
DIFFERENTIAL PULSE POLAROGRAPHIC STUDIES ON SIMPLE AND MIXED LIGAND COMPLEXES OF Cd(II) WITH DIAMINOPROPANE AND ADIPATE LIGANDS

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The composition, stability and equilibria of ternary complexes of Cd(II) with adipate (Adp) as primary ligand and 1,3-diaminopropane (DAMP) as secondary ligand have been studied using differential pulse (d.p.) polarography. The results reveal the presence of three ternary complexes with stoichiometries 1 : 1 : 1, 1 : 1 : 2, and 1 : 2 : 1. Also, the composition and stability of binary species have been determined. The reduction of simple and mixed ligand complexes is reversible and diffusion controlled. The formation constants of mixed complexes were calculated and compared with the observed values.

Mixed-ligand complexes are generally formed when metal ion is present in a mixture of two or more ligands in solution. The DeFord-Hume method¹ for simple complexes was extended to study the formation constants of mixed-ligand species by Schaap and McMasters², which has been extensively used by several workers³⁻⁶.

The modern electroanalytical technique offer a considerable number of advantages compared to conventional polarography, in particular in the determination of the formation constants of metal complex ions in solution^{7,8}. Differential pulse (d.p.) polarography has been shown to be useful for the determination of the formation constants of simple complexes⁷ and in particular of mixed-ligand complexes⁹.

This study concerns the simple and mixed-ligand complexes of Cd(II) with adipate (Adp) and 1,3-diaminopropane systems using d.p. polarography. The graphical method of DeFord-Hume¹ has been used to determine the stability constants of simple complexes (Cd-1,3-diaminopropane and Cd-adipate), and the Schaap-McMasters² graphical method to assess the formation constants of mixed-ligand complexes of Cd(II) with the two ligands.

EXPERIMENTAL

Polarograms were obtained using Metrohm polarographic analysis instrument (626 Polarecord)

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with 663 VA stand. The reference electrode, Ag/AgCl/3M-KCl, was used throughout the measurements.

For fast polarography (DC sampled), a drop time of 1.0 s and a scan rate of 5 mV s^{-1} , and 50 mV (pulse amplitude) was used for differential pulse (d.p.) polarography.

All measurements were made at 25°C , pH 8 and ionic strength of 1.00 mol dm^{-3} was maintained constant using sodium nitrate. The concentration of Cd^{2+} ions was $1 \cdot 10^{-4} \text{ mol dm}^{-3}$.

Reagent-grade chemicals, deionized water and triply distilled mercury were employed in all cases. A maximum suppressor was not used.

THEORETICAL

Heath and Hefter⁷ have modified the DeFord and Hume¹ treatment for determining the consecutive stability constants for the simple complexes for use with d.p. polarography instead of conventional DC polarography. In this modification, it is assumed that the shift in the half-wave potential, $(E_{1/2})_s - (E_{1/2})_c$, is equal to the shift in (d.p.) peak potential, $(E_p)_s - (E_p)_c$. Thus, the modified DeFord-Hume expression is expressed as follows:

$$F_0(X) = \sum B_j C_X^j = \text{antilog} [0.434 (nF/RT) \Delta E_p + \log ((I_p)_s / (I_p)_c)], \quad (1)$$

where B_j is the overall formation constant of the j th complex, C_X is the analytical concentration of the ligand, ΔE_p is the shift in the d.p. peak potential which equals $(E_p)_s - (E_p)_c$ (the subscripts s and c refer to the simple and complex ions, respectively). I_p is the peak height of the d.p. wave.

