# STUDIES ON MIXED COMPLEXES OF Cd(II) WITH DIAMINOPROPANE AND THIOSULPHATE USING DIFFERENTIAL PULSE POLAROGRAPHY

BY

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## ABSTRACT

Ternary complexes of cadmium (II) with thiosulphate (Th) as a primary ligand and diaminopropane (DAMP) as a secondary ligand have been studied using differential pulse (DP) polarography. Schaap and McMasters treatment revealed the presence of two mixed complexes with stoichiometries 1:1:1 and 1:1:2. The reduction of simple and mixed complexes is reversible and diffusion-controlled. The stability constants and the mixing constants of the ternary system were calculated.

## INTRODUCTION

The use of differential pulse polarography for the determination of the stability constants of complex ions has been reported by Heath and Hefter [1]. This technique offers a considerable number of advantages [I] compared to DC-polarography. Moreover, the limitations of the original

Hume [2] treatment using DC-polarography has been documented
[3,4].

In the present work DP polarography was used to investi-
gate the simple complexes of (Cd-diaminopropane and Cd-
thiosulphate) as well as the mixed-ligand complexes of Cd (II)
with the two ligands as a continuation of our earlier work [5,6].

## EXPERIMENTAL

Polarograms were obtained using Metrohm polarographic
analysis instrument (626 Polarecord) with 663 VA stand. The
reference electrode, Ag/AgCl/3M-KCl, was used throughout the
measurements.

For tast polarography (DC sampled), a drop time of 1.0
s and a scan rate of 5 $mV^{-1}$, and in differential pulse DP
polarography, 50 mV pulse amplitude were used.

All measurements were made at 25°C, pH=8 and ionic
strength of 1.0 mol $dm^{-3}$ was maintained constant using sodium
nitrate. The concentration of $Cd^{2+}$ ions was $1.10^{-4}$ mol $dm^{-3}$.

Reagent-grade chemicals, deionized water and triply
distilled mercury were employed in all cases.

## Theoritical

Heath and Heffer [1] have shown that the peak potential

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($E_p$) for a reversible diffusion-controlled process, obtained
from the DP wave, is related to the half-wave potential ($E_{1/2}$)
of DC polarography by:

$$E_p = E_{1/2} - \Delta E/2 \qquad (1)$$

where $\Delta E$ is the pulse amplitude. According to equation (1),
the shift in the half-wave potential ($\Delta E_{1/2}$) is equal to
the shift in peak potential ($\Delta E_p$) from the DP polarograms.

The Deford-Hume expression [2] has been modified accord-
ing to eq. (1), for the DP polarography. This expression may
be written as follows:

$$F_0 (X) = \sum B_j \, C_x^j$$

$$= \text{antilog} \left[ 0.434 \, (nF/RT) \, \Delta E_p + \log \frac{(I_p)_s}{(I_p)_c} \right] \quad (2)$$

In case of mixed systems, the Schaap and McMasters
expression [7] has been modified previously [5], in order to
determine the stability constans. The expression may be written:

$$F_{00} (XY) = \text{antilog} \left[ 0.434 \, (nF/RT) \, \Delta E_p + \log \frac{(I_p)_s}{(I_p)_c} \right] \quad (3)$$

where the sympols have their usual significance. The term log
$\frac{(I_p)_s}{(I_p)_c}$ is normally small because it makes little contribution

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to the $F_{00}$ (XY) function. Thus, eq. (3) might be modified to
the following expression:

$$F_{00} (XY) = \text{antilog} [0.434 \ (nF/RT) \ \Delta E_p] \tag{4}$$

From Schaap and MaMasters expression [7]

$$F_{00} (XY) = A + B [X] + C [X]^2 + D [X]^3$$

where

$$A = B_{00} + B_{01} [Y] + B_{02} [Y]^2 + B_{03} [Y]^3$$

$$B = B_{10} + B_{11} [Y] + B_{12} [Y]^2$$

$$C = B_{20} + B_{21} [Y]$$

$$D = B_{30}$$

The original graphical method [1] may be applied to
$F_{00}$ (XY) function if the activity of one of the ligands is
held constant while that of the other is varied. The intercept
on the $F_{00}$ axis in the plot of $F_{00}$ vs. [X] gives A, and

$$F_{10} = F_{00} - A/[X] = B + C [X] + D [X]^2$$

By a similar plotting of $F_{10}$ vs. [X], B is obtained and then
C and D by iteration.

