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Electrochemical Behavior of Platinum in Solutions Containing Ethylenediaminetetraacetate

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The electrochemical behavior of platinum in solutions of ethylenediaminetetraacetate(EDTA) has been investigated by the measurements of current-potential and current-time curves and by the controlled-potential electrolysis. EDTA gives the anodic limiting current, which is much smaller than that of one-electron transfer obtained for the ordinary diffusion-controlled electrode reaction. Platinum was detected by the spectrophotometric method in the solution which was subjected to the electrolysis at controlled potential. The results suggest that the anodic current is due to the electrolytic dissolution of the platinum electrode by the reactions,

$$Pt + 2H_2O \rightarrow Pt(OH)_2 + 2H^+ + 2e \quad (1)$$

$$Pt(OH)_2 + H_2Y^{2-} \rightarrow PtY^{2-} + 2H_2O \quad (2)$$

where Y^{4-} represents a quadrivalent anion of EDTA.

The anodic limiting current of ethylenediaminetetraacetate (EDTA) which was obtained at the platinum electrode was found to be much smaller than the diffusion-controlled limiting current obtained for the electrode reaction of one-electron transfer and to be independent of the rate of rotation of the platinum electrode. Recently, Stulik and Vydra[1] have investigated the electrode reaction of EDTA at the platinum electrode and stated that the anodic limiting current is due to the oxidation of EDTA itself.

However, our preliminary experiments suggested that the anodic limiting current was due to the electrolytic dissolution of the platinum electrode in the solution of EDTA.

This paper describes the electrochemical behavior of platinum in the solution of EDTA which was revealed from the voltammetric measurements and the controlled-potential electrolysis.

Experimental

Apparatus. A recording polarograph, Yanagimoto Model P 102 was used for the measurements of current-potential and current-time curves. A Hokuto Denko linear scanning unit Model LS-1D, potentiostat PS-500 B and XY recorder F-3B were used for the measurements of cyclic voltammetric curves and for the electrolysis at controlled potential. A Hitachi-Horiba pH meter Model F was used for the measurement of pH. All measurements were made in a thermostat at 25.0°± 0.1°C except those which were made at various temperatures. The measurement of absorbancy was made with a Hitachi Model 139 spectrophotometer.

Electrode. A platinum wire electrode was sealed into a glass tube which was filled with mercury for electrical contact. The electrode was 0.7 mm in diameter and 5 mm in length, its geometric surface area being approximately 0.11 cm^2. The electrode was rotated with a synchronous motor at a rate of 600 rpm. The counter electrode which was used for the

1) K. Stulik and F. Vydra, *J. Electroanal. Chem.*, **16**, 385 (1968).

electrolysis at controlled potential was a platinum spiral of 0.7 mm in diameter and 40 mm in length.

Pretreatment of Electrode. The platinum wire electrode was treated with 10 N nitric acid and washed with distilled water. Before use, it was subjected to several cycles from −0.5 to +1.5 V *vs.* the saturated caromel electrode (SCE) in a deaerated 0.1 M perchloric acid. Then the electrode which was finally polarized anodically was short-circuited against SCE. If the electrode showed such a characteristic that the current decreased practically to zero within 2 or 3 min, it was called a "clean electrode."[2] When the electrode did not show such a characteristic, the cycled polarization was repeated. The clean electrode was stored usually in a deaerated distilled water.

Reagents. All reagents used were of reagent grade.

Spectrophotometric Measurements. The solution (50 m*l*) which was subjected to the controlled potential electrolysis was concentrated to about 1 m*l* in volume. The residual solution was treated with bromine water and concentrated hydrochloric acid and evaporated to almost dryness in order to convert Pt(II) to Pt(IV).[3] Ten milliliters of 1 : 1 hydrochloric acid was added and the solution was concentrated again to about 1 m*l* to remove bromine completely. The residual solution was treated according to Ayres and Meyer:[4] 10 m*l* of 6 N hydrochloric acid, 10 m*l* of 20% ammonium chloride solution and 10 m*l* of 1.0 M tin(II) chloride solution containing 3.5 N hydrochloric acid were added and the developed color was extracted with isoamyl acetate containing 1% resorcinol, of which absorption spectra were obtained.

