Polarographic Behavior of Chloramine-T in an Acidic Solution at a Rotating Platinum Electrode

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The polarographic behavior of chloramine-T at a rotating platinum electrode has been investigated in an acidic solution. Chloramine-T gives a well-defined reduction wave at a relatively positive potential. This is found to be due to the reduction of the non-ionized species of *N*-chloro-*p*-toluenesulfonamide and of dichloramine-T produced by disproportionation reaction of chloramine-T. The chemical process attributed to the disproportionation reaction is involved in the electrode process. The shape of the wave which varies with the recording procedure is correlated with the change of surface conditions. At pH lower than 4, a small prewave of hypochlorous acid produced by hydrolysis is observed at a more positive side. The diffusion current of the total wave, very stable and proportional to the concentration, is due to a two-electron reduction.

Chloramine-T (sodium salt of *N*-chloro-*p*-toluenesulfonamide, CAT) is known to be a stable oxidizing reagent for titrimetric analysis.[1] The purpose of this work is to investigate the electrochemical characteristics of CAT and to develop the end point detection techniques for a redox titration using CAT.

Recent studies[2,3] on the polarographic behavior at a dropping mercury electrode have shown that the over-all reaction of CAT involves two electrons over the pH range 2—13. However, it was impossible to measure the reduction potential of CAT since the reduction occurs at a more positive potential than that of the mercury dissolution. In an acidic solution, the limiting current tends to decrease with time by the reaction with mercury. On the other hand, well-defined reduction waves were observed at considerable positive potential at a rotating platinum electrode (RPE).

The polarographic behavior of CAT at a RPE was investigated in an acidic solution in order to elucidate the nature of the electrode process, the results of which are given in this report.

The free acid of CAT predominates in an acidic solution, producing *N,N*-dichloro-*p*-toluenesulfonamide (dichloramine-T, DCT) by disproportionation.[4,5] Discussion is given on the disproportionation and the effect of the electrode surface conditions on the reduction process.

Experimental

Apparatus and Reagent Used. The apparatus for the measurements of d.c. and a.c. polarograms was essentially the same as that described previously.[3] A Shimadzu synchronous rotator, RE-3, was used with a vertical platinum wire microelectrode (5.0 mm long, 0.5 mm in diameter) at r.p.m., 600. The sensitivity of electrode was 9.28 μA/mM in an electrolyte solution of hexacyanoferrate(III) ion containing 0.1 M KNO_3 and Britton-Robinson buffer at pH 5.0. An electrolytic cell of glass cylinder (50 mm in height and 45 mm in diameter) was used in a thermostat maintained at 25±0.2 °C. N_2 gas was used to deoxygenate the solution, flowing over the surface of the solution during the recording of the polarogram. The potentials are referred to a SCE connected to the solution with a KNO_3-agar salt bridge.

The preparation of the stock solutions of chloramine-T, *p*-toluenesulfonamide and other chemicals has been reported.[3] A satutated solution of *N,N*-dichloro-*p*-toluenesulfonamide (dichloramine-T) was prepared from the reagent grade salt and standardized against an arsenite standard solution. Water was used after distillation of deionized water in the presence of small amounts of $KMnO_4$ and NaOH solutions in a glass apparatus.

Measurement of Polarogram. Before each run for a polarogram of CAT, the polarograms of hexacyanoferrate(III) ion were recorded by use of the electrode which had been pretreated in a 0.1 M $HClO_4$ solution.[6] The values obtained for the diffusion current and the half-wave potential of hexacyanoferrate(III) ion were used to normalize the conditions for the preoxidation and rotation of the electrode, *etc.* An electrolyte solution was prepared by adding an adequate amount of the standard solution of CAT to the base solution, *i.e.*, 0.1 M KNO_3 and Britton-Robinson (B.R.) buffer solution. An aliquot of the solution was deoxygenated in an electrolytic cell. Polarograms were recorded by forward or backward scan. By forward scan, the electrode potential was shifted from positive to negative potentials. By backward scan, the situation was reversed. The rate of the potential scan was 200 mV per minute. A damping condenser of 5 μF was used.