From the knowledge of C, the mixed stability constant
$B_{21}$ may be calculated. In order to determine $B_{11}$ and $B_{12}$, B
must be evaluated at two concentrations of Y.

In the present study X and Y refer to diaminopropane
and thiosulphate ligands. In the stability constants $B_{00}$, the

first subscript refers to the number of diaminopropane, the
second one to the number of thiosulphate ligands.


## RESULTS AND DISCUSSION

The general expression for the half peak width of a DP
wave has been derived by a number of workers [ 8,9 ]. A value
of 62 mV for a reversible two-electron reduction using 50 mV
as a pulse amplitude has been reported [ 8,9 ]. For simple and
mixed camplexes in the present work, the DP polarograms in 1 M
nitrate medium had half peak widths of 62 ± 1 mV as shown
from Tables 1 & 2, indicating the reversibility of the reduc-
tion. For, further confirmation, DC (tast) polarography was
used under the same conditions used for DP polarography.
The plots of log $i/(i_d - i)$ against E were linear of slope
31 ± 1 mV, indicating a high degree of reversibility. On the
other hand, the plots of log $i_1$ versus log h (h=mercury height)
were linear correlations of slopes equal to 0.5 indicating that
the reduction of simple and mixed complexes is diffusion-
controlled (using DC-Sargent-Welch polarograph model 4001)


The formation constants for Cd (DAMP) and Cd (Th)
complexes in nitrate medium ($\mu = 1$, $NaNO_3$) at 25 °C were
determined using eq. (2). The results are given in Table (1).


For Cd (DAMP) system, the results agree well with the
previously reported values [10] using conventional DC
polarography. In case of Cd(Th) system, the stability

constants values are in a good agreement with those obtained earlier [11].

TABLE(1)

| complex species | formation constants | |
| --- | --- | --- |
| $[Cd\ (DAMP)]^{2+}$ | $\log B_{10}$ | 5.60 |
| $[Cd\ (DAMP)_2]^{2+}$ | $\log B_{20}$ | 7.54 |
| $[Cd\ (DAMP)_3]^{2+}$ | $\log B_{30}$ | 8.55 |
| $[Cd\ (Th)]$ | $\log B_{01}$ | 3.10 |
| $[Cd\ (Th)_2]^{2-}$ | $\log B_{02}$ | 4.35 |
| $[Cd\ (Th)_3]^{4-}$ | $\log B_{03}$ | 5.36 |

Ternary Complexes

The concentration of (DAMP) ions was varied while that of (Th) ions was kept contant at two values 0.04 and 0.2 M because at these concentrations 1:1 and 1:2 Cd (Th) complexes, respectively were found to be the predominant species (Fig. 1).

It should be noted that for simple and mixed ligand complexes, the $E_p$ values obtained from DP polarograms were confirmed using D.C (tast) polarography. It was found that the $(\Delta E_p)$ shift agrees well with $(\Delta E_{1/2})$ values and the results were generally repreducible to $\pm$ 1 mV.
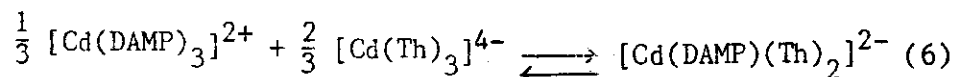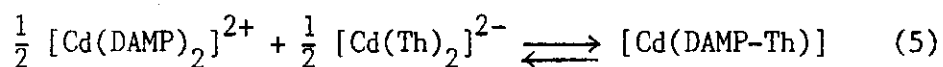
The stability constants of the ternary complexes were calculated using Schaap and McMasters [7] method usi.. . (3) of DP polarograhic wave. The derived function $F_{00}$, $F_{10}$, $F_{20}$ and $F_{30}$ are given in Tables (2 and 3). Figures (2 and 3) show the plots of $F_{10}$ vs. (DAMP) at (Th), 0.04 and 0.2 M, respectively.

