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Studies on Pulse Polarography. IV. Normal Pulse Polarographic Behavior of Fe(II) in an Unbuffered Medium and Catalytic Wave for Fe(II)-Chlorate System

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The normal pulse polarogram of Fe(II) showed a double-wave behavior in an unbuffered solution containing iodate. The results of pulse polarographic and cyclic voltammetric studies indicate that colloidal $Fe(OH)_2$ formed by the reaction between aqua-Fe(II) and OH^- arising from the iodate reduction is responsible for the second wave. A catalytic wave was observed in the presence of chlorate in Tast polarography. The catalytic wave which appears to be a polarographic maximum, has an abnormal form, in which the current increases at every second or third drop because of the depletion of colloidal $Fe(OH)_2$ around the electrode. The catalytic current is due to the reaction of chlorate with colloidal $Fe(OH)_2$ formed in the vicinity of the electrode.

Pulse polarography developed for differentiating the faradaic and charging currents has a better sensitivity as compared with DC polarography and is suitable for trace analysis. In normal pulse polarography, successively increasing potential pulses are applied to the electrode, one pulse per drop with DME, from the initial (resting) potential, which is generally chosen in the potential region where no faradaic process occurs. A current-voltage curve in normal pulse polarography is quite similar to that obtained by current-sampled DC (Tast) polarography.

It has been established that dissolved oxygen is reducible at DME so that high concentration of OH^- is generated at the electrode surface in neutral, unbuffered solution. In the course of the pulse polarographic study of iron-group metals in an unbuffered solution containing dissolved oxygen, it was observed that colloidal $Ni(OH)_2$ generated around the electrode gives an unusual peak on the normal pulse polarogram.[1)]

During the investigation of normal pulse polarographic behavior of Fe(II) in an unbuffered solution, it was found that in the presence of colloidal $Fe(OH)_2$, chlorate gives the current enhancement due to the catalytic process, the nature of which was quite analogous to the nitrate system.[2)] Iodate was used in the case of Fe(II) since dissolved oxygen shows a marked trend to oxidize Fe(II) to Fe(III).

In order to explain the nature of chlorate catalytic wave observed on Fe(II) reduction wave in an unbuffered medium containing dissolved oxygen, Ruvinskii *et al.* postulated a catalytic reaction with participation of Fe(0) hydroxo complex deposited on the electrode surface.[3)] They assumed a catalytic regeneration of Fe(II) hydroxo complex in order to explain a large increase of current.

This paper describes the normal pulse polarographic behavior of Fe(II) in unbuffered solutions containing iodate and also the characteristics of the catalytic current induced by colloidal $Fe(OH)_2$ because their mechanism is not consistent with the results obtained. The mechanism of the process is presented.

Apparatus and Reagents

Apparatus. Polarographic measurements were carried out with a Princeton Applied Research Polarographic Analyzer, Model 174 in conjunction with the Linear Sweep Module Accessory, Model 174/51. This module, which synchronizes the potential scan with DME, permits the scan to start after pre-selected interval during the growth of a drop and to be completed within the lifetime the of drop. The drop time was controlled using a Mechanical Drop Timer, Model 172-A. Polarograms were recorded on a Riken Denshi X-Y Recorder, Model D-8C. The capillary employed had a $m^{2/3}\cdot t^{1/6}$ of 1.45 $mg^{2/3}\,s^{-1/2}$ in 0.1 M KNO_3 solution in an open circuit. One mercury drop was used for HMDE and a fresh drop was suspended from the tip of a mercury plated platinum wire for each measurement unless otherwise stated. The pH of the solution was measured with a Toa Denpa pH Meter, Model HM-8. An external saturated calomel electrode (SCE) was used as a reference electrode. Nitrogen was used to remove dissolved oxygen from the solution. The cell was immersed in water bath maintained at 25±0.1 °C.

