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Anodic Oxidation of Ethylenediaminetetraacetic Acid on Platinum Electrode in Alkaline Medium

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ABSTRACT

The anodic oxidation of ethylenediaminetetraacetic acid (EDTA) was studied in alkaline medium on a smooth platinum electrode. Bulk electrolysis indicated that stable organic intermediates (formaldehyde and glyoxal) are formed during the oxidation of EDTA and that complete oxidation to CO_2 can be achieved. The proposed pathway suggests that the acetate groups in EDTA are initially oxidized, generating formaldehyde and ethylenediamine. The rest potential of EDTA (0.066 to 0.164 V vs. Hg/HgO) was observed to be higher than for other organic species. In alkaline medium, very little EDTA oxidation was found to occur on bare platinum. Limiting-current behavior due to PtO formation was observed immediately positive of the rest potential. Tafel behavior (Tafel slope 120 mV/dec) was observed in the potential region positive of the cessation of the bulk of oxide film formation and negative of the onset of O_2 evolution. The reaction order of EDTA was determined to be ~0.5, and that of OH^- was close to zero. The reaction mechanism consistent with the experimental data involves Temkin-type adsorption and a first-electron-transfer rate-determining step.

Introduction

Ethylenediaminetetraacetic acid (EDTA) forms strong metal complexes and is often used to remove scale from heat-transfer equipment and to decontaminate equipment exposed to radioactive material. However, the resultant waste in the form of EDTA-metal complex is hard to treat due to the high stability of such complexes. Electrochemical oxidation is a promising technique in the destruction of EDTA-metal complexes, since it does not involve the use of other chemicals. However, the design of an electrochemical reactor for such a purpose requires the study of the oxidation reactions involved.

Very little information on the oxidation of EDTA using platinum electrode is available in the literature. Kopeck'a,[1] using a polarographic technique, found that the electrolysis of EDTA on platinum in alkaline medium yielded formaldehyde and amines. Reishakhrit et al.[2] studied the oxidation of EDTA on a platinum rotating disk electrode in acid, neutral, and alkaline media. They found that limiting currents were attained at more positive potentials in acid medium and at more negative potentials in alkaline medium. In addition, the limiting current was found to increase with pH in the range 7.9 to 12.2. The differences in polarization curves with pH were attributed to the varying dissociation equilibria of EDTA with pH. Similar observations were also made by Stulik and Vydra,[3] who studied the polarographic behavior of EDTA on a rotating platinum electrode. A more detailed investigation on the oxidation of EDTA in acidic media (pH range 0.35 to 3.80) using a platinized platinum electrode was carried out by Johnson et al.,[4] who identified several reaction products formed during the electrolysis of EDTA, suggesting a sequential removal of acetate groups. According to their study, EDTA exhibits Tafel behavior (slope ~120 mV/dec) followed by limiting-current behavior during anodic polarization. No such polarization study of EDTA in alkaline medium was found in the literature. During anodic oxidation, platinum is now well known to form a thin oxide film at potentials above 1.0 V vs. a reversible hydrogen electrode (RHE) in both acidic as well as alkaline media.[5-13] Hence, any interpretation of anodic polarization behavior on platinum electrodes should consider the oxide-film formation. However, little or no mention on the oxide film formation on platinum and its effect on the polarization behavior of EDTA was made in earlier studies.[1-4]

The purpose of this investigation was to study the oxidation of EDTA on a platinum electrode in alkaline medium with a focus on understanding the mechanism of the initial oxidation reaction of EDTA. The specific objectives of this work were to determine if EDTA can be oxidized completely to CO_2, to detect some of the chemical interme-

diates formed during the electrolysis of EDTA, to propose a reaction pathway, to study the anodic polarization behavior of EDTA on a platinum electrode, and to propose a mechanism for the initial EDTA oxidation reaction.

Experimental

The electrochemical cell employed for the polarization experiments was a conventional three-compartment design using Hg/HgO as the reference electrode and a platinum gauze with a high surface area as the counterelectrode. The experiments were carried out using a platinum disk with a geometric area of 0.5 cm² as the working electrode (anode). The EDTA concentration was varied from 0 to 0.263 M. The experiments were conducted using the Model 352 SoftCorr System and Model 270 Research Electrochemistry software along with the EG&G Princeton Applied Research potentiostat/galvanostat Model 273A at room temperature (23 ± 1°C).

The EDTA concentration was determined by titrating the test solution against $ZnSO_4$. Erichrome Black T solution (0.2 g in 100 ml deionized water) was used as the indicator. The color change at the end point was from blue to violet red. Prior to the titration, the pH of the test solution was adjusted to around 10 (solution turns blue). Since this technique works on the basis of complexing the EDTA with zinc as opposed to the separation of the species, the method is nonspecific to EDTA and measures partially oxidized intermediates such as ED3A, s-EDDA, u-EDDA, and EDMA; thus, any reference in this paper to EDTA concentration in the bulk electrolysis section refers to the sum of the concentrations of EDTA, ED3A, s-EDDA, u-EDDA, and EDMA.

Formaldehyde was detected using the spot test described by Feigl.[14] The following quantitative technique based on this test was developed in order to measure the concentration of formaldehyde. A 0.2 ml solution containing formaldehyde was taken in a 50 ml flask to which 3 ml of concentrated H_2SO_4 was added followed by 1 ml of 10% chromotropic acid. The flask was then heated in a water-bath for 10 min at 60°C. Finally, the samples were diluted to 50 ml and analyzed using an ultraviolet-visible (UV-vis) spectrophotometer. The peak maximum of the violet color was observed at 575 to 590 nm. The unknown concentration of formaldehyde was determined from the calibration curve constructed previously using standard formaldehyde solutions.

Glyoxal was detected using the spot test described by Feigl.[14] The procedure consisted of treating a drop of the test solution with 2-aminophenol and ignited calcium oxide. In the case when the test solution contains glyoxal, an intense red color appeared within a few minutes due to the deposition of colored calcium salt. The reaction was accelerated by heating the mixture.

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Results and Discussion

Reaction pathway.—Due to relatively large molecules, the oxidation of EDTA is expected to proceed via several organic intermediate species. In order to detect some of these species and to determine the extent of their formation, bulk electrolysis was carried out in a one-liter beaker-type cell using platinum foil (surface area, 12.5 cm^2) as the anode and a platinum gauze as the cathode. The electrolysis was conducted under galvanostatic conditions with an applied current density of 80 mA/cm^2. The initial EDTA concentration and pH were 0.041 M and 12, respectively.

