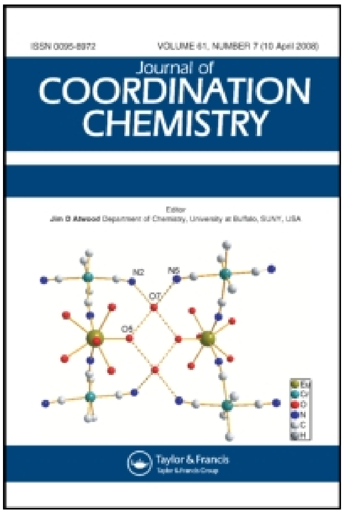

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L. Piszczek[a]; A. Ignatowicz[a]
[a] Institute of Chemistry, University of Gdańsk, Gdańsk, Poland

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A VOLTAMMETRIC STUDY OF THE Cd(II)-TRIETHYLENETETRAMINE SYSTEM

L. PISZCZEK and A. IGNATOWICZ

Institute of Chemistry, University of Gdańsk, ul. Sobieskiego 18, 80-952 Gdańsk, Poland

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The composition and stability of complexes formed between Cd(II) and triethylenetetramine (trien) over a wide range of ligand/metal ratio (A) has been studied by polarographic (DC) and cyclic voltammetric (CV) methods. The system has been found to be reversible over the whole metal/ligand range ($A = 0$–200), and a deformation of the voltammetric curves (CV and DC) at $A < 50$ could be interpreted in terms of the increase of the free ligand concentration at the surface of the electrode due to the electrode process. This plays a key role when a smaller excess of ligand is used. At low ligand/metal ratios, 1 : 1 species have been found to form, but with a large excess of trien, a 2 : 1 complex was detected.

Keywords: Cadmium(II) trien, stability constants, polarography, voltammetry

INTRODUCTION

Triethylenetetramine (trien) has been introduced into analytical practice by Reilley and Sheldon[1,2] owing to the possibility of its application to the titration of transition metals in the presence of alkali metals, alkaline earths and rare earths. Conditions for selective determination of these ions in multicomponent systems have also been discussed. The widespread use of trien in chemical analysis is connected with its capability of forming stable Me–trien complexes with metals which strongly coordinate nitrogen atoms. Stability constants of the 1 : 1 complexes formed under conditions of a stoichiometric ratio of reagents have been determined by potentiometry,[3,4] which is the method of choice in studying such complex systems.

For ions of metals such as cadmium(II), which undergo reversible electrochemical reduction at the mercury electrode, the polarographic method can also be used, a method which allows a study of the complexes formed in the presence of excess ligand.[5-7] However, papers dealing with the Cd(II)–trien system show many incompatibilities with regard to both reversibility of reduction and composition of complexes formed.

A polarographic study of the Cd(II)–trien system, carried out by Douglas *et al.*,[8] revealed its reversibility but only at elevated ligand concentrations (above 0.1 M). According to these authors, in the presence of excess ligand, a 1:1 complex is formed and its stability constant at 298K equals 8.3×10^{13}. Migal and Ivanova[9] claim that the Cd(II)–trien system is reversible over a narrow range of low ligand concentrations (below 0.013 M) and that a 1:2 complex is formed with a stability constant at 298K of 7.3×10^{13}. Jacobsen and Schrøder[10] claim, however, that the Cd(II)–trien system is reversible over the whole range of ligand concentrations. They suggest that the deformation of polarographic waves observed in solutions with a slight excess of the ligand is caused by the presence of other amines contained in trien, which leads to superposition of waves of various complexes.

Because of the above incompatible results and in order to explain these discrepancies, we have undertaken a study of this system by using polarography and cyclic voltammetry; the latter was adapted to the De Ford–Hume's method[11] for determination of stability constants, and which relies on equation (*1*),

$$F = 1 + C_L\beta_1 + C^2{}_L\beta_2 + \ldots + C^j{}_L\beta_j = \exp[nF/RT(E^s{}_{1/2} - E^c{}_{1/2}) + \ln I_s/I_c] \qquad (1)$$

where β_j = the stability constant of the j-th complex, C_L = concentration of ligand, I_s and I_c = diffusion current constants of the ions in the absence of ligand ("free" metal ion) and of the complexed ion, respectively, approximated by appropriate diffusion current alone.