Reagents. All chemicals were of reagent grade and were used without further purification. Water used for preparation of the solutions was de-ionized on an ion-exchange resin bed and then distilled twice with a quartz apparatus.

Results

Normal Pulse Polarographic Behavior of Fe(II) in Unbuffered Solutions Containing Iodate. A typical normal pulse polarogram of 0.6 mM Fe(II) in 0.1 M KCl containing iodate (pH 5.1) is shown in Fig. 1. The reduction of iodate under these conditions proceeds as follows.[4)]

$$IO_3^- + 3H_2O + 6e = I^- + 6OH^- \quad (E_{1/2} = -1.1\ V)$$

When the initial potential was set at −0.70 V, more anodic than the reduction potential of iodate, the normal pulse polarogram of Fe(II) consisted of only one wave with half-wave potential of −1.41 V. However, when the initial potential was chosen in the potential region where the reduction of iodate took place, the polarogram of Fe(II) had two waves. The second wave, which had a peak at the potential of −1.58 V disappeared completely by buffering the solution, indicating that the wave was due to the effect of OH^- arising from the reduction of iodate.

The relationship between the wave heights and pH of the solution is given in Fig. 2. Only a single-step reduction wave was obtained below pH 3.8 since no local high pH values occurred at the electrode. On increasing pH, the peak height of the second wave

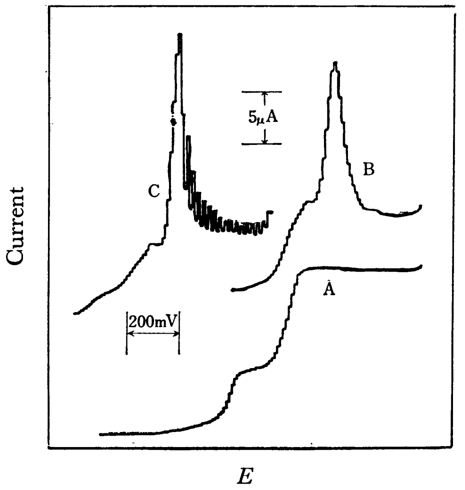

Fig. 1. Normal pulse polarograms of 0.6 mM Fe(II) in 0.1 M KCl (pH 5.1).
Iodate concentration (mM); A) 0.1, $E_i=-0.70$ V. B) 0.1, with violent agitation of capillary. $E_i=-1.20$ V. C) 0.2, with mild agitation of capillary. $E_i=-1.20$ V.
Drop time; 2 s.

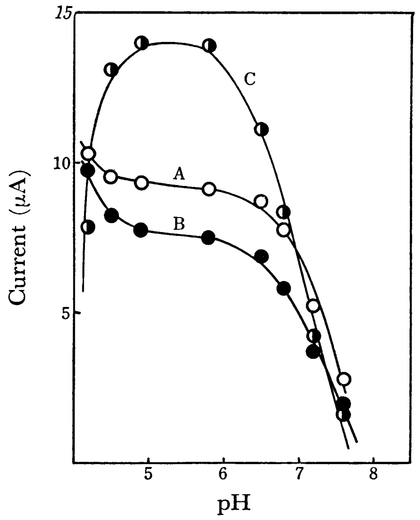

Fig. 2. Effect of pH on pulse polarographic wave of 1.0 mM Fe(II) in 0.1 M KCl containing 0.1 mM iodate.
A) 1st wave, $E_i=-0.70$ V. B) 1st wave, $E_i=-1.20$ V. C) 2nd wave, $E_i=-1.20$ V.
Drop time; 1 s.

increased and reached its limiting value in the pH range 4.8—6.0. The second wave decreased in height above pH 7.0 because of the precipitation of $Fe(OH)_2$ ($K_{sp}=10^{-15}$).[5] The first wave obtained when the initial potential was set at −0.70 V was always greater than that obtained at −1.20 V and decreased gradually with increasing pH in the whole pH range studied. This indicates that the concentration of aqua-Fe(II) decreases around the electrode due to hydrolysis at the initial potential.

