Catalytic Polarographic Wave of Fe(II) in Neutral Thiocyanate Solutions at Dropping Mercury Electrode

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The electrochemical behavior of Fe(II) in neutral thiocyanate solutions has been investigated at a dropping mercury electrode (DME). It was found that Fe(II) in neutral thiocyanate solutions gave a catalytic polarographic wave at potentials prior to the main Fe(II) reduction wave. The mechanism of the catalytic process involves the chemical reduction of thiocyanate ions with $Fe(OH)_{2,aq}$ at the electrode surface. Controlled potential electrolysis suggests that the reduction of thiocyanate ions proceeds with the formation of sulfide and cyanide ions. Sulfide ions produced at the electrode surface can react with Fe(II) diffusing to the electrode to form FeS. The discharge of this is responsible for the catalytic current, while cyanide ions have no essential role in the catalytic process. The effects of surface active substances and iodate ions on the catalytic wave are also discussed.

A number of papers have been devoted to the study of the electrode reactions of the iron group metal ions occurring in thiocyanate solutions.[1-4] Electrode reactions of these systems at a mercury electrode are quite complex, due to the low solubility of these metals in mercury.[5-8]

In the electroreduction of Ni(II) or Co(II) from thiocyanate solutions, catalytic polarographic currents are observed at DME. There are, however, conflicting ideas concerning the origin of the catalytic wave. Itabashi *et al.* proposed a mechanism involving the cyclic regeneration of Ni(II) or Co(II) by the oxidation of electrodeposited metals with thiocyanate ions.[9-11] On the other hand, Krogulec *et al.* explained the catalytic current of the Ni(II)–thiocyanate system in terms of the discharge of hydrogen ions on metallic nickel.[12] However, there seems to be agreement that, with Ni(II) or Co(II) present, the reduction of thiocyanate ions proceeds with the formation of sulfide and cyanide ions at the mercury surface.

The formation of sulfide ions was also observed during the electroreduction of Co(II) in thiosulfate solutions.[13] According to Baranski and Galus,[14] the reduction of transition metal ions in solutions containing sulfur-containing organic compounds resulted in the formation of sulfide ions at the mercury surface.

Stojek and Kublik investigated the process of the reduction and reoxidation of Fe(II) in neutral thiocyanate solutions at a stationary mercury electrode.[15] During the course of the investigation, they observed a small prewave preceding the usual Fe(II) reduction wave. However, they have given no detailed discussion about the reaction mechanism.

In the present paper we report the characteristics of the catalytic current of Fe(II) in neutral thiocyanate solutions. A possible explanation for the catalytic process is proposed.

Experimental

Apparatus. All polarographic measurements were performed with a Princeton Applied Research polarographic analyzer, model 174, and were recorded with a Riken Denshi X-Y recorder, model D-8CP. The controlled potential electrolysis was carried out with a Yanagimoto potentiostat, model V-8. The working electrode for the controlled potential electrolysis was a mercury pool with a surface area of approximately 7 cm^2. Potentials were measured against a saturated calomel electrode (SCE) with the use of a Kikusui Electronics digital voltmeter, model 156-A. The dropping mercury electrode (DME) had a flow rate of 1.95 mg s^{-1} and a drop time of 4.32 s in a 0.1 M KCl solution with an open circuit. The pH of the solutions was measured with a Hitachi-Horiba pH meter, model M-7. Dissolved oxygen was removed from the solution with nitrogen. The cell was immersed in a water bath maintained at (25±0.1) °C.

Reagents. All chemicals were of analytical reagent grade and were used without further purification. All solutions were prepared from redistilled water.

Results

Prewave of Fe(II)–Thiocyanate System. A d.c. polarogram of 1.0 mM† Fe(II) in 0.1 M NaSCN (pH 5.5) is shown in curve a of Fig. 1. A prewave appears at about 0.2 V more positive than the main Fe(II) reduction wave. The current of the prewave was independent of the height of the mercury reservoir, indicating that the electrode process was kinetically controlled.

The relationship between the catalytic wave height and pH of the solution is shown in curve a of Fig. 2. The catalytic wave was obtained in the pH range 4.8—8.2 under the above conditions. By buffering the solution, however, the catalytic wave disappeared completely without any surfactant. With an Fe(II) concentration of 1 mM, the catalytic wave first increased with thiocyanate concentration up to 0.1 M and then decreased above this thiocyanate concentration.

Effect of Iodate Ions on the Catalytic Wave. With iodate ions present, there appeared an increase of the catalytic current in unbuffered thiocyanate solutions. The reduction of iodate ions proceeds as follows:

$$IO_3^- + 3H_2O + 6e = I^- + 6OH^-$$

The iodate reduction process was a source of hydroxide ions, and buffering of the solution caused the catalytic wave to disappear under these conditions.