Our study has been carried out over a range of ligand concentrations of from 0.02 to 0.8 M. It has involved investigation of the reversibility of reduction of the Cd(II)–trien system and the determination of stoichiometry as well as stability constants for the complexes formed over a wide range of ligand/metal concentration ratios, A = 0–200. Interpretation of the voltammetric curves was based on information contained in papers dealing with the relationship between shape of the voltammograms (DC and CV) and experimental conditions and properties of the systems.[12–15]

The composition of the complex was determined on the basis of diffusion current variations of the "free" metals ions and complexed ions as a function of the ligand/metal ratio.

EXPERIMENTAL

Polarograms were measured on an OH-105 (Radelkis, Hungary) polarograph. Experiments were carried out in a thermostatted glass cell with a dropping mercury electrode (DME), a saturated calomel electrode (SCE) as reference, and a spiral platinum electrode as the counter. The capillary constant was $1.28\,\mathrm{mg}^{2/3}\mathrm{t}^{-1/2}$. A mechanical drop life timer (4.0 s) was employed.

A triangular voltage function generator (EG-20, Elpan, Lubawa), a potentiostat (EP-21, Elpan, Lubawa), an XY recorder (KP 6801 Kabid-Press, Warsaw) and a digital voltmeter (Model 4027, Funkwerk, Erfurt) made up the equipment applied in the cyclic voltammetry experiments. A hanging mercury drop electrode (HMDE) with a surface area of about 2.31 mm^2 was the working electrode.[16] Polarograms and cyclic voltammograms were recorded at 25.0 ± 0.1°C, after previous deaeration of the solution (in the cell) by purging with dry argon, purified in a copper column heated to 200°C. All the solutions were prepared in triple distilled water.

Trien (Loba Chemie, Wien-Fischamend) was purified by crystallization as a tetranitrate from aqueous ethanol.[2,4] Cadmium nitrate was crystallized three times from water. Other reagents were of analytical grade. The starting solution containing 0.25 M trien and 1 M $NaNO_3$ was prepared by dissolving a weighed quantity of trien tetranitrate in water containing the amount of NaOH necessary for neutralization of the tetranitrate. The concentration of trien was determined potentiometrically by titration with standard Cd(II) solution. All Cd(II) and trien solutions contained 1 M $NaNO_3$ (stock solution).

In our experiments intended to determine the composition and stability constants of complexes by the De Ford–Hume method, solutions were prepared directly in the cell[17] as follows. To 10 cm^3 of solution S_1 containing 4×10^{-4} $Cd(NO_3)_2$, 1 M $NaNO_3$ and 0.02% carboxymethylocellulose (sodium salt; CMC), solution S_2 was added from a burette, containing 0.25 M trien, 1 M $NaNO_3$ and 4×10^{-4} M $Cd(NO)_3)_2$ (in order to keep the Cd(II) concentration constant).

Solutions used for the determination of stoichiometry on the basis of limiting diffusion current changes of the "free" Cd(II) ions or their complexes were similarly prepared. To 2 cm^3 of solution S_3, containing 5×10^{-3} M $Cd(NO_3)_2$ and 1 M $NaNO_3$ the following two solutions were added: 1) S_4 (1 cm^3), containing 0.2% of CMC and 1 M $NaNO_3$; 2) S_5 containing 5×10^{-3} M trien and 1 M $NaNO_3$; the amount of S_5 was such as to produce the assumed ligand to metal concentration ratio (A). The solution was then made up to 20 cm^3 with 1 M $NaNO_3$.

RESULTS AND DISCUSSION

Cadmium(II) ions undergo a reversible reduction to amalgam at the dropping mercury electrode. In solutions containing an excess of ligand, a single wave appears in the polarograms. A logarithmic analysis of these waves shows that the plot of log $(i_d\text{-}i)/i$ against potential, E, of the working electrode is linear (Figure 1a, c and d). Over the ligand concentration range of 2×10^{-2} to 8×10^{-2} M, the slope of these straight lines is constant and approximately equals 33.8 mV. This proves the reversibility of the electrode process.[5,18]

