ACTA CHEMICA SCANDINAVICA 19 (1965) 2291–2297

Polarography of Copper(II)EGTA Complexes at the Dropping Mercury Electrode

EINAR JACOBSEN and EIVIND SÆTRE

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Oslo 3, Norway

The polarographic behaviour of copper-EGTA complexes has been investigated. In the presence of excess EGTA, two reduction waves are obtained. The effect of pH, temperature, and drop time on the two waves has been studied in detail. The first wave is due to a reversible reduction of copper to the amalgam, and the second wave is assumed to be the result of an inhibited electrode reaction, the inhibition being caused by deposition of the reduction product at the mercury surface. When the applied potential is increased above -0.52 V *vs.* S.C.E., the film is desorbed and the current rises to a diffusion controlled value. The diffusion coefficient of the total wave, $I = 2.65$, is constant independent of pH of the supporting electrolyte. Polarograms recorded in presence of cationic and anionic surface-active substances indicate that a binuclear complex is formed in solutions with copper/EGTA ratios equal to or greater than 2:1. Polarograms of this complex exhibit only one wave.

The complex formation between copper and ethyleneglycol-bis (β-aminoethylether) tetraacetic acid (EGTA) has previously been investigated by various methods and the stability constant of the 1:1 complex has been determined.[1–3] Frausto da Silva *et al.*[4] who studied the complex formation by spectrophotometric and potentiometric methods, claim that a binuclear complex exists at low concentrations of the complexing agent. The polarographic behaviour of copper in presence of excess EGTA has recently been investigated by Schröder.[5] He claims that polarograms of the complex exhibit two reduction waves. The first wave is due to a reversible diffusion controlled reduction of the complex and he suggests that the second wave is due to a slow dissociation of a polarographic inactive polymer into a reducible monomer. Unfortunately, most of the experiments were performed in unbuffered solutions and because hydrogen ions are consumed in the electrode reaction, the pH of the solution in the vicinity of the electrode increases during the electrolysis. Hence, the lack of a suitable buffer resulted in drawn out waves in acidic medium and the effect of temperature and drop time on the second wave could not be measured with any degree of accuracy. The author could therefore not get experimental evidence for the assumption of a slow dissociation of a polymer and the resulting kinetic nature of the second wave.

The present work was carried out in order to redetermine the polarographic behaviour of copper in presence of excess EGTA and to ascertain the existence of a binuclear complex by polarographic methods.

EXPERIMENTAL

Materials. Ethyleneglycol-bis (β-aminoethylether) tetraacetic acid was obtained from Fluka AG, Switzerland. The purity of the product was checked by infra-red analysis. A 0.1 M stock solution was prepared by dissolving 38.036 g EGTA and 8.0 g sodium hydroxide in distilled water and diluting to 1 litre. The titer was checked by complexometric titration of a standard copper(II) solution. Standard copper(II) solution was prepared by dissolving a weighed amount of electrolytic copper in nitric acid. Part of the excess acid was evaporated and the residue diluted to appropriate volume. The remaining chemicals were of reagent grade quality and they were used without further purification. 0.1 M potassium nitrate together with 0.2 M acetate, phosphate, or ammonia buffers were used as supporting electrolytes. The pH of the electrolytes was adjusted to desired value by adding hydrochloric acid or potassium hydroxide and its pH checked with a Beckman Zeromatic pH meter. Dodecylamine perchlorate (Armeen) and sodium dodecylsulphate (SDS) were used as surface-active agents in some experiments. Solutions of these substances were prepared as described previously.[6]

Apparatus. Polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany). The conventional types dropping mercury electrodes and of electrolysis cell were used. The capillary characteristics, measured in 0.1 M potassium nitrate (open circuit) at a mercury height of 51.6 cm, were $m = 3.008$ mg/sec and $t = 3.14$ sec. An external saturated calomel electrode (S.C.E.) connected to the cell by means of an agar bridge, served as reference electrode. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis. All experiments were performed at 25 ± 0.1°C. Half-wave potentials were determined by manual operation of the polarograph, measuring the applied potential with a Hartman and Braun (No. 10018) potentiometer. Half-wave potentials of the reversible waves were taken from the logarithmic plots and were reproducible to ± 2 mV.

