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Mixed Ligand Complexes of Cadmium with Trimethylenediamine and β-picoline using Cyclic Voltammetry Technique

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Linear-scan and cyclic voltammograms were used to determine the overall formation constants of simple and mixed complexes of Cd(II) with β-picoline and trimethylenediamine. DeFord-Hume's treatment suggests that both the ligands form 1 : 3 high complexes separately in aqueous medium and Schaap-McMasters treatment reveals the presence of three mixed complexes with stoichiometry 1 : 1 : 1; 1 : 1 : 2 and 1 : 2 : 1 in the same medium as for the simple complexes. The formation constants of mixed complexes were calculated statistically and compared with the observed values. The equilibria between the mixed ligand species in solution and their equilibrium are also given.

INTRODUCTION

Cyclic voltammetry using hanging mercury dropping electrode (HMDE) has been widely used in investigations of mechanisms of oxidation and reduction of organic compounds[1–3]. It has also been used for the determination of formation constants of simple-ligand[4] and mixed-ligand[5] complexes. In the present work, the simple- and mixed-ligand complexes of Cd(II) ions with β-picoline (Pic) as a primary ligand and trimethylenediamine (TMDA) as the secondary ligand have been studied using linear-scan and cyclic voltammetry techniques.

EXPERIMENTAL

The linear-scan and cyclic voltammograms were measured with Princeton Applied Research Model 174A polarographic analyser. Potential-current curves were recorded on X–Y recorder Type Advance AR-2000. A conventional three electrode cell with saturated calomel electrode (SCE) was employed. The working electrode in linear-scan and cyclic measurements was a PAR 9323 (stationary) hanging mercury drop electrode and the electrode area normally was 0.0408 cm^2. The scan rate was 100 $mV\ s^{-1}$. For polarography (DC sampled mode) measurements, a potential pulse 10 mV, a drop time of 1.0 s and a scan rate of

5 mV s^{-1} were used throughout the measurements. All measurements were made at 25°C and an ionic strength of 1.0 M was maintained by using sodium nitrate. The concentration of Cd^{2+} ions was 2×10^{-4} M.

Reagent grade chemicals, deionised water and triple distilled mercury were employed in all cases. No maximum suppressor was used.

RESULTS AND DISCUSSION

The reversibility of the reduction of simple and mixed systems was very close to the values of the following expression[6]:

$$E_{p_c} - E_{p_a} = \frac{59}{n} \text{ mV} \qquad (1)$$

where E_{p_a} is the anodic peak potential and E_{p_c} is the cathodic peak potential. Also, the peak potential (E_p) was found to be independent of the scan rate, indicating the reversibility. Further confirmation of the reversibility was obtained using the test polarography technique under the conditions used for cyclic volatammetry technique. The plots of $\log (i/i_d - i)$ vs. E were linear with a slope of the order 31 ± 1 mV, indicating the reversibility of the reduction. On the other hand, the plots of peak current (i_p) against square root of the scan rate ($V^{1/2}$) were linear, indicating that the reduction of the present system in nitrate medium was diffusion-controlled which is analogous to the variation of i_d with $h^{1/2}$ in DC polarography.

Simple Systems

For the simple Cd(picoline) and Cd(TMDA) systems, the nature of the reduction, composition and the formation constants for each system were determined separately. With Cd(picoline), the Cd^{2+} ion concentration was kept constant 2×10^{-4} M, and the variation of E_p with picoline concentration was studied at ionic strength ($\mu = 1$ M) using $NaNO_3$ at 25°C and at pH = 8.0. Analysis of the data revealed the formation of 1 : 1, 1 : 2 and 1 : 3 (metal : ligand) complexes. Similarly, Cd(TMDA) system was studied under the conditions used for Cd(picoline). Analysis of the data showed the formation of three complexes. pH = 8.0 was chosen in order to avoid the ligand protonation.

The stability constants of the simple systems were calculated using De Ford-Hume expression[7] as modified by Killa[4] in case of linear sweep voltammetry (LSV) technique instead of DC polarography. This expression may be written in the form

$$\log F_0(X) = \left(\frac{0.434nF}{RT} \Delta E_p \right) \qquad (2)$$

where $\Delta E_p = (E_p)_s - (E_p)_c$ is the shift in the LSV peak potential due to complexation. The stability constants obtained are reported in Table 1, and agree well with the values obtained previously[8, 9] for Cd(picoline) and Cd(TMDA) systems, respectively.

