

Polarography of the Binuclear Copper-diethylenetriaminepentaacetic Acid Complex

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A binuclear copper(II)-DTPA complex is formed in solutions with metal/ligand ratio 2:1. The complex is reduced in two well-defined steps at the dropping mercury electrode. The first step is due to reduction of one half of the copper content to the amalgam. The second wave on the polarogram is due to a nearly reversible 2-electron reduction of copper in the mononuclear complex formed during the electrolysis.

Diethylenetriaminepentaacetic acid (DTPA) forms stable 1:1 complexes with certain metals. The composition and stability of several of these complexes have been determined by spectrophotometric and potentiometric methods.¹⁻⁴ Anderegg *et al.*¹ and Chaberek *et al.*² claim, in contrast to Durham and Ryskiewich³ that binuclear complexes of the type M_2 DTPA are formed in solutions with a metal/ligand ratio of 2:1. Recently we investigated the polarographic behaviour of the mononuclear copper-DTPA complex.⁵ The present work was carried out in order to verify the existence of a Cu_2 DTPA complex and to investigate the polarographic behaviour of the complex.

EXPERIMENTAL

Materials. Diethylenetriaminepentaacetic acid was obtained from Geigy Chemical Corp., New York. Stock solutions of DTPA and copper(II) were prepared and standardized as described previously.⁵ Dodecylammonium perchlorate (Armeen) and sodium dodecyl sulphate (SDS) were used as surface-active agents. The preparation of stock solutions of these substances has been described elsewhere.⁶

Apparatus. Polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany). The conventional types of dropping mercury electrode and of electrolysis cell were used. The capillary characteristics, measured in 0.1 M potassium nitrate (open circuit) at a mercury height of 52.4 cm, were $m = 2.998$ mg/sec and $t = 3.52$ sec. An external saturated calomel electrode (S. C. E.) 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 solutions during the electrolysis. All experiments were performed at $25 \pm 0.1^\circ C$. Half-wave potentials were determined by manual operation of the polarograph, measuring the applied potential with a Hartman and Braun (No. 10018) potentiometer.

RESULTS

Copper (II) and DTPA were mixed in various ratios in 0.2 M acetate buffer with pH 4.6 and polarograms recorded. In the absence of surface active agents, a maximum was observed on the polarograms. Preliminary experiments showed that the maximum is easily suppressed by addition of 0.004 % Armeen to the supporting electrolyte.

The diffusion current of simple copper ions decreased upon addition of small amounts of DTPA to the supporting electrolyte, and a new wave appeared at more negative potentials. Polarograms recorded from solutions with a copper/DTPA ratio 2:1 showed a well-defined double wave and the two waves had exactly the same height. A further increase in the DTPA concentration resulted in an increase in the height of the second wave at the expense of the first one. When the DTPA concentration was equal to or greater than that of copper, only a single wave, corresponding to the reduction of the mononuclear complex,⁵ was observed on the polarograms. A few polarograms of copper in absence and presence of various amounts of DTPA are shown in Fig. 1.

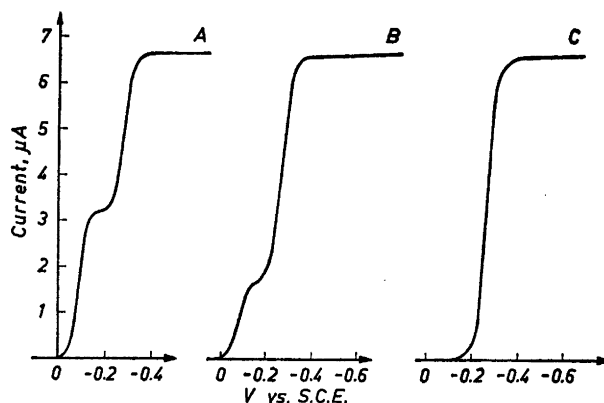


Fig. 1. Polarograms of 10^{-3} M copper in the presence of various amounts of DTPA. 0.2 M acetate buffer with pH 4.6 and 0.004 % Armeen present. Curve A = 5×10^{-4} , B = 7.5×10^{-4} and C = 10^{-3} M DTPA.