RESULTS

Preliminary experiments showed that the copper-EGTA complex produces two reduction waves at all pH values in the region 2—12. A maximum was observed on the first wave on polarograms recorded from solutions with pH less than 6. The maximum was easily suppressed by small amounts of Armeen. The possible distorting effect of this surface-active agent on the polarograms was studied at pH 6. The experiments showed that the height of the two waves and the half-wave potential af the first wave were not effected by the presence of 10^{-3} % Armeen. The half-wave potential of the second wave, however, was shifted to more positive values by the presence of this surfactant. Thus, upon addition of 6×10^{-4} % Armeen to the supporting electrolyte, the half-wave potential of the second wave shifted from -0.52 to -0.41 V *vs.* S.C.E. Other surface active substances tested (SDS, Triton X-100) had a very great distorting effect on both waves. In the following experiments 0.0004 % Armeen was added to solutions with pH less than 4 and 0.0002 % Armeen to solutions in the pH range 4—6.

The effect of pH on the cathodic waves of copper in the presence of excess EGTA was investigated using acetate, phosphate, and ammonia buffers as supporting electrolytes. An increase in pH of the electrolyte resulted in an increase in the height of the second wave at the expense of the first one, the total limiting current remaining constant. The result is shown in Fig. 1.

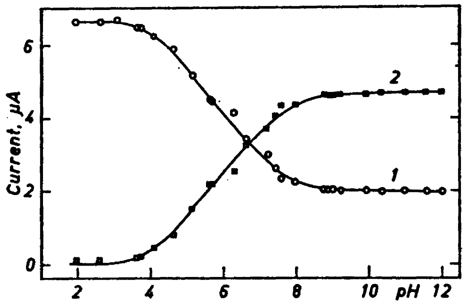

Fig. 1. Limiting currents of the first (1) and second (2) wave of 10^{-3} M copper and 10^{-2} M EGTA at various pH values.

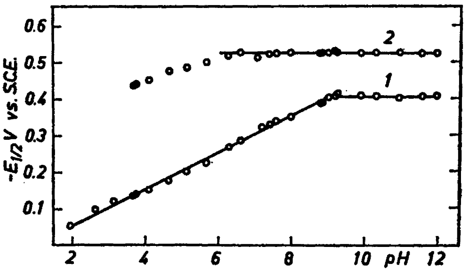

Fig. 2. Half-wave potentials of the first (1) and second (2) wave of 10^{-3} M copper and 10^{-2} M EGTA at various pH values.

The half-wave potential of the first wave was shifted to more negative potentials with increasing pH of the supporting electrolyte as indicated in Fig. 2. The half-wave potential of the second wave was practically constant = -0.52 V *vs.* S.C.E. at all pH values. The apparent shift in the half-wave potential to more positive values in solutions with pH less than 6 is due to the presence of Armeen in these solutions and will be discussed below.

The reversibility of the electrode reactions was tested by plotting log $i/(i_d - i)$ *vs.* the potential. The plots yield straight lines at all pH values for the first wave, and the slopes of the lines (-0.032 to -0.035 V/log unit) indicate a reversible 2-electron reduction of copper to the amalgam. The temperature dependence of the half-wave potential was linear (Table 1). The temperature coefficient of the half-wave potential, -0.4 mV/degree, is of the proper sign and magnitude for that of a reversible process. The half-wave potential

Table 1. Effect of temperature. 10^{-3} M copper and 10^{-2} M EGTA in 0.2 M phosphate buffer with pH = 6.00. No surface-active agent present.

Temp. °C	First wave		Second wave	
	$-E_{\frac{1}{2}}$, V	Current, μA	$-E_{\frac{1}{2}}$, V	Current, μA
25	0.244	4.05	0.52	2.60
30	0.246	4.60	0.52	2.45
35	0.248	5.20	0.51	2.25
40	0.250	5.85	0.51	2.05
45	0.252	6.50	0.52	1.90

shifted to more negative values with an increasing concentration of EGTA, and the plot of the values of $E_{\frac{1}{2}}$ *vs.* the corresponding values of log C_x, resulted in straight lines. The slope of the lines indicated that only one ligand is coordinated in the complex.

The second wave showed an irreversible reduction. The plot of log $i/(i_d - i)$ *vs.* the potential yield curved lines at all pH values. The half-wave potential of this wave, taking $E_{\frac{1}{2}}$ as the point on the curve where $i = i_d/2$, was constant, -0.52 V *vs.* S.C.E., independent of the temperature (Table 1) and the excess of EGTA present.

