

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarography of Some Cadmium Complexes¹BY BODIE E. DOUGLAS,² H. A. LAITINEN² AND JOHN C. BAILAR, JR.

Few complexes of cadmium have been studied by means of the dropping mercury electrode in order to determine the stability of these complexes. The ammonia complex was studied by Dobryszycski,³ but his data are incomplete. Chu⁴ calculated the value 3.3×10^{-7} for the dissociation constant for the ammonia complex from polarographic data. Pines⁵ and Demassieux and Heyrovsky⁶ measured only the 45° tangent reduction potential of cadmium from cyanide solutions. Kolthoff and Lingane⁷ found that the polarographic reduction in cyanide solution was not strictly reversible, but observed that the overvoltage is not very great. Cadmium has also been found to give well-defined waves from tartrate and citrate solutions.⁸ However, dissociation constants were not calculated. The oxalate and pyrophosphate complexes of cadmium have been studied polarographically, but only the 45° tangent reduction potentials were reported.⁹

The cadmium complexes with ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, pyridine, α, α' -dipyridyl and *o*-phenanthroline have been studied by means of the dropping mercury electrode in this investigation. The stabilities of this series of complexes have been evaluated.

Experimental

Apparatus.—Polarograms were recorded with a Sargent model XXI polarograph. Potential measurements were made with a Leeds and Northrup student type potentiometer. An H-cell with a temporary plug of 3% agar-agar in 0.1 *N* potassium nitrate and the bulb-type saturated calomel electrode were used.

The criteria of reversibility of the electrode reactions were the plots of $\log(i_d - i)/i$ vs. E , as reported in Tables I–VII. In all cases, corrections were made for residual current. The values for the half-wave potentials were taken from the logarithmic plots.

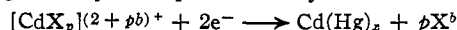
Reagents and Chemicals.—The technical grade aliphatic amines, obtained from the Carbide and Carbon Chemicals Corporation were redistilled with the exception of the triethylenetetramine. The reagent grade pyridine was also redistilled. The solutions of the liquid amines were standardized potentiometrically with hydrochloric acid using a Beckman pH meter. The α, α' -dipyridyl, obtained from the G. Frederick Smith Chemical Company, was once recrystallized. The remaining chemicals were

reagent grade and were used without further purification. A solution of cadmium nitrate was standardized gravimetrically by precipitating the double ammonium phosphate which was ignited to cadmium pyrophosphate.

Potassium nitrate was used as the indifferent electrolyte and gelatin as the maximum suppressor for all complexes. Dissolved oxygen was removed from the solutions for polarographic study with a stream of oxygen-free nitrogen. The temperature of the polarographic cell was maintained at $25 \pm 0.1^\circ$.

Discussion

The reduction of a cadmium complex to the amalgam may be represented by



The equation relating the half-wave potentials of the simple and complex ions is¹⁰

$$(E_{1/2})_0 - (E_{1/2})_c = 0.0296 \log K_d(f_c/f_s)(D_s/D_c)^{1/2} - p0.0296 \log C_X f_X \quad (\text{A})$$

where K_d represents the dissociation constant for the complex, f the activity coefficients of the ions, C_X the concentration of the complexing agent and D the diffusion coefficients of the ions. The *c* and *s* subscripts refer to the complex and simple ions, and the *X* subscript refers to the complexing agent. The number of groups attached to each cadmium ion is represented by p . As a first approximation, the activity coefficients may be assumed to be unity, and in most cases D_s and D_c are nearly equal so that their ratio may also be assumed to be unity.

The formal potential for a complex may be calculated from the equation

$$E_s^\circ - E_c^\circ = 0.0296 \log K_d \quad (\text{B})$$

by substituting the value for the dissociation constant calculated from equation (A), assuming the activity coefficients and the ratio of the diffusion coefficients to be unity.

Data obtained in this investigation are presented in Tables I through VII. The values for

TABLE I

ETHYLENEDIAMINE COMPLEX

Indifferent electrolyte 0.1 *N* KNO₃; 0.01% gelatin maximum suppressor; mercury column 58.2 cm.; $m = 1.313$ mg. sec.⁻¹; $m^2/v^{1/2} = 1.416$ mg.²/sec.^{-1/2}; i_d measured at -1.05 volts.

Concn. en molar	Concn. Cd millimolar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d μ amp.	Diffusion current constant
2.00	1.04	0.964	0.031	3.87	2.62
1.00	0.456	.934	.032	2.04	3.16
1.00	1.04	.934	.032	4.42	3.00
0.500	1.04	.901	.032	4.52	3.07
.100	1.04	.842	.031	4.57	3.10
.100	0.520	.843	.032	2.42	3.29
.010	.520	.775	.033	2.32	3.16

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TABLE II

PROPYLENEDIAMINE COMPLEX

Conditions were the same as those described in Table I.