The half-wave potential of the first wave (curves A and B in Fig. 1) is only slightly more negative than that of uncomplexed copper in the same buffer. In order to verify whether the first wave is due to reduction of uncomplexed copper or a copper-DTPA complex, polarograms of the same mixtures were recorded in the presence of cationic and anionic surface active substances. Earlier experiments in this laboratory⁶ showed that the wave of uncomplexed copper ions is seriously distorted by the presence of the cationic substance Armeen, whereas the waves due to reduction of negatively charged complexes are practically unaffected by even large amounts of this substance. On the other hand, a well-defined reversible wave of uncomplexed copper is obtained in the presence of the anionic substance SDS, whereas the waves of negatively charged complexes are seriously distorted by small amounts of this substance.

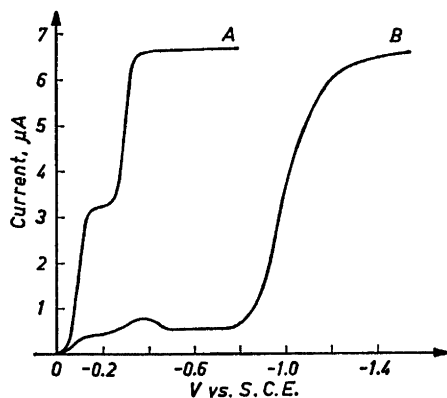


Fig. 2. Polarograms of 10^{-3} M copper and 5×10^{-4} M DTPA recorded in the presence of surface-active substances. Curve A = 0.04 % Armeen, curve B = 0.04 % SDS.

Polarograms recorded from solutions of 10^{-3} M copper and 5×10^{-4} M DTPA in acetate buffer (Fig. 2) showed that the half-wave potentials and the diffusion currents of the two waves are not affected by the presence of 0.04 % Armeen. Both waves are, however, seriously distorted by the presence of small amounts of SDS.

In the presence of 0.04 % SDS both waves are shifted to about -1 V vs. S. C. E. and only a very small wave is left at the potentials where simple copper ions are reduced. These experiments indicate that a negatively charged complex is formed when copper and DTPA are mixed in the ratio 2:1, and that practically no uncomplexed copper is left in the solution.

In order to investigate the electrode reactions of each of the two waves, the following experiments were performed, in which 10^{-3} M copper and 5×10^{-4} M DTPA were mixed in 0.2 M acetate buffer. 0.004 % Armeen was added to each solution in order to suppress the maximum.

The diffusion current of the first and of the second wave was 3.42 and 3.41 μ A, respectively. The height and the ratio of the two waves, compared with the diffusion current of the same amount of copper in the same buffer, but in the absence of DTPA, $i_d = 8.09 \mu$ A, indicate that both waves are due to the reduction of a copper complex. The diffusion current constant of the total wave calculated per mmole copper was $I = 2.66$. This value, compared with the diffusion current constant of the mononuclear copper-DTPA complex ($I = 2.42$), indicates that the two waves involve a two-electron reduction of copper to the amalgam.

The reversibility of the two waves was tested by plotting the curves of $\log i/(i_d - i)$ vs. the applied potential. The points yield straight lines and the slopes indicated a nearly reversible two-electron reduction of copper to the amalgam for both waves. The slight irreversibility is probably due to the lack of excess complexing agent in the solution. The half-wave potentials of the two waves at pH 4.6 were -0.058 and -0.244 V vs. S.C.E., respectively.

The effect of the drop time on the two waves was investigated by recording polarograms at various heights of the mercury column. The height of both waves increased with the height of mercury, and the values i_d/\sqrt{h} , where h

is the height of the column after correction for the "back pressure", were constant, indicating that the electrode reactions are diffusion controlled.

Effect of temperature. In the region 20–50°C the temperature dependence of the diffusion current of both waves was found to be linear. The temperature coefficient of the diffusion current, 1.5 % per degree, is precisely that to be associated with a diffusion-controlled process. The temperature coefficient of the half-wave potential of the first and of the second wave were +0.3 and +0.1 mV per degree, respectively, indicating nearly reversible electrode reactions.

The effect of pH on the half-wave potential of the two waves was investigated using buffers of various pH as supporting electrolytes. The result is plotted in Fig. 3. When pH was increased above 7.5, a precipitate (probably copper hydroxide) was formed, and the measurements were therefore restricted to lower pH values. In the pH range 2.5–5 the half-wave potential of the first wave is shifted 0.026 V/pH unit to more negative values with increasing pH of the electrolyte, indicating that one H⁺ is involved in the reduction. When pH is increased above 5, the half wave potential of the first wave is constant = 0.065 V vs. S.C.E. The half-wave potential of the second wave is shifted 0.060 V/pH unit to more negative potentials in the whole pH range 2.5–7.5, indicating that two H⁺ are involved in this electrode reaction.