The effect of iodate concentration on the catalytic current is shown in Fig. 3. For iodate concentrations

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† 1 M=1 mol dm^{-3}.

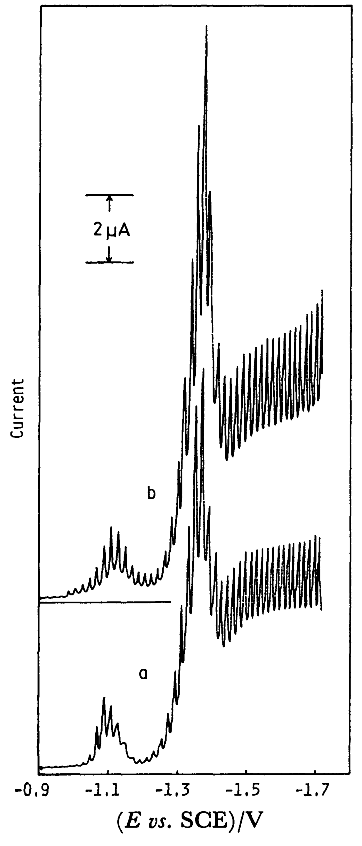

Fig. 1. D. c. polarograms of 1.0 mM Fe(II) in (a) 0.1 M NaSCN (pH 5.5), (b) 0.1 M acetate buffer (pH 5.9) containing 0.2 mM Na_2S.

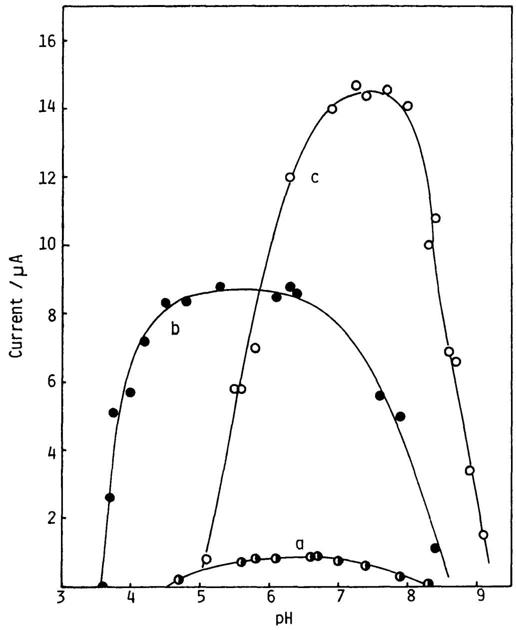

Fig. 2. Relationship between pH and catalytic current of 1.0 mM Fe(II) in (a) 0.1 M NaSCN, (b) solution (a) with 0.01% decylamine, (c) solution (a) with barbital buffer and 0.01% decylamine.

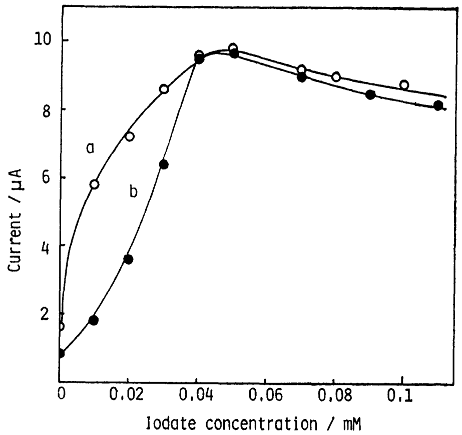

Fig. 3. Catalytic currents of 1.0 mM Fe(II) as a function of iodate concentration in (a) 0.1 M NaSCN (pH 5.6), (b) 0.5 M NaSCN (pH 6.1).

exceeding 0.04 mM, the catalytic current obtained in a 0.5 M NaSCN solution became practically equal to that obtained in a 0.1 M NaSCN solution. The result in Fig. 3 suggests that the increase in pH in the vicinity of the electrode leads to the increase of the rate of the catalytic reaction.

Effect of Surfactant on the Catalytic Wave. The catalytic wave was practically unaffected by the presence of an anionic surfactant such as sodium dodecyl sulfate. However, the presence of a cationic surfactant like decylamine resulted in the appearance of the catalytic wave even in buffered solutions, and caused the current increase in unbuffered media.

