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Dissolution of Metallic Copper in Ethylenediaminetetraacetate Solution in the Presence of Hydrogen Peroxide

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Synopsis. A 50 mg portion of metallic copper (100 mesh) placed in 50 ml of a neutral solution containing 0.1 mol dm^{-3} ethylenediaminetetraacetate (EDTA) was quantitatively dissolved within 20 min at 50 °C after the addition of a small amount of hydrogen peroxide, resulting in blue coloration of the copper(II)–edta complex.

Copper dissolves readily in aqueous ammonia in the presence of oxygen to form copper(II)–ammine complex.[1] A similar reaction is expected in an aqueous solution containing a chelating agent. Quantitative dissolution of copper in EDTA solution in the presence of hydrogen peroxide is reported.

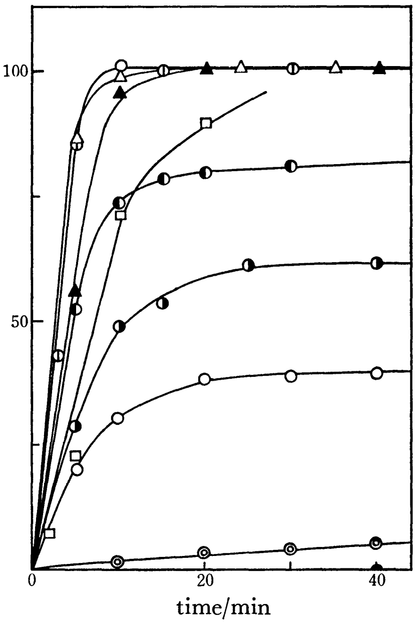

Fig. 1. Effect of hydrogen peroxide on the dissolution of a 50-mg portion of metallic copper in 0.1 M EDTA solution (50 ml, pH 4.8) at 50 °C. Amounts of 30% H_2O_2 solution added; ○: 0.05, ◑: 0.10, ◐: 0.20, ⦶: 0.5, △: 1.0, ▲: 2.5, □: 5.0 ml, ◎: without H_2O_2, ●: the solution deaerated and without H_2O_2.

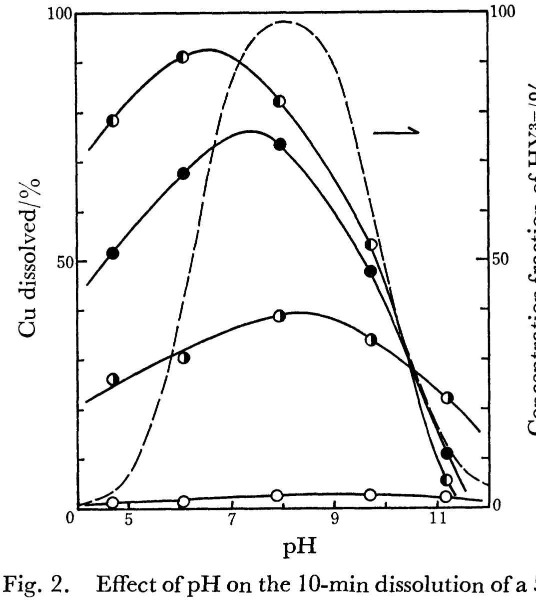

Fig. 2. Effect of pH on the 10-min dissolution of a 50-mg portion of metallic copper. Solution pH was adjusted with mixing 0.1 M EDTA disodium (pH 4.8) and tetrasodium (pH 11.3) salt solutions. Amounts of 30% H_2O_2 solution added; ○: 0, ◑: 0.10, ●: 0.20, ◐: 0.5 ml. The dashed curve indicates the concentration fraction of the HY^{3-} species.

Experimental

Reagents. The following reagents were used. Disodium and tetrasodium salts of ethylenediaminetetraacetic acid (Dotite reagents, Dojindo Laboratories), metallic copper powder of spectrographic standard (99.999 %, 100 mesh, Mitsuwa Pure Chemicals Inc.), and copper(I) oxide (chemically pure grade, Kanto Chemicals Inc.). Other reagents used were of guaranteed grade.