Figure 3 shows the wave heights as a function of Fe(II) concentration. It was found that the first wave increases almost linearly with Fe(II) concentration up to 3 mM but starts asymptotically from the origin, while the relation between the second wave and Fe(II) concentration is not linear.

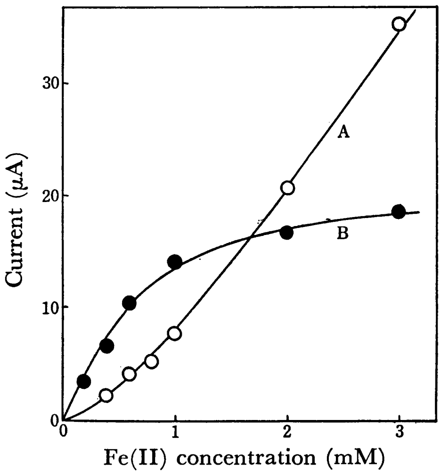

Fig. 3. Pulse polarographic currents as a function of Fe(II) concentration in 0.1 M KCl (pH 5.0) containing 0.1 mM iodate.
A) 1st wave. B) 2nd wave.
$E_i=-1.20$ V, Drop time; 2 s.

With a given Fe(II) concentration, the peak current of the second wave increased almost linearly with iodate concentration up to approximately 0.25 mM. Above this concentration, the second wave went through a maximum and then decreased as shown in Fig. 4, while the first wave decreased gradually on increasing iodate concentration.

From the results, it can be assumed that the first wave corresponds to the reduction of aqua-Fe(II) and the second to that of $Fe(OH)_2$ formed chemically between aqua-Fe(II) and OH^- in the vicinity of the electrode at the initial potential. It was also found that the peak height of the second wave decreases with increase in

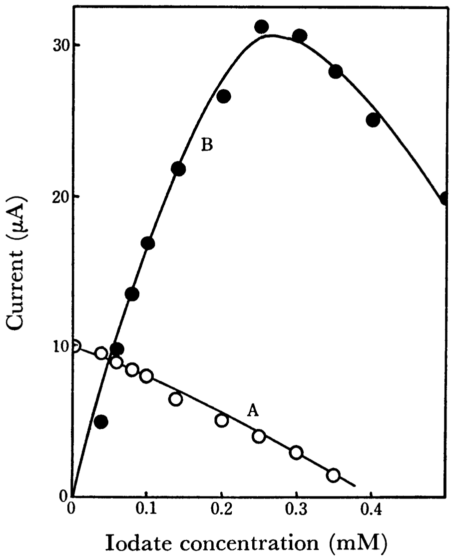

Fig. 4. Effect of iodate concentration on pulse polarographic wave of 1.0 mM Fe(II) in 0.1 M KCl (pH 5.5).
A) 1st wave. B) 2nd wave.
$E_i=-1.20$ V, Drop time; 1 s.

the concentration of the supporting electrolyte. This can be explained by the assumption that the coagulation of colloidal $Fe(OH)_2$ occurs and $Fe(OH)_2$ in the flocculated state can no longer be reduced. It can be confirmed by the fact that colloidal $Ni(OH)_2$ shows a similar behavior, its solubility being almost the same order as that of $Fe(OH)_2$.[1]

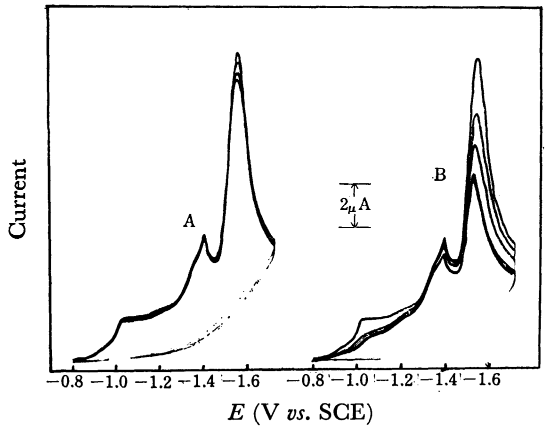

Fig. 5. Linear sweep voltammograms of 0.4 mM Fe(II) in 0.1 M KCl (pH 5.0) containing 0.08 mM iodate at DME.
A) With violent agitation of capillary. B) With mild agitation of capillary.
Pre-selected time; 1 s, Scan rate; 200 mV/s.

