

## Polarography of Lead and Cadmium Complexes with Tetraethylenepentamine and Pentaethylenhexamine

EINAR JACOBSEN and KNUT SCHRØDER

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

The complexes of cadmium and lead with tetraethylenepentamine and pentaethylenhexamine have been studied by means of the dropping mercury electrode. The half-wave potentials and the diffusion current constants have been determined and the complex constants calculated. It has been shown that lead exhibits an amine coordination number of four in both complexes. The amine coordination number of cadmium is probably six in the pentaethylenhexamine. The data obtained seem to indicate that cadmium forms two complexes with both polyamines.

The polarography of copper complexes formed with tetraethylenepentamine ("tetren") and pentaethylenhexamine ("penten") has been thoroughly investigated by Jonassen *et al.*<sup>1</sup> The stability of some tetren complexes have been determined by potentiometric titration<sup>2</sup>. The stability of the penten complexes, however, and the polarographic behaviour of the tetren and penten complexes formed with other metals than copper have previously not been investigated. The present paper is a polarographic study of the cadmium and lead complexes formed with tetren and penten.

### EXPERIMENTAL

*Materials.* The technical grade tetraethylenepentamine, obtained from Fluka AG, Switzerland, was purified and standardized as described by Reilley<sup>3</sup>. Pentaethylenhexamine was obtained as a mixture of amines designated "polyamine H, Special" from Carbide and Carbon Chemicals, New York, and was purified and standardized as described by Jonassen<sup>1</sup>. The purity of the reagents was also checked by infra-red analysis. The remaining chemicals were of reagent grade and were used without further purification. Stock solutions of lead and cadmium were prepared by dissolving the metal salt in redistilled water and standardized by complexometric titration with EDTA. 0.5 M phosphate buffer was used as supporting electrolyte. The buffer was prepared by adding potassium hydroxide to phosphoric acid and its pH measured with a pH meter. In order to avoid precipitation of lead phosphate, 1 M ammonia buffer was used as indifferent electrolyte for the lead complexes. The pH of the electrolyte was adjusted to desired value by addition of hydrochloric acid. 0.004 % of Triton x-100, obtained from Rohm and Haas Co, Philadelphia, was found to be effective as maximum suppressor.

*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 was used. The capillary characteristics, measured in open circuit at a mercury height of 35 cm were  $m = 3.015$  mg/sec, and  $t = 3.36$  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  $25 \pm 0.1^\circ\text{C}$ .

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

## RESULTS AND DISCUSSION

The lead complexes with tetren and penten are reduced directly to the amalgam. The plots of  $\log i/(i_d - i)$  vs. the potentials were straight lines and the slopes indicate that the electrode reactions involve reversible two-electron reductions. The plots of the values of  $E_{1/2}$  vs. the corresponding values of  $\log C_x$  resulted in straight lines and the slopes of the lines indicate that only one group is coordinated in each complex. In the concentration range 0.3–2.6 mM of the complexing agent the half-wave potentials may be expressed by the following equations:

$$\begin{aligned} (\text{Pb tetren})^{2+}: E_{1/2} &= -0.696 - 0.031 \log C_x \\ (\text{Pb penten})^{2+}: E_{1/2} &= -0.710 - 0.034 \log C_x \end{aligned}$$

The half-wave potentials of both lead complexes are shifted to more negative values with increasing pH. Above pH 10.5 the half-wave potentials are constant, independent of the pH of the supporting electrolyte. The dissociation constant,  $K_c$  of the lead complexes was calculated from the half-wave potentials assuming  $C_x$  equal to the total concentration in the pH region 10.5–11.5. The following values were calculated:

$$\begin{aligned} (\text{Pb tetren})^{2+}: & \quad \text{p}K_c = 10.9 \\ (\text{Pb penten})^{2+}: & \quad \text{p}K_c = 11.0 \end{aligned}$$

The  $\text{p}K_c$  values for the tetren complex is in good agreement with the value ( $\text{p}K_c = 10-11$ ) previously determined by potentiometric titration<sup>2</sup>. The  $\text{p}K_c$  of both complexes is about the same as that of the corresponding triethyl-enetetramine complex ( $\text{p}K_c = 10.4$ )<sup>4</sup>, and seems to indicate that four lead to nitrogen bonds exist in all the three lead polyamine complexes.

