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Electrocatalytic Reaction of $Fe^{2+/3+}$ Aqua Ions by $[Mo(CN)_8]^{4-/3-}$ Complexes

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Synopsis. The catalysis of the oxidation of Fe^{2+} aqua ion by $[Mo(CN)_8]^{3-}$ ion, which is formed on an electrode surface, and that of the reduction of Fe^{3+} aqua ion by $[Mo(CN)_8]^{4-}$ ion were examined by means of hydrodynamic voltammetry at a rotating disk pyrolytic graphite electrode. The rate constants of the electron transfer cross-reaction of the $Fe^{2+}/[Mo(CN)_8]^{3-}$ and $Fe^{3+}/[Mo(CN)_8]^{4-}$ systems were estimated to be $(7.0\pm0.5)\times10^6$ and $(6.6\pm0.5)\times10^6$ $cm^3\ mol^{-1}\ s^{-1}$, respectively.

In previous papers[1,2] we have examined the catalysis of the electrode process of $Fe^{2+/3+}$ redox couple by $[Mo(CN)_8]^{4-/3-}$ complexes bound electrostatically to graphite electrodes coated with the protonated poly(4-vinylpyridine) (PVP) film. It has been shown therein that $[Mo(CN)_8]^{4-/3-}$ complexes are strongly incorporated into the protonated PVP film and the resulting metalated film electrode can catalyze both the oxidation of Fe^{2+} aqua ion and the reduction of Fe^{3+} aqua ion present in a bulk solution. The catalytic reaction of the $Fe^{2+}/[Mo(CN)_8]^{3-}$ and $Fe^{3+}/[Mo(CN)_8]^{4-}$ systems can be considered to be simple and outer-sphere electron transfer cross-reaction. However, no kinetic study on the catalytic reaction of both systems in a bulk solution at an uncoated electrode has been reported yet.

In this paper, we will thus examine the catalysis of the oxidation of Fe^{2+} ion by $[Mo(CN)_8]^{3-}$ ion, which is formed on a graphite electrode surface, and that of the reduction of Fe^{3+} ion by $[Mo(CN)_8]^{4-}$ ion by means of hydrodynamic voltammetry at a rotating disk pyrolytic graphite electrode.

Experimental

Electrochemical apparatus and the experimental procedures have been described previously.[1-3,8] The exposed area of each electrode was 0.17 cm^2. Potassium octacyanomolybdate(IV) dihydrate ($K_4[Mo(CN)_8]\cdot2H_2O$) was synthesized according to the standard procedure.[4] Solutions were freed of air with prepurified argon prior to the electrochemical measurements. Experiments were conducted at 25 °C. Potentials are reported with respect to a sodium chloride saturated calomel electrode (SSCE).

Results and Discussion

Current-potential curves A, B, and C shown in Fig. 1 demonstrate typical steady-state current-potential curves obtained at a rotating disk graphite electrode in an each 0.2 M CF_3COONa solution containing 0.2 mM $[Mo(CN)_8]^{4-}$, 2 mM Fe^{2+} and 0.2 mM $[Mo(CN)_8]^{4-}$+2 mM Fe^{2+} ions. When the current-potential curves were measured at a graphite electrode in the solution containing both 0.2 mM $[Mo(CN)_8]^{4-}$ and 2 mM Fe^{2+} ions, two waves were observed and each of their half-wave potentials were about 0.5 and 0.7 V *vs.* SSCE. The first wave observed at about 0.5 V corresponds to the oxidation of $[Mo(CN)_8]^{4-}$ ion. The conventional log-plot of $\log\{i/(i-i_{lim})\}$ against E (where i_{lim} is the limiting current and i is the current at any potential, E) of the current-potential curve A yields straight lines with the reciprocal slopes of 59 ± 1 mV, in accordance with the fact that the first wave is the reversible one-electron oxidation wave. From the similar log-plot of the current-potential curve B, the oxidation of Fe^{2+} ion was proved to be close to irreversible. The standard heterogeneous rate constant for the oxidation of Fe^{2+} ion at a graphite electrode is 6×10^{-5} cm s^{-1}.[8] As can readily be seen from the comparison of the limiting currents of the steady-state current-potential curves A and C shown in Fig. 1, the limiting current for the oxidation of $[Mo(CN)_8]^{4-}$ ion in the solution containing Fe^{2+} ion is several times larger than the corresponding limiting current in the absence of Fe^{2+} ion. As the concentration of Fe^{2+} ion increased under the constant concentration of $[Mo(CN)_8]^{4-}$ ion, the height of the first wave increased, but the half-wave potential at about 0.5 V remained constant. At the constant concentrations of Fe^{2+} and $[Mo(CN)_8]^{4-}$ ions, the height of the first wave unchanged with changes in the rotation rate between 400 and 3600 min^{-1}, but the total limiting current was proportional to the square root of the rotation rate. These facts suggest the catalytic oxidation of Fe^{2+} ion by $[Mo(CN)_8]^{3-}$ ion, which is formed on an electrode surface by the electrochemical oxidation of the $[Mo(CN)_8]^{4-}$ ion present in a bulk solution.