The effect of temperature on the height of the two waves was investigated in phosphate buffer of pH 6.0. At this pH value the two waves are very well separated and no maximum occurs on the waves. The result, which is reported in Table 1, showed that the height of the first wave increased about 3 % per degree with increasing temperature, whereas the height of the second wave decreased about 1.5 % per degree in the same temperature range. The total wave increased +1.3 % per degree, indicating that the limiting current of the total wave is diffusion controlled.

The diffusion current constant was determined by measuring the limiting current of various amounts of copper in the presence of 10^{-2} M EGTA. At a given pH value the height of both waves increased proportionally to the concentration of copper. The limiting current of the *total wave* was independent of pH and the diffusion current constant $I = 2.65$. Comparison of this value with the diffusion current constants of the copper-EDTA complex,[7] $I = 2.85$, and of the copper-DTPA complex,[8] $I = 2.42$, indicates that the total wave is caused by a two-electron reduction of copper to the amalgam.

The effect of drop time was investigated by recording polarograms of 10^{-3} M copper and 10^{-2} EGTA in phosphate buffer of pH 6.0 at various heights of the mercury column. The height of the first wave increased with the height of mercury; the value $i/\sqrt{h}$, where h is the height of the column after correction for the "backpressure", was constant, indicating that the electrode reaction is diffusion controlled (Table 2). The height of the second wave was found to increase proportionally to the height of mercury, indicating that an absorption takes place at the electrode and that the current is controlled by the rate of penetration of the complex through an adsorbed film.[8,9]

Table 2. Effect of pressure of mercury. 10^{-3} M copper and 10^{-2} M EGTA in 0.2 M phosphate buffer with pH = 6.00. No surface-active agent present.

h, cm	First wave		Second wave	
	i_d, μA	$i_d/\sqrt{h}$	i, μA	i/h
39.2	3.65	0.58	2.05	0.052
44.2	3.95	0.59	2.35	0.053
49.2	4.05	0.58	2.60	0.053
54.2	4.35	0.59	2.85	0.053
59.2	4.55	0.59	3.10	0.052

In order to verify the existence of the binuclear complex reported by Frausto da Silva *et al.*,[4] a few polarograms were recorded from solutions with excess copper. A 0.2 M acetate buffer with pH = 4.65 was used as supporting electrolyte and 0.0004 % Armeen was added as maximum suppressor. The diffusion current of simple copper ions decreased upon addition of small amounts of EGTA and a new wave appeared at more negative potentials. Polarograms recorded from solutions with a copper/EGTA ratio 2:1 showed only the new wave with a half-wave potential about 0.1 V more negative than that of copper ions in the same medium (Table 3). In order to ascertain that this wave is due to reduction of a copper complex, the experiments were repeated in the presence of the surface-active substance SDS. Earlier experiments in this laboratory[6,10] showed that the waves of negatively charged copper complexes are seriously distorted in the presence of SDS, whereas the waves due to reduction of uncomplexed copper are practically unaffected by even large amounts of this substance. As indicated in Fig. 3, the first wave on

Table 3. Half-wave potentials and limiting currents of 10^{-3} M copper in the presence of various amounts of EGTA. Polarograms recorded from 0.2 M acetate buffer with pH 4.65. 0.0004 % Armeen was added as maximum suppressor.

Conc. EGTA	Cu/EGTA Molar ratio	$-E_{\frac{1}{2}}$ V *vs.* S.C.E.	Limiting current, μA
0	1:0	0.017	7.85
2.5×10^{-4}	4:1	0.02, 0.11	7.2
5×10^{-4}	2:1	0.10	6.9
10^{-3}	1:1	0.14	6.8
10^{-2}	1:10	0.17	6.8

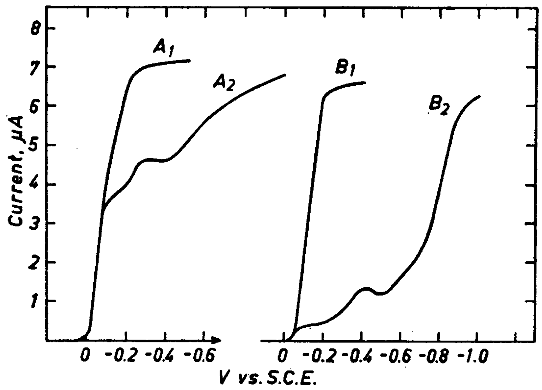

Fig. 3. Polarograms of copper-EGTA mixtures in 0.2 M acetate buffer with pH 4.65. Copper/EGTA ratio = 4:1 (curves A) and 2:1 (curves B). Curves A_1 and B_1 recorded in presence of 0.0004 % Armeen and the curves A_2 and B_2 recorded in the presence of 0.008 % SDS.

