

Polarography of Lead in Presence of 2,2'- Diaminodiethylether-N,N,N',N'-tetraacetic Acid

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Polarograms of lead in the presence of excess EEDTA exhibit two waves at the dropping mercury electrode. In the pH range 3-6, the second wave is due to reduction of the PbY^{2-} complex to the amalgam and the first wave, which is kinetic in nature, corresponds to reduction of free lead ions dissociated from the complex. The limiting current of the total wave is diffusion controlled, whereas that of the first wave is partly controlled by the rate of the reaction $PbY^{2-} + 2H^+ \rightleftharpoons Pb^{2+} + H_2Y^{2-}$. The effect of drop time, temperature, pH, and of ionic surfactants on the two waves has been investigated.

Diaminodiethylethertetraacetic acid (EEDTA) forms stable complexes with several metals,^{1,2} and it has been reported to have certain advantages over other complexans as spectrophotometric reagent for copper,³ iron,⁴ and vanadium⁵ and in complexometric titration of barium.⁶ During a preliminary polarographic study of various EEDTA complexes we observed that the lead complex gives rise to a poorly defined doublet wave at the dropping mercury electrode. However, upon addition of the surface-active substance dodecylamine perchlorate to the supporting electrolyte, the drawn out wave was separated into two well-defined and apparently reversible waves.

The present work was carried out in order to investigate the polarographic behaviour of the lead-EEDTA complex and to study the effect of surface-active substances on the electrode reactions.

EXPERIMENTAL

Materials. 2,2'-Diaminodiethylethertetraacetic acid was obtained from Geigy Chemical Corp., New York. The commercial product (Chel ME) was recrystallized twice from hot water and dried in vacuum. The purity of the product was checked by infra-red analysis. A 0.1 M stock solution was prepared by dissolving 33.631 g EEDTA and 8.0 g sodium hydroxide in distilled water and diluting to one litre. The titer was checked by complexometric titration of a standard copper(II) solution. Standard 0.01 M solution of lead was prepared by dissolving reagent grade lead nitrate (E. Merck AG, Germany) in distilled

water and standardized by EDTA titration. 0.2 M acetate buffers together with 0.1 M potassium nitrate were used as supporting electrolytes. The pH of the electrolytes was adjusted to desired value by adding hydrochloric acid or potassium hydroxide and the pH was checked with a Beckman Zeromatic pH meter. Dodecylamine perchlorate (Armeen) and sodium dodecylsulphate (SDS) were used as surface-active agents. Solutions of these substances were prepared as described previously.⁷

Apparatus. D.C. 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 corrected mercury height of 49.2 cm, were $m = 3.008$ mg/sec and $t = 3.14$ 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 $25 \pm 0.1^\circ\text{C}$. Halfwave potentials were determined by a manual set-up. A.C. polarograms were obtained manually by a polarograph built in this laboratory.⁸

RESULTS

Polarograms recorded from acidic solutions of the lead-EEDTA complex showed two poorly separated waves. Upon increasing pH of the electrolyte the height of the second wave increased at the expense of the first one, and when pH was increased above 6 only the second wave was observed on the polarogram.

The effect of surface-active substances on the two waves was investigated using 0.2 M acetate buffer of pH 4.65 as supporting electrolyte. As indicated in Fig. 1 the presence of SDS has a great distorting effect on the second wave, whereas two well-defined waves are obtained in the presence of Armeen. The effect of different amounts of the two surfactants on the polarogram is reported in Table 1. The reversibility of the electrode reactions was checked for each polarogram by noting the difference in $E_{1/2} - E_{1/4}$ and the result is included in the table.

Table 1. Effect of surfactants on the polarographic waves of 10^{-3} M lead and 10^{-2} M EEDTA in 0.2 M acetate buffer at pH 4.65.

Surfactant added, %	First wave			Second wave		
	i , μA	$-E_{1/2}$, V	$E_{1/2} - E_{1/4}$	i , μA	$-E_{1/2}$, V	$E_{1/2} - E_{1/4}$
0	3.60	0.488	-0.030	2.60	0.594	-0.050
0.0004 Armeen	3.20	0.489	-0.030	3.00	0.616	-0.040
0.0010 »	2.85	0.488	-0.030	3.35	0.626	-0.035
0.0016 »	2.78	0.486	-0.032	3.41	0.629	-0.030
0.002 »	2.80	0.487	-0.033	3.40	0.630	-0.029
0.003 »	2.78	0.486	-0.033	3.42	0.629	-0.030
0.005 »	2.80	0.486	-0.034	3.40	0.628	-0.028
0.010 »	2.82	0.486	-0.033	3.40	0.628	-0.030
0.0008 SDS	3.00	0.483	-0.029	3.20	0.63	-0.055
0.0020 »	2.72	0.483	-0.030	3.50	0.71	-0.070
0.004 »	2.60	0.484	-0.028	3.60	0.80	-0.075
0.008 »	2.52	0.483	-0.028	3.70	0.87	-0.085
0.010 »	2.50	0.481	-0.028	Distorted		