TABLE 1. RELATIONSHIP BETWEEN SCAN RATE (v) AND PEAK CURRENT OF 0.4 mM Fe(II) IN 0.1 M KCl

v (mV/s)	$v^{1/2}$	i_1[a] (μA)	$i_1/v^{1/2}$	i_2[b] (μA)	$i_2/v^{1/2}$
10	3.16	2.60	0.82	1.61	0.51
20	4.47	3.60	0.81	3.83	0.86
50	7.07	5.45	0.77	9.23	1.31
100	10.0	8.33	0.83	14.5	1.45
200	14.1	10.89	0.77	23.23	1.64

a) 1st wave without iodate. b) 2nd wave with 0.1 mM iodate.

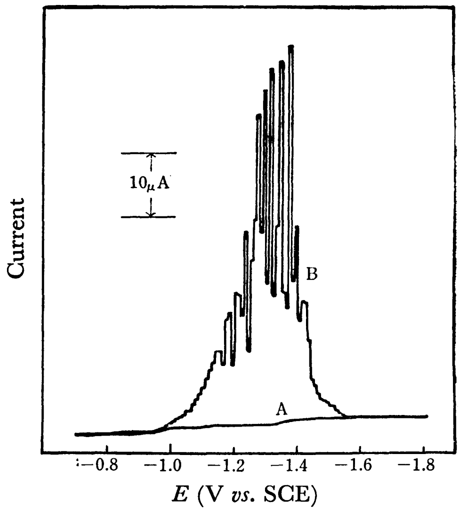

Fig. 6. Tast polarograms.
A) 0.4 mM Fe(II) in 0.1 M KCl (pH 5.0) containing 0.1 mM iodate. B) Solution (A) with 40 mM chlorate.
Drop time; 1 s.

A periodical alternation of high and low currents appeared at every second drop with mild agitation of capillary (Fig. 1). The unusual phenomenon was also investigated by means of linear sweep voltammetry at DME. The current-voltage curve exhibited the same two peaks with peak potentials, −1.40 and −1.55 V, respectively as observed in normal pulse polarography (Fig. 5). On increasing iodate concentration, the first wave decreased with an increase of the second one. This might be ascribed to the reduction of colloidal $Fe(OH)_2$ formed in the vicinity of the electrode. Reproducible current-voltage curves were obtained in the multiple cathodic scans either when the capillary was agitated violently or when the solution was stirred with a magnetic stirrer. However, with mild agitation of the capillary, the second peak decreased gradually in the multiple scans. The results suggest that the reproducible production of colloidal $Fe(OH)_2$ at every drop cannot be obtained in a quiet solution.

In order to clarify the nature of Fe(II)–OH^- system, a number of cyclic voltammetric studies have been carried out with the use of HMDE. Table 1 gives the relationship between scan rates and peak currents of 0.4 mM Fe(II) in 0.1 M KCl containing 0.1 mM iodate. The value of $i_p/v^{1/2}$ is practically constant for the first wave, indicating that the process was diffusion controlled. However, the peak current of the second wave shows an abnormal current increase at greater scan rates.

Chlorate Catalytic Wave in Tast Polarography.