Similarly, the Schaap and McMasters expression² has been modified by Killa et al.⁹ to determine the stability constants of mixed-ligand complexes, using differential pulse (d.p.) polarography:

$$F_{00}(XY) = \text{antilog} [0.434 (nF/RT) \Delta E_p + \log ((I_p)_s / (I_p)_c)], \quad (2)$$

where $\Delta E_p = (E_p)_s - (E_p)_c$ is the shift in the peak potential due to complexation in the presence of X and Y ligands. The term $\log ((I_p)_s / (I_p)_c)$ is normally small because it makes little contribution to the $F_{00}(XY)$ function. Thus, Eq. (2) might be modified to an expression of the form:

$$F_{00}(XY) = \text{antilog} [0.434 (nF/RT) \Delta E_p]. \quad (3)$$

In the present work, the formation constants of simple complexes were evaluated using Eq. (1), and for mixed-ligand species Eq. (3) was used in case of d.p. wave, as described in the previous paper⁹.

RESULTS AND DISCUSSION

Nature of Reduction

The polarographic reduction of [Cd(II)-1,3-diaminopropane], and [Cd(II)-adipate] complexes in 1M sodium nitrate is reversible, with $n = 2$. The reversibility is confirmed in this study by measuring the half-peak width of the differential-pulse polarograms. Values 62 ± 1 mV were found for all of the polarograms recorded for either Cd^{2+} , Cd(DAMP), and Cd(Adp) systems. This is consistent with the prediction of Dillard and Hanck¹⁰ that, for a fully reversible two-electron reduction with an applied pulse amplitude of 50 mV, the value of the half-peak width is 62 mV. Similarly, the d.p. polarograms for the ternary system, Cd-diaminopropane-adipate, in 1M nitrate had a half-peak widths of 62 ± 1 mV, indicating a high degree of reversibility.

It is important to recall that the reversibility of the binary and ternary systems was confirmed using the DC sampled (tast mode) technique under the conditions used for the d.p. polarography. The plots of $\log [i/(i_d - i)]$ against E were linear with a slope of 31 ± 1 mV. Also, the plots of i_d vs $h^{1/2}$ were linear and passed through the origin indicating that the reduction of binary and ternary systems was diffusion controlled (using DC Sargent-Welch polarograph model 3001).

The Simple Systems

For the system Cd(DAMP), the Cd^{2+} ions concentration was kept constant at $1 \cdot 10^{-4}$ mol dm^{-3} and the variation of E_p with varying concentration of 1,3-diaminopropane was studied at constant ionic strength (1.0 mol dm^{-3} using NaNO_3) at 25°C. Analysis of the data in the concentration range 0.02 to 0.4 mol dm^{-3} of the amine indicate the formation of 1 : 1, 1 : 2, and 1 : 3 (metal-ligand) complexes. The data were, therefore, analysed on the basis of the DeFord-Hume expression¹ in the form modified by Heath and Hefter⁷ for d.p. polarography. Three complexes were observed, the stability constants being $\log B_{10} = 5.60$, $\log B_{20} = 7.54$, and $\log B_{30} = 8.55$. The obtained values agree well with those obtained by Gupta et al¹¹ using conventional DC polarography.

For the Cd(Adp) system, the conditions were similar to those of the Cd(DAMP) system. Application of the DeFord-Hume method as modified by Heath and Hefter⁷ suggested the formation of 1 : 1, 1 : 2, and 1 : 3 complex species. The formation constants obtained are: $\log B_{01} = 1.35$, $\log B_{02} = 1.84$, and $\log B_{03} = 2.89$, in good agreement with those obtained earlier¹².

Mixed (Ternary) Systems

In the ternary system, the concentrations of adipate ion were kept constant at

0.1 mol dm⁻³ and 0.25 mol dm⁻³ because at these concentrations 1:1 and 1:2 complex species were found to be predominant.

In the first set solutions containing $1 \cdot 10^{-4}$ mol dm⁻³ Cd²⁺ ions, 0.1 mol dm⁻³ adipate ions and concentrations of DAMP varying from 0.03 to 0.4 mol dm⁻³ were examined (Table I). The ionic strength was maintained constant (1.0 mol dm⁻³) using NaNO₃. The same procedure was adopted in the second set in which adipate ion concentration was kept constant at 0.25 mol dm⁻³ (Table II).

