

## A Polarographic Study of the Interaction between Copper(II) and Ethyleneglycol-bis( $\beta$ -aminoethylether)N,N,N',N'-tetraacetic Acid

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EGTA forms 1:1 complexes with divalent copper. In neutral and alkaline solutions, two polarographic reduction waves appear. The first is due to reversible and diffusion controlled reduction of the complex. The second wave seems to be due to a slow dissociation of a not reducible polymer to a reducible monomer. An equilibrium between six- and four-coordination of the divalent copper is discussed. The polymerization could result from bonds between neighbouring mononuclear complexes on increase of the coordination of number of copper from four to six.

Ethyleneglycol-bis( $\beta$ -aminoethylether) N,N,N',N'-tetraacetic acid (EGTA) has gained increasing interest in the last few years as a reagent in complexometric analyses. The nature of the complexes and the stability constants have been studied by pH and potentiometric methods<sup>1-2</sup>. The great difference between the stability of the calcium and the magnesium complexes has been utilized for simultaneous determinations of the metals<sup>3-8</sup>. Since many of the metal complexes are coloured, they have been used in colourimetric determinations<sup>9-13</sup>. A polarographic study of the complexes has not been performed, but half-wave potentials are often used to characterize the chelating power of new complexones, and polarography is recommended for the qualitative analysis of complexone mixtures<sup>14-15</sup>. The present paper deals with the polarographic behaviour of the copper(II)-EGTA compounds.

### EXPERIMENTAL

*Apparatus and technique.* The Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany), was used to record the d.c. polarograms. These were recorded in the conventional way without use of the tast technique. The conventional type of dropping mercury

\* The first part of the work has been performed at University of Oslo, Department of Chemistry A, Blindern, Norway. I am indebted to Professor Haakon Haraldsen for the facilities placed at my disposal.

electrode was used. An external saturated calomel electrode (S.C.E.) served as reference electrode, and was connected to the cell with an agar-KCl bridge. The total a.c. resistance of the cell, agar bridge and reference electrode was measured to 780  $\Omega$ . The temperature of the solutions was kept within  $\pm 0.1^\circ\text{C}$  and all the experiments were performed at  $25.0^\circ\text{C}$  (except in the temperature studies). Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 5 min and passing it over the solution during the electrolysis. The a.c. polarograms were recorded with Cambridge Univector a.c. polarograph, Krizik polaroscope P-570, and Davis Cathode Ray Polarograph A-1660. The potentials were measured *vs.* mercury pool.

The  $\log i/(i_d - i)$  *vs.* the potentials were measured by manual operations. An external potentiometer (Leeds and Northrup type K) was used for these measurements. The amperometer on the polarograph functioned as zero-point indicator. The slopes were determined and the interpolated potentials with zero log plots were taken to be the half-wave potentials. For some badly defined polarographic waves, the (approximate) half-wave potentials (measured with the external potentiometer), were taken to be the potentials at the points on the polarograms where  $i = \frac{1}{2}i_d$ .

The mercury height was corrected for the "back pressure". This height was measured from the top of the capillary. The "back pressure" for the capillary was determined by plotting different mercury heights *vs.* the inverse droptime, and extrapolate to  $1/t = 0$ . The experiments were performed in 0.1 M  $\text{NH}_3 - \text{NH}_4\text{Cl}$  buffer at open circuit.

*Materials.* *Purum p.a.* ethyleneglycol-bis( $\beta$ -aminoethylether) N,N,N',N'-tetraacetic acid was obtained from Fluka A.G., Switzerland. Stock solutions were made by dissolving a known amount of the reagent in redistilled water. To increase the solubility, NaOH (*p.a.*) was added to pH about 6. Stock solutions of copper(II) were made by dissolving a known amount of *p.a.* metallic copper in nitric acid, and diluting. Different supporting electrolytes were used. All the chemicals were of reagent grade.

## RESULTS

Preliminary investigations at different pH showed that EGTA was not reduced at the dropping mercury electrode before the reduction of the supporting electrolyte. In alkaline medium a maximum appeared at the potential where oxidation of mercury takes place. There seems to be a connection between the maximum and the presence of a mercury-EGTA complex; this point is being investigated further. The maximum could be avoided by using a start potential of  $-0.2$  V (S.C.E.), where no mercury is oxidized and no complex is formed. No maxima were observed on the copper waves. Consequently no maximum suppressors were used.