Fe(II) in unbuffered solutions catalyzes the reduction of chlorate in Tast polarography (Fig. 6). This catalytic wave did not yield a limiting current but showed a maximum (peak) on the rising portion of Fe(II) reduction wave. The average peak current obtained in DC polarography was practically independent of the height of the mercury reservoir. Its temperature coefficient was +4.9% per degree, indicating that the current was kinetically controlled.

The relationship between the catalytic currents and chlorate concentration with 0.4 mM Fe(II) in 0.1 M KCl at different concentrations of iodate is shown in Fig. 7.

The catalytic wave could be obtained in the pH range 4.1—6.5, the range agreeing closely with that at which the second wave was obtained in normal pulse polarography (Fig. 2).

The catalytic wave decreased with an increase in the concentration of the supporting electrolyte and disappeared on buffering the solution.

Figure 8 shows the effect of iodate concentration on the catalytic wave. At the same Fe(II) and chlorate concentrations, the catalytic wave first increased and then decreased gradually when the iodate concentration was increased beyond 0.25 mM. This effect is in line with the observation made on varying iodate concentration in normal pulse polarography (Fig. 4).

The current-time curves of an individual drop at various potentials for the catalytic wave were recorded. The instantaneous i-t curves show the current increase at every second or third drop. However, the current

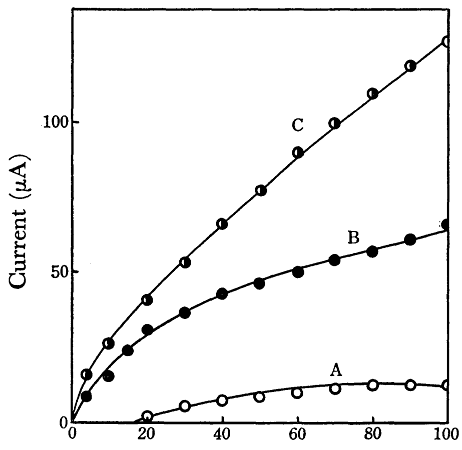

Fig. 7. Catalytic currents as a function of chlorate concentration in the solution 0.4 mM Fe(II) in 0.1 M KCl (pH 5.3).
Iodate concentration (mM); A) 0, B) 0.04, C) 0.2.
Drop time; 1 s.

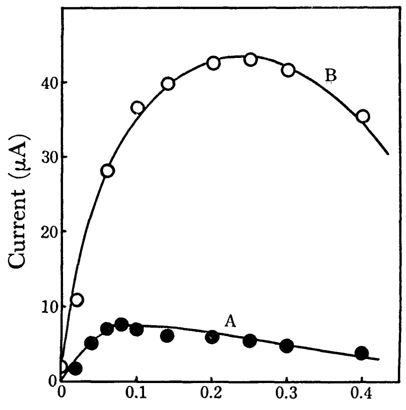

Fig. 8. Effect of iodate concentration on chlorate catalytic currents in the solution 0.4 mM Fe(II) in 0.1 M KCl (pH 5.5).
Chlorate concentration (mM); A) 2.0, B) 20.
Drop time; 1 s.

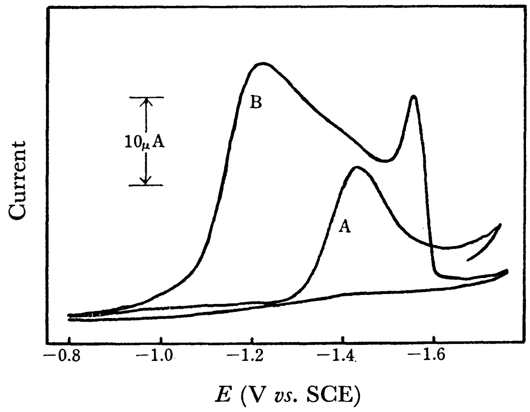

Fig. 9. Cyclic voltammograms.
A) 0.4 mM Fe(II) in 0.1 M KCl (pH 5.0) containing 1 mM chlorate. B) Solution (A) with 0.05 mM iodate. Scan rate; 100 mV/s.