The extent of formation of stable organic intermediates during oxidation of EDTA in alkaline medium can be seen in Fig. 1, which shows the concentrations of EDTA and total organic carbon (TOC) as a function of the time for which the solution has been electrolyzed. After 15 h of electrolysis, EDTA was found to be destroyed (converted to other organic species), while 50% of the TOC was still present in the solution. This clearly indicates that stable organic intermediates are formed during EDTA oxidation and that the rate of oxidation of some of these intermediates may be slower than that of EDTA. This finding suggests that the kinetics of the oxidation reactions of the intermediate species must be studied as well, prior to any design of an electrochemical reactor to be used to destroy EDTA by oxidation.

The CO$_2$ formed during the oxidation of EDTA stays in the solution as carbonate ion due to the alkalinity of the solution according to the reaction

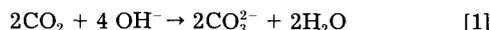$$2CO_2 + 4\,OH^- \rightarrow 2CO_3^{2-} + 2H_2O \qquad [1]$$

Figure 2 shows the concentration of carbon dioxide in the solution in terms of the total inorganic carbon (TIC) as a function of the time for which the solution was electrolyzed. As expected, the TIC concentration increases as the organic species in the solution are oxidized (*i.e.*, TOC decreases). After an initial increase, the TIC concentration was found to remain constant, suggesting the possibility of carbonate saturation in the solution.

Using the procedures of Feigl[14] discussed above in the Experimental section, formaldehyde and glyoxal were

Fig. 2. Total organic carbon and total inorganic carbon content as a function of the time of electrolysis.

detected in the partially electrolyzed solution of EDTA. In addition, Lawrence *et al.*[15] detected oxalate and formate in similar partially electrolyzed EDTA solution, using an ion chromatography technique. Figure 3 shows a possible pathway for the oxidation of EDTA to CO$_2$ in alkaline medium.

Figure 4 shows the concentrations of formaldehyde and EDTA as a function of the time for which the solution was electrolyzed. The concentration of formaldehyde was found to increase from zero to a maximum value at a time corresponding to the complete conversion of EDTA to other intermediates. The increase in the concentration of formaldehyde during the initial period of EDTA oxidation, the observed maximum concentration of formaldehyde at a time corresponding to the complete conversion of EDTA, and the absence of formaldehyde thereafter, suggests that the acetate groups in EDTA are initially oxidized, yielding formaldehyde in a manner similar to that in acidic media,[4] *i.e.*
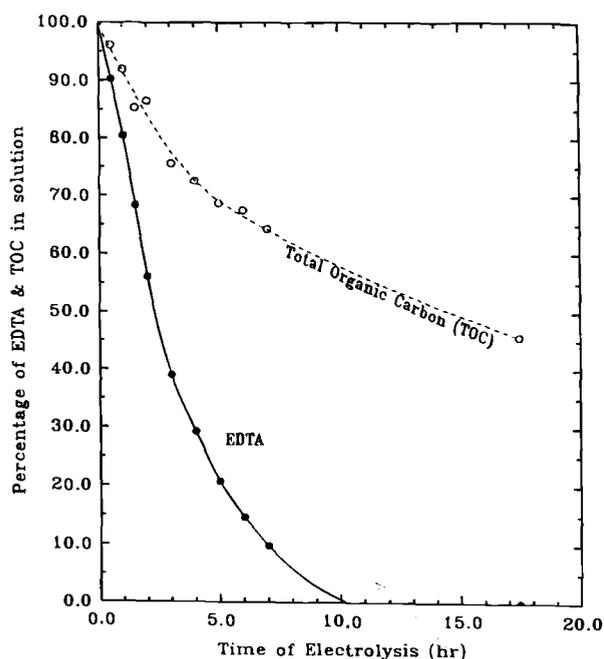

Fig. 1. Percent initial EDTA concentration and percent initial total organic carbon content remaining in the cell as a function of the time of electrolysis.
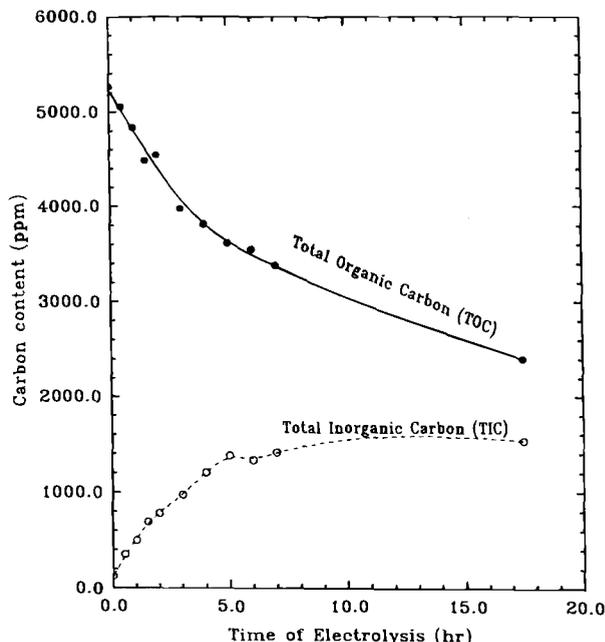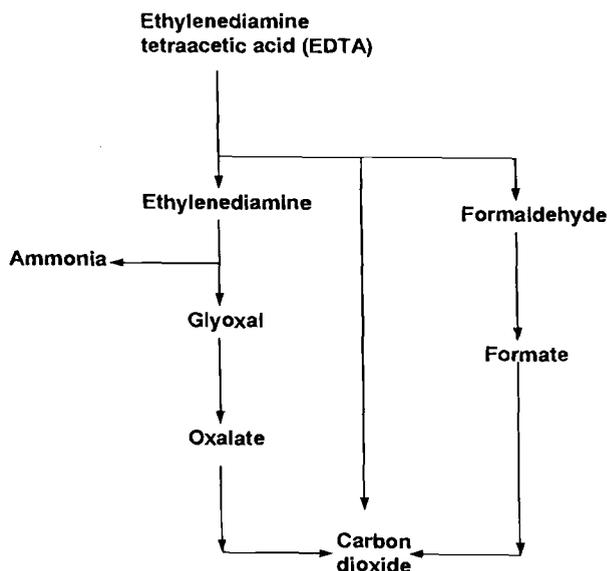

