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Alternating Current Polarography of Copper in Presence of Diethylenetriaminepentaacetic Acid

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A. C. polarograms of the copper-DTPA complex exhibit two waves when recorded from acetate or phosphate buffers. The effect of pH, temperature, and droptime on the two waves has been investigated. The experimental results indicate that the overall electrode reaction process consist of two simultaneous reactions, one which proceeds at the clean electrode surface and the other one at the electrode surface covered with the adsorbed reduction product of the first reaction. In the presence of high concentrations of ammonia a mixed ligand complex is formed which is not adsorbed at the electrode. Polarograms of this complex exhibit only one wave.

D. C. polarograms of the copper-DTPA complex exhibit two waves when recorded from supporting electrolytes at pH above 5. The double wave is assumed to be the result of an inhibited electrode reaction, the inhibition being caused by adsorption of the reduction product at the electrode surface.[1] Preliminary experiments showed that the apparently irreversible second wave gives rise to a well-defined A. C. peak, indicating a reversible step in the overall electrode reaction. The present study was performed in order to investigate this electrode reaction by alternating current polarography.

EXPERIMENTAL

Materials. Stock solutions of copper and of diethylenetriaminepentaacetic acid (DTPA) were prepared and standardized as described previously.[1] 0.1 M acetate and phosphate buffers together with 0.1 M potassium nitrate were used as supporting electrolytes. The pH of the electrolytes was adjusted to desired value by adding hydrochloric acid or potassium hydroxide to the solution and its pH measured with a Beckman Zeromatic pH meter.

Apparatus. A. C. polarograms were obtained manually by a polarograph built in this laboratory.[2] The superimposed sinusoidal voltage was of the main frequency (50 c/sec) and was stabilized by an Advance voltstat from Hainault, Essex, England. The con-

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ventional type of dropping mercury electrode (d.m.e.) was used. The capillary characteristics measured in 0.1 M potassium nitrate (open circuit) at a corrected mercury height of 49.0 cm were $m = 2.578$ mg/sec and $t = 3.54$ sec. An external saturated calomel electrode (S.C.E.) served as reference electrode. The polarographic cell was a so-called "pool-condenser" electrode.[3] A shunt capasitor of 2000 μF was connected between the mercury pool in the cell and the calomel electrode. All experiments were performed at 25 $\pm$ 0.1°C.

RESULTS

Preliminary experiments showed that A. C. polarograms of the copper-DTPA complex exhibit only one peak in acid medium. In order to avoid maxima which occur on D. C. polarograms at pH values less than 5,[1] the polarograms were obtained from solutions with a copper concentration of 10^{-3} M. The summit potential shifted to more negative values with increasing pH and at a given pH value the summit potential coincided with the D. C. half-wave potential.

When pH of the supporting electrolyte was increased above 5 a new A. C. peak appeared at a more negative potential. A further increase in pH resulted in an increase in the height of the second peak, whereas that of the first one decreased. At a given pH the summit potential of the first A. C. wave coincided with the half-wave potential of the first D. C. wave. The summit potential of the second A. C. wave was, however, about 30 mV more negative than the half-wave potential of the second D. C. wave. A few typical polarograms are shown in Fig. 1. No maximum is observed on D. C. polarograms recorded from solutions with pH above 5, and a copper concentration of 4×10^{-3} M was used at these pH values.

The effect of temperature on the two waves was investigated using phosphate buffer of pH 6.42 as supporting electrolyte. As indicated in Table 1, the height of the first wave increased about + 2.6 % per degree, whereas that of the second wave was practically independent of the temperature.

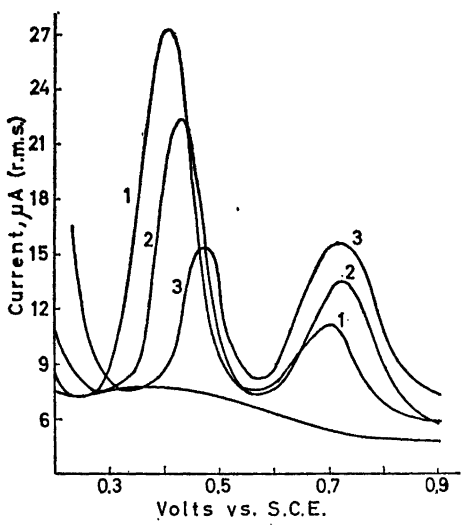

Fig. 1. A. C. polarograms of 4×10^{-3} M copper and 10^{-2} M DTPA in 0.1 M phosphate buffer of pH 6.42 (curve 1), pH 7.10 (curve 2), and pH 8.08 (curve 3).

Table 1. Effect of temperature on the height of the waves of 6×10^{-3} M Cu and 10^{-2} M DTPA in phosphate buffer of pH 6.42.

Temperature °C	First wave μA r.m.s.	Second wave μA r.m.s.
25	27.3	9.9
30	31.5	9.9
35	35.4	9.9
40	40.8	9.9

The effect of the drop time was investigated by measuring the height of the two waves at different heights of the mercury column. The height of the first wave appeared to be independent of the height of the column. The height of the second wave, however, increased linearly with the height of mercury. As indicated in Table 2 the height of the second wave increases about 40 % upon increasing the mercury head from 20 to 60 cm above the capillary.