The results of A, B, C and D values are presented in Tables (2 and 3). From the values of B at different thiosulphate concentrations, the formation constants of [Cd(DAMP)(Th)] and $[Cd(DAMP)(Th)_2]^{2-}$ were calculated and found to be: log $B_{11}$ = 7.59 and log $B_{12}$ = 7.27, respectively.

From the two values of C, it was found that the log $B_{21}$ is negative value (log $B_{21}$ = -8.66) which indicates the absence of the mixed complex species $[Cd(DAMP)_2(Th)]$ in the solution. At the same time, the two values of log D are 8.65 and 8.83 which agree well with the experimentally determined log $B_{30}$ value of 8.55.

The mixing constants [12] (log $K_m$) for the following reactions are given below:

$$\frac{1}{2} [Cd(DAMP)_2]^{2+} + \frac{1}{2} [Cd(Th)_2]^{2-} \rightleftharpoons [Cd(DAMP-Th)] \quad (5)$$

$$\frac{1}{3} [Cd(DAMP)_3]^{2+} + \frac{2}{3} [Cd(Th)_3]^{4-} \rightleftharpoons [Cd(DAMP)(Th)_2]^{2-} \quad (6)$$

$$\log K_{m_{11}} = \log B_{11} - \frac{1}{2} (\log B_{20} + \log B_{02})$$

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$$\log K_{m_{12}} = \log B_{12} - (\frac{1}{3} \log B_{30} + \frac{2}{3} \log B_{03})$$

Which yield $\log K_m$, 1.65 and 0.85 for reactions 5 and 6, respectively. On the other hand, the stabilization constant $\log K_s$ is expressed as follows [13]:

$$\log K_s = (\log K_m - \log 2)$$

which yield $\log K_s$, 1.35 and 0.55 for reactions 4 and 5, respectively. The positive values of $\log K_m$ and $\log K_s$ show that the mixed complexes are more stable than the simple complexes.

### Waters-Dewitt expressions

The formation constants obtained for mixed systems can be compared with that statistically predictable which were evaluated according to the following expression [14]:

$$B_{11} = 2 \left[ \frac{4}{9} B_{02} B_{20} \right]^{1/2}$$

$$B_{12} = 3 B_{30}^{1/3} B_{03}^{2/3}$$

The values of the stability constants (log values) calculated from the above expression are 6.1 and 6.9, respectively. The observed values of the mixed complexes are higher than the statistically calculated values. This has been explained by many authors [14,15] considering the enhancement due to some weak bonding between unlike ligands. This may also be explained by the neutralization of charge on ions [12].

Table (2): Differential pulse polarographic data for the [Cd(DAMP) (Th.)] system. Ionic strength 1.0 mol. $dm^{-3}$, 1 x $10^{-4}$ M $Cd^{2+}$, 0.04 M thiosulphate, 25 °C.

