(CN)_8^{4-/3-}$ couple incorporated into the protonated PVP film.[1,26]

Kurimura et al.[43] have studied the kinetics of electron-transfer reactions between Fe^{2+} and *cis*-$Co(en)_2XCl^{2+}$ (where en = ethylenediamine, X = pyridine (py) or poly(4-vinylpyridine) (PVP)), which can be considered to be very similar to the electrode reactions at polymer-coated electrodes under consideration of the fact that in both cases reactants are confined in the polymeric domains. They[43] have reported that both the activation entropy and enthalpy for the electron-transfer reaction of the *cis*-$Co(en)_2PVPCl^{2+}$–Fe^{2+} system are larger than those for the *cis*-$Co(en)_2pyCl^{2+}$–Fe^{2+} system, and consequently the rate constant is smaller in the former than in the latter. The kinetics of electron-transfer reaction between $Co(phen)_3^{2+}$ and $Co(phen)_3^{3+}$ ions (phen = *o*-phenanthroline) in dilute aqueous solutions containing anionic polyelectrolytes have been investigated by Brückner et al.,[44] who have mentioned that the polyelectrolytes produce an increase in the activation energy for the reaction considered, for which the very clustering of the reactant ions into the densely charged polyelectrolyte domains might be responsible. Recently, Bard et al.[20,32,38] have reported that the apparent heterogeneous rate constant of electron-transfer reaction for the $Ru(bpy)_3^{2+/3+}$ (bpy = 2,2′-bipyridine) couple in a Nafion film, which was estimated to be about 1×10^{-5} cm s^{-1} from the digital simulation of cyclic voltammograms for the oxidation–reduction of $Ru(bpy)_3^{2+/3+}$ confined to a Nafion film, is much lower than the corresponding heterogeneous rate constant in an aqueous solution ($\sim 7 \times 10^{-2}$ cm s^{-1}). They have suggested that the changes in the structure of the polymer layer upon oxidation and reduction, which are equivalent to a fast following reaction, contribute to the large peak separation between anodic and cathodic peak potentials of cyclic voltammograms and therefore to the low apparent heterogeneous rate constant. The model involving the "equivalent of a following reaction" seems to be partly successful in interpreting the shape and location of the cyclic voltammetric waves obtained with the polymer-coated electrodes, where the polymer itself is electroactive (e.g., poly(vinylferrocene) modified electrode[17]), or electroactive species are trapped in the electroinactive polymer film (e.g., Nafion-coated electrode in which $Ru(bpy)_3^{2+}$ is held[20,38]). However, it can be considered that the digital simulation of cyclic voltammograms for polymer electrodes is insufficient to probe the nature of the processes occurring in the polymer films, since the variety of possible processes and the number of adjustable parameters do not allow unambiguous determination of the kinetic parameters (i.e., $k°$ and α). Recently, Sharp et al.[45] have adopted a simple elastic electron tunnelling model[46,47] in order to account for the kinetics of electron transfer between a platinum electrode and a ferrocene redox center which is covalently attached to its surface. They have suggested that the surface reaction involving electron transfer between platinum and ferrocene is markedly nonadiabatic in character, as opposed to the similar reaction for dissolved species, and that the entropy of activation for this process is small. However, we have now no data to support that such a elastic electron tunnelling model applies straightforwardly to the present system. At the present stage, we cannot conclude what is attributable to the changes of $k°$ and α against Γ_M/Γ_{PVP} (Figure 6). In this report, it should be noted that the kinetic parameters of the electrode reactions at polymer-coated electrodes could be obtained by means of NPV, which is one of the most suitable methods for the examination of electrode kinetics in fairly fast electrode reaction processes ($k°(\tau/D_{app})^{1/2} \leq 2.5$),[22-24] without the severe perturbation by the uncompensated resistance in the polymer film by using positive feedback techniques to minimize such an uncompensated resistance.