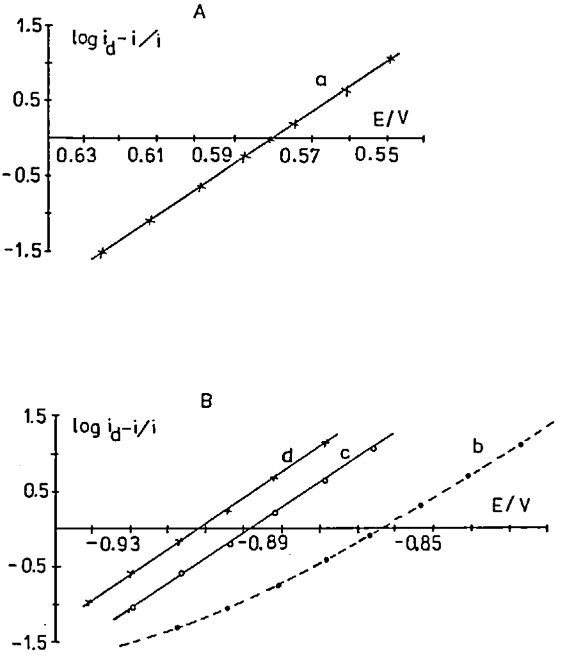

FIGURE 1 Logarithmic analysis of polarograms for the Cd(II)-trien system. T = 25.0 ± 0.1°C, I = 1.0, [Cd(II)] = 4×10^{-4} M, [trien]: 0 (a), 9.615×10^{-3} (b), 3.814×10^{-2} (c) and 6.481×10^{-2} M (d).

Polarographic waves obtained in solutions containing a small excess of ligand (<0.02 M) undergo, however, some deformation (Figure 1b). This deformation can be attributed neither to irreversibility of the system nor to ligand impurity, but rather to variation of the ligand concentration in the vicinity of the working electrode, which takes place during the recording of the polarogram. The occurrence of a similar deformation in the Cd(II)-CN^- system, which was due to an increase of ligand concentration at the electrode surface brought about by reduction of the complex, has been observed by Koryta.[19] Theoretical considerations of Macovschi[13] and Elenkova[14] also led to the conclusion that deformation of the polarographic wave occurred when the "free" ligand concentration in solution was distinctly lower than total ligand concentration.

In experiments carried out by the cyclic voltammetry method, the reduction of complexed Cd(II) ions in the presence of a sufficient excess of trien as well as reduction of the "free" Cd(II) ions at the HMDE is also reversible. Figure 2 shows cyclic voltammograms of the "free" Cd(II) ion (curve a) and of the complexed ion (curves b, c). Over the ligand concentration range $2\text{–}8 \times 10^{-2}$ M, the difference between cathodic and anodic peak potentials on the CV curve is about 30 mV. This is proof of the reversible character of the process.[18,20,21]

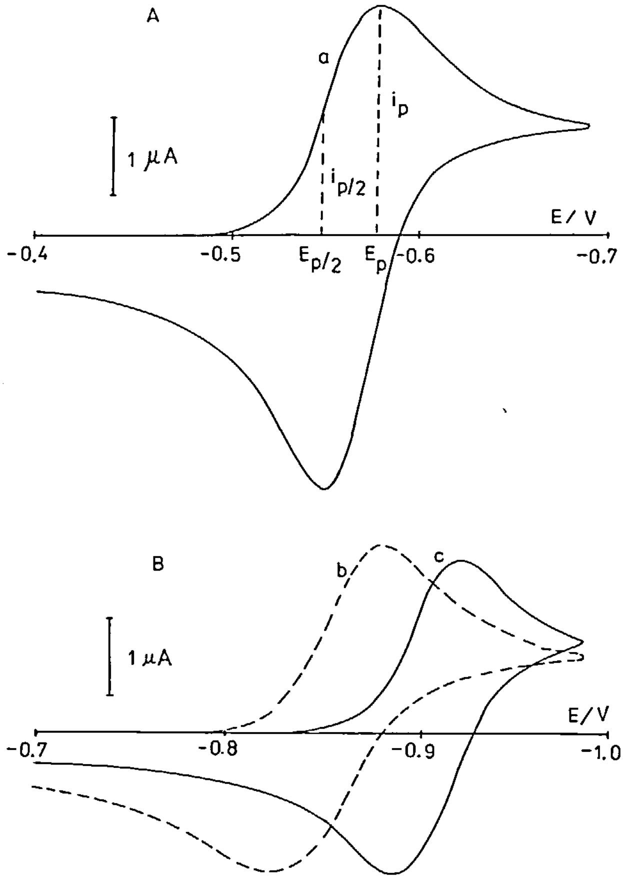

FIGURE 2 Cyclic voltammograms of the Cd(II)-trien system. T = 25.0 ± 0.1°C, I = 1.0, [Cd(II)] = 4×10^{-4} M, [trien]: 0 (a), 9.615×10^{-3} (b) and 7.759×10^{-2} M (c).