Results and Discussion

Current-potential Curves. Current-potential curves of 5 mM EDTA in 0.1 M acetate buffer solutions were obtained with the rotated or stationary platinum electrode in the absence of oxygen, which are shown in Fig. 1. An arrow sign represents the direction of scanning potential. In both cases, the anodic limiting currents gave almost the same value which was independent of the rate of rotation of the electrode and was much smaller than that of one-electron transfer of ordinary compounds at this electrode. This indicates that the anodic current is not controlled by diffusion. In addition, the cathodic peak current was smaller in the presence of EDTA than in the absence of EDTA in the solution. This may indicate that the oxide film produced on the electrode surface was dissolved partly by the chemical reaction with EDTA.

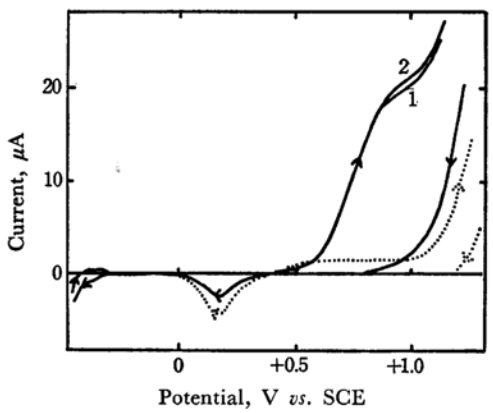

Fig. 1. Voltammetric curves of 5 mM EDTA in 0.1 M acetate buffer solutions at (1) rotated and (2) stationary Pt electrode. ····· indicates voltammetric curve of 0.1 M acetate buffer.

The anodic current increased with the increase of the concentration of EDTA, but it was not exactly proportional to the latter, as is given in Table 1. In the acetate buffer solution, the anodic current decreased with increasing pH's, and at higher pH's adjusted with other buffers no anodic current could be obtained. (Fig. 2).

The above results suggest that the anodic current is due to the electrode reaction given by

$$Pt + 2H_2O \rightarrow Pt(OH)_2 + 2H^+ + 2e \quad (1)$$

$$Pt(OH)_2 + H_2Y^{2-} \rightarrow PtY^{2-} + 2H_2O \quad (2)$$

Table 1. Anodic currents at 0.9 V at various EDTA concentrations in 0.1 M acetate buffer solutions

Concentration of EDTA, mM	Anodic current at +0.9 V, μA	
	Observed	Corrected for residual current*
1	6.0	3.5
5	14.5	12.0
10	23.0	20.5
20	36.5	34.0

* Residual current due to platinum oxide formation.

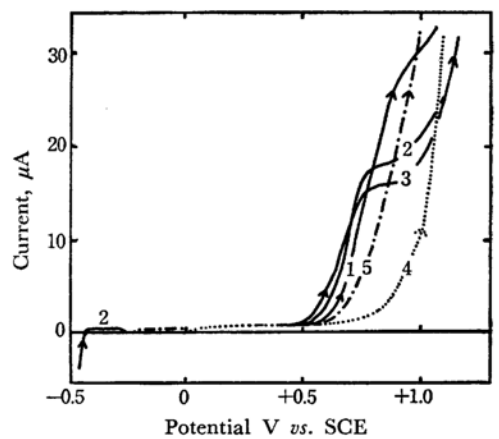

Fig. 2. Voltammetric curves of 5 mM EDTA at pH (1) 3.6 (2) 4.7 (3) 5.1 (4) 9.3 (0.1 M borate buffer) and (5) 13 (0.1 M NaOH).

2) I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, **26**, 632 (1954).

3) D. T. Napp and S. Bruckenstein, *ibid.*, **40**, 1036 (1968).

4) G. H. Ayres and A. S. Meyer, Jr., *ibid.*, **23**, 299 (1951).

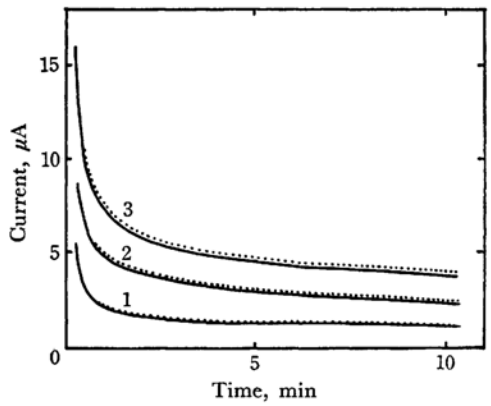

Fig. 3. Current-time curves of (1) 1×10^{-3} M, (2) 3×10^{-3} M and (3) 5×10^{-3} M EDTA obtained at 0.9 V *vs.* SCE in 0.1 M acetate buffer solution. ····· indicates $i-t$ curves at stationary and ——, at rotated Pt electrode.