*Choice of supporting electrolyte.* Most of the experiments were performed in  $\text{NH}_3 - \text{HClO}_4$  media. No complex between the copper ions and the supporting electrolytes were formed, as identical polarograms were obtained, at equal pH, from solutions containing other supporting electrolytes ( $\text{KNO}_3$ , HCl, KOH). To find the effect of ionic strength and buffer concentration, some polarograms were recorded in  $\text{NH}_3 - \text{NH}_4\text{Cl}$  buffer of different concentrations. As with the other supporting electrolytes, double waves appeared. A slight increase of the buffer concentration did not affect the polarographic waves, but at very high concentrations, an ammonia complex or mixed complex with ammonia is formed.

*pH studies.* Fig. 1 shows the effect of pH-variations. With the most acid solutions, only one wave appeared, but above  $\text{pH} = 4$ , the wave is split up into a double wave. The half-wave potentials and diffusion current of the two waves at different pH are shown in Table 1. As seen in the figure both waves are very well defined, but for the most alkaline solutions the waves are not

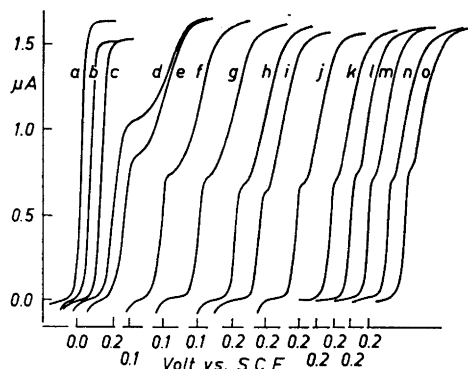


Fig. 1. Polarograms of  $2.40 \times 10^{-4}$  M  $\text{Cu}^{2+}$  and  $2.83 \times 10^{-3}$  M EGTA in 0.1 M  $\text{HClO}_4$ .  $\text{NH}_3$  is added to change pH. (a, pH = 1.20, b, pH = 2.10, c, pH = 3.60, d, pH = 4.65, e, pH = 5.25, f, pH = 5.85, g, pH = 6.25, h, pH = 7.00, i, pH = 7.65, j, pH = 7.90, k, pH = 8.10, l, pH = 8.60, m, pH = 8.70, n, pH = 8.95, o, pH = 9.20).

well separated and the values given for the potentials and currents are therefore approximate. The  $\log i/(i_d - i)$  vs.  $-E$  were calculated from the polarograms. For the second waves the slopes are of the order of magnitude 100 mV/log unit; for the first ones, slopes are indicated in the table. The half-wave potentials of the two waves vs. pH are plotted in Fig. 2.

The temperature has a pronounced effect on the waves. For each solution at different pH, temperature studies were performed from 25 to 40°C. Independent of pH, the first wave increased markedly with increasing temperature while the second decreased. The total sum increased. Some typical curves at pH 4.65 are shown in Fig. 3.

Table 1. Half-wave potentials and diffusion current at different pH.  $\alpha$  indicates the log-slope of the first wave.

$2.40 \times 10^{-4}$  M  $\text{Cu}^{2+}$ , 0.1 M  $\text{HClO}_4$ ,  $\text{NH}_3$  added to change pH.  
Temp. 25°C. ( $m^2/s, t^2/s = 2.590$  measured at  $-0.7$  V (SCE). pH = 9.20).

pH	First wave			Second wave	
	$-E_{1/2}$	$i_d(\mu\text{A})$	$\alpha$ (mV)	$-E_{1/2}$	$i_d(\mu\text{A})$
1.20				**	
2.10	+ 0.006	1.63	33	**	
3.60	0.040	1.53	32	**	
4.65	0.111	1.54	34	**	
5.25	0.175	1.06	58	0.491	0.57
5.85	0.226	0.88	56	0.500	0.75
6.25	0.242	0.83	50	0.49	0.82
7.00	0.256	0.75	44	0.49	0.84
7.65	0.287	0.74	39	0.50	0.84
7.90	0.313	0.72	38	0.49	0.86
8.10	0.334	0.70	30	0.50	0.86
8.60	0.335	0.81	*	0.51	0.76
8.70	0.365	0.79	*	0.52	0.78
8.95	0.372	0.82	*	0.52	0.75
9.20	0.386	0.84	36	0.52	0.68
	0.397	0.99	45	0.52	0.60

\* not recorded. \*\* single wave.