Results and Discussion

Polarograms of Chloramine-T at Various pH Values. Figure 1 shows typical polarographic waves of 0.4 mM chloramine-T (CAT) in a supporting electrolyte solution containing 0.1 M KNO_3 and B.R. buffer at various pH values. The reduction waves in an acidic solution appeared at more positive potential than the reduction potential of platinum oxide. A maximum current on the plateau of the forward curves is due to the cathodic dissolution pattern of platinum oxide film. With the electrode covered with the oxide film, the waves shifted to negative potential and became drawn out, as shown on the forward curves, the results thus becoming less reproducible. This indicates that the electrode reaction is strongly inhibited by the oxide film. On the other hand, when the potential was scanned backward with the electrode reduced at an adequate negative potential after preoxidation, well-defined waves were observed at more positive side, the results being reproducible. On these curves, the main wave was two-stepped at pH lower than 7, a small prewave being observed at the more positive side at pH lower than 4 and a single wave at pH about 8.

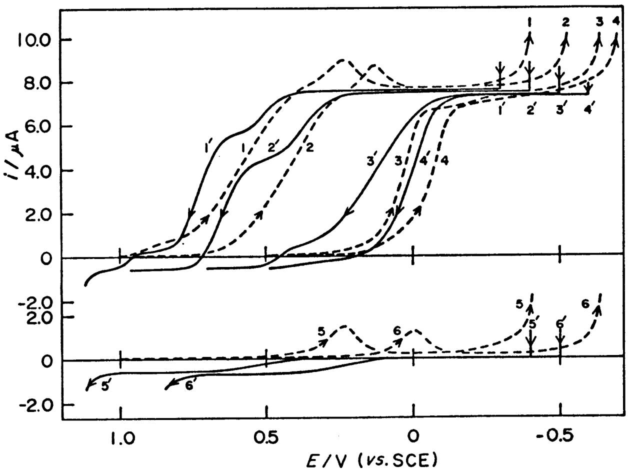

Fig. 1. Polarograms of 0.4 mM CAT in a solution containing 0.1 M KNO$_3$ and B.R. buffer at various pH values. (1,1′) pH 3.40; (2,2′) pH 5.05; (3,3′) pH 7.10; (4,4′) pH 8.10. Lower polarograms are residual current curves at various pH values. (5,5′) pH 3.40; (6,6′) pH 7.10. Dotted lines are forward curves recorded from +1.0 or +0.5 V after preoxidation at an adequate positive potential. Solid lines are backward curves recorded from between −0.3 and −0.6 V after the preoxidation.

The relations between pH and limiting current and between pH and half-wave potential of the backward wave are given in Figs. 2 and 3, respectively. The values of limiting current have been corrected for the residual current. On the main wave, the value of $\Delta E_{1/2}/\Delta$pH for the first step was −65 mV per unit pH, except at pH *ca.* 2. For the second step, the value was −80 mV per unit pH in the pH range 2—6. The limiting current of the first step varied with pH in the above pH range, giving a maximum value at pH 4—5. On the second step at pH higher than 6, the slope became remarkably drawn out, the half-wave potential shifting to negative potential. The results suggest that the reduction wave in an acidic solution can be characterized with the two-stepped wave at pH lower than 6 and that its electrode reaction differs from that at pH about 8. The half-wave potential shifts slightly to negative potential at pH *ca.* 2, which is considered to be attributable to the deactivation of the electrode surface. This tendency for the electrode surface to be rapidly deactivated, especially in an acidic solution, was also observed for the reduction of *N*-bromosuccinimide.7)

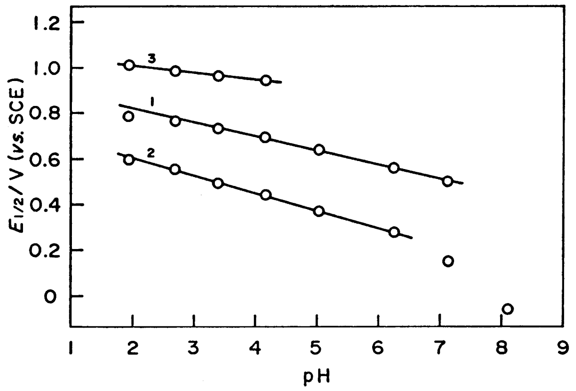

Fig. 3. Relation between the half-wave potential of the backward wave and pH for 0.4 mM CAT. (1) First wave; (2) second step; (3) prewave.