Fig. 3. Possible reaction pathway for the complete oxidation of EDTA in alkaline medium.
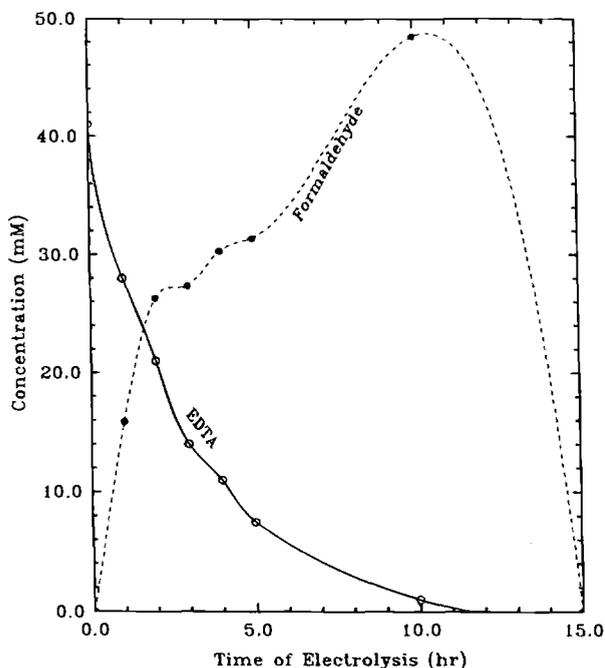
Fig. 4. Concentrations of EDTA and formaldehyde as a function of the time of electrolysis.
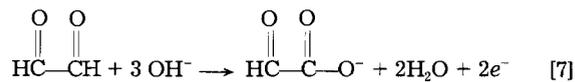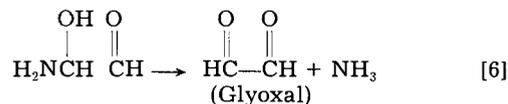
$$\begin{array}{ccc} ^-OOCCH_2 & & CH_2COO^- \\ \diagdown & & \diagup \\ & NCH_2CH_2N & + \ OH^- \\ \diagup & & \diagdown \\ ^-OOCCH_2 & & CH_2COO^- \\ & (EDTA) & \end{array}$$

$$\longrightarrow \begin{array}{ccc} ^-OOCCH_2 & & H \\ \diagdown & & \diagup \\ & NCH_2CH_2N & + \ HCHO \quad [2] \\ \diagup & & \diagdown \\ ^-OOCCH_2 & & CH_2COO^- \\ & (ED3A) & \\ & + \ CO_2 + 2e^- & \end{array}$$
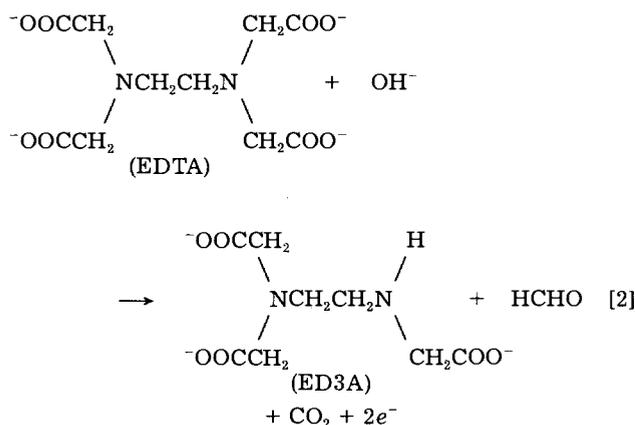
The number of electrons participating in the initial EDTA oxidation reaction was determined by electrolyzing EDTA solution under constant current conditions and measuring the CO_2 content in the alkaline solution using TIC analysis. According to Eq. 2, 1 M of CO_2 is expected to be produced per 2 F of charge passed. Efficiencies less than 100% (based on Eq. 2) were found, indicating that two electrons may be participating in the initial EDTA oxidation reaction.

The acetate groups on ED3A can be expected to be oxidized sequentially in a manner similar to Eq. 2, yielding U-EDDA, $(^-OOCCH_2)_2NCH_2CH_2NH_2$ [or S-EDDA, $(^-OOCCH_2)HNCH_2CH_2NH(CH_2COO^-)$]; EDMA, $H_2NCH_2CH_2NH$ (CH_2COO^-); and ethylenediamine $H_2NCH_2CH_2NH_2$.

The oxidation of ethylenediamine was studied by Rozhkova *et al.*,[16] who suggested the following reaction pathway as one of the possible mechanisms for its oxidation

$$\underset{}{H_2NCH_2CH_2NH_2} + 2\ OH^- \longrightarrow \overset{OH}{\underset{|}{H_2NCH_2CHNH_2}}$$
$$+ H_2O + 2e^- \quad [3]$$

$$\overset{OH}{\underset{|}{H_2NCH_2CHNH_2}} \longrightarrow \overset{O}{\underset{\|}{H_2NCH_2CH}} + NH_3 \quad [4]$$

$$\overset{O}{\underset{\|}{H_2NCH_2CH}} + 2\ OH^- \longrightarrow \overset{OH\ O}{\underset{|\ \ \ \|}{H_2NCH\ CH}} + H_2O + 2e^- \quad [5]$$

$$\overset{OH\ O}{\underset{|\ \ \ \|}{H_2NCH\ CH}} \longrightarrow \overset{O\ \ \ O}{\underset{\|\ \ \ \|}{HC-CH}} + NH_3 \quad [6]$$
$$\text{(Glyoxal)}$$

$$\overset{O\ \ \ O}{\underset{\|\ \ \ \|}{HC-CH}} + 3\ OH^- \longrightarrow \overset{O\ \ \ O}{\underset{\|\ \ \ \|}{HC-C-O^-}} + 2H_2O + 2e^- \quad [7]$$

