

(6) Magnetic moments and Δ values of a particular complex anion, $[\text{CoX}_4]^{2-}$ vary, somewhat (usually $\sim 4\%$, occasionally as much as 10%) from one compound to another due, presumably, to variations in compression forces in the crystal lattices.

(7) Solvent effects on the spectra of $[\text{CoX}_4]^{2-}$ species are often significant. True spectra can usually be obtained in nonaqueous solutions by adding excess X^- ion, but in aqueous solutions, even saturated with HX or LiX , full conversion of Co(II) to $[\text{CoX}_4]^{2-}$ species does not seem to occur.

(8) Co(OH)_2 dissolves in concentrated alkali metal hydroxide to form, at least partly, one or more tetrahedral species. It is believed that these are $[\text{Co(OH)}_3(\text{H}_2\text{O})]^-$, $[\text{Co(OH)}_4]^{2-}$ or both.

(9) The intensities of the ν_2 and ν_3 bands in all tetrahedral Co(II) complexes studied to date appear to be $\sim 10^2$ times as great as the band intensities in octahedral Co(II) complexes. This ratio is comparable to those found for Ni(II) ²¹ and

Mn(II) ²⁹ and in agreement with previously reported observations, notably those of Gill and Nyholm,¹¹ Ballhausen and Jørgensen⁸ and Bufagni and Dunn.¹⁶

(10) The Δ values for $[\text{CoX}_4]^{2-}$ complexes are 80–85% of those in the corresponding $[\text{NiX}_4]^{2-}$ complexes.²¹ Whereas the $[\text{NiI}_4]^{2-}$ and $[\text{Ni-Br}_4]^{2-}$ complexes had Δ values which were equal within experimental error, the Δ value for $[\text{Co-Br}_4]^{2-}$ is 5–10% greater than that for $[\text{CoI}_4]^{2-}$.

Acknowledgments.—We thank Dr. Richard H. Holm for some of the data on aqueous solutions. Financial support was provided by the United States Atomic Energy Commission (Contract No. AT(30-1)-1965) and the National Institute of Health (Research Grant No. 7445). We also thank Dr. H. A. Weakliem and Professor H. G. Drickamer for communicating some of their results in advance of publication.

(29) D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1961); F. A. Cotton, D. M. L. Goodgame, M. Goodgame, *J. Am. Chem. Soc.*, in press.

[CONTRIBUTION NO. 1023 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

A Polarographic Study of Mixed-ligand Complex Formation; Complexes of Copper and Cadmium with Oxalate Ion and Ethylenediamine

BY WARD B. SCHAAP AND DONALD L. McMASTERS¹

RECEIVED MAY 15, 1961

The polarographic method for the study of mixed-ligand complexes is discussed and then applied to the determination of the formation constants of the mixed-ligand complexes of copper(II) and cadmium(II) in the presence of both oxalate ion (ox) and ethylenediamine (en). Results for the one mixed complex of copper, $[\text{Cu(en)(ox)}]$, agree well with results based on other physical measurements. The constants for the three possible mixed complexes of cadmium are $\log K_{11} = 7.9$ for $[\text{Cd(en)(ox)}]$, $\log K_{12} = 8.8$ for $[\text{Cd(en)(ox)}_2]^{-2}$ and $\log K_{21} = 11.5$ for $[\text{Cd(en)}_2(\text{ox})]$. The effects of the relative charges of the unsaturated complex and the incoming ligand on the stepwise formation constants are those predicted by charge neutralization and entropy considerations when a second ligand adds to either copper or cadmium; abnormal effects accompany the addition of a third ligand to cadmium.

Introduction

An increasing number of studies of mixed-ligand complex formation has appeared during the past decade. Mixed-ligand complexes are those in which more than one kind of ligand, other than the solvent molecule, are present in the innermost coordination sphere of the central metal ion and can be represented by the general formula $[\text{MX}_i\text{Y}_j\text{Z}_k \dots]$. Most of the previous studies have made use of spectrophotometric measurements,^{2–12} some have involved potentiometric measurements using metal-metal ion or oxidation-reduction elec-

trodes,^{2,3,13,14} while others made use of data obtained from *pH* titration curves.^{3,15–19}

The formation constants evaluated in the above studies, as well as purely statistical considerations, indicate that mixed-ligand complex formation is a general and common phenomenon whenever two or more ligands are present in solution and that actually mixed complexes should be preferred over simple complexes whenever the concentrations of the ligands involved are such that the products of the formation constants for the simple complexes and the concentrations of the ligands, raised to the appropriate power, are approximately equal, *i.e.*, $K_{\text{MX}_i}[\text{X}]^i = K_{\text{MY}_j}[\text{Y}]^j = K_{\text{MZ}_k}[\text{Z}]^k \dots$

Although the polarographic method has been widely used in the study of single-ligand systems, no general discussion of the application of the method to the study of mixed-ligand complexes

(1) Based in part on the Ph.D. thesis of Donald L. McMasters submitted June, 1959.