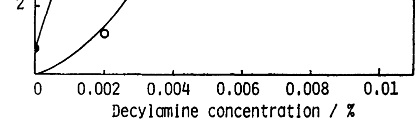

Fig. 4. Catalytic currents of 1.0 mM Fe(II) as a function of decylamine amount in (a) 0.1 M acetate buffer and 0.1 M NaSCN (pH 5.9), (b) 0.1 M NaSCN (pH 6.0).

The effect of the amount of decylamine on the catalytic current is given in Fig. 4. In the solution containing 0.1 M acetate buffer and 0.1 M NaSCN, the current increased gradually on increasing the amount of decylamine up to 0.01%, while it reached a limiting value when 0.002% decylamine was present in the 0.1 M NaSCN solution. Hence, most of the following experiments were carried out in a solution containing 0.01% decylamine.

In the presence of 0.01% decylamine, the catalytic wave was observed in the pH range of 3.6—8.5 and 5.1—9.1 in unbuffered and barbital buffer solutions, respectively (curves b and c in Fig. 2).

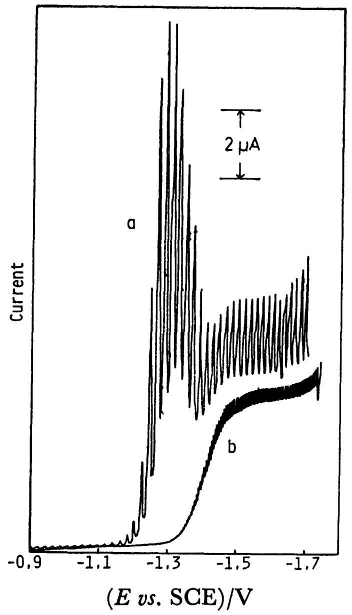

Fig. 5. D. c. polarograms of 1.0 mM Fe(II) in 0.1 M acetate buffer (pH 5.9), 0.1 M NaSCN and 0.01% decylamine with (a) natural drop, (b) a drop time of 0.5 s.

Figure 5 shows d. c. polarograms of 1.0 mM Fe(II) in the solution containing 0.1 M acetate buffer (pH 5.9), 0.1 M NaSCN, and 0.01% decylamine, using natural drop and forced drop (t=0.5 s) methods. No catalytic wave was observed with a drop time of 0.5 s. It is well known that catalytic and kinetic currents can be minimized or eliminated with rapid DME.[16,17] From comparison of a with b in Fig. 5, it follows that the catalytic wave was obtained at potentials before the reduction of aquairon(II) ions reached its limiting plateau. This result clearly shows that the catalytic reaction takes place under the conditions where aquairon(II) ions exist at the electrode surface.

Effect of Thiocyanate and Fe(II) Concentrations on the Catalytic Wave. Figure 6 presents the relationship between the catalytic current and thiocyanate concentrations. In buffered solutions, the catalytic current increased with thiocyanate concentrations up to 0.1 M. Above this concentration, the current went through a maximum and then decreased. In unbuffered solutions, however, the current increased over the thiocyanate concentration range studied.

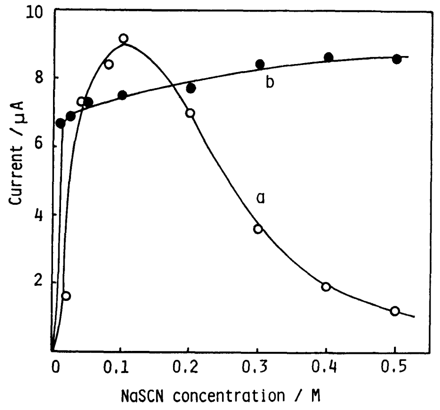

Fig. 6. Catalytic currents of 1.0 mM Fe(II) as a function of thiocyanate concentration in (a) 0.1 M acetate buffer (pH 5.9), (b) 0.1 M $NaClO_4$ (pH 6.0). Each solution contains 0.01% decylamine.

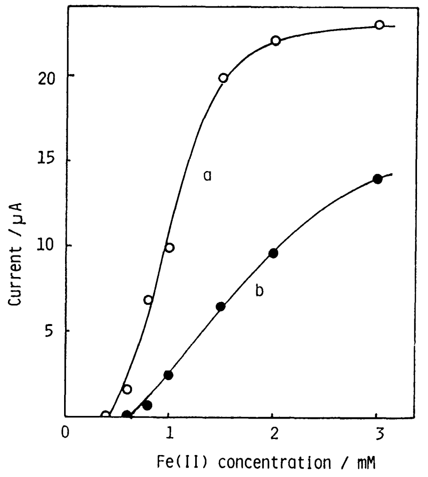

Fig. 7. Catalytic currents as a function of Fe(II) concentration in 0.1 M acetate buffer (pH 5.9) and 0.01% decylamine containing (a) 0.1 M NaSCN, (b) 0.5 M NaSCN.