increased at every drop when the solution was stirred. This anomalous behavior is quite similar to recent observations on the nitrate system.[2]

Cyclic voltammetric investigations with HMDE were carried out in order to investigate more precisely the role of $Fe(OH)_2$ in the reduction of chlorate. Figure 9 shows the current-voltage curve (B) recorded in the solution 0.4 mM Fe(II) in 0.1 M KCl containing 1 mM chlorate and 0.25 mM iodate. The curve shows two peaks with peak potentials, −1.22 and −1.56 V, respectively. The first wave is ascribed to the catalytic wave, probably involving the discharge of aqua-Fe(II), the second one being responsible for the reduction of colloidal $Fe(OH)_2$. When the cathodic potential scan was carried out up to −1.4 V (more positive than the second wave), the catalytic wave continued to increase in height in the multiple cathodic scans. However, when colloidal $Fe(OH)_2$ was electroreduced in the first scan, the catalytic wave could no longer be observed in the following scans. Similarly, in the absence of iodate, the curve corresponded to the reduction of aqua-Fe(II) (curve (A) in Fig. 9). This indicates that if iron exists as colloidal $Fe(OH)_2$ around the electrode, the catalytic reaction can take place.

The heights of the peaks obtained after the initial electrolysis at various potentials are shown in Fig. 10. When the initial electrolysis was carried out at a potential between −1.05 and −1.35 V for 0.4 mM Fe(II) in 0.1 M KCl containing 1 mM chlorate, the current-voltage curve was found to be almost the same as the one obtained in the presence of both iodate and chlorate (curve (B), Fig. 9). Similar experiments were carried out for 0.4 mM Fe(II) in 0.1 M KCl containing 0.04 mM iodate. The results are also shown in Fig. 10. We see that the first wave (the reduction wave of

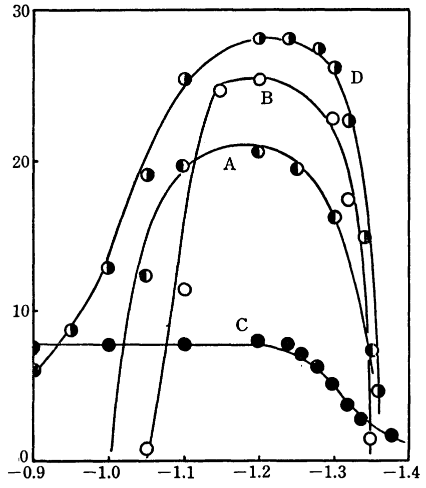

Fig. 10. Relationship between the initial potential and peak currents of 0.4 mM Fe(II) in 0.1 M KCl containing.
1 mM chlorate; A) 1st wave, $E_p = -1.22$ V. B) 2nd wave, $E_p = -1.56$ V.
0.04 mM iodate; C) 1st wave, $E_p = -1.42$ V. D) 2nd wave, $E_p = -1.56$ V.
Initial electrolysis time; 30 s. Scan rate; 200 mV/s.

aqua-Fe(II)) decreases in the potential region between −1.25 V and −1.40 V, since aqua-Fe(II) is partly reduced directly to Fe(0) at the initial potential and the concentration of aqua-Fe(II) diminishes around the electrode. The second wave (the reduction wave of colloidal $Fe(OH)_2$) then appears after the initial electrolysis at potentials more positive than the reduction potential of aqua-Fe(II).

