

## Polarography of Some Complexes with N-Hydroxyethylethylenediamine-triacetic Acid

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The complexes of copper, cadmium and lead with N-hydroxyethylethylenediamine-triacetic acid have been studied by means of the dropping mercury electrode. The half-wave potentials and the diffusion current constants have been determined. It is found that the copper complexes are reduced reversibly while cadmium and lead show irreversible reductions, but all the reductions are diffusion controlled. The complex constants of copper have been calculated.

The complexes of some metals with N-hydroxyethylethylenediamine-triacetic acid (HEDTA) have earlier been studied by potentiometric methods<sup>1-3</sup>. The HEDTA complexes with iron have been studied by pH and redox potential titrations as well as by polarographic and spectrophotometric measurements<sup>4</sup>. The stabilities of the rare earth complexes have been determined by Spedding and co-workers<sup>5</sup>.

The present paper is a polarographic study of the copper(II), cadmium and lead complexes formed with HEDTA.

### EXPERIMENTAL

*Materials.* The trisodium hydroxyethylethylenediamine-triacetate, Chel DM-41, and the corresponding HEDTA-acid, Chel DM acid, obtained from Geigy Industrial Chemicals, were used without further purifications and both samples gave identical results. Impurities of sequestering agents with higher stabilities than HEDTA (*e.g.* ethylenediamine-tetraacetic acid, diethylenetriamine-pentaacetic acid, *etc.*) were found not to be present, because the half-wave potentials with the above quality reagents and the potentials of the corresponding complexes with *p.a.* HEDTA were identical (*p.a.* HEDTA was not available until near the end of the experiments). The reagent was standardized by complexometric titration with a standard solution of lead. The remaining chemicals were of reagent grade. Stock solutions of copper, cadmium and lead were prepared by dissolving the corresponding metal salt in redistilled water, and standardized by complexometric titrations with EDTA. A 0.1 M  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer was used if not otherwise stated. To vary pH,  $\text{NH}_3$  was added to a 0.1 M HCl solution or HCl was added to a 0.2 M  $\text{NH}_3$  solution; to keep the ionic strength constant ( $\mu = 0.1$ ) the first method was preferred when possible. The most alkaline solutions were made up with KOH. The pH was meas-

ured with a conventional pH meter with glass electrode. For studies of the shifts of half-wave potentials with pH, the Beckman so-called "stomach" electrode, directly inserted in the polarographic cell, was found convenient for the pH measurements. Unless specified, the concentration of complexing agent is 12 mM and of metal ions, 0.2 mM.

*Apparatus and technique.* Polarograms were recorded with a Tast-polarograph, Selector D (Atlas Werken, Bremen, Germany). The conventional type of dropping mercury electrode and of electrolysis cell were used. The capillary characteristics, measured in open circuit at a mercury height of 35 cm were

$$m = 3.015 \text{ mg/sec, and } t = 3.36 \text{ sec.}$$

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 solution during the electrolysis. All experiments were performed at  $25 \pm 0.1^\circ\text{C}$  (except in the temperature coefficient studies). The total a.c. resistance of the cell, agar bridge and reference electrode was 800  $\Omega$ .

The reversibility of the electrode reactions was tested from the temperature coefficient of the half-wave potentials and the slopes of  $\log i/(i_d - i)$  vs. the potential curves. Corrections were made for the residual current. The data for the log plots were obtained by manual operations of the polarograph. The applied potentials were measured with a Leeds and Northrup Type K potentiometer. Half-wave potentials were taken from the logarithmic plots and were reproducible to  $\pm 1$  mV.

*Calculations.* The HEDTA becomes protonated to varying degrees depending upon the pH of the solution. The following values for the dissociation constants were used to calculate the actual concentrations<sup>2</sup>:

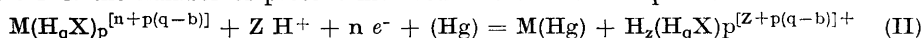
$$pK_1 = 2.64, \quad pK_2 = 5.33, \quad pK_3 = 9.73$$

For the reversible processes, the stability constants ( $pK_c$ ) of the complexes were calculated from the shifts in the half-wave potentials to more negative values on addition of sequestering agent, as described by Kolthoff and Lingane<sup>3</sup>.