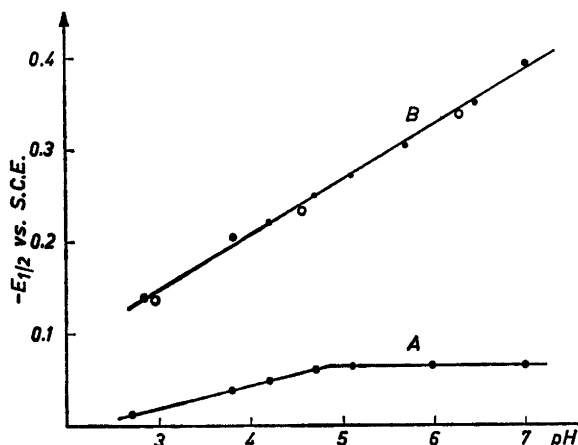


Fig. 3. Effect of pH on the half-wave potential of the first (curve A) and the second wave (curve B) of 10^{-3} M copper and 5×10^{-4} M DTPA. Open circles in curve B represent the half-wave potentials of 10^{-3} M copper and 10^{-3} M DTPA in the same buffers.

Polarograms of mixtures of copper and DTPA in the ratio 1:1 exhibit only a single wave in acid medium. The variation of the half-wave potential of this wave with pH of the electrolyte is also plotted in Fig. 3. As indicated in the figure, the half-wave potential of this wave is also shifted -0.060 V/pH unit to more negative potentials. At a given pH value, the half-wave potential of this 1:1 complex almost coincides with the half-wave potential of the second wave of the binuclear complex.

DISCUSSION

It is evident from the experimental results that a binuclear complex is formed when copper and DTPA are mixed in the ratio 2:1. If the amount of DTPA is increased, a mixture of the binuclear and the more stable mononuclear complex is obtained. When the molar DTPA concentration is equal to or greater than that of copper, only the mononuclear copper-DTPA complex is formed.

The binuclear copper-DTPA complex is reduced in two well-defined steps with equal height at the dropping mercury electrode. Each step corresponds to a two-electron reduction of copper to the amalgam and indicate that one of the copper atoms in the complex is more loosely coordinated, and hence more easily reduced than the other. This is in accordance with the structure of the complex suggested by Chaberek *et al.*², in which one copper atom is coordinated to two nitrogen and two carboxylate groups, whereas the other one is coordinated to only one nitrogen, two carboxylate groups and the fourth coordination site is occupied by water. Thus, when the potential is increased above a certain value, the more loosely bounded copper atom is reduced to the amalgam. At the same time the more stable mononuclear complex is formed. This complex is reduced at more negative potentials causing the second wave on the polarogram.

On the basis of the present results the following electrode reactions are suggested.

In the pH range 2.5–5:

1. wave



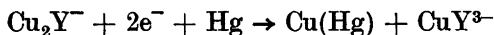
2. wave



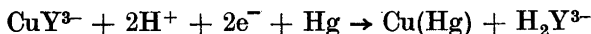
where H_5Y denotes DTPA.

At pH values above 5, the half-wave potential of the first wave is independent of pH and the second wave is shifted 0.060 V/pH unit to more negative potentials, indicating the electrode reactions:

1. wave



2. wave



The electrode reaction of the second wave is identical with that of the mononuclear complex previously reported.⁵

REFERENCES

1. Anderegg, G., Nägeli, P., Müller, F. and Schwarzenbach, G. *Helv. Chim. Acta* **42** (1959) 827.
2. Chaberek, S., Frost, A. E., Doran, M. A., Bicknell, N. J., Vandegaer, J. and Harder, R. *J. Inorg. Nucl. Chem.* **11** (1959) 184.
3. Durham, E. J. and Ryskiewich, D. P. *J. Am. Chem. Soc.* **80** (1958) 4814.
4. Wänninen, E. *Acta Acad. Aboensis, Math. Phys.* **21** (1960) 17.
5. Jacobsen, E. and Kalland, G. *Talanta* **11** (1964) 139.
6. Jacobsen, E. and Kalland, G. *Anal. Chim. Acta.* **30** (1964) 240.

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