Table 2. Effect of the height of the mercury column on the height of the second wave of copper in phosphate buffer at pH 6.42 and 10^{-2} M DTPA present. The current was measured half way through the drop and corrected for the base current.

h cm	4×10^{-3} M Cu i_s, μA	6×10^{-3} M Cu i_s, μA	8×10^{-3} M Cu i_s, μA
20	4.05	7.05	10.10
30	4.89	8.10	11.50
40	5.40	9.12	12.85
50	5.91	10.10	14.25
60	6.36	11.00	15.45

The summit potentials and the height of the two waves were not affected by the excess of DTPA. The summit potentials were also independent of the concentration of copper within a certain concentration range. At pH 6.42 this range was 5×10^{-4} to 1.5×10^{-3} M. Upon a further increase in the copper concentration, the summit potentials were shifted slightly to more negative values (Table 3). As indicated in Fig. 2 the height of the two waves increased proportionally to the concentration of copper. The constant i_s/C, where i_s is the current at the summitpotential, had, however, a different value at copper concentrations below and above 2×10^{-3} M.

DISCUSSION

The experimental results indicate that the overall reduction process of the copper-DTPA complex proceeds through two reaction paths with different degrees of reversibility in solutions of pH > 5. One reaction proceeds at the clean electrode surface and the other one at the electrode surface covered with the adsorbed reduction product.

Table 3. Summit potentials of the copper-DTPA complex obtained from 0.1 M phosphate buffer at pH 6.42 and 10^{-2} M DTPA present.

Conc. of Cu mmole	First wave, volts *vs.* S.C.E.	Second wave, volts *vs.* S.C.E.
0.5	−0.38	−0.68
1.0	−0.38	−0.68
1.5	−0.38	−0.68
2.0	−0.39	−0.69
4.0	−0.41	−0.71
6.0	−0.42	−0.72
8.0	−0.43	−0.73

The first reaction path gives rise to the first A. C. peak which is accompanied by a reversible D. C. polarographic step. During this reaction the reduction product is probably adsorbed at the electrode. When the applied potential is increased above a certain value, the depolarizer will penetrate the adsorbed layer as indicated in Table 2. The height of the resulting second A. C. wave increases linearely with increasing height of the mercury column as in the case of "A. C. penetration waves",[2] and indicates that the electron transfer is preceded by a slow reaction.[4] The rate determining step is probably the penetration through the adsorbed film. Hence the height of the second wave is partly controlled by the rate of penetration through the adsorbed layer.

The degree of adsorption and hence the degree of coverage of the mercury drop, increases with increasing pH and concentration of the complex in the bulk of the solution. Above a certain coverage of the mercury surface, the rate of the first electrode reaction is probably also affected as indicated by the nonlinear variation of the height of the wave in the concentration range 1—2 × 10^{-3} M copper reported in Fig. 2.

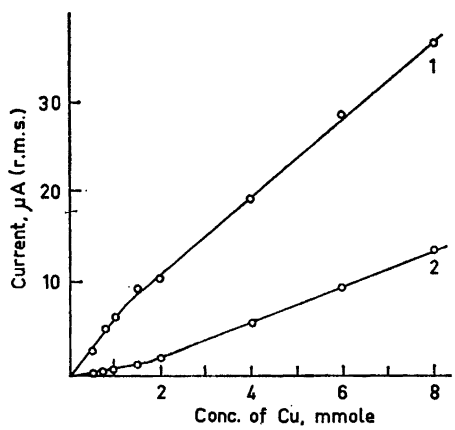

Fig. 2. Peak height of the first (curve 1) and second (curve 2) wave of copper in 0.1 M phosphate buffer of pH 6.42 and 10^{-2} M DTPA present.

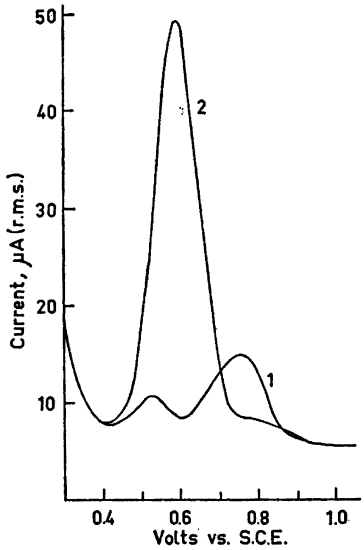

Fig. 3. A. C. polarograms of 4×10^{-3} M copper and 10^{-2} M DTPA at pH 11.2. Supporting electrolyte: 0.1 M potassium nitrate and 0.1 M phosphate buffer (curve 1) and 0.1 M potassium nitrate and 3 M ammonia (curve 2).

According to Kirson and Citron [5] the copper-EDTA complex exists as a polymer in solution. Upon addition of ammonia to the solution the polymer is disrupted into single $[Cu(NH_3)_2\ EDTA]^{2-}$ units.[6] A similiar polymer and single mixed ligand units are probably formed also in copper-DTPA solution. When ammonia was added to the supporting electrolyte, the height of the first wave increased, whereas that of the second one decreased and in the presence of 3 M ammonia the second penetration wave was almost completely suppressed. As indicated in Fig. 3 the height of the first wave obtained from 3 M ammonia is several times greater than that one obtained from a phosphate buffer with the same pH. The summit potential is shifted to more negative values in the presence of ammonia, indicating the formation of a more stable mixed ligand complex. These experiments indicate that the complex exists as a polymer in acetate and phosphate buffers and that the polymer is responsible for the surface-active behaviour of the copper-DTPA complex. In the presence of ammonia the polymer is disrupted into less surface-active single mixed ligand units which are reversibly reduced at the d.m.e.

The great temperature coefficient of the first wave reported in Table 1 is probably due to partly disruption of the polymer into single and less surface-active units with increasing temperature.

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