Monatshefte für Chemie 110, 657—661 (1979)

Monatshefte für Chemie

Studies on Mixed Complexes of Cd(II) With Propylenediamine and Trimethylenediamine at the Dropping Mercury Electrode

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(Received 7 October 1977. Accepted 12 December 1977)

Propylenediamine and trimethylenediamine have been found to form mixed complexes with Cd(II) in aqueous medium with stoichiometries 1:1:1 and 1:1:2. The overall formation constants of these mixed complexes have been evaluated using *Schaap* and *McMaster*'s method. The tendency of the complexes (simple and mixed) to add and substitute another ligand is discussed.

[Keywords: Cd(II)*-Complexes, mixed; Polarography]*

Polarographische Untersuchungen an gemischten Komplexen von Cd(II) *mit Propylendiamin und Trimethylendiamin*

Propylendiamin und Trimethylendiamin bilden in wäßr. Lösung gemischte Komplexe mit Cd(II) in den stöchiometrischen Zusammensetzungen 1:1:1, 1:1:2 und 1:2:1. Die Bildungskonstanten dieser Komplexe wurden mit der Methode nach *Schaap* und *McMaster* bestimmt. Die Tendenz der (einfachen und gemischten) Komplexe, mit anderen Liganden Addition oder Substitution einzugehen, wird diskutiert.

Introduction

Simple Cd(II) complexes with propylenediamine[1] (*PDA*) and trimethylenediamine[2] (*TMDA*) are well known. *DeFord* and *Hume*'s[3] method for the determination of stability constants of simple complexes was extended by *Schaap* and *McMaster*[4] to determine the stability constants of mixed complexes. The method of *Schaap* and *McMaster* has been extensively used by several workers[5–8]. In the present investigation we report polarographic studies on mixed complexes of amines with metal ions which have not been carried out until now using this technique.

0026-9247/79/0110/0657/$ 01.00

Experimental

All the solutions used were $1 \times 10^{-3} M$ with respect to the metal ion. The ionic strength was maintained constant by using KNO_3 as supporting electrolyte. All the chemicals used were of reagent grade purity. The solutions were prepared in double distilled water. 0.001 per cent titron X-100 was used to suppress maximum in each solution. For mixed complexes the two fixed concentrations of *TMDA* were $0.02 M$ and $0.04 M$. All the measurements were carried out at 300 K. The temperatures were maintained constant using a thermostate within ± 0.1 K variation. The capillary of the d.m.e. used had the following characteristics: $m = 2.14$ mg/s, $t = 4$–6 s open circuit.

Results

Simple Complexes

The reduction of Cd^{2+} in solutions containing propylenediamine and trimethylenediamine separately was found reversible and diffusion controlled. The slope of the straigth plot of $\log\frac{1}{(i_d-1)}$ vs. E_{de} was 32 mV and the plot of i_d vs. $h\frac{1/2}{\text{eff.}}$ (of the mercury column) was a straight line passing the origin.

Overall formation of the simple complexes were determined according to *DeFord* and *Hume*:

Complex Species	Overall formation constant at 300 K
$[Cd(TMDA)]^{2+}$, $\log \beta_{01}$	5.3802
$[Cd(TMDA)_2]^{2+}$, $\log \beta_{02}$	7.4771
$[Cd(TMDA)_3]^{2+}$, $\log \beta_{03}$	8.9542
$[Cd(PDA)]^{2+}$, $\log \beta_{10}$	7.9031
$[Cd(PDA)_2]^{2+}$, $\log \beta_{20}$	9.6021
$[Cd(PDA)_3]^{2+}$, $\log \beta_{30}$	11.3404

Mixed Complexes

The nature of reduction of Cd^{2+} in solutions containing both amines was the same as in the simple case. The *Schaap* and *McMaster* function F_{00} was calculated over the given range; variable concentrations of propylenediamine at two fixed concentrations of *TMDA*. F_{00} functions and other function values together with the polarographic data are recorded in Tables 1 and 2.