A model general enough to understand the electrode reactions at polymer-coated electrodes may be too much to hope for, but many experimental data are needed to make clear some interesting problems mentioned above. For example, it is of great interest to obtain the electrochemical activation parameters from the temperature dependence of rate constant ($k°$), although the obtained activation parameters seem not to be straightforwardly associated with the electron transfer reaction itself at electrode/film interface, because the changing of temperature would cause the change of the morphology, the swelling and the solubility of the polymer itself, and further may result in the change of the structure of the electrical double layer at electrode/film interface. Study on the effect of ion strength and the kind of supporting electrolyte upon the kinetic parameters of electrode reactions would

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also give further information. Experiments with this objective have been in progress.

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Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3; PVP, 9003-47-8; graphite, 7782-42-5.

Preparation and Crystal and Molecular Structure of $S_4N_4H^+BF_4^-$. Molecular Orbital Study of the Protonation of Tetrasulfur Tetranitride

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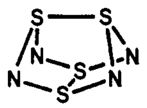
Abstract: The reaction of tetrasulfur tetranitride with tetrafluoroboric acid diethyl etherate in methylene chloride solution produces $S_4N_4H^+BF_4^-$, the first simple salt of S_4N_4. the crystal and molecular structure of $S_4N_4H^+BF_4^-$ has been determined by X-ray crystallography. Crystals of the compound are monoclinic, space group $P2_1/n$, $a = 6.563$ (2) Å, $b = 11.717$ (2) Å, $c = 11.409$ (2) Å, $\beta = 101.63$ (2)°, $V = 859.3$ (6) Å^3, and $Z = 4$. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares procedures to give a final R of 0.042 for 1428 observed reflections. The structure of the $S_4N_4H^+$ cation consists of a boat-shaped 8-membered ring with approximately coplanar (to within 0.02 Å) sulfur atoms. The reasons for the structural rearrangement which the protonation of S_4N_4 induces are discussed in the light of MNDO molecular orbital calculations on a number of idealized conformations of $S_4N_4H^+$ unit.

In spite of the lack of evidence usually regarded as diagnostic of aromatic behavior, e.g., heats of formation and[2] diamagnetic ring currents,[3] the descriptions of the electronic structures of cyclic binary sulfur nitride derivatives often allude to their aromatic character. The empirical rules devised by Banister[4] and the symmetry-based molecular orbital arguments of Gleiter[5] and of Gimarc and Trinajstić[6] emphasize the preponderance of cyclic π systems containing $4n + 2$ electrons. However, the need for such a complement vanishes in molecules possessing less than 3-fold symmetry.[7] Recently several cyclic molecules containing $4n$ π electrons have been reported.[8,9]

The observed structure of tetrasulfur tetranitride (**1**) has long been regarded as a manifestation of the $4n + 2$ rule. In his extended Hückel analysis of S_4N_4, Gleiter pointed out that the 12-π-electron ground state of a planar S_4N_4 would be orbitally degenerate and as such unstable with respect to Jahn–Teller distortion.[10] However, as indicated above, there is no a priori reason to suppose that the cage shape will be more stable than a cyclic structure if the symmetry of the molecule is lowered by the attachment of an exocyclic ligand. Certainly the structural evidence obtained from numerous Lewis acid adducts, e.g., $S_4N_4{\cdot}A$ (**2**),[11-17] indicates that the coordination of a lone pair of electrons on nitrogen to an acceptor site is a sufficient perturbation to cause the cage to open. However, the electronic factors that dictate this conformational change have not hitherto been addressed. In order to develop some understanding of this rearrangement we have carried out a synthetic, structural, and molecular orbital (MNDO) study of $S_4N_4H^+BF_4^-$, the first simple salt of S_4N_4 to be structurally characterized. The results provide an insight into the factors that govern the conformational preferences of sulfur-nitrogen rings.



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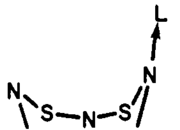

2

Experimental Section

Reagents and General Procedures. Tetrasulfur tetranitride, S_4N_4, was prepared according to a published method.[18] Fluoroboric acid–diethyl ether complex was obtained commercially (Aldrich) and used without further purification. Methylene chloride (reagent grade) was dried by distillation from phosphorus pentoxide. Infrared spectra were recorded on Nujol mulls (CsI cells) by using a Perkin-Elmer 467 grating spec-

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