However, at a slight excess of ligand, this difference is larger than 30 mV, and the anodic peak has a characteristic "broadened" shape (Figure 2, curve b). These phenomena are mostly due to the high stability of the complex formed. This is in accordance with theoretical considerations and experimental results obtained by Killa and Philp[22,23] for the Cu(II)-ethylenediamine system.

In preliminary studies it was found that a better precision and reproducibility could be obtained when the half-peak potential rather than peak potential was measured. Table I lists values of half-wave potentials, $E^C_{1/2}$, for the reduction of the Cd(II) complex in the presence of excess ligand, determined from logarithmic analysis of the polarographic waves. The corresponding variations of $\Delta E^C_{1/2}$ in relation to the half-wave potential of the "free" Cd(II) ion and the values of the limiting diffusion current, i^C_d, are also included. In Table I values of half-peak potential for complex reduction ($E^C_{p/2}$) are shown, as well as variations of these potentials ($\Delta E^C_{p/2}$) in relation to $E_{p/2}$ for the reduction of "free" Cd(II) ion. Peak current values, i^C_p, are also included.

TABLE I

Cyclic voltammetric and DC polarographic data for the cadmium(II)-trien system[a].

10^2 [trien] /M	cyclic voltammetry			DC polarography		
	$-E^c_{p/2}$/ mV *vs* SCE	$-\Delta E^c_{p/2}$/ mV *vs* SCE	i^c_p/μA	$-E^c_{1/2}$/ mV *vs* SCE	$-\Delta E^c_{1/2}$/ mV *vs* SCE	$i^c d$/μA
	558.9[b]		3.05[b]	579.6[b]		1.83[b]
2.273	866.6	307.1	2.76	887.7	308.1	1.64
2.679	870.0	311.1	2.70	891.0	311.4	1.63
3.070	873.1	314.2	2.67	894.0	314.4	1.61
3.448	875.9	317.0	2.65	895.8	316.2	1.59
3.814				898.1	318.5	1.59
3.992	878.9	320.0	2.64			
4.167	880.9	322.0	2.63	901.0	321.4	1.58
4.592	882.2	323.3	2.61	903.4	323.8	1.57
5.000	885.1	326.2	2.57	905.5	325.9	1.56
5.392	887.1	328.2	2.55	907.5	327.9	1.54
5.769	889.0	330.1	2.52	910.3	330.6	1.53
6.481	891.7	332.8	2.50	911.9	332.3	1.52
7.143	893.9	335.0	2.48	914.8	335.2	1.50
7.759	895.5	336.6	2.46	916.6	337.0	1.49
8.333	877.9	338.9	2.44	918.1	338.5	1.49

[a] T = 25.0 ± 0.1°C, I = 1.0; [b] values for "free" Cd(II) ions; $E^c_{p/2}$ = half peak potential, i^c_p = peak current, $E^c_{1/2}$ = half wave potential, i^c_d = limiting diffusion current.

Stability constants for complexes formed in the Cd(II)-trien system, determined by the least-squares method from polarographic ($\Delta E^C_{1/2}$, i^C_d) and voltammetric ($\Delta E^C_{p/2}$, i^C_p) data are presented in Table II. The results show that both the 1:1 and 1:2 complexes are formed in this system. The results of the polarographic and voltammetric measurements are fully compatible. Such agreement requires maintaining identical experimental conditions, solution concentration and reagent purity. It also requires preparation of solutions directly in the cell and a great precision in potential measurements.

TABLE II
Stability constants for the Cd(II)-trien system.[a]

	cyclic voltammetry		DC polarography	
Model	β_i	δ	β_i	δ
ML_1,ML_2	$\log\beta_1 = 11.50 \pm 0.07$ $\log\beta_2 = 13.47 \pm 0.02$	0.041	$\log\beta_1 = 11.45 \pm 0.05$ $\log\beta_2 = 13.47 \pm 0.01$	0.027
ML_2	$\log\beta_2 = 13.56 \pm 0.01$	0.087	$\log\beta_2 = 13.56 \pm 0.02$	0.076

[a] T = 25.0 ± 0.1°C, I = 1.0, δ = standard deviation.