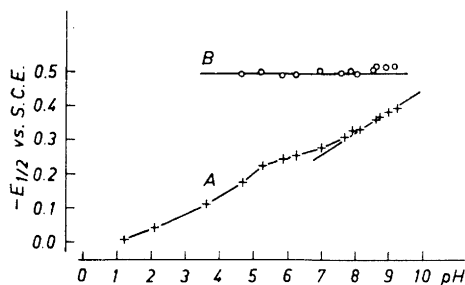


Fig. 2. Plots of half-wave potentials of  $2.40 \times 10^{-4}$  M  $\text{Cu}^{2+}$  in  $2.83 \times 10^{-3}$  M EGTA vs. pH. (A = first step, B = second step).

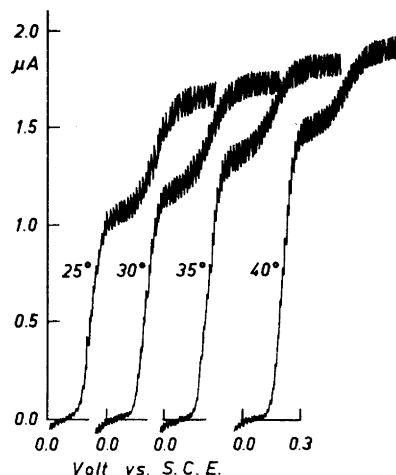


Fig. 3. Polarograms of  $2.40 \times 10^{-4}$  M  $\text{Cu}^{2+}$  in  $2.83 \times 10^{-3}$  M EGTA, pH = 4.65, at different temperatures.

Variation of the concentration of copper(II)-ions from  $4.8 \times 10^{-5}$  to  $2.0 \times 10^{-3}$  M showed that the ratio of the diffusion current of the two waves was constant, and that the currents were both proportional to the concentration of copper.

Polarograms recorded with constant concentration of copper and different amounts of EGTA indicate that the nature of the two waves is independent of the concentration of the reagent. The ratio of the two wave-heights was approximately constant, but the half-wave potentials shifted to more negative values with increasing concentration of EGTA. The shifts were about  $-30$  mV for both waves on ten-fold increase in concentration.

Increase of the height of the mercury reservoir increased both waves at all pH where double waves appeared. The first wave-height was approximately proportional to the square root of the mercury height (corrected for the "back pressure"), but the second one could not be measured exactly enough to find the dependence on the mercury height. The reduction which corresponds to the first wave is therefore assumed to be diffusion controlled. The second will be explained later.

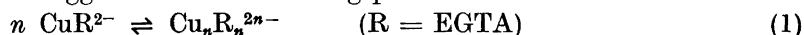
Electrocapillary curves were plotted for solutions with and without copper and in different supporting electrolytes. The diagrams were all of the same shape with maxima at about  $-0.5$  V (S.C.E.) and all without inflections due to adsorption on the mercury surface.

#### DISCUSSION

The copper complexes studied here are reduced to give two waves except in the most acid solutions, and this is independent of the supporting electrolyte. The reductions could be from  $\text{Cu(II)}$  to  $\text{Cu(I)}$  and then to amalgam, but

because the ratio of the two waves is not unity and is very dependent of temperature, two waves due to reductions in two steps seem improbable, and the author believes that the copper(II)-compounds are directly reduced to amalgam. The first wave would then be due to reduction of a normal Cu-(EGTA)-complex. From Fig. 2 is seen that the half-wave potential of the first wave is shifted to more negative values with increasing pH, while the second is approximately constant. As the EGTA is protonized to varying degrees dependent of pH, protons will be involved in the electrode reaction and this will explain the shifts in the half-wave potential with increasing pH.