The species H_2Y^{2-} is predominant in a pH range where the anodic current is obtained.

Current-time Curves. Current-time curves of EDTA were measured with the rotated and the stationary electrodes at +0.9 V. They are shown in Fig. 3 after correction for the residual current. Although the current decreased rapidly at first, it was nearly constant after the elapse of 5 min. There was practically no difference in current at the rotated and at the stationary electrode. The product $it^{1/2}$ which was found not to be constant also supports that the anodic current is not diffusion-controlled.[5]

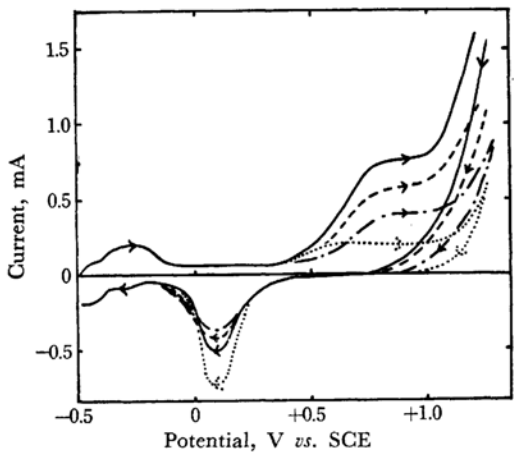

Fig. 4. Cyclic voltammetric curves of 5 mM EDTA in 0.1 M acetate buffer solutions at 25°C (—·—), 40°C (——) and 55°C (——). ····· indicates that of base electrolyte at 55°C. Scan rate is 0.2 V/sec.

5) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York (1954), p. 51.

Cyclic Voltammetric Curves. Cyclic voltammetric curves of 5 mM EDTA in 0.1 M acetate buffer solutions were measured at various temperatures. Some of the curves are given in Fig. 4. The cathodic peak current obtained in the presence of EDTA was found to be always smaller than that obtained in the absence of EDTA. The anodic limiting current was enhanced with increasing temperature.

Electrolysis at Controlled Potentials. The solutions containing 5 or 10 mM EDTA and 0.1 M acetate buffer were electrolyzed for 10 hr at controlled potential of +0.9 V or at potentials cycled in the range of −0.1 V to +1.3 V, and the ultraviolet absorption spectra were obtained with the procedure mentioned above, which are shown in Fig. 5. The absorption band is considered to be due to the formation of Pt(IV)-Sn(II) complexes. In Fig. 5, the absorption spectra of the solution which was prepared with a standard platinum(IV) solution and a tin(II) chloride solution are shown. These spectra clearly indicate that platinum is dissolved electrochemically into the solution to a greater amount in the presence of EDTA than in the absence of EDTA.

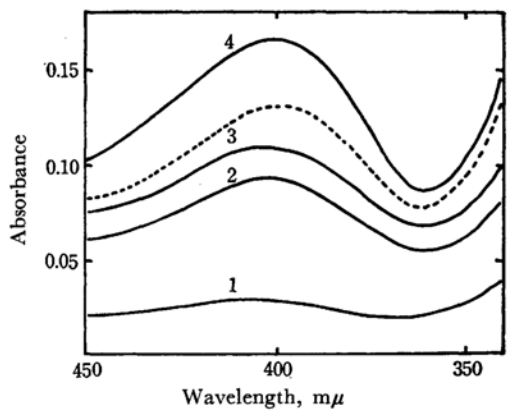

Fig. 5. Absorption spectra of Pt(IV)-Sn(II) chloride complex in isoamyl acetate solution. —— indicates absorption spectra of the solutions which were prepared with the solution subjected to the electrolysis at potentials cycled in the range of −0.1 to +1.3 V (1, 2 and 3) and at controlled potential at +0.9 V (4) for 10 hr. The concentrations of EDTA in electrolysis solutions were 0(1), 5(2) and 10 (3 and 4) mM. ---- indicates absorption spectra of the solution which was prepared with 2.45 mM Pt(IV) standard solution and tin(II) chloride solution.

Conclusion. From all of the results obtained in this study, it may be concluded that the anodic current obtained in the solution of EDTA is not due to the oxidation of EDTA itself but due to the electrolytic dissolution of platinum electrode with EDTA.