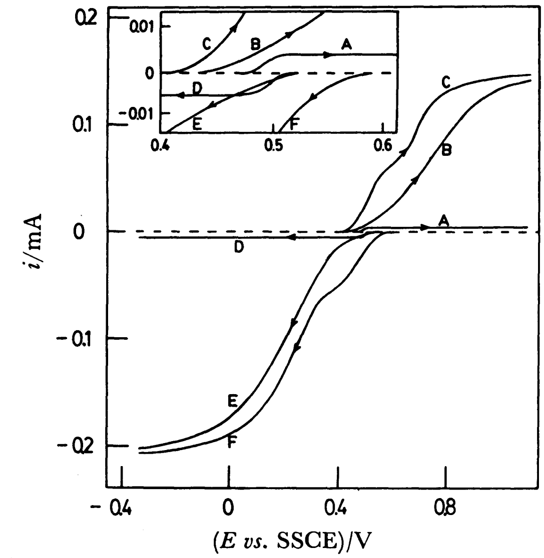

Fig. 1. Typical steady-state current-potential curves demonstrating the catalysis of the oxidation of Fe^{2+} ion by $[Mo(CN)_8]^{3-}$ ion and of the reduction of Fe^{3+} ion by $[Mo(CN)_8]^{4-}$ ion at rotating disk pyrolytic graphite electrodes.
Oxidation of (A): 0.2 mM $[Mo(CN)_8]^{4-}$; (B): 2 mM Fe^{2+}; (C): 0.2 mM $[Mo(CN)_8]^{4-}$+2 mM Fe^{2+}; Reduction of (D): 0.2 mM $[Mo(CN)_8]^{3-}$; (E): 2 mM Fe^{3+}; (F): 0.2 mM $[Mo(CN)_8]^{3-}$ +2 mM Fe^{3+}.
Supporting electrolyte: 0.2 M CF_3COONa–CF_3COOH (pH 1.5). Electrode rotation rate: 800 min^{-1}.

Thus, the overall electrode reaction can be expressed by the following scheme:

$$[\mathrm{Mo(CN)_8}]^{4-} - \mathrm{e} \rightleftharpoons [\mathrm{Mo(CN)_8}]^{3-} \qquad (1)$$

$$[\mathrm{Mo(CN)_8}]^{3-} + \mathrm{Fe}^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Mo(CN)_8}]^{4+} + \mathrm{Fe}^{3+}. \qquad (2)$$

Under the conditions that the concentration of Fe^{2+} ion is so high compared with that of $[\mathrm{Mo(CN)_8}]^{4-}$ ion, it can be assumed that the concentration Fe^{2+} ion remains constant during the whole electrochemical process. Thus, we obtain Eq. 3 which characterizes the catalytic current, i_{cat}, of the reaction process expressed by Eqs. 1 and 2, together with the conditions expressed by Eq. 5 which must be fulfilled to maintain the validity of Eq. 3:[5,6]

$$\frac{i_{\mathrm{cat}}}{i_{\mathrm{L}}} = \frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}}, \qquad (3)$$

with

$$\lambda = (1+K)k_1 C_{\mathrm{Fe}^{2+}}\delta^2/D, \qquad (4)$$

and

$$\frac{C_{\mathrm{Fe}^{2+}}}{C_{[\mathrm{Mo(CN)_8}]^{3-}}} \gg \frac{i_{\mathrm{cat}}}{i_{\mathrm{L}}}, \qquad (5)$$

where i_{L} is the Levich current[5] for the oxidation of $[\mathrm{Mo(CN)_8}]^{4-}$ ion, k_1 and k_2 are the forward and backward rate constants of reaction 2, respectively, the equilibrium constant, K, is k_2/k_1, $C_{[\mathrm{Mo(CN)_8}]^{3-}}$ and $C_{\mathrm{Fe}^{2+}}$ denote the concentrations of $[\mathrm{Mo(CN)_8}]^{3-}$ and Fe^{2+} ions, respectively, D is the common value of the diffusion coefficients of $[\mathrm{Mo(CN)_8}]^{4-}$ and $[\mathrm{Mo(CN)_8}]^{3-}$ ions and δ is the steady-state thickness of the diffusion layer ($\delta = 1.62\ D^{1/3}\nu^{1/6}\omega^{-1/2}$, ν: the kinematic viscosity, ω: the electrode rotation rate).