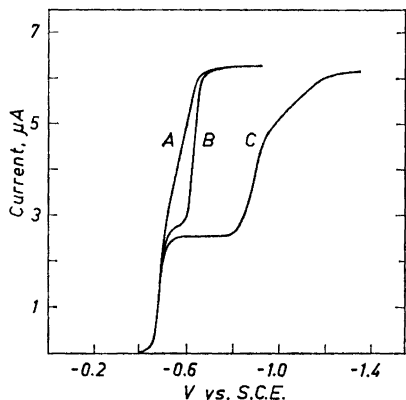


Fig. 1. Polarograms of 10^{-3} M lead and 10^{-2} M EEDTA in 0.2 M acetate buffer at pH 4.65 in the absence of surfactants (curve A) and in the presence of 0.01 % Armeen (curve B) and 0.01 % SDS (curve C).

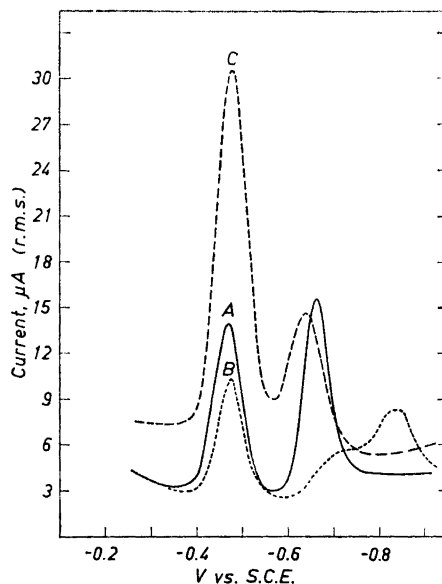


Fig. 2. A.C. polarograms of 2.5×10^{-3} M lead and 10^{-2} M EEDTA in 0.2 M acetate buffer at pH 4.65 in the presence of 0.002 % Armeen (curve A), 0.002 % SDS (curve B), and in the absence of surfactants (curve C).

The height of the second wave increased at the expense of the first one and the half-wave potential of the second wave was shifted to more negative values with increasing amount of either of the two surfactants. However, the most interesting result in Table I is the effect of the surfactants on the reversibility of the second wave. As indicated in the last column of the table, the second wave appears to be more reversible in the presence of the cationic substance Armeen and more irreversible in the presence of the anionic substance SDS. These results were confirmed by A.C. polarography. The peak height of the second wave increased upon addition of Armeen to the supporting electrolyte and the wave was greatly distorted in the presence of SDS (Fig. 2). The distorting effect of SDS indicates that the second wave is due to reduction of a negatively charged complex.⁷

The A.C. as well as the D.C. polarograms were not affected upon increasing the Armeen concentration above 0.0015 %, and the following experiments were performed in the presence of 0.002 % Armeen.

The effect of drop time was investigated by recording polarograms at various heights of the mercury column. The limiting current of the total wave increased with the height of mercury; the value $i/\sqrt{h_{\text{corr}}}$, where h_{corr} is the height of the column after correction for the "back pressure", was constant, indicating that the overall electrode reaction is diffusion controlled. The height of the first wave increased also with increasing h_{corr} , but much less rapidly than the

square-root relationship would predict (Table 2), which is a characteristic feature of kinetic waves. The half-wave potential of the first wave was constant and independent of the drop time, whereas the second wave was shifted to more negative values with decreasing drop time. The value $\Delta E_{1/2}/\Delta \log t_{1/2}$, where $t_{1/2}$

Table 2. Effect of pressure of mercury on the polarographic waves of 10^{-3} M lead and 10^{-2} M EEDTA in acetate buffer, pH 4.70, and 0.002 % Armeen present.

h_{corr} cm	First wave		Second wave		Total wave	
	Current μA	$-E_{1/2}$ Volt	Current μA	$-E_{1/2}$ Volt	Current μA	$i_d/\sqrt{h_{\text{corr}}}$
34.2	2.50	0.485	2.70	0.629	5.20	0.888
39.2	2.52	0.484	3.05	0.630	5.57	0.888
44.2	2.55	0.486	3.37	0.631	5.92	0.889
49.2	2.57	0.485	3.65	0.632	6.22	0.888
54.2	2.60	0.484	3.90	0.633	6.50	0.885
59.2	2.62	0.485	4.20	0.634	6.82	0.886

is the drop time at the half-wave potential, was -16 mV which is close to the theoretical value for a quasi-reversible 2-electron process.⁹ The reversible electron-transfer step is probably preceded by a slow reaction, *i.e.* the penetration through the adsorbed Armeen layer.