polarograms recorded from a solution with copper/EGTA ratio 4:1 is not affected by the presence of 0.008 % SDS and the half-wave potential (—0.02 V *vs.* S.C.E.) coincides with that of uncomplexed copper in the same medium. The second wave is seriously distorted in the presence of SDS, indicating complex formation of about one half of the copper content in this mixture. Polarograms of solutions with a copper/EGTA ratio 2:1 were completely distorted by the presence of SDS. These experiments indicate that a negatively charged complex is formed when copper and EGTA are mixed in the ratio 2:1 and that practically no uncomplexed copper is left in the solution.

DISCUSSION

It is evident from the experimental data that the first wave on polarograms recorded from solutions with excess EGTA is due to a reversible, diffusion controlled reduction of the mononuclear copper-EGTA complex. The observed half-wave potentials are linear functions of the pH in the regions 3—9 and 9—12. The slopes of the curves are —0.058 and 0 V/pH unit, respectively, indicating that the following reactions take place at the electrode

$$\mathrm{CuY^{2-} + 2H^+ + 2e^- \xrightarrow{pH\ 3-9} Cu(Hg) + H_2Y^{2-}}$$

$$\mathrm{CuY^{2-} + 2e^- \xrightarrow{pH\ 9-12} Cu(Hg) + Y^{4-}}$$

where H_4Y represents EGTA.

The non-linear variation of the half-wave potential with pH previously reported in the literature,[5] is probably due to the lack of a suitable buffer in these experiments.

The effect of the drop time on the height of the second wave shows that this wave is the result of an absorption on the electrode. The current is obviously not controlled by any kinetic reaction occurring in the bulk of the solution as previously suggested.[5] The diffusion current constant and the temperature dependence of the limiting current of the total wave indicate that both waves are due to reduction of copper in the complex to the amalgam. The splitting of the wave is therefore assumed to be the result of an inhibited electrode reaction. The EGTA liberated at the electrode during the electrolysis is probably surface-active and accumulates on the electrode surface during the life of a drop. When the drop is completely covered, the electrode reaction is inhibited until the desorption potential of EGTA is reached. When the applied potential is increased above this value (—0.52 V *vs.* S.C.E.) the EGTA film is desorbed and the current rises to its original value.

The height of the second wave increases with increasing pH and indicates that EGTA is less surface-active in acidic medium. The degree of absorption, and hence the degree of inhibition, decreases with increasing temperature and explains the great positive temperature coefficient of the first wave and the negative temperature coefficient of the second wave.

The desorption potential of EGTA and hence the half-wave potential of the second wave is constant, —0.52 V *vs.* S.C.E., independent of pH of the electrolyte, but it is shifted to more positive potentials by the presence of Armeen. These experiments indicate that Armeen is more strongly absorbed on the mercury surface and thus partly prevents the absorption of EGTA. The same effect of the cationic substance Armeen has previously been reported for copper-DTPA complexes.[6]

REFERENCES

1. Holleck, L. and Liebold, G. *Naturwiss.* **44** (1957) 582.
2. Holloway, J. H. and Reilley, C. N. *Anal. Chem.* **32** (1960) 249.
3. Ringbom, A. and Saariaho, E. *Complexation in Analytical Chemistry,* Interscience Publ., London 1963, p. 334.
4. Frausto da Silva, J. J. R. and Calado, J. G. *Rev. Port. Quim.* **5** (1963) 121.
5. Schrøder, K. H. *Acta Chem. Scand.* **17** (1963) 1087.
6. Jacobsen, E. and Kalland, G. *Anal. Chim. Acta* **30** (1964) 240.
7. Pecsok, R. L. *Anal. Chem.* **25** (1953) 561.
8. Jacobsen, E. and Kalland, G. *Talanta* **11** (1964) 139.
9. Biegler, T. *J. Electroanal. Chem.* **4** (1962) 317.
10. Kalland, G. and Jacobsen, E. *Acta Chem. Scand.* **18** (1964) 1412.

Received August 27, 1965.