The limiting current of the total wave was independent of the recording procedure, provided that the correction for the residual current in each case was applied. Its value remained constant within deviation of ±2.0% in the pH range 2—8, being proportional to the concentration from 0.05 to 0.6 mM CAT (Table 1). The plot of log $^{T}i_d$ *vs.* log N (N is r.p.m. of the electrode, which varied from 600 to 1200) gave a straight line, the slope of which was determined to be 1/3 (Fig. 4). A similar result was obtained for the diffusion current of hexacyanoferrate(III) ion. The temperature coefficient of $^{T}i_d$ measured in the temperature range 15—40 °C was 1.8% per degree. The limiting current can be concluded to be controlled by diffusion.

The value of $^{T}i_d/C$ for the total wave found to be 18.18±0.32 μA/mM in the above pH range. It can be seen that this value corresponds to a two-electron reduction on the basis of a similar calculation.6) The values of diffusion coefficient used for this calculation were 0.79×10^{-5} cm^2 s^{-1} and 0.85×10^{-5} cm^2 s^{-1} for CAT5) and hexacyanoferrate(III) ion,5) respectively. The resut with respect to the limiting current of the

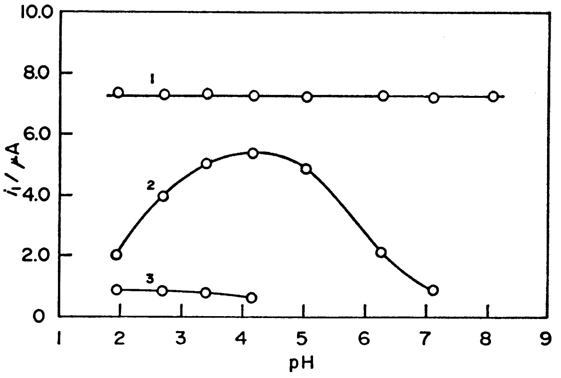

Fig. 2. Relation between the limiting current of the backward wave and pH for 0.4 mM CAT. (1) Total wave; (2) first step; (3) prewave.

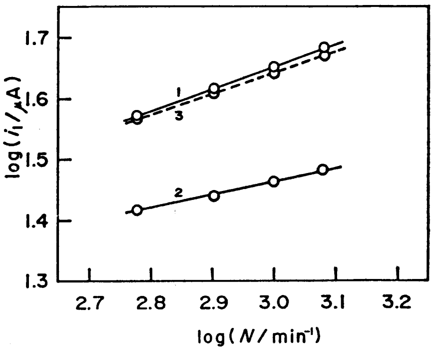

Fig. 4. Plots of log i_l *vs.* log N for (1) total wave, (2) first wave on the backward wave of 0.4 mM CAT and (3) reduction wave of 0.8 mM K$_3$Fe(CN)$_6$ in 0.1 M KNO$_3$ and B.R. buffer at pH 5.05.

TABLE 1. POLAROGRAPHIC DATA FOR THE REDUCTION WAVE OF CAT[a)]

pH	C/mM	Total wave		First step			Second step	Prewave		
		${}^{T}i_d$/µA	${}^{T}i_dC^{-1}$ µA mM^{-1}	${}^{I}i_l$/µA	${}^{I}i_lC^{-1}$/ µA mM^{-1}	${}^{I}E_{1/2}$/V (vs. SCE)	${}^{II}E_{1/2}$/V (vs. SCE)	${}^{P}i_d$/µA	${}^{P}i_dC^{-1}$/ µA mM^{-1}	${}^{P}E_{1/2}$/V (vs. SCE)
5.05	0.600	10.71	17.85	6.88	11.47	+0.641	+0.380	b)		
	0.500	8.93	17.86	5.82	11.64	+0.640	+0.380	b)		
	0.400	7.22	18.05	4.90	12.25	+0.643	+0.376	b)		
	0.200	3.59	17.95	2.54	12.70	+0.642	+0.390	b)		
	0.100	1.790	17.90	1.300	13.00	+0.642	c)	b)		
	0.0500	0.910	18.20	0.743	14.68	+0.645	c)	b)		
3.40	0.600	10.84	18.07	7.16	11.93	+0.725	+0.505	1.16	1.93	+0.960
	0.500	8.99	17.98	6.36	12.72	+0.725	+0.510	0.94	1.88	+0.960
	0.400	7.36	18.40	5.11	12.77	+0.730	+0.505	0.76	1.91	+0.965
	0.200	3.64	18.20	2.83	14.15	+0.728	+0.510	0.38	1.90	+0.965
	0.100	1.790	17.90	1.442	14.42	+0.730	c)	b)		
	0.0500	0.920	18.40	0.742	14.84	+0.733	c)	b)		

a) Values were obtained from backward waves in a supporting electrolyte solution containing 0.1 M KNO_3 and Britton-Robinson buffer at various pH values. b) No prewave. c) No second step.