Concn. pn molar	Concn. Cd millimolar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d , μ amp.	Diffusion current constant
2.00	1.04	0.966	0.032	4.24	2.88
1.00	1.04	.938	.034	3.68	2.50
1.00	0.456	.937	.032	1.50	2.32
1.00	0.456	.937	.032	1.76	2.74
0.500	1.04	.910	.034	4.04	2.74
.100	1.04	.848	.032	4.30	2.92
.100	0.520	.847	.033	2.31	3.13
.010	.520	.782	.036	2.22	3.02

TABLE III

DIETHYLENETRIAMINE COMPLEX

Conditions were the same as those described in Table I except that i_d was measured at -1.10 volts.

Concn. dien molar	Concn. Cd millimolar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d , μ amp.	Diffusion current constant
1.00	0.456	0.993	0.032	1.50	2.32
1.00	.520	.989	.033	2.10	2.86
0.500	.520	.969	.030	2.00	2.72
.250	.260	.952	.032	1.12	3.05
.250	.520	.943	.033	2.23	3.03
.100	.520	.929	.032	2.30	3.13
.050	.520	.913	.032	2.24	3.05
.010	.520	.878	.035	2.35	3.19

TABLE IV

TRIETHYLENETETRAMINE COMPLEX

Conditions were the same as in Table I except for these changes: $5.20 \times 10^{-4} M$ Cd(NO₃)₂; mercury column 60.0 cm.; $m = 1.506$ mg. sec.⁻¹; $m^2/t^{1/2} = 1.732$ mg.²/sec.^{-1/2}.

Concn. trien molar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d , μ amp.	Diffusion current constant
1.00	0.986	0.034	1.68	1.88
0.500	.976	.032	3.66 ^a	2.04
.300	.970	.033	1.94	2.16
.200	.956	.034	2.20	2.46
.100	.949	.037	2.16	2.41
.01	.871	.050	2.79	3.11

^a This solution contained $1.04 \times 10^{-3} M$ Cd(NO₃)₂.

the reciprocal slopes of the plots of $\log(i_d - i)/i$ against the potential indicate that the electrode reactions involve reversible two electron reductions in all cases except for the solution containing 0.01 M triethylenetetramine. The reduction process for this solution is apparently irreversible.

The number of groups coordinated to each cadmium ion is obtained from the slope of the plots of equation A. The results are presented in Table VIII. This table also includes the dissociation constants calculated from equation A after making the simplifying assumptions previously described. The formal potential values were calculated from these dissociation constants

TABLE V

PYRIDINE COMPLEX

Conditions were the same as in Table IV except for these changes: $m^2/t^{1/2} = 1.747$ mg.²/t^{1/2}; i_d measured at -0.80 volt.

Concn. py molar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d , μ amp.	Diffusion current constant
2.00	0.680	0.029	2.10	2.32
1.00	.643	.030	0.87 ^a	2.40
1.00	.641	.031	2.28	2.52
1.00	.642	.034	2.23	2.46
0.400	.615	.031	2.37	2.61
.200	.604	.031	2.53	2.79
.100	.592	.030	1.32 ^a	3.00
.010	.578	.033	2.29	2.52

^a These solutions contained $2.08 \times 10^{-4} M$ Cd(NO₃)₂.

TABLE VI

DIPYRIDYL COMPLEX

Conditions were the same as in Table V except for these changes: 0.005% gelatin maximum suppressor; $1.04 \times 10^{-4} M$ Cd(NO₃)₂; i_d measured at -0.85 volt.

Concn. dipy molar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d , μ amp.	Diffusion current constant
0.040	0.766	0.031	0.41	2.26
.040	.758	.031	.40	2.20
.020	.732	.031	.42	2.31
.010	.708	.031	.42	2.31
.005	.691	.032	.44	2.42
.100 ^a	.767	.031	.30	1.65
.060 ^a	.752	.032	.31	1.71
.040 ^a	.735	.031	.30	1.65
.010 ^a	.687	.032	.30	1.65

^a These solutions contained 28.5% ethyl alcohol (by volume).

TABLE VII

o-PHENANTHROLINE COMPLEX

Conditions were the same as in Table V except for these changes: $1.04 \times 10^{-4} M$ Cd(NO₃)₂; i_d measured at -0.90 volt.

Concn. o-phen molar	$-E_{1/2}$ vs. S. C. E.	Reciprocal slope of log plot $(i_d - i)/i$	i_d , μ amp.	Diffusion current constant
0.020	0.878	0.032	0.38	2.09
.010	.846	.033	.32	1.77
.010	.845	.033	.75 ^b	2.04
.005	.820	.034	.34	1.87
.030 ^a	.861	.030	.34	1.87
.020 ^a	.852	.031	.33	1.82
.010 ^a	.835	.033	.32	1.77
.005 ^a	.794	.036	.33	1.82

^a These solutions contained 28.5% ethyl alcohol (by volume). ^b This solution contained $2.08 \times 10^{-4} M$ Cd(NO₃)₂.

using equation B. The changes in activities and the liquid junction potentials were neglected for the alcoholic solutions.

