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

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Synopsis. Chloramine-T in alkaline solutions at pH higher than 8 gives a single reduction wave at a rotating platinum electrode. This wave results from the two-electron reduction of the anionic species of *N*-chloro-*p*-toluenesulfonamide. The electrode reaction is polarographically irreversible. Reproducible waves were observed with a freshly reduced electrode. The diffusion current was proportional to the concentration over the range from 0.05 to 0.6 mM chloramine-T.

Chloramine-T (CAT) exhibits a reduction wave in alkaline solutions at a rotating platinum electrode (RPE), as reported previously.[1,2] In this report, the polarographic behavior of CAT at the RPE was further investigated over the pH range from 7 to 13 in order to elucidate the nature of the wave from an analytical viewpoint.

Experimental

The polarograph and synchronous rotator used were the same as those described previously.[1] A vertical platinum-wire microelectrode (5.0 mm, 0.5 mm in diameter) was used at 600 r.p.m. The sensitivity of the electrode was 8.90 μA/mM for hexacyanoferrate(III) in 0.1 M KNO_3 and a Britton-Robinson (B.R.) buffer at pH 10.

Pretreatment of the electrode was performed by means of repetition of electrolytic oxidation and reduction in 0.1 M $HClO_4$.[3] Polarograms were recorded by either forward or backward scans. For forward scans, the electrode potential was shifted from positive to negative potential, and *vice versa*. The scan rate was 200 mV per minute. The cathodic current was taken to be positive.

Preparation of the solutions and other experimental conditions have been reported elsewhere.[1]

Results and Discussion

Polarographic waves of CAT at pH 10 are shown in Fig. 1, and similar waves were obtained over the pH range from 8 to 13. A single reduction wave appeared at a potential near the reduction potential of platinum oxide. Although the slope of the wave was dependent on the direction of scanning, well-developed and reproducible waves were obtained for backward scans with a freshly reduced electrode (curve 1). The values of the half-wave potential of the waves obtained in a manner similar to those shown in curve 1 were reproducible to within ±10 mV. The value of $\Delta E_{1/2}/\Delta$pH was −50 mV per unit pH over the pH range from 8 to 13 (Table 1).

The magnitude of the limiting current was independent of the direction of scanning, provided that a correction for the residual current in each case was applied. This correction remained constant to within ±2% over the above pH range (Table 1), and was

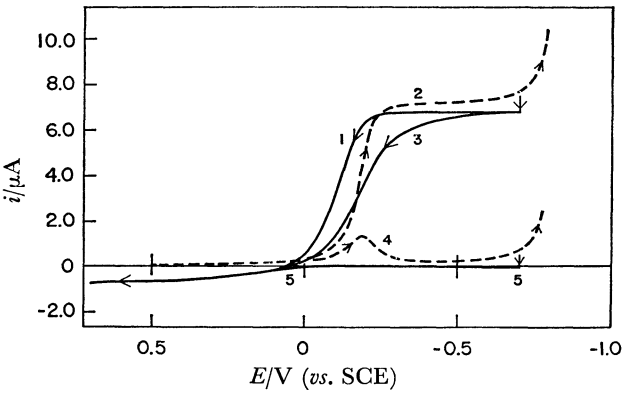

Fig. 1. Polarograms of 0.4 mM CAT in a solution containing 0.1 M KNO_3 and B. R. buffer pH 9.95. Recording procedures: (1) Backward from −0.7 V after preoxidation at +1.3 V for 2 min; (2) forward from +0.5 V after preoxidation at +1.3 V for 2 min; (3) backward from −0.7 V after polarization at −0.5 V for about 5 min; (4) same as in curve 2 (residual current); (5) same as in curve 1 (residual current).