$$\overset{O\ \ \ O}{\underset{\|\ \ \ \|}{HC-C-O^-}} + 3\ OH^- \longrightarrow \overset{O\ \ \ O}{\underset{\|\ \ \ \|}{^-O-C-C-O^-}} + 2H_2O + 2e^- \quad [8]$$
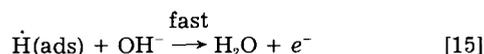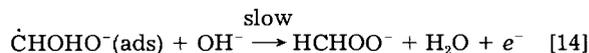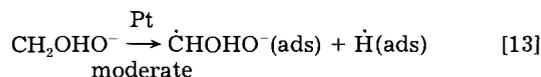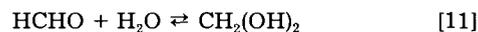$$\text{(Oxalate)}$$
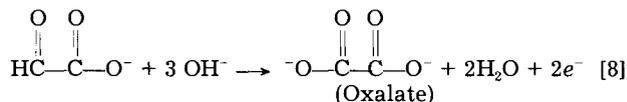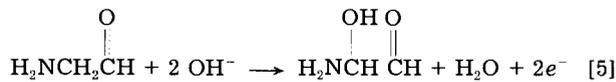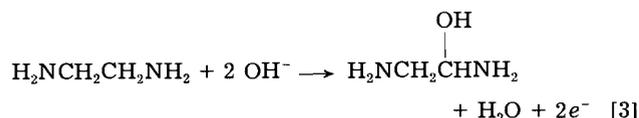
The two species, glyoxal and oxalate, predicted by the above mechanism were detected during the oxidation of EDTA in alkaline solution, suggesting that EDTA oxidation may follow the mechanism presented above. The oxalate thus formed is oxidized to CO_2[17] as follows
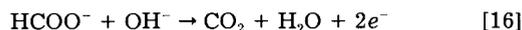
$$\overset{O\ \ \ O}{\underset{\|\ \ \ \|}{^-O-C-C-O^-}} \longrightarrow 2CO_2 + 2e^- \quad [9]$$
$$\text{(Oxalate)}$$
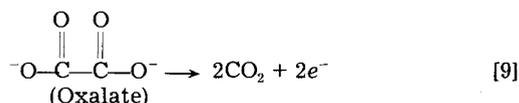
The formaldehyde formed during the initial oxidation of EDTA is oxidized to formate according to the reaction

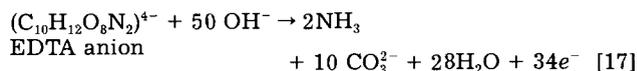$$HCHO + 3\ OH^- \rightarrow HCOO^- + 2H_2O + 2e^- \quad [10]$$

Buck and Griffith[18] proposed the following mechanism for the oxidation of formaldehyde to formate in alkaline medium on a platinum electrode

$$HCHO + H_2O \rightleftarrows CH_2(OH)_2 \quad [11]$$

$$CH_2(OH)_2 + OH^- \rightleftarrows CH_2OHO^- + H_2O \quad [12]$$

$$CH_2OHO^- \overset{Pt}{\underset{moderate}{\longrightarrow}} \overset{\cdot}{C}HOHO^-(ads) + \overset{\cdot}{H}(ads) \quad [13]$$

$$\overset{\cdot}{C}HOHO^-(ads) + OH^- \overset{slow}{\longrightarrow} HCHOO^- + H_2O + e^- \quad [14]$$

$$\overset{\cdot}{H}(ads) + OH^- \overset{fast}{\longrightarrow} H_2O + e^- \quad [15]$$

Formate is generally less electroactive than other organic species and can be expected to be oxidized to CO_2 according to the reaction[18]

$$HCOO^- + OH^- \rightarrow CO_2 + H_2O + 2e^- \quad [16]$$

The overall EDTA oxidation reaction may be written as

$$\underset{\text{EDTA anion}}{(C_{10}H_{12}O_8N_2)^{4-}} + 50\ OH^- \rightarrow 2NH_3$$
$$+ 10\ CO_3^{2-} + 28H_2O + 34e^- \quad [17]$$

Electrolysis of EDTA was carried out for an extended period of time to determine if the EDTA is completely oxidized to CO_2. As shown in Fig. 5, the TOC was found to approach zero concentration, suggesting that EDTA is completely oxidized without any refractory intermediates. The decrease in pH of the solution (Fig. 5) is due to the consumption of OH^- during EDTA oxidation (Eq. 17) and the direct oxidation of OH^- to oxygen.

Rest potentials.—The rest potential measurements were carried out in a three-compartment cell using a platinum disk electrode of area 0.5 cm^2. After the initial cleaning, any oxide buildup on the electrode was reduced by applying a potential close to the hydrogen-evolution potential (−0.650 V *vs.* Hg/HgO). Nitrogen gas was bubbled through the solution prior to and during the rest-potential measurements. The rest potential of the platinum electrode was first determined in NaOH solution (pH 12) and in the absence of EDTA to be 0.190 V *vs.* Hg/HgO reference elec-

trode. According to Damjanovic et al.,[13] the PtO formation commences at about 1.0 V vs. RHE. On a Hg/HgO scale, this potential (1.0 V vs. RHE) in pH 12 solution is 0.193 V, which is close to the rest potential measured in the supporting electrolyte. Hence the rest potential measured in the absence of EDTA in the electrolyte is suspected to be primarily due to PtO formation together with the reduction of oxygen on the electrode surface.

The pH of the electrolyte in the first set of rest-potential measurement experiments was maintained at 12 and the concentration of EDTA in the electrolyte was varied from 0.001 to 0.316 M. As shown in Fig. 6, the rest potential decreases with the addition of EDTA in the solution, indicating that the open-circuit potential of EDTA is less than 0.190 V. The observed rest potential for EDTA in alkaline solution (0.066 to 0.164 V vs. Hg/HgO) is higher than the rest potential of other organic compounds in alkaline medium. For example, in 1 N NaOH, the rest potentials of methanol, acetylene, and ethylene reported in the literature are −0.441 V, −0.481 V, and −0.461 V[21] vs. Hg/HgO, respectively. Similar observation of EDTA oxidation occurring at higher potentials than other organic compounds in acidic media was made by Johnson et al.[4] In alkaline medium, since the observed rest potentials for EDTA are close to the potential at which oxide film formation commences, little or no oxidation of EDTA on bare platinum is expected.

The rest potential measured at a constant EDTA concentration of 0.056 M showed little variation with pH (Fig. 7). The dependence of the rest potential on EDTA concentration and not on pH suggests that the initial electrochemical reaction involves EDTA species and not OH⁻ ions. Thus the rest potential may reflect a reaction such as

$$R_1 - CH_2COO^- \rightarrow R_1 - CH_2\cdot + CO_2 + e^- \quad [18]$$
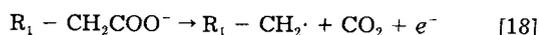
The Nernst equation for the above reaction (Eq. 18) can be written as

$$E = E^\circ - 0.0591 \log \left[\frac{R_1 - CH_2COO^-}{[R_1 - CH_2\cdot][CO_2]} \right] \quad [19]$$

As in the case of acidic media,[4] the lack of knowledge of the concentrations and free energies of $R_1 - CH_2\cdot$ and CO_2 precludes the calculation of the open-circuit potential of EDTA and its comparison with the measured rest potential. However, assuming the concentrations of $R_1 - CH_2\cdot$ and CO_2 to be small and constant, Eq. 19 provides a relation between the rest potential and the concentration of EDTA

$$E = \overline{E^\circ} - 0.0591 \log [R_1 - CH_2COO^-] \quad [20]$$

The slope of 59.1 mV predicted by Eq. 20 agrees closely with the measured slope of 53.5 mV (Fig. 6).