(2) G. Schwarzenbach and A. Willi, *Helv. Chim. Acta*, **34**, 528 (1951).

(3) G. Schwarzenbach and J. Heller, *ibid.*, **576**, 1876, 1889 (1951).

(4) J. I. Watters and E. D. Loughran, *J. Am. Chem. Soc.*, **75**, 4819 (1953).

(5) J. I. Watters, J. Mason and A. Aaron, *ibid.*, **75**, 5212 (1953).

(6) R. DeWitt and J. I. Watters, *ibid.*, **76**, 3810 (1954).

(7) M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1591, 1603 (1955).

(8) W. E. Bennett, *J. Am. Chem. Soc.*, **79**, 1290 (1957).

(9) D. L. Leussing and R. C. Hansen, *ibid.*, **79**, 4270 (1957).

(10) L. Newman and D. N. Hume, *ibid.*, **79**, 4571, 4581 (1957).

(11) A. A. Schilt, *ibid.*, **79**, 5421 (1957).

(12) A. A. Schilt, *ibid.*, **82**, 3000 (1960).

(13) J. L. Watters and J. Mason, *ibid.*, **78**, 285 (1956).

(14) J. I. Watters, J. Mason and O. E. Schupp, III, *ibid.*, **78**, 5782 (1956).

(15) S. Fronaeus, *Acta Chem. Scand.*, **4**, 72 (1950).

(16) A. E. Martell, *et al.*, *J. Am. Chem. Soc.*, **79**, 3036 (1957); *ibid.*, **80**, 2121, 4170 (1958).

(17) W. E. Bennett, *ibid.*, **81**, 246 (1959).

(18) J. I. Watters, *ibid.*, **81**, 1560 (1959).

(19) J. I. Watters and R. DeWitt, *ibid.*, **82**, 1333 (1960).

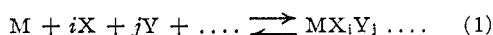
has been published. This application involves an extension of the DeFord and Hume polarographic method for studying single-ligand complexes.²⁰ Such an extension was made by Davis²¹ in this Laboratory in an unpublished study of basic tin pyrophosphate complexes. Also, Watters and Mason¹⁸ derived the equation of the polarographic wave for the special case of mixed-ligand complexes of mercury and used their equation to test polarographic reversibility of the mixed complexes but not to determine their formation constants.

The copper-ethylenediamine-oxalate system was investigated prior to this study by DeWitt and Watters⁶ using spectrophotometric techniques. It was included in the present study to allow comparison of results obtained by the two methods. Recently, Watters¹⁸ has reinvestigated this system using pH titration measurements and has obtained essentially the same results as in his spectrophotometric study.

The cadmium-ethylenediamine-oxalate system provides an example of a hexacoördinate system and has not been studied previously. A study of the analogous nickel system with these ligands was reported recently by Watters and DeWitt.¹⁹

Theoretical

The mathematical treatment of polarographic data for the determination of the formation constants of successive single-ligand complexes has been described in detail by DeFord and Hume²⁰ and makes use of the graphical approach of Leden.²² This treatment can be extended to the more general case in which more than one kind of ligand can add to a given central ion to form mononuclear complexes,^{13,21} *i.e.*



(For simplicity and generality, charges will not be included in the equations.) The activity of each species may be expressed

$$[MX_iY_j \dots] = K_{ij} \dots [M][X]^i[Y]^j \dots \quad (2)$$

The constants, $K_{ij} \dots$, are the over-all complexity constants for the indicated complexes. If the total analytical concentration of the metal ion present in all forms is designated Σ_M and if N is the maximum number of ligands coördinated, then

$$[M] = \Sigma_M \left/ \sum_{i+j+\dots=0}^N K_{ij} \dots [X]^i [Y]^j \dots / f_{MX_iY_j} \dots \right. \quad (3)$$

where f is an activity coefficient and $K_{00} \dots = 1$. In equation 3, Σ_M is easily known and $[M]$ is obtainable from polarographic measurements, as described below. The activity coefficients are usually not known, so are most often held as constant as possible by maintaining a constant ionic strength and are incorporated into the equilibrium constants, which are then valid only for the conditions of the experiment. By definition, Leden's F_0 function for this more general case becomes

(20) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(21) J. A. Davis, Ph.D. Thesis, Dept. of Chem., Indiana Univ. Bloomington, Ind., 1955.