The half-wave potentials for the cadmium complexes in 0.01 M solutions of ethylenediamine,

TABLE VIII

FORMULAS AND STABILITIES OF COMPLEXES STUDIED

Formula of complex	CX range molar	Reciprocal slope of plot of Eq. A	K_d	$-E_0'$
[Cd(en) ₃] ⁺⁺	0.1-2	0.094	6.7×10^{-13}	1.26
[Cd(pn) ₃] ⁺⁺	0.1-2	.090	5.4×10^{-13}	1.26
[Cd(dien) ₂] ⁺⁺	0.05-1	.060	7.6×10^{-16}	1.31
[Cd(trien)] ⁺⁺	0.3-1	.031	1.2×10^{-14}	1.31
[Cd(py) ₄] ⁺⁺	1-2	.127	3.2×10^{-3}	0.96
[Cd(py) ₂] ⁺⁺	0.4-1	.063	7.2×10^{-3}	.96
[Cd(dipy) ₃] ⁺⁺	0.01-.04	.084	3.4×10^{-11}	1.21
^a [Cd(dipy) ₃] ⁺⁺	0.01-.1	.087	1×10^{-10}	1.19
[Cd(<i>o</i> -phen) ₃] ⁺⁺	0.005-.02	.097	6.4×10^{-16}	1.35
^a [Cd(<i>o</i> -phen) ₂] ⁺⁺	0.01-.03	.055	7×10^{-14}	1.29

^a These solutions contained 28.5% ethyl alcohol (by volume).

propylenediamine and diethylenetriamine fall below the straight lines in the plots of equation A, indicating the possible formation of complexes having a lower mole ratio in these solutions. In the concentration range of 0.1 to 0.4 *M* pyridine, the slope of the line resulting from the plot of equation A is 0.038, indicating that a complex having a lower mole ratio is present in these solutions. The formula for the complex approaches [Cd(py)]⁺⁺, but the change is probably more or less continuous in this range. The half-wave potentials for the solutions containing 0.1 and 0.2 *M* triethylenetetramine do not lie on the straight line in the plot of equation A and were not included. Deviation from theoretical behavior for these solutions is not unexpected, since the reduction process in the 0.01 *M* triethylenetetramine solution was found to be irreversible. The half-wave potential for cadmium in 0.005 *M* α, α' -dipyridyl solution lies below the straight line plot, indicating the possible formation of a lower mole ratio complex.

The formulas found here agree with those reported in the literature for the tris-(ethylenediamine)-cadmium(II) ion,¹¹ tris-(propylenediamine)-cadmium(II) ion,¹² tris-(α, α' -dipyridyl)-cadmium(II) ion^{13,14} and tris-(*o*-phenanthroline)-cadmium(II) ion.¹⁴ These complexes have been prepared in the solid state and analyses are given. Pyridine complexes have been prepared in which two and six molecules of pyridine are attached to

each cadmium ion.^{15,16} The preparation of complex cadmium(II) perchlorate salts containing four and six molecules of pyridine has also been reported.¹⁷

The marked stabilization due to chelation is evident from the dissociation constants given in Table VIII. Monodentate groups usually give a coordination number of four for the cadmium ion, but the coordination number six seems to be more common for polydentate groups. The coordination number for cadmium in triethylenetetramine solution is apparently four, but this method of study does not differentiate between a coordination number of four or six, if two positions are occupied by the solvent. A coordination number of four for cadmium would seem especially likely in this case, since a completely closed structure would result. The change in the coordination number of cadmium in alcoholic solutions containing *o*-phenanthroline is unusual in view of the great stability of the tris-(*o*-phenanthroline)-cadmium(II) complex and the fact that the change is not observed for the α, α' -dipyridyl complex. A high energy of solvation of the *o*-phenanthroline in alcohol could be one factor, but it seems unlikely that this alone could account for the formation of a bis-(*o*-phenanthroline) complex even in alcoholic 0.03 *M* *o*-phenanthroline solution.

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Summary

1. Polarographic studies indicate the existence of complexes having the formulas [Cd(en)₃]⁺⁺, [Cd(pn)₃]⁺⁺, [Cd(dien)₂]⁺⁺, [Cd(trien)]⁺⁺, [Cd(dipy)₃]⁺⁺ and [Cd(*o*-phen)₃]⁺⁺ in the presence of one hundred to two thousandfold excess of the respective complexing agent. In solutions containing 28.5% ethyl alcohol (by volume), the formula for the *o*-phenanthroline complex is [Cd(*o*-phen)₂]⁺⁺.

2. Four pyridine molecules are coordinated to each cadmium ion in the presence of 1 to 2 *M* pyridine. In the presence of 0.4 to 1 *M* pyridine, two molecules of pyridine are coordinated.

3. Dissociation constants and formal potentials have been evaluated for these complexes.

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