Figure 7 shows the catalytic currents as a function of Fe(II) concentration. As can be seen, the wave height was dependent on Fe(II) concentration, although it was not a linear function.

D.c. Polarography of Fe(II) in an Acetate Buffer Containing Na_2S. To identify the Fe(II) species responsible for the catalytic current, d. c. polarograms of Fe(II) in neutral solutions containing sodium sulfide were also recorded. As an example, curve b in Fig. 1 shows a d. c. polarogram of 1.0 mM Fe(II) in 0.1 M acetate buffer (pH 5.9) containing 0.2 mM Na_2S. There appeared a prewave preceding the main Fe(II) reduction wave. The kinetic character of the prewave was verified by its dependence of the height of the mercury reservoir. Both catalytic waves of Fe(II) obtained in thiocyanate and sulfide solutions are very similar in appearance in d. c. polarography, suggesting that the same species of Fe(II) is responsible for the catalytic currents. In this case, however, an addition of decylamine had no effect on the catalytic current.

In cyclic voltammetry at a hanging mercury drop electrode (HMDE), Itabashi recently found a similar prewave of Fe(II) in unbuffered perchlorate solutions containing Na_2S; he ascribed the prewave to the reduction of FeS.[18]

Pulse Polarography for an Anodic Scan. Normal pulse polarograms for anodic scans of 1.0 mM Fe(II) in 0.1 M NaSCN (pH 6.0) are shown in Fig. 8. When the initial potential was set at −1.5 V, no oxidation current of iron was obtained, as shown in curve a. However, when the initial potential was chosen at a potential where the catalytic wave appeared (at −1.15 V), an oxidation current was observed with a half-wave potential of −0.53 V.

On the basis of cyclic voltammetry, Stojek and Kublik

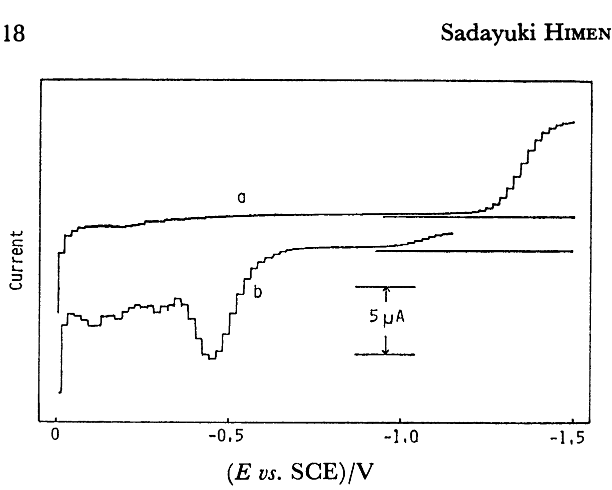

Fig. 8. Normal pulse polarograms for anodic scans of 1.0 mM Fe(II) in 0.1 M NaSCN (pH 6.0). Initial potential, (a) −1.50 V, (b) −1.15 V. Drop time, 2 s.

suggested that metallic iron electrodeposited at potentials of the catalytic wave stayed on the mercury surface, while iron deposited in the main reduction wave penetrated into the electrode.[15] The result obtained by pulse polarography seems to be in line with their observations and shows that, in the potential region of the catalytic wave, Fe(II) is reduced to metal which stays on the electrode surface.

Controlled Potential Electrolysis. For the purpose of elucidating the reaction mechanism, controlled potential electrolysis experiments were carried out with 25 ml of a 2.0 mM Fe(II) solution in 0.5 M NaSCN (pH 5.3) containing 0.01% decylamine at a potential of −1.25 V. After the solution was carefully deoxygenated, the electrode potential was held at −0.9 V to remove any remaining traces of oxygen dissolved in the solution. The pH of the solution increased during the electrolysis and the precipitation of Fe(II) as the hydroxide was observed. This result is in accord with the work of Stojek and Kublik, who explained this behavior in terms of the decomposition of water on an electrodeposited metallic iron. Hence, the following experiments were performed in acetate buffer solutions.

Electrolysis was carried out with a 25 ml solution containing 2.0 mM Fe(II), 0.1 M acetate buffer (pH 5.9), 0.5 M NaSCN, and 0.01% decylamine at −1.25 V. During the course of the electrolysis, gas evolution was observed on the mercury surface. The gas was introduced into a 0.25 M NaOH solution and was analyzed by d. c. polarography. The polarogram obtained showed a single anodic wave with a half-wave potential of −0.36 V, which corresponded to that of cyanide ions. A black solid was obtained on the mercury surface after the progress of the electrolysis. After the black solid was washed carefully with distilled water, it was dissolved in a 5 M H_2SO_4 solution. Bubbles of gas were observed. The polarographic analysis revealed the presence of sulfide ions in the solutions. The sulfuric acid solution was treated with thiocyanate ions and the solution turned red on the addition of hydrogen peroxide. This result indicates that the black solid is FeS.