The diffusion current constant  $I = i_d/C m^{2/3} t^{1/2}$  at pH 10.3 was found to be 3.3 and 3.1 for the lead tetren and lead penten complex, respectively.

The cadmium complexes with tetren and penten are reduced directly to the amalgam. The half-wave potentials of both complexes are shifted to more negative values with increasing pH. Above pH 10.5 the half-wave potentials were constant and independent of pH of the supporting electrolyte. The plots of  $\log i/(i_d - i)$  vs. the potential were straight lines with the same slope of  $-0.044$  V/log unit for the tetren complex. The log plots of the corresponding penten complex were curved at all concentrations of the reagent in the pH

range 9.5–11.5 of the supporting electrolyte. By careful examination of the undamped so-called Tast polarograms, it was verified that the polarograms of the cadmium penten complex consist of two waves. Exactly the same polarograms were obtained using ammonia buffer as supporting electrolyte.

The polarograms were perfectly reproducible and seem to indicate that the waves are due to two different cadmium complexes being reduced at almost the same potential. Because of the very small difference in half-wave potentials the individual diffusion currents and half-wave potentials could not be measured.

The limiting current of the tetren and penten complexes varied with the height of mercury above the capillary. The value  $i/\sqrt{h}$ ,  $h$  being the height of the mercury after correction for the "back pressure", was constant, indicating that the electrode reactions are diffusion controlled. The following values for the diffusion current constants,  $I = i_d/C m^{2/3} t^{1/6}$ , were found:

Cadmium tetren (pH 11.2):	$I = 2.75$
Cadmium penten (total wave pH 10.5):	$I = 2.07$

The half-wave potentials (taking  $E_{1/2}$  of the penten complex as the point on the Tast polarogram where  $i = i_d/2$ ) shifted to more negative values with increasing concentration of the reagents. In the concentration range 0.3–8 mM of the complexing agents, the plot of  $E_{1/2}$  vs.  $\log C_x$  resulted in straight lines which may be expressed by the equations:

Cadmium tetren: $E_{1/2} = -1.075 - 0.050 \log C_x$
Cadmium penten: $E_{1/2} = -1.22 - 0.050 \log C_x$

The temperature coefficient of the diffusion currents was + 1.3 %/degree and the shift in the half-wave potentials was about + 1 mV/degree for the cadmium tetren and penten complexes. This seems to indicate that both cadmium penten complexes are reversibly reduced at the dropping mercury electrode and that the wave of the tetren complex (slope of log plot = -0.044 V/log unit) also is due to reversible reduction of two complexes being reduced at almost the same potential.

By amperometric titrations of different amounts of cadmium with standardized tetren and penten solutions, it was verified that exactly one mole of the reagent was consumed in the complex formation with one mole of the cadmium ions, indicating that only one ligand is coordinated in each complex. The diffusion current constants of the total waves indicate that the reduction of the complexes involve two electrons.

By assuming reversible reduction of the complexes, the mean values for the dissociation constants of the two tetren and the two penten complexes were calculated. The half-wave potentials obtained from polarograms of solutions with pH > 10.5 were used in the calculation assuming  $C_x = C$  in this pH region. The following values were obtained:

Cadmium tetren:	$pK_c = 14.7$
Cadmium penten:	$pK_c = 19$

The stability of cadmium tetren complex has previously been determined by potentiometric titration<sup>2</sup> and the  $pK_c$  value was found to be = 14.0.

Considering the great difference in ionic strength in the potentiometric and the present polarographic determination, the agreement is satisfactory.

The large increase of the stability of the tetren and penten complexes over that of the cadmium triethylenetetramine complex <sup>4</sup> ( $pK_c = 10.8$ ) indicates that the amine coordination number of cadmium is greater than four in the tetren and penten complexes and probably six in the penten complex.

## REFERENCES

1. Jonassen, H. B., Bertrand, J. A., Groves, F. R. and Stearns, R. I. *J. Am. Chem. Soc.* **79** (1957) 4279.
2. Reilley, C. N. and Holloway, J. H. *J. Am. Chem. Soc.* **80** (1958) 2917.
3. Reilley, C. N. and Vavoulis, A. *Anal. Chem.* **31** (1959) 243.
4. Reilley, C. N. and Schmid, R. W. *J. Elisha Mitchell Soc.* **73** (1957) 279.

Received January 15, 1962.