As the concentration of the free ligand available for complex formation varies with pH of the solution, a plot of  $(E_{1/2})_c$  vs. pH has a slope  $a$  given by

$$a = \frac{0.0591}{n} \cdot Z \quad (\text{I})$$

where  $Z$  is the number of protons involved in the reduction process:



## RESULTS AND DISCUSSION

(a) *Copper.* All complexes with copper are reduced directly to the amalgam. The reduction is thermodynamically reversible in the measured pH-range and with all the used concentrations of HEDTA, since the  $\log i/(i_d - i)$  vs.  $E$  slopes are all nearly theoretical ( $n = 2$ ), and since the temperature coefficient of the diffusion current is only  $+ 1.3$  %/degree and the shift in half-wave potential only  $+ 0.78$  mV/degree.

The slopes of the polarograms are very dependent on the presence of surface active substances. Thus, 0.0004 % Triton X-100 highly affects the diffusion current and half wave-potential and no wave is observed with concentrations of Triton X-100 exceeding 0.005 % before components of the supporting electrolytes are reduced. No maximum suppressor is used in the measurements below.

*pH studies.* Fig. 1 shows plots of  $(E_{1/2})_c$  vs. pH for copper(II) with excess of HEDTA. The slope gives the value of  $Z$  in eqn. (II). The slopes of  $\log i/(i_d - i)$  vs.  $E$  were all in the range 33–36 mV per log unit, giving  $n = 2$ . The magnitudes of the half-wave potentials for  $\text{pH} < 2.5$  are rather approxi-

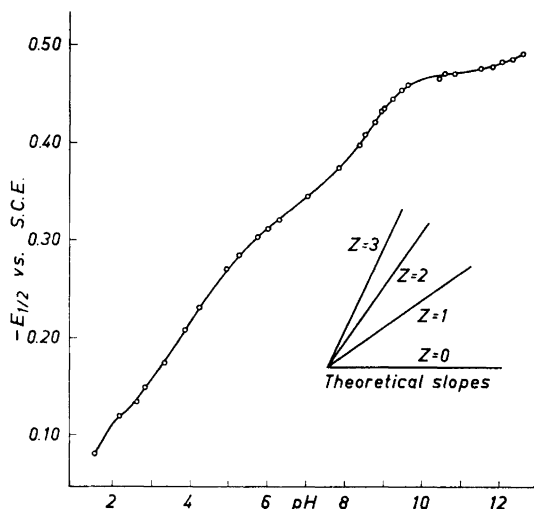
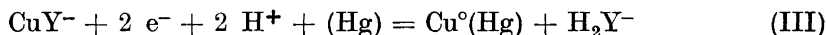


Fig. 1. Variation of half-wave potentials of copper complexes of HEDTA with pH of the solution.

mate because dissolution of mercury took place at almost the same potentials as the reduction of the copper complexes.

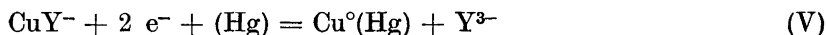
A comparison with eqn. (I) indicates that different complexes are formed. The unprotonated complex appears above  $\text{pH} = 8$ . Up to  $\text{pH} = 9$ ,  $Z = 2$ , giving the following reduction process ( $\text{H}_3\text{Y} = \text{HEDTA}$ ):



In the pH-range 9–10,  $Z$  is changing from 2 to 0. ( $Z = 1$  will give:

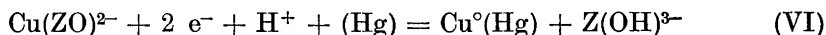


In the pH-range 10–11.5,  $Z = 0$ :



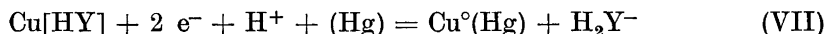
(Here the mole ratio of metal ion and ligand is assumed to be unity, as stated later.)