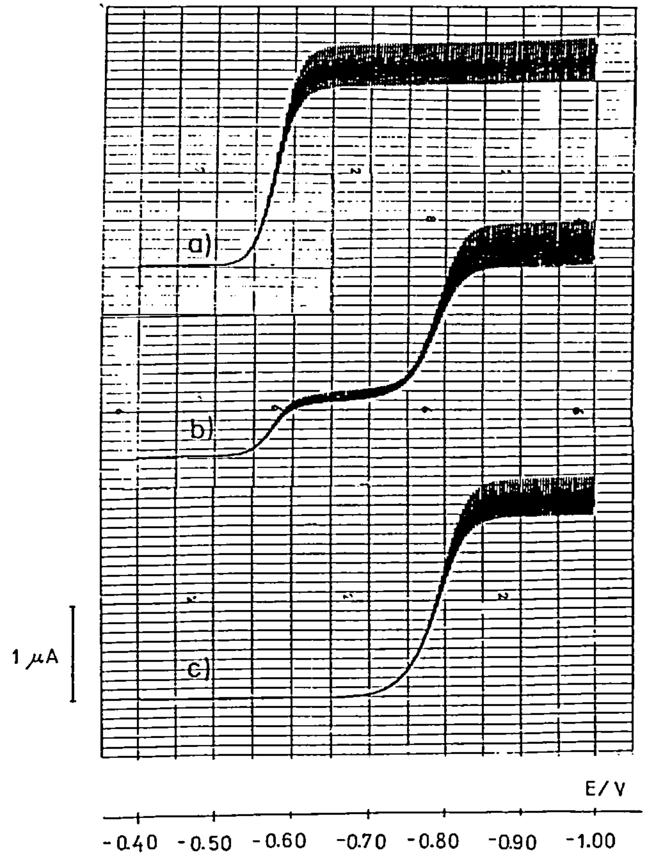

FIGURE 3 Polarograms of the Cd(II)-trien system. T = 25.0 ± 0.1°C, I = 1.0. Ligand to metal concentration ratio A: 0 (a), 0.75 (b) and 1.125 (c).

At low trien/Cd(II) ratios the shape of the polarographic waves differs from those recorded with a great excess of ligand. Figure 3 shows polarograms taken at various ligand/metal ratios, A, in solution. For A = 0, only one wave appears on the polarogram, corresponding to the reduction of the "free" Cd(II) ion (curve a); for $A > 1$ one wave also appears due to reduction of the complex (curve c), and this is displaced toward more negative potentials. Over the intermediate range of A values ($0 < A < 1$), both waves are seen (curve b). In this region, the height of the wave due to reduction of the "free" Cd(II) ion decreases with increasing A at the expense of the height of that due to the reduction of complex. Figure 4 shows the dependence of diffusion current of the reduction of the "free" Cd(II) ion (curve a) and the complex (curve b) on the composition of the solution. The break point on the curves clearly indicates the composition of the complex (1:1) over the low ligand concentration range.

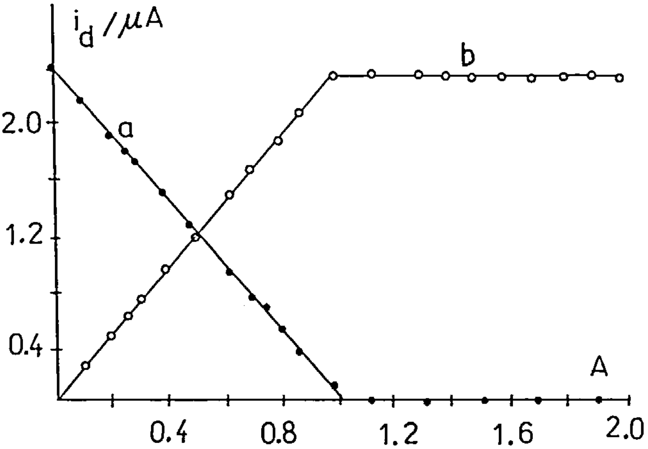

FIGURE 4 Plots of i_d vs A for the Cd(II)-trien system. T = 25.0 ± 0.1°C, I = 1.0. a) i_d of "free" Cd(II) ions, b) i^c_d of complexed Cd(II)-trien ions.

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