Procedure. A 50 mg portion of copper powder was taken into 50 ml of a 0.1 M (1 M=1 mol dm^{-3}) EDTA solution in a 100-ml Erlenmeyer flask placed in a thermostat kept at 50 °C, a small amount of hydrogen peroxide being added to the solution with stirring. The course of the reaction was followed by pipetting out a 3-ml portion of the reaction solution at certain time intervals and determining the concentration of copper(II)–edta complex spectrophotometrically at 720 nm with a Shimadzu Spectronic 88 spectrophotometer. The amount of dissolved copper was evaluated from the calibration curve obtained by means of copper sulfate in a solution of the same composition as the reaction solution. After the absorption measurement the solution was returned quickly to the reaction vessel to keep the volume constant.

Results and Discussion

Effect of Hydrogen Peroxide. In the presence of dissolved oxygen, copper reacts slowly with EDTA to form a blue colored copper(II)–edta complex, but no copper dissolves when oxygen is purged by nitrogen. Addition of a small amount of hydrogen peroxide was highly effective in promoting the dissolution (Fig. 1). A 50 mg portion of copper in 50 ml of a 0.1 M Na_2H_2-edta solution (pH 4.8) was quantitatively dissolved within 20 min after the addition of 0.4—2.4 ml of 30% hydrogen peroxide solution when the reaction solution was stirred at 50 °C. At a higher initial concentration of hydrogen peroxide, evolution of oxygen took place in the solution, the dissolution of copper being depressed.

Effect of pH. The pH dependence of the reaction was examined by varying the concentration of hydrogen peroxide. The reaction solution was gently shaken in an incubator. Rapid dissolution of copper took place in the pH range 6—8, as shown in Fig. 2, in which the proportion of copper dissolved during the first 10 min is plotted against pH of the initial solution. After quantitative dissolution of copper, the pH of solution was found to increase by *ca.* one unit. The rate of dissolution depends upon the concentration of $Hedta^{3-}$. When the pH was higher than 9, the decomposition of hydrogen peroxide took place with increase in the initial concentration of hydrogen peroxide, no quantitative dissolution of copper taking place.

Dissolution Reaction. The kinetics of the corrosion of copper in aqueous solution was reported by Hill.[2] In the presence of oxygen, copper is oxidized to copper(I) ion, forming copper(I) oxide. The formation of copper(I) oxide is hindered in the presence of acetate ion owing to the absorption of acetate ion on the copper surface.

Thus the following sequence of reactions is suggested in the presence of hydrogen peroxide and EDTA.

$$2Cu + H_2O_2 + 2H^+ \longrightarrow 2Cu^+ + 2H_2O, \qquad (1)$$

$$2Cu^+ + H_2O_2 + 2HY^{3-} \longrightarrow 2CuY^{2-} + 2H_2O, \qquad (2)$$

where HY^{3-} denotes EDTA anion predominating near pH 8. The overall reaction is given by

$$Cu + HY^{3-} + H_2O_2 + H^+ \longrightarrow CuY^{2-} + 2H_2O. \qquad (3)$$

This indicates the consumption of proton, experimentally confirmed as the increase in pH after the dissolution of copper.

Reaction of Copper Oxide with EDTA. The reactions of copper(I) and copper(II) oxides with EDTA solution were tested. Each sample of the oxides containing 7.89×10^{-4} mol copper was taken into a 0.1 M Na_2H_2-edta solution. Copper(I) oxide reacts readily with EDTA in an air-saturated solution, an appreciable dissolution taking place even in a deaerated EDTA solution. On the other hand, copper(II) oxide dissolves slightly into an EDTA solution even in the presence of hydrogen peroxide.

References

1) J. Halpern, *J. Electrochem. Soc.*, **100**, 421 (1953).
2) G. R. Hill, *J. Electrochem. Soc.*, **100**, 345 (1953).