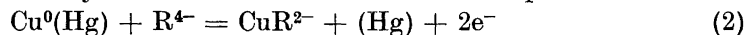
It is earlier reported<sup>1</sup> that EGTA forms 1:1 complexes with divalent copper, and the author suggest that the following products are formed:



The polymer is in slow equilibrium with the monomer, and because of steric hindrance or other reasons the reduction of the polymer does not occur before reduction of the supporting electrolyte. (There might also be two isomers in equilibrium ( $n = 1$ )). The second wave is probably due to a current caused by a slow dissociation to the monomer and reduction of the latter. The second wave is not due to reduction of complexes containing hydrogen or hydroxyl ions, or compounds with the mole ratio metal to ligand different from unity, because change in pH and concentration of metal and ligand had no influence on the ratio of the height of the two waves. With increasing temperature the equilibrium of eqn. 1 is assumed to be shifted to the left, which explains the increase of the first wave.

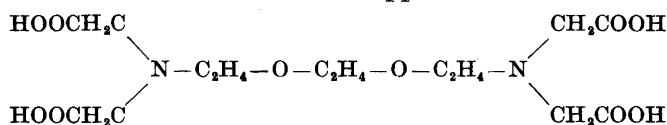
The first wave is due to a reversible and diffusion controlled reduction, and the second one results from an irreversible process which is probably controlled by eqn. 1.

The current controlling factor was tested, by changing the height of the mercury reservoir. The reversibility was studied through the temperature dependence of the half-wave potentials and the slopes of  $\log i/(i-i_a)$  vs.  $E$ . With the Atlas d.c. polarograph, the reversibility tests were inconclusive (some of the plots from Table 1 deviate from the values for  $n = 2$ ), and therefore the reversibility was also checked with a.c. instruments. The Cambridge Univector a.c. polarograph gave polarograms with two peaks, the second one was very small, indicating irreversibility. The Czech Krizik polaroscope "P-570" gave irregular oscillograms which was probably due to a surface effect. With the Davis Cathode Ray Polarograph A 1660, two peaks appeared with a start potential of  $-0.2$  V (vs. Hg-pool), corresponding to the two waves found in the d.c. polarography. With reversed sweeps, starting at  $-1.0$  V, only one peak was formed and at exactly the same potential as for the first peak of the forward recording. This is proof of the reversibility of the reduction corresponding to the first wave and irreversibility of the second wave. For reversed sweeps the amalgam formed prior to the electrolysis probably is oxidized to the monomer complex when EGTA is present:



and the polymerization will not be a current controlling process. (In the reaction above, protons and  $\text{HR}^{3-}$  etc. are involved, but omitted in eqn. 2 for convenience).

EGTA is maximum octadentate as appears from its formula:



Schwarzenbach and co-workers<sup>1</sup> found that the ether oxygen atoms could take part in complex formation. Copper(II) usually forms four-coordinated  $dsp^2$  bonds. For polydentate ligands, *e.g.* ethylenediaminetetraacetic acid, the excess of bonding groups is assumed not to take part in the four-coordinate bonds. Very careful examination of polarograms of copper(II)-EDTA solutions, however, shows a slight irregularity on the last part of the wave, which possibly is due to polymerization. With increasing polydentity, the excess bonding groups could bring about six-coordination of copper. Another possibility then arises. The two new coordination sites need not be occupied by the already four-coordinating ligand molecule, but at least one bond could be from a free donor site of another complex. This could be a possible reason for the polymerization. The difference between EDTA-complexes of copper and the corresponding EGTA complexes may be due to the presence of the new (ether) coordination sites, or to steric factors, *e.g.* the difference in distance between the two nitrogen atoms. For complexes with ligands having one less coordination site, *e.g.* N-hydroxyethylethylenediaminetriacetic acid, where the hydroxyethyl-oxygen bond to copper(II) is very weak, polarographic studies<sup>16</sup> show no irregularity, which may be due to the fact that copper is only four-coordinated and no polymerization occurs. With six-coordinated metal complexes of EDTA, the polarographic reductions to amalgams are irreversible, and this might be so also in the case of six-coordinated complexes of divalent copper with EGTA.

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