TABLE 1
OVERALL STABILITY CONSTANTS (log B_i) OF SIMPLE SYSTEMS AT 25°C, $\mu = 1.0$ M ($NaNO_3$) and at pH = 8.0

System	Complex species	log B_i
Cd(picoline)	$[Cd(pic)]^{2+}$	log $B_{01} = 1.45$
	$[Cd(pic)_2]^{2+}$	log $B_{02} = 2.14$
	$[Cd(pic)_3]^{2+}$	log $B_{03} = 3.30$
Cd(TMDA)	$[Cd(TMDA)]^{2+}$	log $B_{10} = 5.48$
	$[Cd(TMDA)_2]^{2+}$	log $B_{20} = 7.54$
	$[Cd(TMDA)_3]^{2+}$	log $B_{30} = 8.31$

Mixed Complexes

The stability constants of the mixed ligand complexes were evaluated using Schaap and McMasters expression[10] in case of LSV mode. This expression can be given as follows:

$$\log F_{00}(XY) = \left(\frac{0.434nF}{RT}\Delta E_p\right) \quad (3)$$

where $\Delta E_p = (E_p)_s - (E_p)_c$ is the shift in the peak potential due to complexation. Since Cd^{2+} forms hexacoordinate complexes with (TMDA) and (pic) individually. Thus, the maximum mixed species formed has three complexes and Leden's approach[11] may be written in the form:

$$F_{00}(XY) = A + B(X) + C(X)^2 + D(X)^3 \quad (4)$$

where

$$A = B_{00} + B_{01}(Y) + B_{02}(Y)^2 + B_{03}(Y)^3$$
$$B = B_{10} + B_{11}(Y) + B_{12}(Y)^2$$
$$C = B_{20} + B_{21}(Y)$$
$$D = B_{30}$$

where (X) and (Y) refer to (TMDA) and (picoline) ligands, respectively.

The original graphical method[7] may be aplied to F_{00} function if the activity of one ligand 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

$$F_{10} = \frac{F_{00} - A}{(X)} = B + C(X) + D(X)^2$$

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_{21}, B must be evaluated at two concentrations of Y.

In the mixed system, the concentration of (TMDA) was varied while that of the (picoline) ligand was kept costant at two values, 0.10 M and 0.25 M. Table 2 represents the shift in the peak potential (E_p) of Cd(TMDA-Pic) system at 0.10 and 0.25 M picoline. The results show the formation of three mixed species.

TABLE 2
LINEAR-SWEEP VOLTAMMETRIC DATA FOR Cd(TMDA-Pic) SYSTEM

Series I: [Pic] = 0.10 M (fixed)			Series II: [Pic] = 0.25 M (fixed)		
[TMDA], M	$-E_p$, V	ΔE_p, V	[TMDA], M	$-E_p$, V	ΔE_p, V
0.00	0.596	—	0.0	0.596	—
0.04	0.746	0.150	0.04	0.758	0.162
0.05	0.753	0.157	0.05	0.761	0.165
0.06	0.758	0.162	0.06	0.763	0.167
0.07	0.764	0.168	0.07	0.766	0.170
0.08	0.766	0.170	0.08	0.772	0.176
0.10	0.773	0.177	0.10	0.778	0.182
0.15	0.785	0.189	0.15	0.788	0.192
0.20	0.794	0.198	0.20	0.797	0.201
0.25	0.802	0.206	0.25	0.804	0.208
0.30	0.808	0.212	0.30	0.811	0.215

$[Cd^{2+}] = 2 \times 10^{-4}$ M, $\mu = 1.0$ M ($NaNO_3$), pH = 8.0 and T = 25°C.

The results of A, B, C and D are presented in Table 3. For the two values of B, the stability constants B_{11}, B_{12} were calculated. The two values of C gave two values for log $B_{21} = 8.01$, 8.08 in good agreement with each other. On the other hand, the average value of D (log B_{30}) from both series is 8.54. This agrees well with the value of log $B_{30} = 8.31$ calculated for the $[Cd(TMDA)_3]^{2+}$ complex from the simple system. The values of the stability constants are given in Table 4.

TABLE 3
MIXED LIGAND STABILITY CONSTANTS PARAMETERS OF Cd(TMDA-Pic) SYSTEM AT 25°C, $\mu = 1.0$ M AND pH = 8.0

Picoline concentration	Log A (calculated)	log B	log C	log D
0.10M	0.86	6.00	7.65	8.62
0.25M	1.68	6.40	7.81	8.46

TABLE 4
STABILITY CONSTANTS OF Cd(TMDA-Pic) SYSTEM AT 25°C, $\mu = 1.0$ M and pH = 8.0

Complex species	Stability constants log B_i
$[Cd(TMDA)(pic)]^{2+}$	log B_{11}= 6.76
$[Cd(TMDA)(pic)_2]^{2+}$	log B_{12}= 7.11
$[Cd(TMDA)_2(pic)]^{2+}$	log B_{21} = 8.05