Figure 2 shows the plots of the ratio $i_{\mathrm{cat}}/i_{\mathrm{L}}$ against the inverse square root of the electrode rotation rate at the various concentrations of Fe^{2+} and $[\mathrm{Mo(CN)_8}]^{4-}$ ions, together with the similar plots for the $\mathrm{Fe}^{3+}/[\mathrm{Mo(CN)_8}]^{4-}$ system. The value of k_1 was evaluated by curve fitting method and estimated to be $(7.0\pm0.5)\times10^{6}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ by using $\nu = 1\times10^{-2}\ \mathrm{cm^2\ s^{-1}}$,[7] $K = 4.7$ (calculated using the standard redox potentials,[1] *i.e.*, 0.49 and 0.53 V *vs.* SSCE for $\mathrm{Fe}^{2+/3+}$ and $[\mathrm{Mo(CN)_8}]^{4-/3-}$ couples, respectively) and $D = 5.0\times10^{-6}\ \mathrm{cm^2\ s^{-1}}$. The value of D was the average value of the diffusion coefficients for $[\mathrm{Mo(CN)_8}]^{4-}$ and $[\mathrm{Mo(CN)_8}]^{3-}$ ions obtained from the limiting currents of the steady-state current-potential curves by using the Levich equation.[5] The solid lines shown in Fig. 2 represent the best fit curves calculated by using Eq. 3, which are seen to reproduce the experimental results. As can easily be seen from Fig. 2, the plots of $i_{\mathrm{cat}}/i_{\mathrm{L}}$ *vs.* $\omega^{-1/2}$ give the straight lines whose slopes are proportional to the square root of the concentration of Fe^{2+} ion, indicating that in this case the r.h.s. of Eq. 3 can be reduced to $\sqrt{\lambda}$, *i.e.*, $\tanh\sqrt{\lambda}\approx1$, as can be expected for a fast catalytic reaction. By introducing the obtained value of k_1 and other known values of D, ν, ω and $C_{\mathrm{Fe}^{2+}}$ into the right-hand side of the inequality (Eq. 5), it was confirmed that this inequality is fulfilled under the experimental conditions employed.

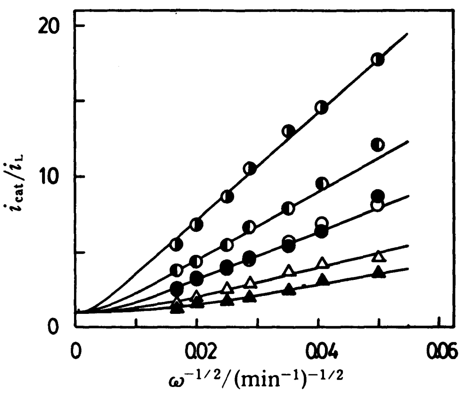

Fig. 2. Plot of the ratio, $i_{\mathrm{cat}}/i_{\mathrm{L}}$, against the inverse square root of the rotation rate, $\omega^{-1/2}$.
○: 0.2 mM $[\mathrm{Mo(CN)_8}]^{4-}+2$ mM Fe^{2+}; ◐: 0.2 mM $[\mathrm{Mo(CN)_8}]^{4-}+4$ mM Fe^{2+}; ◑: 0.2 mM $[\mathrm{Mo(CN)_8}]^{4-}+10$ mM Fe^{2+}; ●: 0.05 mM $[\mathrm{Mo(CN)_8}]^{4-}+2$ mM Fe^{2+}; ▲: 0.2 mM $[\mathrm{Mo(CN)_8}]^{3-}+2$ mM Fe^{3+}; △: 0.2 mM$[\mathrm{Mo(CN)_8}]^{3-}+4$ mM Fe^{3+}.
Supporting electrolyte and scan rate of electrode potential are the same as in Fig. 1. Solid lines are the best fit curves calculated by Eq. 3.

From the current-potential curves E and F shown in Fig. 1, it is also apparent that the reduction of Fe^{3+} ion present in a bulk solution is catalyzed by the $[\mathrm{Mo(CN)_8}]^{4-}$ ion formed on a graphite electrode surface. By means of the same method as described above, the rate constant (k_2) of the electron transfer cross-reaction between Fe^{3+} and $[\mathrm{Mo(CN)_8}]^{4-}$ ions was estimated to be $(6.6\pm0.5)\times10^{6}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$.

The values of k_1 and k_2 are by 1 to 2 orders of magnitude larger than those ($k_1 = 3.8\times10^{5}$ and $k_2 = 1.0\times10^{4}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$) reported in a previous paper,[2] where the $[\mathrm{Mo(CN)_8}]^{4-}$ or $[\mathrm{Mo(CN)_8}]^{3-}$ ion was bound electrostatically to the protonated poly(4-vinylpyridine) (PVP) film on a graphite electrode and Fe^{2+} or Fe^{3+} ion was present in a bulk solution. The similar results have been previously reported in the case of the catalysis of the oxidation of Fe^{2+} ion by the $[\mathrm{IrCl_6}]^{2-}$ ion bound to the protonated PVP film on an electrode or present in a bulk solution.[8] This may be mainly attributed to the differences in the reaction media in which the rate constants were measured.

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