total wave was identical with that obtained at a dropping mercury electrode.[3)] It could be assumed, therefore, that the non-ionized species of *N*-chloro-*p*-toluenesulfonamide is mainly reduced in an acidic solution. However, the fact that the limiting current of the first step varies with pH as shown in Fig. 2 and that it has a kinetic character suggest that the electrode process of the main wave can not be accounted for by the reduction process of the non-ionized species only.

The limiting current of the first step was not proportional to the concentration (Table 1). The plot of log ${}^{I}i_l$ *vs.* log N gave a straight line, the slope of which was determined to be 1/5. The temperature coefficient of ${}^{I}i_l$ determined in the temperature range 15—40 °C was 2.8% per degree, indicating that the limiting current has a kinetic character.

Effect of Surface Conditions of Electrode. In order to clarify the nature of the two-stepped wave, the effect of surface conditions of the electrode was investigated around pH 5.

With the reduced electrode, current-time curves were recorded in 0.4 mM CAT solution at pH 5.10 at +0.6 and +0.5 V, on the rising portion and the plateau of the first step, respectively, and at +0.4 V on the rising portion of the second step. As seen in Fig. 5, currents increased at these potentials, except at +0.6 V, after the electrode had been allowed to stand for 90 seconds at a natural electrode potential in an open-circuit condition. The natural electrode potential in this solution was found to be +0.8 V *vs.* SCE. At this potential, the platinum electrode would be oxidized (Fig. 6, curve 5). The increase of current is thus considered to be attributable to the formation of the oxide film. It is assumed that the current might not increase at +0.6 V, since the thin oxide film was produced at an earlier stage of the curve.

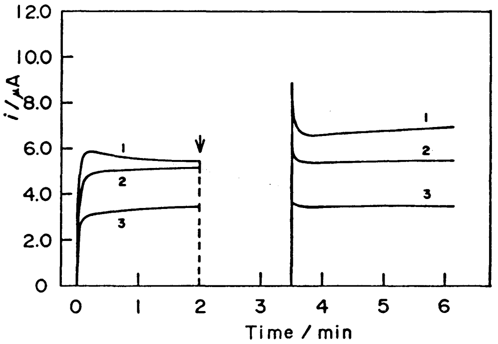

Fig. 5. Current-time curves of the reduction wave of 0.4 mM CAT at pH 5.10. (1) At +0.4 V; (2) at +0.5 V; (3) at +0.6 V. The point of open-circuit is denoted by arrow on the time-axis.

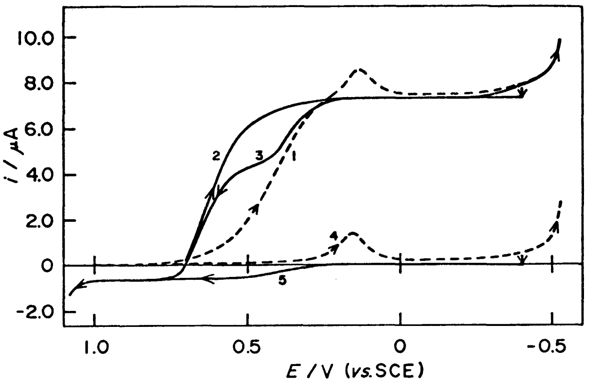

Fig. 6. Effect of the recording procedures on the polarogram of 0.4 mM CAT at pH 5.10.

(1) Forward scan from +1.0 V after preoxidation at +1.5 V; (2) forward scan from +0.7 V after preoxidation at +1.5 V followed by polarization at −0.4 V for a few minutes; (3) backward scan from −0.4 V after preoxidation at +1.5 V; (4) same as in curve (1) (residual current), (5) same as in curve (3) (residual current).