Cyclic voltammetry.—Since the current due to O_2 evolution cannot be completely avoided in alkaline solutions at higher anodic potentials, an effort was made in this work to reduce its interference by choosing a suitable pH. Figure 8 shows cyclic voltammograms on a platinum disk electrode obtained at pH values of 13.5, 13, 12, 11, and 10. As expected, the current due to oxygen evolution at pH values of 10, 11, and 12 is much smaller than at 13, and 13.5, suggesting that it would be beneficial to study EDTA oxidation at lower pH. However, tetrasodium EDTA, being a basic salt, forms a pH 11.3 solution when it is dissolved in water. Hence the pH of the solution cannot be made below 11.3 without adding other species (e.g., H_2SO_4, HCl, or HNO_3). A pH of 12 was therefore chosen throughout this study in order to decrease the oxygen evolution and to investigate the EDTA oxidation without the interference of anions other than EDTA.

The predominance of EDTA oxidation over oxygen evolution at higher anodic potentials can be seen in Fig. 9, which shows cyclic voltammograms obtained using a platinum electrode in NaOH solution (pH 12) for different EDTA concentrations. The contribution of oxygen evolu-

tion to the total current can be seen in Fig. 9 to become smaller at higher EDTA concentrations. For example, at 1.5 V vs. Hg/HgO in the absence of EDTA in the electrolyte, the current due to O_2 evolution is about 0.4 mA, compared to 18.2 mA at a concentration of 0.263 M. The voltammograms did not show any large diffusion-controlled peak in the presence of EDTA. A small peak at 1.15 V vs. Hg/HgO was observed at lower EDTA concentrations.

Figure 10 shows the cyclic voltammograms obtained at pH 12 in the presence of 0.105 M EDTA. The scan rates were varied from 5 to 100 mV/s. The increase in the limiting current with scan rate shows that the process is diffusion controlled. The Levich equation was tested by studying the variation of current density with the square root of rotation speed (Fig. 11). The linear dependence observed in Fig. 11 indicates that the Levich equation holds true and that EDTA oxidation at high overpotentials is controlled by diffusion of EDTA electroactive species.

Polarization measurements.—Unlike in acidic media, the polarization behavior in alkaline media is more complicated due to interference of oxygen evolution and oxide film formation on the electrode. In order to identify the potential region where EDTA polarization behavior could best be studied without the interference of oxygen or oxide film formation, potentiodynamic scans (1 mV/s) were obtained in the presence and absence of EDTA in pH 12 solution. As seen in Fig. 12, the current density in the absence of EDTA in the electrolyte is almost an order of magnitude lower than in the case when 0.263 M EDTA was present in the electrolyte, suggesting that O_2 evolution does not significantly influence EDTA polarization behavior. Also, as shown in Fig. 12, in both cases (i.e., in the presence and absence of EDTA) limiting currents were observed immediately positive to the rest potentials. A similar current plateau in alkaline medium due to oxide film formation was earlier observed by Damjanovic et al.[13] at potentials just above 1.0 V vs. RHE (corresponding to 0.193 V on a Hg/HgO scale). This potential is close to the rest potential observed in both cases (i.e., with and without EDTA), clearly indicating that the limiting current behavior observed in the presence of EDTA immediately positive to the rest potential is due to oxide film formation. Johnson et al.[4] also observed limiting currents when EDTA was oxidized in acidic media around 1.0 V normal hydrogen electrode (NHE), and found that these limiting currents do not obey linear relationships with EDTA concentrations. The authors attributed this phenomenon to
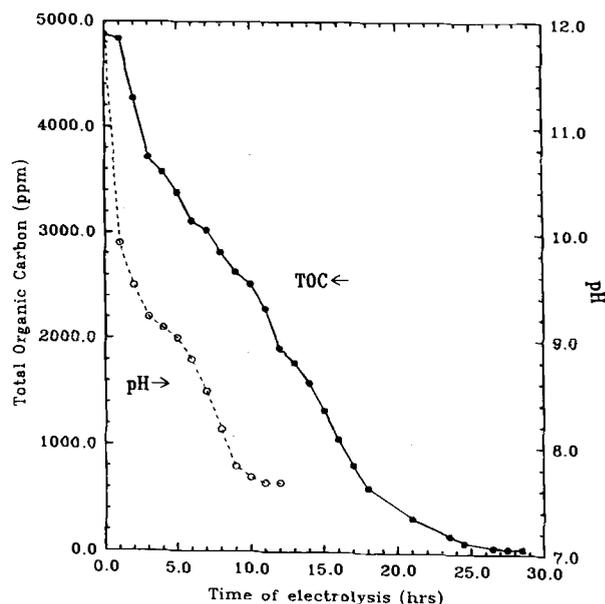

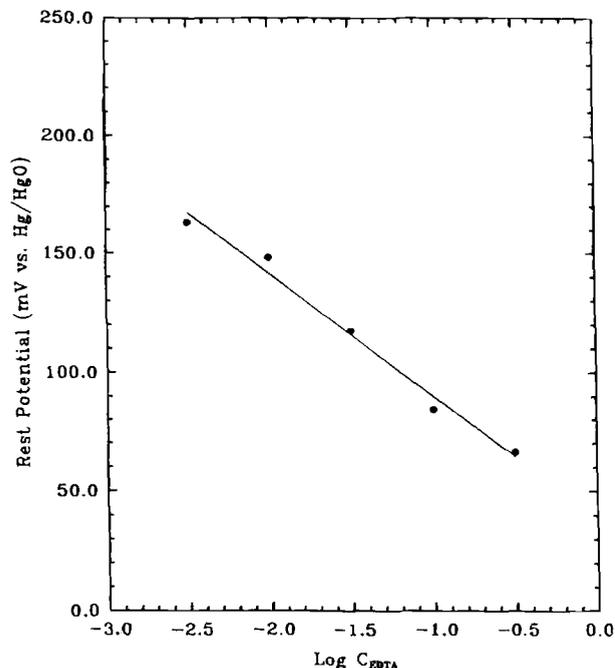Fig. 5. Total organic carbon and pH as a function of the time of electrolysis.