Diaminopropane and adipate species are considered as bidentate ligands. Thus, the maximum number for the two species which can associate with Cd(II) ions is three, hence at most three mixed complex species can occur. Consequently, the Schaap and McMasters treatment for the ternary complexes can be written as follows:

$$F_{00}(XY) = A + B[X] + C[X]^2 + D[X]^3, \quad (5)$$

where

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

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

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

$$D = B_{30}.$$

TABLE I

Differential pulse polarographic data for the [Cd(DAMP)(Adp)] system. Ionic strength 1.0 mol . dm⁻³, $1 \cdot 10^{-4}$ M-Cd²⁺, 0.1M-(Adp), 25°C

DAMP mol dm ⁻³	ΔE_p mV	$F_{00} \cdot 10^4$	$F_{10} \cdot 10^6$	$F_{20} \cdot 10^8$	$F_{30} \cdot 10^8$
0.03	144	7.42	—	—	—
0.04	153	14.96	2.49	—	—
0.06	161	27.90	3.82	0.503	—
0.08	168	48.13	5.39	0.574	—
0.10	174	76.80	7.18	0.638	1.78
0.15	185	180.90	11.73	0.729	1.79
0.20	194	364.63	17.98	0.854	1.99
0.25	200	581.84	23.07	0.891	1.72
0.30	207	1 003.61	33.29	1.080	2.07
0.35	212	1 481.45	42.18	1.180	2.06
0.40	216	2 022.94	50.45	1.240	1.95

X and Y refer to diaminopropane and adipate ligands, respectively. In the stability constants B_{00} , the first subscript refers to the number of DAMP ligands, the second one to the number of Adp ligands.

The formation constants were evaluated using Eq. (3). According to this equation, the function $F_{00}(X, Y)$ can be obtained. Also, the functions F_{10} , F_{20} , and F_{30} are obtained from the relations:

$$F_{10} = (F_{00} - A)/[\text{DAMP}] \quad (6)$$

$$F_{20} = (F_{10} - B)/[\text{DAMP}] \quad (7)$$

$$F_{30} = (F_{20} - C)/[\text{DAMP}]. \quad (8)$$

The intercepts at $[\text{DAMP}] = 0$ of the plots (Figs 1 and 2) of F_{00} , F_{10} , F_{20} and F_{30} vs $[\text{DAMP}]$ give the respective values of A , B , C , and D . From these values the stability constants B_{11} , B_{12} and B_{21} of the Cd(DAMP-Adp) system were thus calculated:

(I) $[\text{Adp}] = 0.10 \text{ mol dm}^{-3}$ (Fig. 1).

$$A_1 = 5 \cdot 10^4, B_1 = 8 \cdot 10^5, C_1 = 4.6 \cdot 10^7, D_1 = 1.90 \cdot 10^8.$$

(II) $[\text{Adp}] = 0.25 \text{ mol dm}^{-3}$ (Fig. 2).

$$A_2 = 1.0 \cdot 10^5, B_2 = 2.30 \cdot 10^6, C_2 = 5.50 \cdot 10^7, D_2 = 2.70 \cdot 10^8.$$

TABLE II

Differential pulse polarographic data for the Cd[(DAMP)(Adp)] system. Ionic strength $1.0 \text{ mol} \cdot \text{dm}^{-3}$, $1 \cdot 10^{-4} \text{M-Cd}^{2+}$, 0.25M-(Adp) , 25°C

DAMP mol dm^{-3}	ΔE_p mV	$F_{00} \cdot 10^4$	$F_{10} \cdot 10^6$	$F_{20} \cdot 10^8$	$F_{30} \cdot 10^8$
0.03	157	2.040	3.470	—	—
0.04	161	2.790	4.480	0.545	—
0.06	168	4.810	6.350	0.675	—
0.08	174	7.680	8.350	0.756	2.58
0.10	179	11.34	10.34	0.804	2.54
0.15	189	24.70	15.80	0.900	2.33
0.20	198	49.79	24.39	1.105	2.78
0.25	204	79.45	31.38	1.163	2.45
0.30	210	126.78	41.93	1.321	2.57
0.35	216	202.29	57.51	1.577	2.93
0.40	220	276.24	68.81	1.663	2.78