The height of the first step decreased due to the addition of *p*-toluenesulfonamide (TSA), a reduction product. The decrease was not detected in the presence of potassium chloride. A.c. base-current was recorded in both the presence and absence of TSA by the conventional a.c. polarographic method[3)] with the reduced electrode. It decreased in the presence of TSA at the potential region in which the platinum electrode is

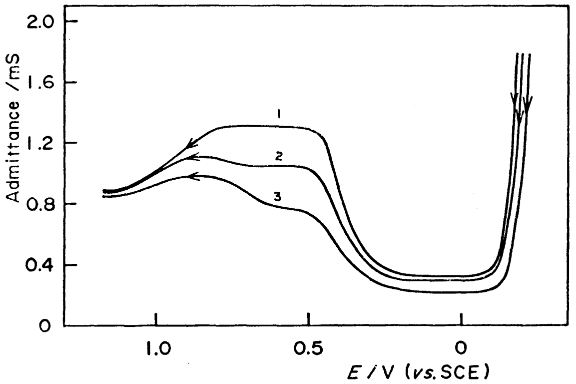

Fig. 7. Effect of TSA on the a.c. base-current curve in a solution containing 0.1 M KNO_3 and B.R. buffer at pH 5.10. (1) TSA was not added; (2) TSA was added in 0.1 mM; (3) TSA was added in 0.4 mM.

reduced (Fig. 7), which indicates that TSA is adsorbed on the surface of the reduced electrode.

It can be seen that TSA is adsorbed on the oxide-free surface and is desorbed partly by the formation of the oxide film. Thus, the two-stepped wave would be correlated with the adsorption of TSA. In fact, the curve recorded by the forward scan with an electrode covered thinly with the oxide film showed a single wave (Fig. 6, curve 2). This result is in line with the fact that the current increases as a result of the formation of the oxide film (Fig. 5).

Comparison with Reduction Wave of Dichloramine-T. Non-ionized species of CAT undergoes disproportionation in an acidic solution into dichloramine-T (DCT) and *p*-toluenesulfonamide (TSA)[4,5] according to

$$2RSO_2NHCl \rightleftarrows RSO_2NCl_2 + RSO_2NH_2, \qquad (1)$$

where $R=CH_3C_6H_4$. DCT as well as CAT act as a relatively strong oxidizing reagent in an acidic solution.[8] It can be expected, therefore, that a reduction wave of DCT is involved in the reduction wave of the CAT. A comparison with the reduction wave of DCT was made.

The value of the equilibrium constant (K_d) of the disproportionation is reported[4,5] to be 6.1×10^{-2} at 25 °C. DCT hydrolyzes to hypochlorous acid, the hydrolysis constant being 8×10^{-7}. If we assume that the amount of hydrochlorous acid is negligibly small and the non-ionized species predominates in the bulk solution, the equilibrium concentration of DCT can be calculated to be approximately 0.02 mM in the solution of 0.4 mM CAT.

DCT in an acidic solution gave a reduction wave (Fig. 8). The shape of the wave was very similar to that of CAT. The values of the half-wave potential and $\Delta E_{1/2}/\Delta pH$ for the first step were idential with those for the first step of CAT (Fig. 3). Although the slope of the second step became slightly drawn out, the value of $\Delta E_{1/2}/\Delta pH$ was close to that of CAT. At pH lower than 5, the height of the total wave remained constant. The wave obtained by the same recording procedure (Fig. 6, curve 2) became a single wave. Consequently, the behavior was identical with that of the reduction wave of CAT. The value of the diffusion current of the total wave at pH lower than 5 was found to correspond to a four-electron reduction.

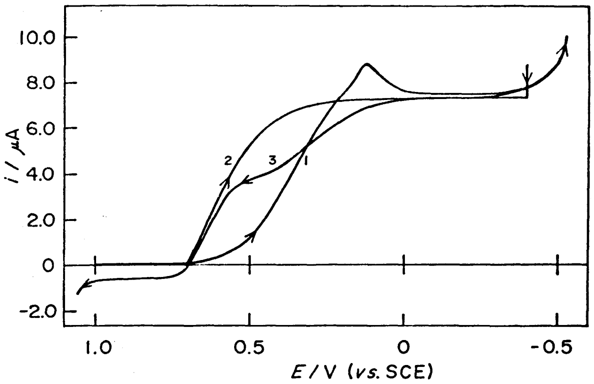

Fig. 8. Polarograms of 0.2 mM DCT in a solution containing 0.1 M KNO_3 and B.R. buffer at pH 5.20. (1) Forward scan from +1.0 V after preoxidation at +1.5 V; (2) forward scan from +0.7 V after preoxidation at +1.5 V followed by polarization at −0.4 V for a few minutes; (3) backward scan from −0.4 V after preoxidation at +1.5 V.