Fig. 6. Variation of rest potential with EDTA concentration.

the preferential participation of some of the EDTA species. Since oxide films are also formed in acidic media at 1.0 V RHE (*i.e.*, 1.0 V NHE at pH 0), the limiting currents observed by Johnson *et al.*[4] were probably due to PtO formation as well.

Figure 13 presents polarization curves obtained in pH 12 solution as a function of EDTA concentration. Note that the starting potentials shown in Fig. 13 are above the potential range where bulk of the oxide film is formed. As shown in Fig. 13, the current density and Tafel slopes were found to depend upon the concentration of EDTA in the electrolyte. This is due to the fact that the applied potential was at least 300 mV above the rest potential, where a diffusion limitation could be expected. In order to minimize diffusion limitations, the concentration of EDTA in
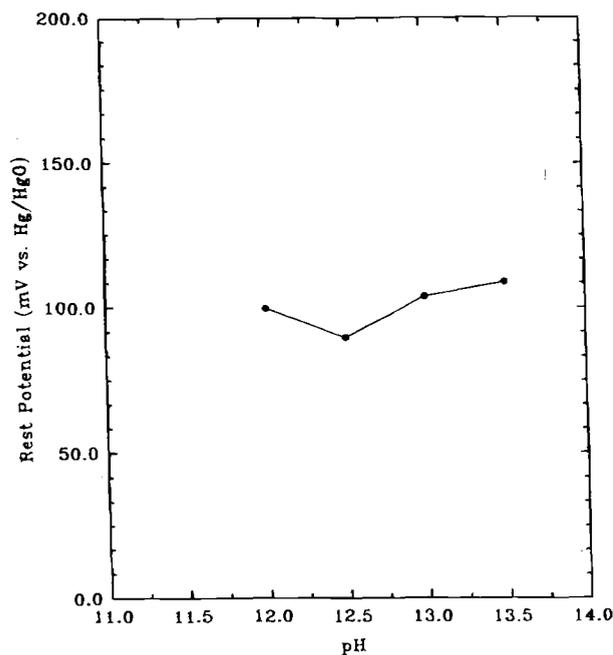
the bulk was gradually increased. As seen in Fig. 13, increasing the EDTA concentration has an effect of "steadying" the Tafel slope (due to decrease in diffusion limitations), and finally at 0.263 *M* EDTA, a Tafel slope of 119 mV/dec was observed.

In Fig. 14, log *i* is plotted as a function of log C_{EDTA} at constant pH 12 for three different potentials (0.7, 0.8, and 0.9 V *vs.* Hg/HgO) in the diffusion-limiting region. The concentration dependence (reaction order) of the EDTA electroactive species was obtained from the slope of the plot in Fig. 14 to be

Reaction order for EDTA

$$= \rho_1 = \left(\frac{\partial \log i}{\partial \log C_{EDTA}} \right)_{T,P,E,pH} = 0.54 \quad [21]$$

Since the EDTA concentration effect is positive, the rate-determining step (rds) involves EDTA species.

Figure 15 shows the potential *vs.* log *i* dependences as a function of pH. The experiments were carried at constant EDTA concentration of 0.263 *M*, using a scan rate of 1 mV/s. As shown in Fig. 15, the reaction order of OH⁻ was close to zero in the Tafel region, indicating that the rds of EDTA oxidation does not involve OH⁻ species. At high overpotentials (0.65 V to 1.0 V *vs.* Hg/HgO), oxygen evolution becomes significant, and as shown in Fig. 15, the limiting-current density increases with an increase of OH⁻ concentration.

Reaction mechanism for the oxidation of EDTA.—The oxidation reaction of EDTA to ED3A in alkaline medium can be written as
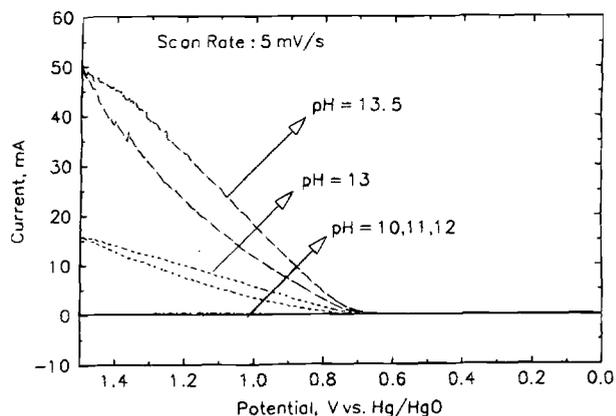

Fig. 8. Cyclic voltammograms as a function of pH in NaOH solution (no EDTA) using a platinum electrode.
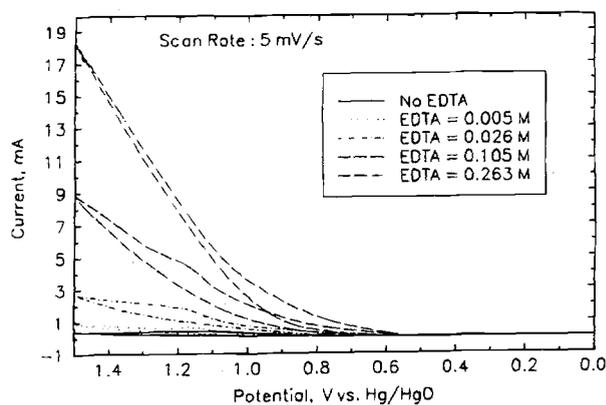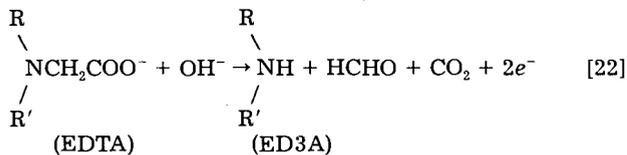

Fig. 7. Variation of rest potential with pH(C_{EDTA} = 0.056 *M*).
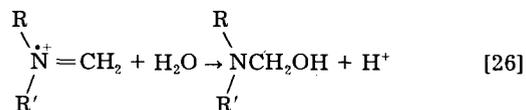

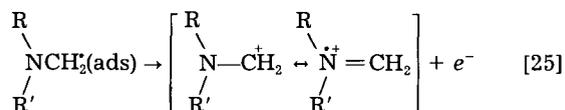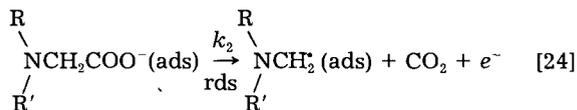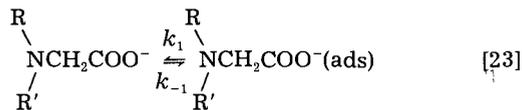**Fig. 9. Cyclic voltammograms as a function of EDTA concentration in NaOH solution (pH 12) using a platinum electrode.**

$$\begin{array}{cc} R & R \\ \backslash & \backslash \\ NCH_2COO^- + OH^- \rightarrow NH + HCHO + CO_2 + 2e^- \\ / & / \\ R' & R' \\ \text{(EDTA)} & \text{(ED3A)} \end{array} \quad [22]$$

Note that in alkaline media of pH $\geq$ 12, EDTA is primarily in the form of Y^{4-} species.