| [DAMP] mol.dm$^{-3}$ | half-peak width (mV) | $\Delta E_p$ (mV) | $F_{00} \cdot 10^4$ | $F_{10} \cdot 10^5$ | $F_{20} \cdot 10^7$ | $F_{30} \cdot 10^7$ |
|---|---|---|---|---|---|---|
| 0.04 | 62 | 150 | 11.63 | 2.95 | --- | ---- |
| 0.05 | 62 | 154 | 16.15 | 3.23 | --- | ---- |
| 0.06 | 62 | 161 | 27.86 | 4.54 | 4.73 | ---- |
| 0.08 | 63 | 170 | 56.16 | 7.02 | 6.29 | 47.25 |
| 0.10 | 61 | 176 | 69.60 | 8.95 | 6.96 | 52.60 |
| 0.15 | 61 | 189 | 246.55 | 16.44 | 9.63 | 52.87 |
| 0.20 | 62 | 197 | 459.77 | 22.98 | 10.49 | 44.00 |
| 0.25 | 62 | 205 | 857.55 | 34.29 | 12.92 | 44.66 |
| 0.30 | 62 | 212 | 1478.56 | 49.26 | 15.76 | 45.87 |
| 0.35 | 61 | 217 | 2182.42 | 62.35 | 17.24 | 44.40 |
| 0.40 | 62 | 222 | 3221.36 | 80.53 | 19.63 | 44.83 |
| | | | $\log A_1 =$ 2.00 | $\log B_1 =$ 6.30 | $\log C_1 =$ 7.37 | $\log D_1 =$ 8.65 |

Table (3): Differential pulse polarographic data for [Cd(DAMP)(Th)] system. Ionic strength 1.0 M $dm^{-3}$, 1 x $10^{-4}$ M $Cd^{2+}$, 0.2 M thiosulphate, 25 °C