Discussion

On the basis of pulse polarographic and cyclic voltammetric experiments, we can assume that the main product of the reaction between aqua-Fe(II) and OH^- produced around the electrode is colloidal $Fe(OH)_2$, which is responsible for the second wave. This assumption is also supported by the thermodynamic data that the formal potentials of Fe(II)/Fe(0) and $Fe(OH)_2$/Fe(0) are equal to −0.44 and −0.88 V, respectively.[5]

It has been established that the initial adsorption of the depolarizer produces an unusual peak on the normal pulse polarogram.[6–9] Wopschall and Shain have also stated that a significant increase in the current function at faster scan rates is an indication of the presence of weak adsorption in cyclic voltammetry with HMDE.[10] Thus, from the shape of the normal pulse polarogram and the results in Table 1, we can conclude that colloidal $Fe(OH)_2$ is adsorbed weakly on the electrode surface at the initial potential. This is in line with the work of Dahms, who reported the presence of adsorption of $Fe(OH)_2$ on DME by means of galvanostatic charging curves.[11]

From the fact that the peak currents of the second wave are about 30 μA in both normal pulse polarography (Fig. 4) and cyclic voltammetry (Fig. 10), the second wave might be ascribed to the discharge of both adsorbed $Fe(OH)_2$ and colloidal $Fe(OH)_2$ in the neighborhood of the electrode but not to the discharge of adsorbed $Fe(OH)_2$ only.

Ruvinskii *et al.*[3] postulated that the current enhancement with chlorate is due to the chemical reaction between chlorate and Fe(0) hydroxo complex formed on the electrode surface by the reduction of Fe(II) hydroxo complex and the current drop is due to the decomposition (amalgamation) of Fe(0) hydroxo complex deposited on the electrode surface.

$$\begin{tikzcd} \mathrm{Fe(II)(OH)}_x \arrow[r, "2e"] & \mathrm{Fe(0)(OH)}_x \arrow[r] \arrow[l, bend left, "\mathrm{ClO_3^-}"] & \mathrm{Fe(Hg)} + x\mathrm{OH^-} \end{tikzcd}$$

$x = 1, 2, \text{and } 3$

However, this seems to be improbable since no catalytic wave can be observed when colloidal $Fe(OH)_2$ is electroreduced (Fig. 9). It can be seen in Fig. 10 that colloidal $Fe(OH)_2$ can no longer be produced at the plateau potentials of Fe(II) reduction wave (more negative than −1.4 V) because of the direct reduction of aqua-Fe(II) to Fe(0). The potential coincides with that at which the catalytic current drops abruptly to the reduction current of Fe(II). This indicates that participation of Fe(0) hydroxo complex in the catalytic process is negligible and the nature of the catalytic process is related to the chemical reaction of colloidal $Fe(OH)_2$ with chlorate.

The mechanism for the catalytic effect might be as follows: Chlorate is chemically reduced by colloidal $Fe(OH)_2$ formed in the vicinity of the electrode; the unstable Fe(III) hydroxo complex is then reduced at the cathode, resulting in a catalytic reduction current.

Cyclic voltammetric studies with HMDE (Fig. 10) show that the catalytic wave also appears in the absence of iodate when the initial electrolysis is carried out in the potential region between −1.05 and −1.35 V. It is impossible to explain completely the occurrence of the catalytic wave under these conditions. However, this is probably because a trace of colloidal $Fe(OH)_2$ exists around the electrode. It should be noted that the second wave, whose peak potential is identical to that of the reduction of colloidal $Fe(OH)_2$ can also be observed (curve (B), Fig. 10). This suggests that OH^- is liberated in the vicinity of the electrode by the reduction of chlorate, although the reduction product of chlorate cannot be detected. This is easily realized by the fact that no second wave appears when the electrolysis is carried out in a buffered solution (pH 5.5). Since the amount of OH^- produced in this way is directly related to the formation of colloidal $Fe(OH)_2$, the process may acquire an autocatalytic character.

It can be seen that the amount of colloidal $Fe(OH)_2$ formed at every drop is not reproducible in a quiet solution (Figs. 1(C) and 5). If stirring of the solution is insufficient after detachment of the individual mercury drops, accumulation of aqua-Fe(II) in the close neighborhood of the electrode cannot be made constant at every drop. The anomalous *i-t* curves obtained for the catalytic wave may be explained in this way.

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