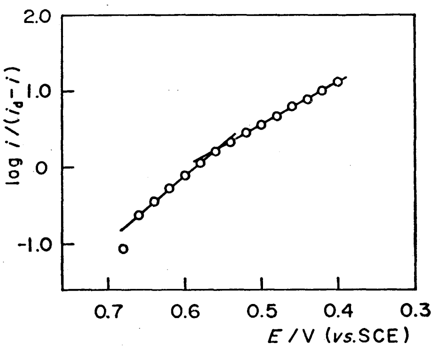

Fig. 9. Plot of log $[i/(i_d-i)]$ *vs.* E for the reduction wave of 0.4 mM CAT at pH 5.10, which was obtained by recording procedure as in curve 2 of Fig. 6.

The results suggest that the electrode process of the reduction wave in the CAT solution is essentially the same as that of DCT.

Electrode Process of the Reduction Wave of Chloramine-T. On the single wave (Fig. 6, curve 2), the plot of log-$[i/(i_d-i)]$ *vs.* E consists of two straight lines (Fig. 9). The potential at the point of intersection corresponds to that on the plateau of the first of the two-stepped wave. A similar result was obtained on the single wave in the DCT solution (Fig. 8).

The electrode process of the reduction wave in the CAT solution at pH lower than 6 can be explained as follows.

The reduction wave is made up of the following reactions:

$$RSO_2NCl_2 + H^+ + 2e^- \longrightarrow RSO_2NHCl + Cl^- \qquad (2)$$

$$RSO_2NHCl + H^+ + 2e^- \longrightarrow RSO_2NH_2 + Cl^- \qquad (3)$$

Reaction 2 occurs fast and is followed by Reaction 3. With the electrode from which TSA is desorbed, the two reactions occur continuously and the resulting wave becomes a single wave. With the electrode surface adsorbed with TSA, Reaction 3 is inhibited and the resulting wave becomes a two-stepped wave. It seems that, on the two straight lines of the log-plot, the leftside branch from the point of intersection corresponds to Reaction 2 and the right-side branch to Reaction 3, *viz.*, the two-stepped wave; the first step is due to Reaction 2 and the second step to Reaction 3. According to Higuchi *et al.*,[9] the rate of disproportionation given by Reaction 1 is relatively great. We might thus expect that, over the potential region where only Reaction 2 occurs, DCT undergoes transformation on the surface by the chemical process attributed to Reaction 1. The limiting current of the first step is greater than that corresponding to the equilibrium concentration of DCT, which can be accounted for by this chemical process. This consideration is supported by the fact that the limiting current of the first step has a kinetic character and that its pH-dependence (Fig. 2, curve 2) is the same as that of the forward rate constant for Reaction 1.[9]

As regards the behavior at pH higher than 7, the reduction of ionized species might be considered.

Behavior of Prewave. The value of $\Delta E_{1/2}/\Delta\text{pH}$ was determined to be -33 mV per unit pH on the small prewave obtained by backward scan with the reduced electrode at pH lower than 4. The limiting current was proportional to the concentration of CAT (Table 1) and found to be controlled by diffusion.

Hypochlorous acid gives a reduction wave at a relative positive potential on a platinum electrode,[10,11] giving a reduction wave at the same potential as that of the prewave under the same experimental conditions as in this study. The behavior was the same as that of the prewave. Thus, it is concluded that the prewave results from the reduction of hypochlorous acid produced by hydrolysis in the CAT solution.[4,5]

The value of i_d/C for the reduction wave of hypochlorous acid was determined separately to be 26.9 μA/mM in the same electrolyte solution. By use of this value and the value of the prewave (Table 1), the amount of hypochlorous acid in the solution of 0.4 mM CAT is calculated to be *ca.* 0.03 mM at pH 3. This is in line with the interpretation that the fraction of hypochlorous acid present in the CAT solution is much less than 10%.[3]

Analytical Aspect. When current-time curves were recorded at several potentials on the plateau of the total wave, no detectable variations of current were observed over a period of 10 min at pH lower than 6. This indicates that the limiting current of the total wave is remarkably stable and reproducible over the pH range studied. This behavior is advantageous for analysis as compared with that of a dropping mercury electrode,[3] in which the limiting current decrease is due to the reaction with mercury or maximum suppressor.

It can be concluded that the limiting current in an acidic solution is useful for amperometric titration in the short-circuit method.

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