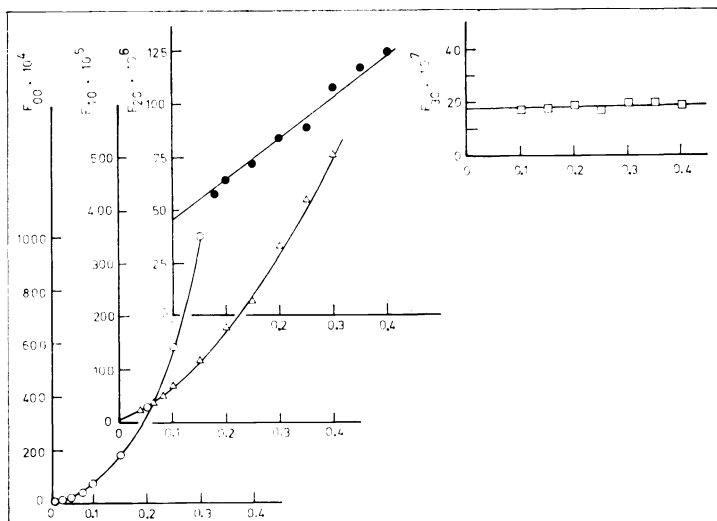


FIG. 1
Plots of F_{i0} vs [DAMP] (mol dm^{-3}) at [Adp] = 0.1 mol dm^{-3}

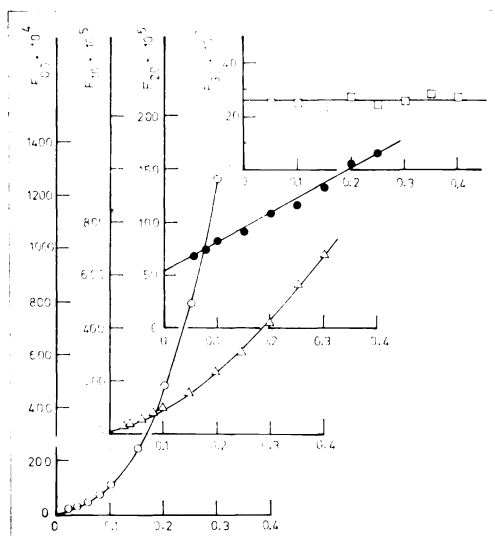


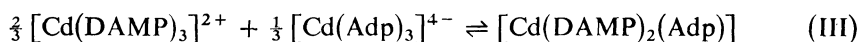
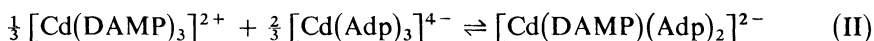
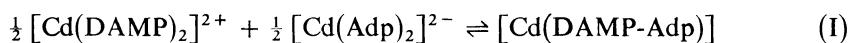
FIG. 2
Plots of F_{i0} vs [DAMP] (mol dm^{-3}) at [Adp] = 0.25 mol dm^{-3}

The values of C_1 and C_2 gave two values for $\log B_{21} = 7.72, 7.91$, in good agreement with each other. From the two values B_1 and B_2 , the stability constants $\log B_{11}$ and $\log B_{12}$ were calculated and were found to be 6.21 and 7.38, respectively. It should be noted that the two values of $\log D$ from both series are 8.28 and 8.43 (average 8.36 ± 0.08), which agrees well with the value of $\log B_{30}$ (8.55).

Comparison of Mixed Complexes with Binary Ones

The shift in peak potential (E_p) of Cd(II) ions in the presence of the mixture of adipate and diaminopropane ions is greater than in (DAMP) alone. This suggests the formation of Cd(DAMP-Adp) mixed complexes.