Table 1. *Polarographic measurements and F_{ij} functions of* Cd-*PDA and TMDA mixed system at 300 K; [TMDA] 0.04 M fixed;* i_d of simple metal ion = 0.65 div; $-E_{1/2}$ of simple metal ion = 0.6030 V vs. *SCE*

c_{PDA} (mol/dm^3)	$-E_{1/2}$ V vs. *SCE*	i_d (div)	F_{00}	F_{10}	F_{20}	F_{30}
0.00	0.6030	65	—	—	—	—
0.01	0.8180	59	161.6×10^5	16.16×10^8	7.16	2.16×10^{12}
0.02	0.8340	58	561.6×10^5	28.08×10^8	9.54	2.27×10^{12}
0.03	0.8455	57	$1,381.0 \times 10^5$	46.03×10^8	12.34	2.44×10^{12}
0.04	0.8535	56	$2,598.0 \times 10^5$	64.95×10^8	13.98	2.24×10^{12}
0.05	0.8605	56	$4,446.0 \times 10^5$	88.92×10^8	15.99	2.19×10^{12}
0.06	0.8665	55	$7,047.0 \times 10^5$	117.45×10^8	18.07	2.17×10^{12}
0.07	0.8715	54	$10,730.0 \times 10^5$	153.28×10^8	20.61	2.23×10^{12}

A 3×10^5; *B* 9×10^8; *C* 5×10^{10}; $D_{av.}$ 2.23×10^{12} (see ref. [4]).

Table 2. *Polarographic measurements and* F_{ij} *functions of* Cd-*PDA*-*TMDA mixed system at 300 K*; [*TMDA*] *0.02 M fixed*

c_{PDA} (mol/dm^3)	$-E_{1/2}$ V vs. *SCE*	i_d (div)	F_{00}	F_{10}	F_{20}	F_{30}
0.00	0.6030	65	—	—	—	—
0.01	0.8105	63	83.22×10^5	8.32×10^8	4.32	1.02×10^{12}
0.02	0.8260	59	298.00×10^5	14.90×10^8	5.45	1.07×10^{12}
0.03	0.8365	58	680.50×10^5	22.68×10^8	6.82	1.11×10^{12}
0.04	0.8455	58	$1,358 \times 10^5$	33.95×10^8	7.48	1.04×10^{12}
0.05	0.8520	57	$2,275 \times 10^5$	45.50×10^8	8.30	1.00×10^{12}
0.06	0.8575	56	$3,532 \times 10^5$	60.00×10^8	9.4	1.01×10^{12}
0.07	0.8625	56	$5,182 \times 10^5$	75.50×10^8	10.00	1.10×10^{12}
0.08	0.8695	55	$9,002 \times 10^5$	112.52×10^8	13.50	1.27×10^{12}

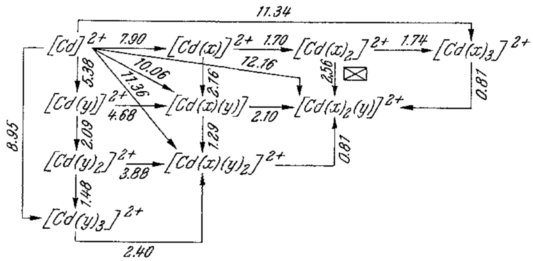
A 2.40×10^5; B 4×10^8; C 3.3×10^{10}; $D_{\text{av.}}$ 1.06×10^{12} (see ref. [4]).

The mixed stability constants at 300 K are determined using equations $B = \beta_{10} + \beta_{11}(Y) + \beta_{12}(X)^2$ [$\log \beta_{11} = 10.06$; $\log \beta_{12} = 11.35$] and $C = \beta_{20} + \beta_{21}(Y)$ [at two fixed concentrations of the weaker complexing agent trimethylenediamine; $\log \beta_{21} = 12.61$; see ref. [4]].

Discussion

Propylenediamine and trimethylenediamine form hexacoordinated complexes with Cd(II), propylendiamine forming more stable complexes than trimethylenediamine.

The log K values of the stepwise equilibrium constants at 300 K are schematically shown below: [X and Y stands for propylenediamine and trimethylenediamine respectively].



It is seen from the scheme that the complex $[Cd(Y)]^{2+}$ can add X more easily than the complex $[Cd(X)]^{2+}$ is able to add Y and that the tendency of $[Cd(Y)]^{2+}$ to add X is greater than to add Y. In the same way complex $[Cd(X)(Y)]^{2+}$ can add X more easily than Y. Close inspection of all possible combinations shows that in all cases the approach of X to the metal ion is less hindered than the approach of Y, and that X forms stronger complexes than Y with Cd(II).

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