| [DAMP] mol.$dm^{-3}$ | half-peak width (mV) | $\Delta E_p$ (mV) | $F_{00} \cdot 10^5$ | $F_{10} \cdot 10^7$ | $F_{20} \cdot 10^7$ | $F_{30} \cdot 10^7$ |
|---|---|---|---|---|---|---|
| 0.04 | 63 | 166 | 4.11 | 1.03 | 3.25 | ---- |
| 0.05 | 63 | 170 | 5.52 | 1.12 | 4.40 | ---- |
| 0.06 | 63 | 172 | 6.55 | 1.09 | 3.17 | ---- |
| 0.08 | 62 | 180 | 12.23 | 1.53 | 7.83 | 67.25 |
| 0.10 | 61 | 185 | 18.06 | 1.81 | 9.10 | 65.00 |
| 0.15 | 62 | 196 | 42.53 | 2.84 | 12.63 | 69.53 |
| 0.20 | 62 | 205 | 85.72 | 4.29 | 16.95 | 72.25 |
| 0.25 | 61 | 213 | 159.83 | 6.39 | 21.96 | 77.84 |
| 0.30 | 62 | 218 | 235.92 | 7.86 | 23.20 | 69.00 |
| 0.35 | 63 | 223 | 346.23 | 9.95 | 25.86 | 66.74 |
| 0.40 | 61 | 227 | 475.49 | 11.89 | 27.48 | 62.45 |
| | | | log $A_2$= 3.47 | log $B_2$= 6.95 | log $C_2$= 7.40 | log $D_2$= 6.63 |
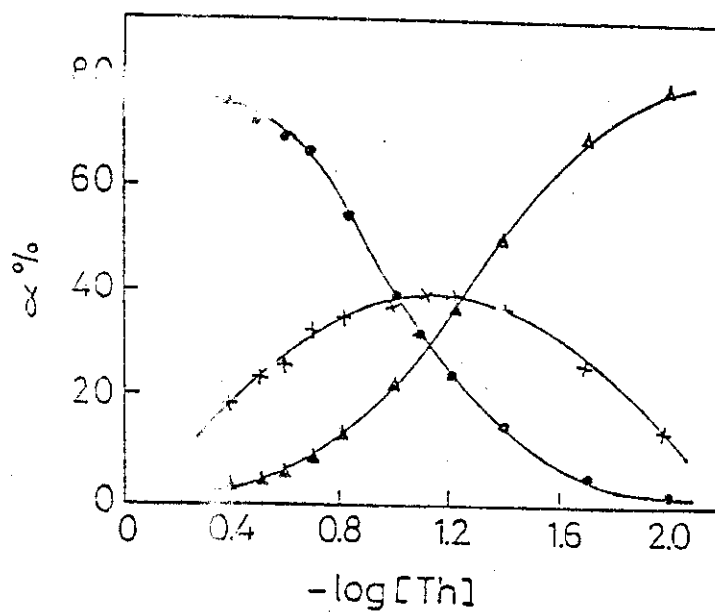
Fig.1: The percentage distribution of Cd(II) in
its various forms: ▲ [ Cd(Th) ]
+ [Cd(Th)$_2$]$^{2-}$  ● [ Cd(Th)$_3$]$^{+-}$
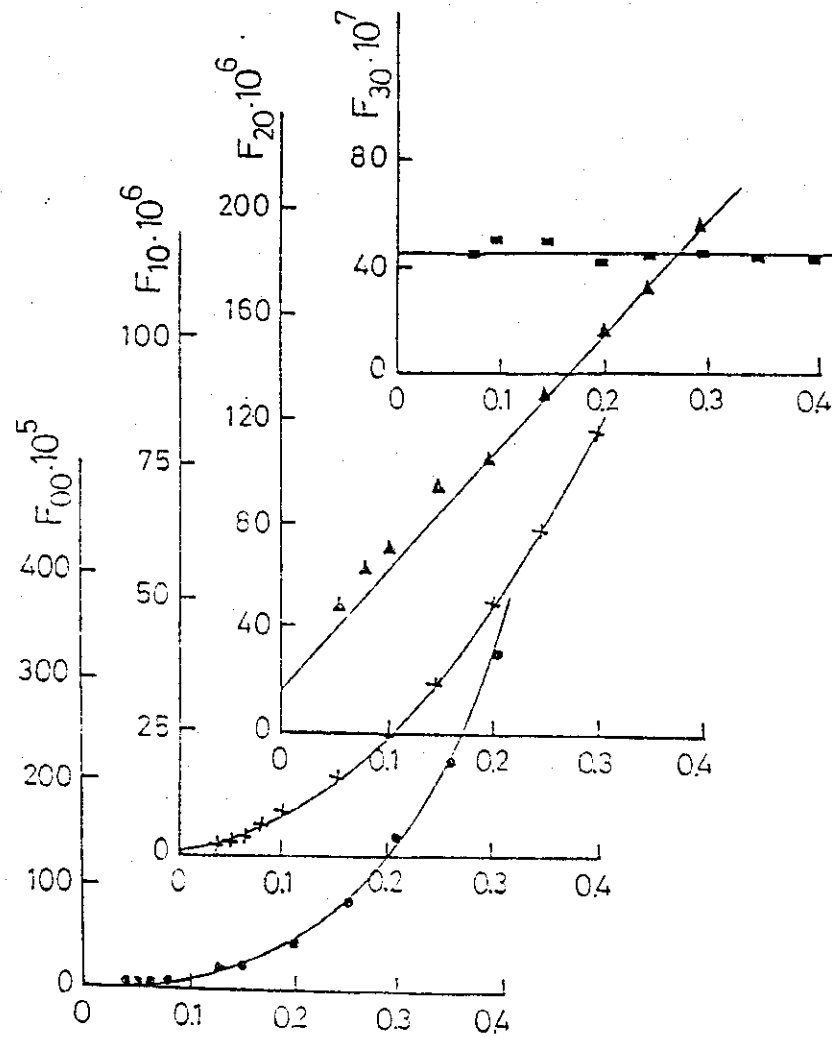
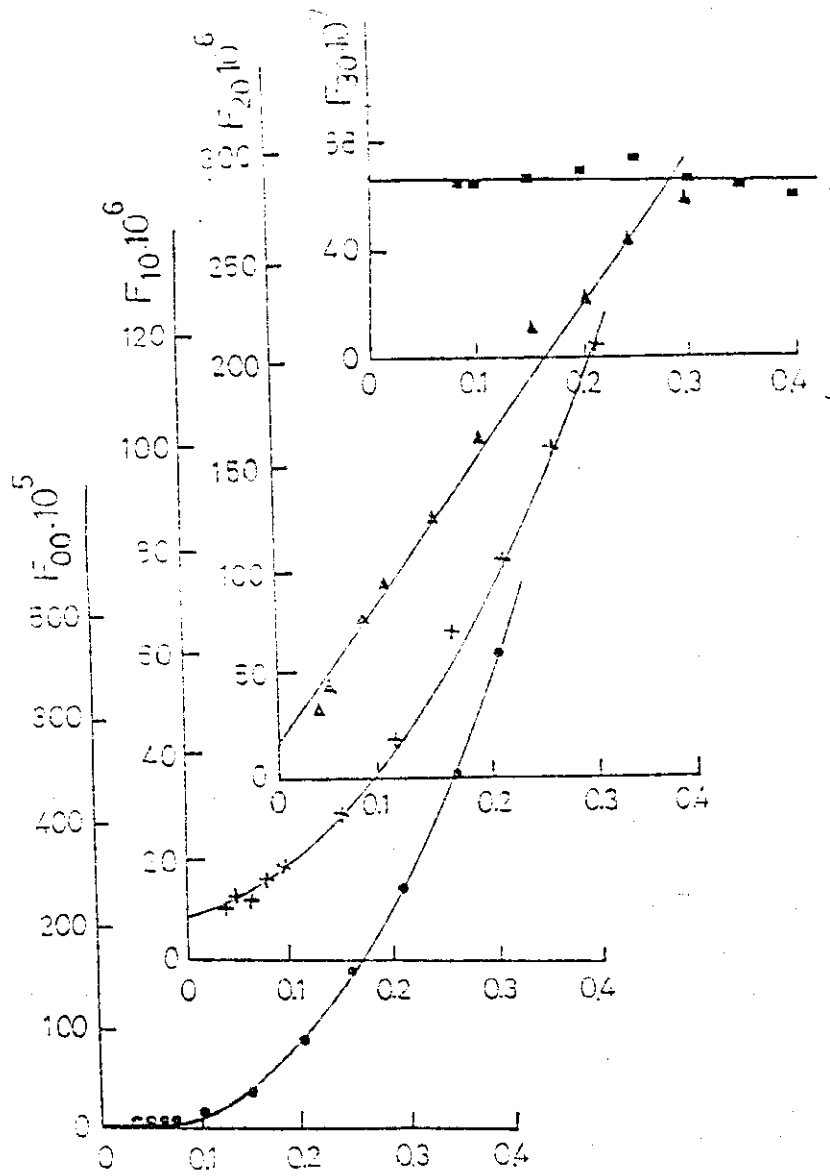Fig.2: Plots of $F_{i0}$ vs. [DAMP] (mol dm$^{-3}$) at [Th] = 0.04 mol dm$^{-3}$