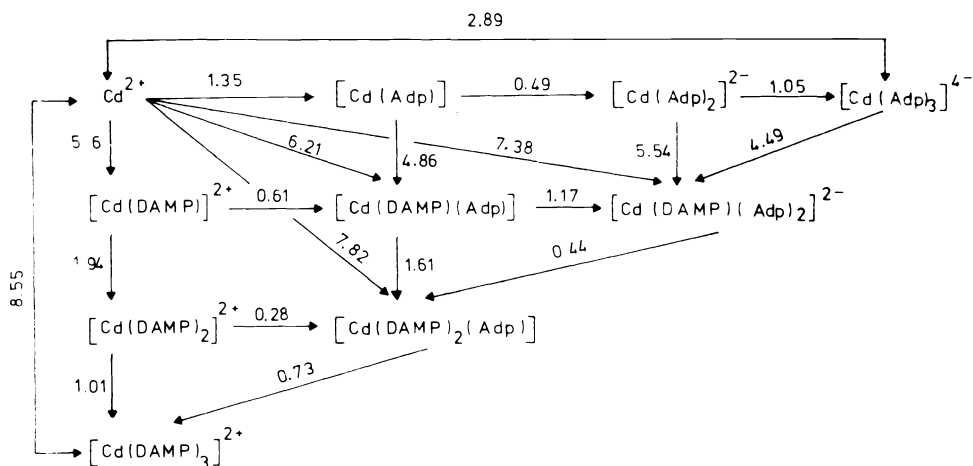
The mixing constants¹³ ($\log K_m$) for the following reactions are given below:



$$\log K_m(\text{I}) = \log B_{11} - \frac{1}{2} (\log B_{20} + \log B_{02})$$

$$\log K_m(\text{II}) = \log B_{12} - \left(\frac{1}{3} \log B_{30} + \frac{2}{3} \log B_{03} \right)$$

$$\log K_m(\text{III}) = \log B_{21} - \left(\frac{2}{3} \log B_{30} + \frac{1}{3} \log B_{03} \right)$$



SCHEME 1

The equilibria between mixed-ligand species and the log K values for these equilibria

which indicate the relative stability of ternary complexes in solution as compared to parent binary complexes. The values of $\log K_m$ of the above reactions are 1.52, 3.02 and 1.15, respectively. The positive values of mixing constants show that mixed complexes are more stable than simple complexes.

The various complexation reactions along with their stepwise stability constants are shown in Scheme 1.

The $\log K$ value for $[\text{Cd}(\text{DAMP})^{2+}]$ to $[\text{Cd}(\text{DAMP})_2]^{2+}$ is 1.94 while the value for $[\text{Cd}(\text{Adp})]$ to $[\text{Cd}(\text{DAMP})(\text{Adp})]$ is 4.86. Likewise, the $\log K$ value of the formation of $[\text{Cd}(\text{DAMP})(\text{Adp})]$ from $[\text{Cd}(\text{DAMP})]^{2+}$ is 0.61 while the value of the formation $[\text{Cd}(\text{Adp})_2]^{2-}$ from $[\text{Cd}(\text{Adp})]$ is 0.49. The $\log K$ values obtained from the addition of neutral (DAMP) as a third ligand to $[\text{Cd}(\text{Adp})_2]^{2-}$, $[\text{Cd}(\text{DAMP})(\text{Adp})]$, and $[\text{Cd}(\text{DAMP})_2]^{2+}$ are 5.54, 1.61, and 1.01. These results show that the mixed species are preferred.

Watters and DeWitt¹⁴ derived the following expression for the prediction of stability constants of ternary complexes from statistical factors:

$$B_{11} = 2 [(4/9) B_{02} \cdot B_{20}]^{1/2}$$

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

$$B_{21} = 3B_{30}^{2/3} \cdot B_{03}^{1/3}$$

The values of stability constants (log values) calculated from the above expressions are 4.78, 5.25 and 7.13, respectively. The experimental values for the mixed complexes are higher than the statistically calculated values. This has been explained by many workers^{2,15} considering the cooperative effects of electrostatic forces between different kinds of ligands and steric effects. This may also be accounted for the neutralization of charge¹³.

Cd(II) can be determined using differential pulse (d.p.) polarography technique, in the presence of adipate and 1,3-diaminopropane.

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