Comparison between mixed and simple complexes

In order to compare the stabilities of simple and mixed complexes, it is better to calculate the disproportionation constant, log K_{dis}, for the reaction:

$$2[Cd(X)(Y)]^{2+} = [Cd(X)_2]^{2+} + [Cd(Y)_2]^{2+} \quad (5)$$

which is given by:

$$\log K_{dis} = \log K_{Cd(X)_2} + \log K_{Cd(Y)_2} - 2 \log K_{Cd(XY)} \quad (6)$$

where X and Y refer to the (TMDA) and (Pic) ligands, respectively. The log K_{dis} value was –3.84. The negative log K_{dis} value reveals the stability of the mixed complexes.

The mixing constants K_M for the reactions:[12]

$$\frac{1}{2}[Cd(X)_2]^{2+} + \frac{1}{2}[Cd(Y)_2]^{2+} = [Cd(X)(Y)]^{2+} \quad (7)$$

$$\frac{1}{3}[Cd(X)_3]^{2+} + \frac{2}{3}[Cd(Y)_3]^{2+} = [Cd(X)(Y)]^{2+} \quad (8)$$

$$\frac{2}{3}[Cd(X)_3]^{2+} + \frac{1}{3}[Cd(Y)_3]^{2+} = [Cd(X)(Y)]^{2+} \quad (9)$$

The values of log $K_{M_{11}}$, log $K_{M_{12}}$ and log $K_{M_{21}}$ of the above reactions are 1.92, 2.14 and 1.41, respectively. The positive values of the mixing constants (log K_M) indicate the relative stability of mixed complexes in solution compared to parent binary species.

Three mixed complexes exist in solution in the equilibria shown in Table 5. The equilibrium constants (log values) have been calculated and written against each equilibrium. It is seen from the equilibria that (TMDA) adds to $[Cd(TMDA)(Pic)]^{2+}$ complex more easily than (Pic) as shown from the equilibria (6 and 10). The saturated mixed complexes can accommodate (TMDA) in place of (Pic) [equilibria 9, 11 and 12]. Thus, the complexing tendency of (TMDA) is much more than (Pic). On the other hand, equilibria (4, 5, 7, 8 and 9) favour mixed complexation over simple ones.

TABLE 5
EQUILIBRIA INVOLVED IN THREE MIXED COMPLEXES AND EQUILIBRIUM (k) CONSTANT VALUES FOR Cd(TMDA-Pic) SYSTEM

	Equilibria			log K
1.	Cd + (TMDA) + (Pic)	=	[Cd(TMDA)(Pic)]	6.76
2.	Cd + (TMDA) + 2(Pic)	=	$[Cd(TMDA)(Pic)_2]$	7.11
3.	Cd + 2(TMDA) + (Pic)	=	$[Cd(TMDA)_2(Pic)]$	8.05
4.	[Cd(TMDA)] + (Pic)	=	[Cd(TMDA)(Pic)]	1.28
5.	$[Cd(TMDA)_2]$ + (Pic)	=	$[Cd(TMDA)_2(Pic)]$	0.51
6.	[Cd(TMDA)(Pic)] + (Pic)	=	$[Cd(TMDA)(Pic)_2]$	0.35
7.	[Cd(Pic)] + (TMDA)	=	[Cd(TMDA)(Pic)]	5.31
8.	$[Cd(Pic)_2]$ + (TMDA)	=	$[Cd(TMDA)(Pic)_2]$	4.97
9.	$[Cd(Pic)_3]$ + (TMDA)	=	$[Cd(TMDA)(Pic)_2]$ + (Pic)	3.81
10.	[Cd(TMDA)(Pic)] + (TMDA)	=	$[Cd(TMDA)_2(Pic)]$	1.29
11.	$[Cd(TMDA)(Pic)_2]$ + (TMDA)	=	$[Cd(TMDA)_2(Pic)]$ + (Pic)	0.94
12.	$[Cd(TMDA)_2(Pic)]$ + (TMDA)	=	$[Cd(TMDA)_3]$ + (Pic)	0.26

The charges are neglected for simplicity.

The stability constants of mixed complexes have been estimated theoretically using the method of Watters and De Witt[13]. The values are

$$\log B_{11} = 4.96, \quad \log B_{12} = 5.45 \quad \text{and} \quad \log B_{21} = 7.12$$

These values are less than the observed values (Table 4). This has been explained by many authors[10, 14, 15] considering the cooperative effects of electrostatic forces between different kinds of ligands and steric effects.

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