It seems that the weak ethanolic group of the ligand possibly dissociates a proton above  $\text{pH} = 11.5$ , giving a new complex. The slope in Fig. 1 seems to fit for a reaction with  $Z = 1$  ( $\text{H}_3(\text{OH})\text{Z} = \text{HEDTA}$ ):

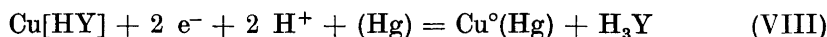


A detailed study of this complex is not possible since this will need to high pH.

In more acid solutions than  $\text{pH} = 8$ , Fig. 1 shows the appearance of a protonated complex with  $Z = 1$  in the pH-range 5–8:



Below  $\text{pH} = 5$ ,  $Z = 2$  and the reaction is:



(Here too, the mole ratio of metal ion and ligand is assumed to be unity, as stated later.)

*Stability studies.* The polarographic data were used to determine the composition of the complexes and the stability constants.

Plots of the values of  $(E_{1/2})_c$  vs. the corresponding values of the logarithm of the concentration of the complexing agent show straight lines. In 0.1 M  $\text{NH}_3\text{—NH}_4\text{Cl}$  buffer,  $\text{pH} = 9.25$ , and in 0.1 M sodium acetate-acetic acid buffer,  $\text{pH} = 4.70$ , the found values of the half-wave potentials in the concentration range 0.3–20 mM HEDTA may be expressed by the following equations:

$$E_{1/2} = -0.529 - 0.033 \log C_x \text{ and} \quad (\text{IX})$$

$$E_{1/2} = -0.335 - 0.032 \log C_x \quad (\text{X})$$

These equations correspond to the complexes  $\text{CuY}^-$  and  $\text{Cu}[\text{HY}]$ , respectively. Therefore, by means of the protolysis constants of HEDTA,  $C_x$  is calculated to be the excess of  $\text{Y}^{3-}$  and  $\text{HY}^{2-}$  in the two solutions. The slopes of the lines indicate that the mole ratio of metal ion and ligand is unity in both complexes. The half-wave potential of the  $\text{Cu}_{\text{aq}}^{2+}$  complex,  $(E_{1/2})_s$ , is taken to be +0.04 V vs. S.C.E. The stability constants are defined as follows:

$$K_{c1} = \frac{[\text{Cu}^{2+}] \cdot [\text{Y}^{3-}]}{[\text{CuY}^-]} : \text{p}K_{c1} = 18.8 \quad (\text{XI})$$

$$K'_{c2} = \frac{[\text{Cu}^{2+}] \cdot [\text{HY}^{2-}]}{[\text{Cu}(\text{HY})]} ; \text{p}K'_{c2} = 12.4 \quad (\text{XII})$$

To bring eqn. (XII) to a more familiar form, it is combined with (XI) and the dissociation constant  $\text{p}K_3$ , giving

$$K_{c2} = \frac{[\text{CuY}^-] \cdot [\text{H}^+]}{[\text{Cu}(\text{HY})]} ; \text{p}K_{c2} = 3.3 \quad (\text{XIII})$$

The values become slightly different if calculated with eqn. (IX) and (X) because of deviations from theoretical slopes.

Potentiometrically<sup>2</sup>,  $\text{p}K_{c1}$  has been measured to 17.4. The difference between the potentiometric and polarographic results cannot at present be explained, but similar discrepancy has been observed with related metal complexes.

The reduction of the  $\text{CuY}^-$  complex is found to be diffusion controlled, obeying Ilkovič's equation, since the diffusion current varies linearly with the concentration of added copper(II) ions in the concentration range studied (from  $1.8\text{—}9.0 \times 10^{-4}$  M) and with the square root of the height of mercury (from 30–45 cm, corrected for the "back pressure").