According to our studies, the following qualitative conclusions can be drawn about the reaction mechanism of EDTA oxidation in alkaline solution: (*i*) the observed maximum formaldehyde concentration at a time corresponding to complete conversion of EDTA to other species suggests that acetate groups on EDTA are initially oxidized in a sequential manner yielding CO_2 and HCHO. From CO_2 efficiency studies it appears that two electrons are transferred to the faradaic circuit during the reaction. (*ii*) A positive pH effect in the initial EDTA oxidation was not observed, indicating that OH^- ion is not involved as a reactant during or prior to the rds. (*iii*) The fractional concentration effect of EDTA indicates that EDTA species are adsorbed. (*iv*) The positive concentration effect of EDTA

Fig. 10. Cyclic voltammograms as a function of scan rate in NaOH solution (pH 12) and with an EDTA concentration of 0.105 *M* using a platinum electrode.

Fig. 11. Variation of limiting current i_l with $\omega^{1/2}$ at 0.421 *M* EDTA and 1.8 V vs. Hg/HgO.

suggests that the rds involves EDTA species. Based on these conclusions and the information obtained from the reaction-order study, the Tafel-slope and the rest-potential studies, the following mechanism is suggested for the initial oxidation reaction of EDTA in alkaline medium

$$\begin{array}{cc} R & R \\ \backslash & k_1 \quad \backslash \\ NCH_2COO^- & \rightleftharpoons NCH_2COO^-(ads) \\ / & k_{-1} \; / \\ R' & R' \end{array} \quad [23]$$

$$\begin{array}{cc} R & R \\ \backslash & k_2 \quad \backslash \\ NCH_2COO^-(ads) & \rightarrow NCH_2^\cdot(ads) + CO_2 + e^- \\ / & \text{rds} \; / \\ R' & R' \end{array} \quad [24]$$

$$\begin{array}{c} R \\ \backslash \\ NCH_2^\cdot(ads) \rightarrow \left[\begin{array}{cc} R & R \\ \backslash & \backslash \cdot\cdot \\ N-\overset{+}{C}H_2 \leftrightarrow \overset{\cdot+}{N}=CH_2 \\ / & / \\ R' & R' \end{array} \right] + e^- \end{array} \quad [25]$$

$$\begin{array}{cc} R & R \\ \backslash\overset{\cdot+}{\;} & \backslash \\ N=CH_2 + H_2O \rightarrow NCH_2OH + H^+ \\ / & / \\ R' & R' \end{array} \quad [26]$$

$$H^+ + OH^- \rightarrow H_2O \quad [27]$$

$$\begin{array}{cc} R & R \\ \backslash & \backslash \\ NCH_2OH \rightarrow NH + HCHO \\ / & / \\ R' & R' \end{array} \quad [28]$$
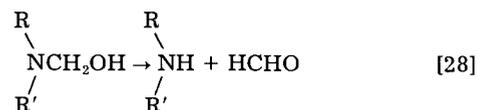
The observed fractional reaction order of EDTA indicates that intermediate coverages are involved where Temkin isotherm is often assumed. For the rds in the above mech-
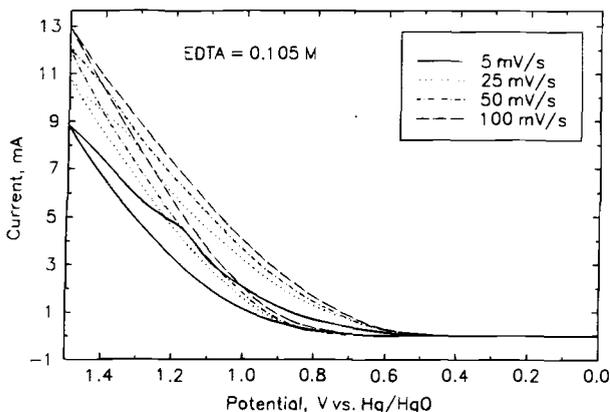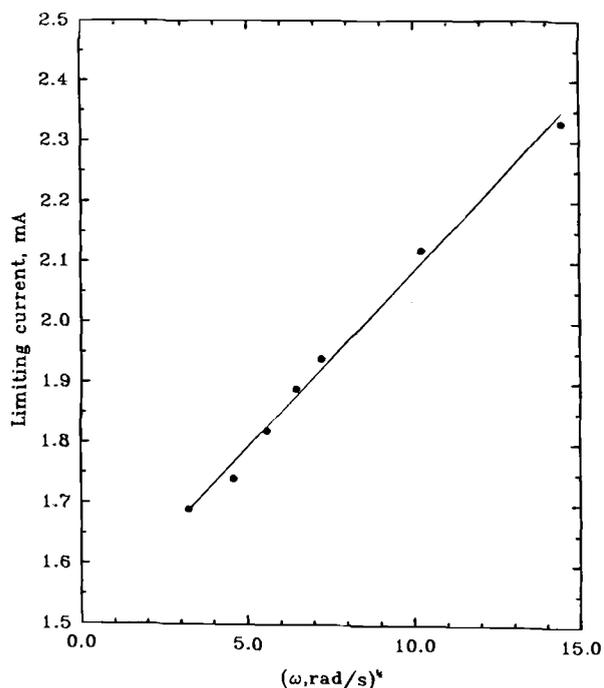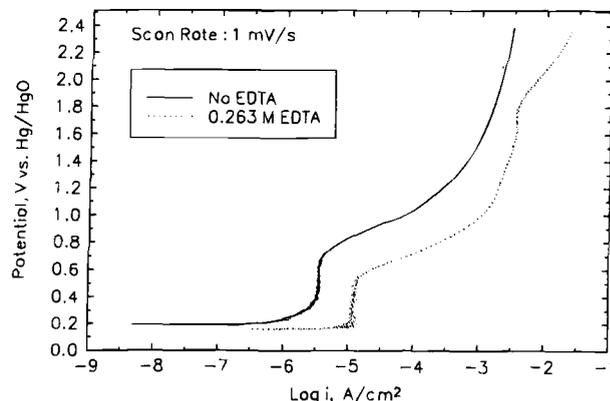