Table 1. Polarographic data for the reduction wave of 0.4 mM CAT[a]

pH	$i_d/\mu A$	$i_d C^{-1}/\mu A mM^{-1}$	$E_{1/2}$/V (*vs.* SCE)
7.15	6.91	17.3	—[b]
8.20	6.92	17.3	−0.040
9.04	6.95	17.4	−0.080
9.95	6.93	17.3	−0.122
11.05	6.91	17.3	−0.177
11.85	6.93	17.3	−0.220
12.89	6.81	17.0	−0.265

a) These values were obtained in a supporting electrolyte solution containing 0.1 M KNO_3 and a B.R. buffer for various pH values and in the case of backward polarograms. b) No single wave appeared.

proportional to concentrations from 0.05 to 0.6 mM CAT. A plot of log i_d *vs.* log N (N is the number of revolutions per minute, which varied from 600 to 1200 min^{-1}) gave a straight line with a slope of 1/2.7. A similar result was obtained for the diffusion current of the hexacyanoferrate(III) ion. The temperature coefficient of i_d measured in the temperature range from 15 to 40 °C was 1.7% per degree. The limiting current can be concluded to be controlled by diffusion.

The value of i_d/C was found to be (17.3±0.3) μA/mM in the above pH range. This value corresponds to a two-electron reduction, which was calculated from a comparison with the value of i_d/C for the hexacyanoferrate(III) ion. This result suggests that monovalent

positive chlorine is reduced to a chloride ion by the electrode reaction. According to a previous report[4] the *N*-chloro-*p*-toluenesulfonamide anion predominates in alkaline solutions of CAT. It is, therefore, concluded that a single wave results from the reduction of the anion given by the reaction

$$RSO_2NCl^- + 2H_2O + 2e^- \longrightarrow RSO_2NH_2 + Cl^- + 2OH^-,$$

where $R=CH_3C_6H_4$. For the wave obtained in the backward scan with a freshly reduced electrode, a plot of log $[i/(i_d-i)]$ *vs.* E showed a straight line. The values of these slopes were found to be (85 ± 10) mV per log unit over the pH range from 8 to 13. The electrode reduction is considered to be polarographically irreversible.

It has been stated[5] that CAT is hydrolyzed in alkaline solutions and then the hypochlorite produced acts as an active species. In this study, the hypochlorite added to the CAT solution gave a single wave, the half-wave potential of which was more positive than that of the reduction wave of CAT. The value of the half-wave potential for the reduction wave of hypochlorite was the same as that reported previously.[6,7] It is concluded, therefore, that the reduction wave in the CAT solution is free from reduction of the hypochlorite.

The effect of the direction of scanning on the polarogram, as is shown in Fig. 1, can be explained as follows. When the curve was recorded for forward scan with the oxidized electrode, a deformed wave was observed, with the rising portion shifted to more negative potentials (curve 2). This result means that the electrode reduction of CAT is inhibited in the rising portion of the wave by the partially remaining oxide. In fact, the wave obtained for forward scan from 0 V with the reduced electrode was well-defined.

When the curve was recorded in backward scan with the electrode previously polarized at -0.5 V for about 5 min, the wave became markedly ill-defined (curve 3). The half-wave potential tended to shift to more negative potentials with increasing polarization time. The results are considered to be due to the deactivation of the electrode surface that occurred during polarization. This deactivation may be attributed to the adsorption of some constituents on the electrode surface. For example, adsorption of *p*-toluenesulfonamide (TSA), one of the reduction products, could be considered responsible on the basis of the following result. The a.c. polarographic base current used with the RPE with a reduced surface was recorded either in the presence or the absence of TSA. The base current decreased in the presence of 0.2 mM TSA in the potential region over which the platinum electrode had been reduced.

On the other hand, when the curve was recorded in backward scan with a freshly-reduced electrode, after preoxidation, the value of the half-wave potential was more positive than values obtained by other procedures, and the slope was independent of the starting potential (curve 1). This indicates that the electrode surface is free from formation of the oxide and the adsorption of constituents. This result is in line with the fact[3,8] that the electrode reaction tended to be more reversible on the platinum electrode with a fresh layer of finely-divided platinum.

The results described above indicate that the slope of the wave is strongly dependent on the history of the electrode, and that, for amperometric studies, careful attention should be paid to the selection of the potential for which the current is measured.

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