The diffusion constant, defined as

$$I = i_d / C \cdot m^{2/3} \cdot t^{1/6}$$

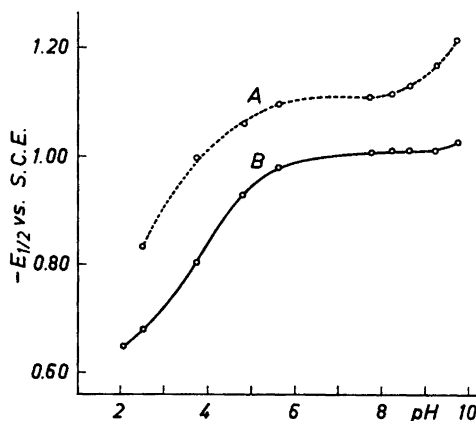


Fig. 2. Variation of half-wave potentials of (A) cadmium- and (B) lead complexes of HEDTA with pH of the solutions.

is measured to 3.03 and 3.13 in solutions containing  $1.2 \times 10^{-2}$  M HEDTA in 0.1 M ammonia or acetic acid buffer (pH = 9.25 and 4.70) and correspond to the complexes  $\text{CuY}^-$  and  $\text{Cu}[\text{HY}]$ .

(b) *Cadmium and lead.* The polarographic reduction of these metal complexes with HEDTA was found to be irreversible. The plots of  $\log i/(i_d - i)$  vs.  $E$  are curved at all concentrations of the reagent and all values of pH, and the slopes are approximately twice the theoretical values. The irreversibility is probably due to too slow reduction rates. Koryta and Kössler<sup>7</sup> found the same effects with the related sequestering agents nitrilotriacetic acid and ethylenediaminetetraacetic acid.

The polarograms of the cadmium and lead complexes are, like the corresponding copper complexes, very sensitive to surface active substances.

Plots of the half-wave potentials vs. pH for the two metal complexes are shown in Fig. 2. Two waves appeared in acid solutions (pH < 4). The first

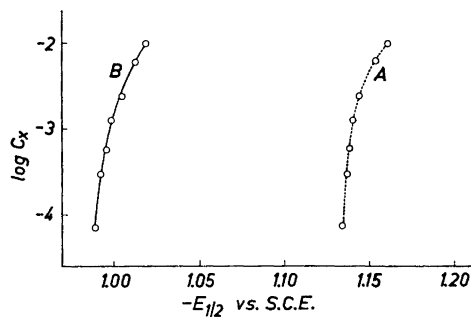


Fig. 3. Variation of half-wave potentials of (A) cadmium- and (B) lead complexes of HEDTA with the logarithm of the concentration of the chelating agent ( $C_x = [\text{Y}^{3-}]$ ). pH = 9.25.

one is reversible and is due to reduction of uncomplexed cadmium or lead ions. Because of the irreversibility, no conclusions can be drawn about the nature of the complexes, but comparing with Fig. 3 showing shifts in half-wave potentials with excess of HEDTA, it seems that the reasons for the irreversibility are the same for both complexes since the shapes of the A and B curves are very similar.

The diffusion constants are 2.85 and 3.26 for cadmium and lead complexes, respectively ( $1.2 \times 10^{-2}$  M HEDTA, ammonia buffer with pH = 9.25). The diffusion current varies linearly with the square root of the mercury height, measured from 30–45 cm, and with concentrations of metals from  $1.8-9 \times 10^{-4}$  M, indicating that the reductions are diffusion controlled. All the polarographic waves are very well defined. The observed half-wave potentials are shown in Figs. 2 and 3.

Chaberek and Martell<sup>2</sup> find that the reduction of iron(III)-HEDTA complexes is reversible and it must be concluded that the mechanism of reduction of the copper and iron complexes is different from that of the cadmium and lead complexes.

#### REFERENCES

1. Chaberek, S. and Bersworth, F. C. *Science* **118** (1953) 280.
2. Chaberek, S. and Martell, A. E. *J. Am. Chem. Soc.* **77** (1955) 1477.
3. Holloway, J. H. and Reilley, C. N. *Anal. Chem.* **32** (1960) 249.
4. Shochdopole, R. and Chaberek, S. *J. Inorg. & Nuclear. Chem.* **11** (1959) 222.
5. Spedding, F. H., Powell, J. E. and Wheelweight, E. J. *J. Am. Chem. Soc.* **78** (1956) 34.
6. Kolthoff, I. M. and Lingane, J. J. *Polarography*. Interscience, New York 1952, p. 214.
7. Koryta, J. and Kössler, I. *Collection Czechoslov. Chem. Commun.* **15** (1950) 241.

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