Table 3. Effect of temperature on the polarographic waves of 10^{-3} M lead and 10^{-2} M EEDTA in 0.2 M acetate buffer, pH 4.65, and 0.002 % Armeen present.

Temp. $^{\circ}\text{C}$	First wave		Second wave		Limiting current μA
	Current μA	$-E_{1/2}$ Volt	Current μA	$-E_{1/2}$ Volt	
25	2.80	0.486	3.50	0.630	6.30
30	3.35	0.485	3.44	0.629	6.79
35	3.90	0.487	3.32	0.628	7.22
40	4.46	0.486	3.20	0.630	7.66
45	4.99	0.487	3.10	0.629	8.09
50	5.48	0.486	2.98	0.628	8.46

The effect of temperature on the two waves was tested in acetate buffer at pH 4.65. In the temperature region 25–50°C the height of the first wave increased whereas that of the second wave decreased. The temperature coefficients calculated from the data reported in Table 3 are +2.7 and -0.7 % per degree for the height of the first and of the second wave, respectively. The

temperature coefficient for the limiting current of the total wave is + 1.2 % per degree and indicates that the overall electrode reaction is diffusion controlled. The half-wave potentials of both waves were constant and independent of the temperature within the experimental error.

Table 4. Effect of pH on the polarograms of 10^{-3} M lead and 10^{-2} M EEDTA. 0.002 % Armeen was added to each solution.

pH	First wave		Second wave	
	Current, μ A	$-E_{1/2}$, V	Current, μ A	$-E_{1/2}$, V
3.20	6.2	0.427	0.4	0.55
4.10	4.5	0.465	1.8	0.60
4.65	2.8	0.48	3.4	0.630
5.18	1.6	0.50	4.5	0.660
5.70	0.7	0.51	5.4	0.690
6.20			6.2	0.712
6.65			6.3	0.721
7.00			6.2	0.722

The effect of pH on polarograms of the lead-EEDTA complex was investigated using acetate and phosphate buffers as supporting electrolytes. The result is given in Table 4. The height of the first wave decreased and that of the second one increased with increasing pH, and above pH 6 only the second wave was observed on the polarogram. When pH of the supporting electrolyte was increased above 7, the wave became increasingly more irreversible both in presence and in absence of Armeen. The experiments were therefore restricted to lower pH values. The half-wave potential of the second wave was shifted linearly to more negative values with increasing pH as indicated in Fig. 3. In the pH range 3–6 the slope of the curve was -0.058 V/pH unit, indicating that two H^+ ions are involved in the electrode reaction.

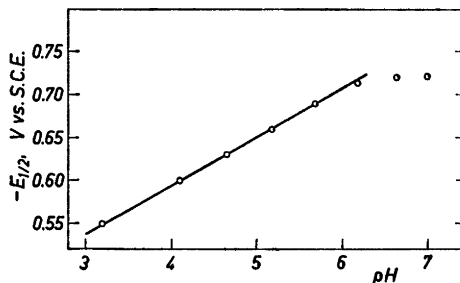
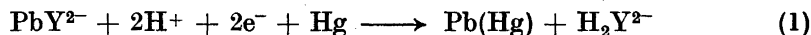


Fig. 3. Effect of pH on the half-wave potential of the second wave of 10^{-3} M lead and 10^{-2} M EEDTA and 0.002 % Armeen present.

DISCUSSION

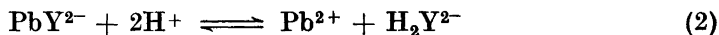
It is evident from the experimental results that the second wave corresponds to a reversible 2-electron reduction of a lead-EEDTA complex. The dissociation constants of EEDTA² indicate that the species PbY^{2-} is predominantly present in the pH region 3–8 and because two H^+ are consumed during the reduction, the following electrode reaction is suggested:



where H_4Y denotes EEDTA. The stability constant of PbY^{2-} , calculated from the summit potential of A.C. polarograms obtained in the absence of Armeen was $\text{p}K_c = 14.7$, which compares favourably to the value 14.4 previously determined potentiometrically by Holloway and Reilley.²

The half-wave potential of the first wave is only slightly more negative than that of lead ions in the same buffer but in the absence of EEDTA. This indicates that the first wave is due to the reduction of free lead ions (or acetate complexes of lead) dissociated from the PbY^{2-} complex.

From the stability constant $K = [\text{Pb}^{2+}][\text{Y}^{4-}]/[\text{PbY}^{2-}]$ and the dissociation constants of EEDTA, the concentration of free lead ions in the presence of a tenfold excess of EEDTA was calculated at different pH values. The limiting current corresponding to the equilibrium concentration of lead ions, was much lower than the experimental height of the wave (Fig. 4). The difference must be due to a kinetic contribution according to:



According to this equation, the presence of an excess EEDTA would be expected to alter the height of the first wave. As indicated in Fig. 5, this assumption was verified experimentally, the height of the first wave decreases and that of the second wave increases with increasing excess of EEDTA.