The electrolysis of 1.0 mM Fe(II) in a 0.1 M acetate buffer (pH 5.9) containing 0.8 mM Na_2S was also performed at a potential of −1.20 V. There appeared a black solid on the mercury surface. Analysis of the black compound according to the procedure mentioned above showed the presence of FeS, suggesting that the prewave was due to the reduction of FeS.

Discussion

The catalytic current can not be ascribed to the formation of Fe(II)–thiocyanate complexes, since Fe(II) and thiocyanate ions form only a weak complex, $FeSCN^+$,[19] and the increase of thiocyanate concentrations is not necessarily related to the increase of the catalytic current. As shown in Fig. 7, on the other hand, the catalytic current is closely related to the Fe(II) concentration.

Wells and Salam investigated the hydrolysis of Fe(II) in perchlorate media.[20] According to them, $Fe(OH)^+$ exists in equilibrium with Fe^{2+} at about pH 3. Above pH 4, the predominant species is $Fe(OH)_{2,aq}$, which is converted slowly to a hydrated dimer. Since such polymerization reactions are known to be slow,[21] we can assume that the predominant species of Fe(II) in the pH range where the catalytic wave appears is $Fe(OH)_{2,aq}$ which has a much stronger reducing ability than Fe^{2+}.[22]

Controlled potential electrolysis shows that thiocyanate ions are reduced to sulfide and cyanide ions in the presence of Fe(II). The formation of these ions by the reduction of thiocyanate ions has also been observed in the solution of either Ni(II) or Co(II).[4,9–12] Taking account of the resemblance of the catalytic wave of Fe(II) in thiocyanate solutions to that in sulfide media, we can ascribe the current to the discharge of FeS formed at the electrode surface. In an attempt to check the effect of cyanide ions on the catalytic reaction, sodium cyanide was added to the thiocyanate-free Fe(II) solution. The presence of cyanide ions only caused the decrease of the main Fe(II) reduction wave and no contribution of Fe(II)–cyanide complexes in the catalytic process could be observed.

Wroblowa *et al.* observed that the adsorption of thiocyanate ions on the mercury electrode occurred in the potential region of the catalytic wave.[23]

On the basis of these observations, the reaction mechanism of the Fe(II)-thiocyanate system can be written as the following sequence of reactions:

$$SCN^-_{bulk} \longrightarrow SCN^-_{ads}$$

$$2Fe(OH)_{2,aq} + SCN^-_{ads} + 2OH^- \longrightarrow 2Fe(OH)_3 + CN^- + S^{2-}$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS \xrightarrow{2e} Fe(0)_{metal} + S^{2-}.$$

The fact that the catalytic current is greatly enhanced by the presence of iodate ions can be accounted for by the increase of $Fe(OH)_{2,aq}$ in the vicinity of the electrode. In the absence of iodate ions, hydroxide ions produced by the decomposition of water on the metallic iron are available for the formation of $Fe(OH)_{2,aq}$ at the electrode surface. As shown in Fig. 2, therefore, no catalytic wave may be observed in buffered media below pH 5. However, we cannot fully explain why we can obtain greater catalytic currents in buffered media than in unbuffered media.

As long as the electrode potential is more positive than the main Fe(II) reduction potentials, aquairon(II) ions are continuously supplied at the electrode surface and can react with hydroxide ions and sulfide ions. At the limiting plateau of the main Fe(II) reduction wave, on the other hand, the formation of either $Fe(OH)_{2,aq}$ or FeS becomes impossible because of the direct reduction of aquairon(II) ions to the metal. As shown in Figs. 1 and 5, therefore, no catalytic current is observed in the limiting region of the main Fe(II) reduction wave.

It is possible to assume that, in the potential region of the catalytic wave, $FeSCN^+$ adsorbs on the electrode surface, and in the adsorbed state it stimulates the catalytic reaction. On the basis of this adsorption process, however, we cannot explain the effect of the surfactants on the catalytic wave. Thus we excluded the participation of this process in the overall electrode reaction.

The effect of decylamine on the catalytic current may be attributed to the formation of a bridge between thiocyanate ions, the positively charged surfactant, and the negatively charged mercury surface. The adsorption of thiocyanate ions onto the mercury surface may thus take place more easily.

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