Fig. 12. Potentiodynamic scans using a platinum electrode (presence and absence of EDTA) in pH 12 solution.
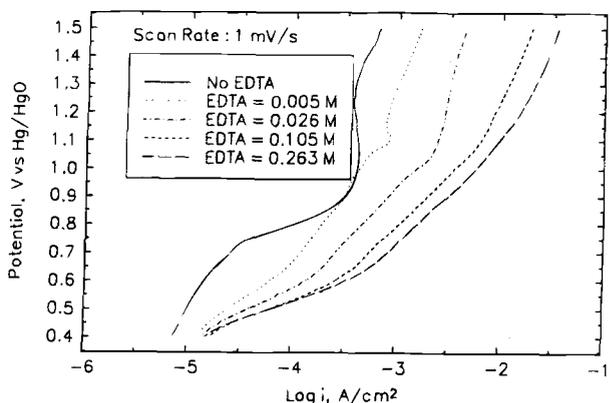

Fig. 13. Potentiodynamic scans using a platinum electrode (variation with EDTA concentration) in pH 12 solution.

anism, Temkin-type adsorption gives a Tafel slope of 120 mV and a fractional dependence upon EDTA concentration. Thus, the rate of the first reaction (Eq. 23) may be written as

$$r_1 = k_1 C_{EDTA} \exp\left(-\beta \frac{r\theta}{RT}\right) = k_{-1} \exp\left[(1-\beta)\frac{r\theta}{RT}\right] \quad [29]$$

or

$$\exp\left(\frac{r\theta}{RT}\right) = \frac{k_1}{k_{-1}} C_{EDTA} \quad [30]$$

The rate of the rds Eq. 24 can be written as

$$r_2 = k_2 \exp\left[(1-\beta)\frac{r\theta}{RT}\right] \exp\left(\beta \frac{EF}{RT}\right) \quad [31]$$

where β is the symmetry factor and r is the rate of change of Gibbs energy of adsorption with coverage. The current density is given by

$$i = nFr_2 = nFk_2 \exp\left[(1-\beta)\frac{r\theta}{RT}\right] \exp\left(\beta \frac{EF}{RT}\right) \quad [32]$$

Substituting Eq. 30 into Eq. 32 gives

$$i = nFk_2\left(\frac{k_1}{k_{-1}}\right)^{1-\beta} C_{EDTA}^{1-\beta} \exp\left(\beta \frac{EF}{RT}\right) \quad [33]$$

Assuming the symmetry factor, β, to be 0.5, the Tafel slope is $b = 2.3RT/\beta F = 120$ mV, and the reaction order for initial EDTA oxidation is: $(\partial \log i/\partial \log C_{EDTA})_{T,pH,E} = 0.5$, which agrees well with the experimentally determined values of 119 mV and 0.54, respectively.

Conclusions

Bulk electrolysis of EDTA in alkaline medium showed that EDTA can be completely oxidized to CO_2. A possible reaction pathway suggests that the acetate groups on EDTA are sequentially oxidized, generating ethylenediamine which is further oxidized to CO_2 via glyoxal and oxalate. The formaldehyde generated is oxidized to CO_2 via formate ion.
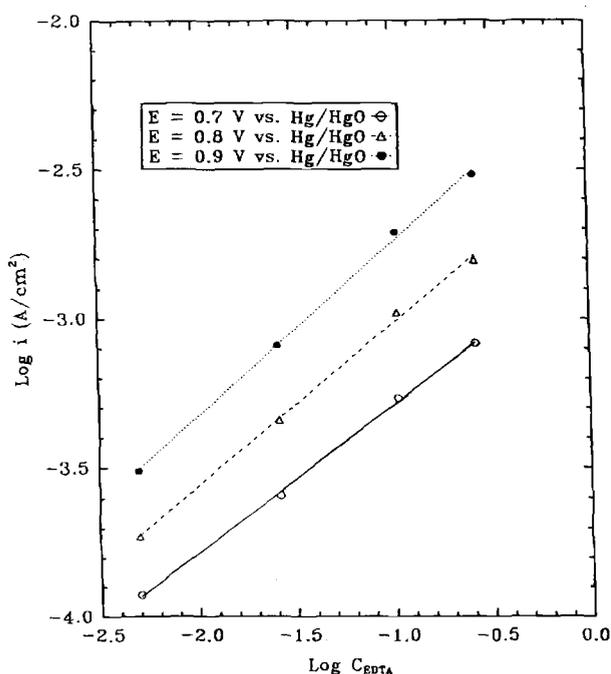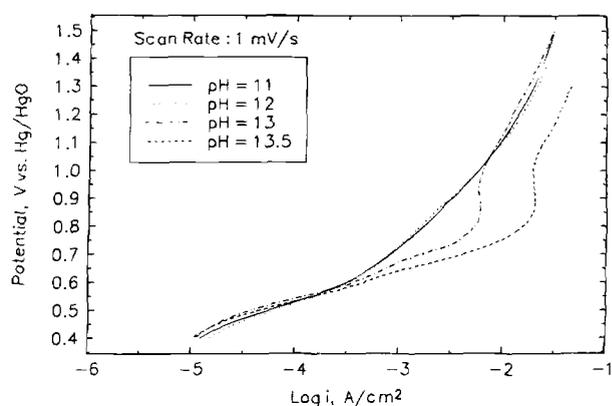

Fig. 15. Potentiodynamic scans using a platinum electrode (variation with pH). EDTA concentration 0.263 *M*.

Rest potentials of EDTA were observed to be higher than the rest potentials of other organic compounds in alkaline medium. The observed rest potential of EDTA was close to the potential at which oxide film formation commences (*i.e.*, 1.0 V *vs.* RHE). Small limiting currents immediately after the rest potential were observed and attributed to oxide film formation.

A Tafel slope close to 120 mV was observed in the potential region above the oxide film formation. The reaction order of the rds with respect to EDTA was found to be 0.54, while the reaction order with respect to OH^- was close to zero. The electrochemical kinetic data indicated Temkin-type adsorption of the EDTA species followed by the first electron rate-determining decarboxylation step.

Fig. 14. Log *i* as a function of log C_{EDTA} at constant pH 12 for different values of potential.

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