The Anodic Oxidation of Ethylenediaminetetraacetic Acid and Its Divalent Metal Chelates at the Carbon Paste Electrode

By Toyokichi KITAGAWA and Syōichirō TSUSHIMA

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka

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Recent works in voltammetry[1,2] have shown the existence of oxide films on platinum electrodes after they had been anodized at highly positive potentials. Therefore, it is not suitable to use a platinum electrode as an indicator electrode at a positive potential region. A carbon paste electrode (graphite intimately mixed with Nujol) has been reported to possess unique advantages and to be very precise in anodic voltammetry.[3]

A single anodic wave of EDTA is observed in the pH range from 1.8 to 2.5, with $E_{P/2}$ of $+0.93$ V. (vs. SCE) varying slightly with the pH. A second wave appears in the pH range from 4 to 6. The second wave shifts to less positive potentials with an increase in the pH and merges into the first wave.

The peak current - concentration relationship is linear for the first wave in the range from 10^{-2} mM to 1 mM at any pH less than 5 and is reproducible within ±2 to 3%.

The anodic oxidation of metal-EDTA complexes containing a slight excess of metal ions in a 0.1 M HOAc - 0.1 M NaOAc buffer solution with 0.005% polyacrylamide was also investigated at the carbon paste electrode. According to the anodic oxidation potential of metal-EDTA complexes, the following four situations arise, as is shown in Fig. 1: (a) Co(II)EDTA is oxidized more easily than EDTA. The anodic oxidation of Co(II)EDTA to Co(III)EDTA was confirmed by chronopotentiometry. (b) Ni(III)EDTA shows an anodic wave at almost the same potential as that of EDTA. The peak current is, however, about one-half that of EDTA. (c) The anodic wave of Cu(II)EDTA appears at a potential less negative than that of EDTA. This peak current is also about one-half that of EDTA at the same concentration. (d) Cd(II)EDTA does not show any anodic wave until the final increase in the background current appears. Pb(II)EDTA and Zn(II)EDTA behave the same way.

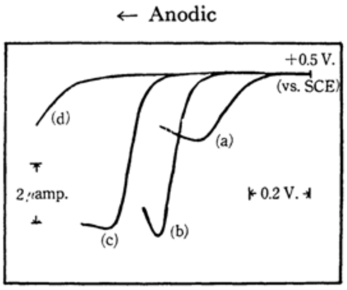

Fig. 1. Current-voltage curves for the oxidation of metal-EDTA complexes in 0.1 M HOAc - 0.1 M NaOAc buffer solution.
1 mM metal EDTA, 0.005% polyacrylamide
(a) Co(II)EDTA (b) Ni(II)EDTA
(c) Cu(II)EDTA (d) Cd(II)EDTA
Scanning rate 0.2V./min.,
Electrode area 0.0853 cm²

The details of the mechanisms of these electrode reactions will be reported later.

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[1] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, **26**, 623 (1954).

[2] H. A. Laitinen and C. G. Enke, *J. Electrochem. Soc.*, **107**, 773 (1960).

[3] C. Olson and R. N. Adams, *Anal. Chim. Acta*, **22**, 582 (1960).