Fig. 3: Plots of $F_{i0}$ vs. [DAMP] (mol $dm^{-3}$) at [Tn] = 0.2 $mol\ dm^{-3}$

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دراسات على المتراكبات المختلطة لأيونات الكادميوم مع ليجاندات
ثنائى أمينو بوبان والثيوسلفات باستخدام الريفرنشال بلس
بولاروجـــــــراڧى.

+ أميرة محمود حسنين ـ ++ مصطفى محمود مصطفى ـ ++ مصطفى ابراهيم مصطفى
++ السيد محمود مبـــــروك
+ قسم الكيمياء ـ كلية التربية ـ بكفــر الشيخ ـ جامعـــة طنطـــا
++ قسم الكيمياء ـ كلية العلــــــوم ـ جامعـــة بنها ـ بنها

يتضمن هذا البحث دراسة المتراكبات المختلطة لايونات الكادميوم مع
الثيوسلفات كليجاند ابتدائى وثنائى امينو بروبان كليجاند ثانوى باستخـــدام
الريفرنشــال بلس بولاروجرافى وقد اثبتت النتائج تكوين متراكبان فى المحلول
بنسب 1:1:1 ، 2:1:1 وان اختزال ايونات الكاديوم فى وجود الثيوسلفات
وثنائى امينو بروبان يتم بطريقة انعكاسية عن طريق الانتشار وقد تم تعين
ثوابت التكوين للمتراكبات البسيطة والمختلطة.