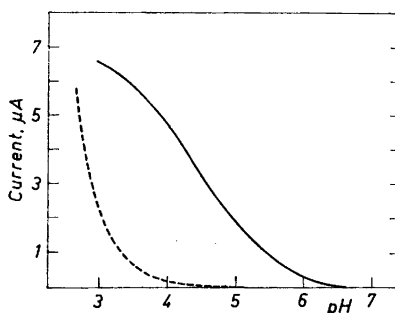


Fig. 4. Limiting current of the first wave of 10^{-3} M lead and 10^{-2} M EEDTA as a function of pH. The dashed curve is the diffusion current corresponding to the calculated equilibrium concentrations of lead and the solid curve represents the experimental values.

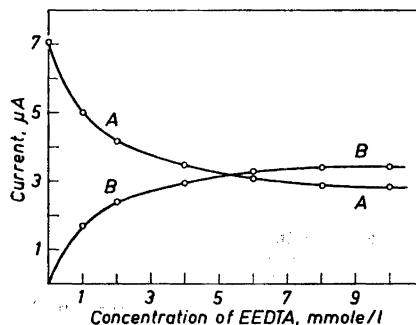


Fig. 5. Effect of excess EEDTA on the height of the first (curve A) and the second (curve B) wave of 10^{-3} M lead in 0.2 M acetate buffer at pH 4.65 and 0.002% Armeen present.

The decrease in the height of the second wave with increasing temperature and the great temperature coefficient of the first wave (+ 2.7 % per degree), is probably attributed to an increase in the dissociation of the complex with increasing temperature. The dissociation of the complex represented by eqn. 2 is also responsible for the kinetic behaviour of the first wave reported in Table 2.

Negatively charged complexes may easily penetrate through an adsorbed Armeen layer, whereas the electrode reaction of positively charged species is greatly decelerated in the presence of this cationic surfactant.⁷ Consequently, the decrease in the height of the first wave with increasing Armeen concentration reported in Table 1, is probably the result of a reduced rate in the reduction of free Pb^{2+} ions and hence in the kinetic contribution to the current. Because the limiting current of the total wave is diffusion controlled, the height of the second wave is correspondingly increased. When the Armeen concentration is increased above 0.002 %, the electrode is probably completely covered by the surfactant and the polarogram is therefore not affected by a further increase in the Armeen concentration.

A kinetic step in the polarographic reduction of metal chelates has previously been reported for cadmium complexes with EDTA¹⁰ and TTHA¹¹ and for cadmium,¹²⁻¹⁴ lead,¹⁵ and zinc¹⁶ complexes with NTA.

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REFERENCES

1. Schwarzenbach, G., Senn, H. and Anderegg, G. *Helv. Chim. Acta* **40** (1957) 1886.
2. Holloway, J. H. and Reilley, C. N. *Anal. Chem.* **32** (1960) 249.
3. Bermejo-Martinez, F. and Blas-Pérez, A. G. *Anal. Chim. Acta* **27** (1962) 459.
4. Bermejo-Martinez, F. and Blas-Pérez, A. G. *Inform. Quim. Anal. (Madrid)* **16** (1962) 129.
5. Bermejo-Martinez, F. and Blas-Pérez, A. G. *Chemist-Analyst* **52** (1963) 18.
6. Schwarzenbach, G. *Complexometric Titrations*, Interscience, New York 1960, p. 103.
7. Jacobsen, E. and Kalland, G. *Anal. Chim. Acta* **30** (1964) 240.
8. Jacobsen, E. *Anal. Chim. Acta* (1966). *In press*.
9. Meites, L. *Polarographic Techniques*, 2nd Ed., Interscience, New York 1965, p. 253.
10. Schmid, R. W. and Reilley, C. N. *J. Am. Chem. Soc.* **80** (1958) 2101.
11. Conradi, G., Kopanica, M. and Koryta, J. *Collection Czech. Chem. Commun.* **30** (1965) 2029.
12. Koryta, J. *Collection Czech. Chem. Commun.* **24** (1959) 3057.
13. Papoff, P. *J. Am. Chem. Soc.* **81** (1959) 3254.
14. Tanaka, N., Ebata, K., Takahari, T. and Kumagai, T. *Bull. Chem. Soc. Japan* **35** (1962) 1836.
15. Pryszeewska, M., Ralea, R. and Koryta, J. *Collection Czech. Chem. Commun.* **24** (1959) 3796.
16. Kodama, M. and Hashimoto, M. *Bull. Chem. Soc. Japan* **35** (1962) 1802.

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