(22) I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

$$F_{00} \dots (X, Y \dots) = \sum_{i+j+\dots=0}^N K_{ij} \dots [X]^i [Y]^j \dots / f_{MX_iY_j} \dots \quad (4)$$

If the expression for $[M]$ in eqn. 3 is substituted into the Nernst equation describing the potential of a dropping mercury electrode at whose surface the metal ion is reduced to a soluble amalgam, then

$$E_{d.m.o.} = E_a^0 - \frac{RT}{nF} \ln \frac{C_a^0 f_a \left[\sum_{i+j+\dots=0}^N K_{ij} \dots [X]^i [Y]^j \dots / f_{MX_iY_j} \dots \right]}{\left[\sum_{i+j+\dots=0}^N [MX_iY_j \dots]^0 / f_{MX_iY_j} \dots \right]} \quad (5)$$

The definitions of the various symbols used in equation 5 and below are well known and will not be repeated here.^{13,20,23}

It can be shown that $C_a^0 = i/kI_a$ and that

$$(i_d - i) = k \sum_{i+j+\dots=0}^N I_{ij} \dots (C_{MX_iY_j} \dots - C_{MX_iY_j}^0) \dots$$

It is not necessary to assume that the diffusion coefficient for each complex, $I_{ij} \dots$, is the same, as done by Watters and Mason, rather let I_c be the observable "weighted average" diffusion coefficient for all diffusing species giving rise to the electrode current in a given solution.²⁰ Thus

$$\sum_{i+j+\dots=0}^N [MX_iY_j \dots]^0 / f_{MX_iY_j} \dots = (i_d - i) / kI_c \quad (6)$$

The equation of the polarographic wave then becomes

$$E_{d.m.o.} = E_a^0 - \frac{RT}{nF} \ln \frac{f_a I_c}{I_a} - \frac{RT}{nF} \ln \sum_{i+j+\dots=0}^N K_{ij} \dots [X]^i [Y]^j \dots / f_{MX_iY_j} \dots - \frac{RT}{nF} \ln \frac{i}{i_d - i} \quad (7)$$

The first three terms on the right-hand side of equation 7 represent the half-wave potential of the complexed metal, $(E_{1/2})_c$. The difference between the half-wave potential of the uncomplexed ("simple") metal ion, $(E_{1/2})_s$, and that of the complexed ion is

$$(E_{1/2})_s - (E_{1/2})_c = - \frac{RT}{nF} \ln \frac{I_M}{f_M I_c} + \frac{RT}{nF} \ln \sum_{i+j+\dots=0}^N K_{ij} \dots [X]^i [Y]^j \dots / f_{MX_iY_j} \dots \quad (8)$$

Thus, $F_{00} \dots (X, Y \dots) =$

$$\text{antiln} \left\{ \frac{nF}{RT} [(E_{1/2})_s - (E_{1/2})_c] + \ln \frac{I_M}{I_c f_M} \right\} \quad (9)$$

All terms in equation 9 are readily evaluated from polarographic data except for f_M , which is usually incorporated into the equilibrium constants.

For the sake of brevity and clarity, the description of the analysis of the $F_{00} \dots$ function for the formation constants of the mixed-ligand system will be restricted to the case of two different ligands of the same functionality, assuming that at most a total of three can add to the central ion.

(23) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, New York, 1952, Chapters XI and XII.

(In the studies of Cu^{+2} and Cd^{+2} reported below, a total of two and three of the bidentate ligands can add, respectively.) Further extension of the treatment to apply to the addition of a total of four or more ligands, or to more than two types of ligands, will be obvious from the discussion below. In the latter case, however, considerably more data would be needed to evaluate the constants.

The $F_{00}(\text{X}, \text{Y})$ function can be factored and written in the form

$$F_{00}(\text{X}, \text{Y}) = \{K_{00} + K_{01}[\text{Y}] + K_{02}[\text{Y}]^2 + K_{03}[\text{Y}]^3\}[\text{X}]^0 \\ + \{K_{10} + K_{11}[\text{Y}] + K_{12}[\text{Y}]^2\}[\text{X}] \\ + \{K_{20} + K_{21}[\text{Y}]\}[\text{X}]^2 \\ + \{K_{30}\}[\text{X}]^3 \quad (10)$$

$$\text{or } F_{00}(\text{X}, \text{Y}) = A + B[\text{X}] + C[\text{X}]^2 + D[\text{X}]^3 \quad (11)$$

where the quantities A , B , C and D are defined by eq. 10 and are constant at each given value of $[\text{Y}]$.

If experimental data are obtained under conditions such that the activity of one of the ligands remains constant while the other is varied, which is particularly easy to do if the ligands vary significantly in basicity, then the resulting F_{00} data can be readily analyzed by a Leden-type approach.

The value of the constant A at a given activity of Y can be calculated if the consecutive formation constants are known for the simple system containing the metal ion with Y alone. This value of A may be compared with the value of A obtained by plotting F_{00} versus $[\text{X}]$ at the same value of $[\text{Y}]$. The plot represents a cubic equation whose intercept at $[\text{X}] = 0$ is A and whose limiting slope at $[\text{X}] \rightarrow 0$ is B .

If the intercept value of A is subtracted from F_{00} and the resulting quantity divided by $[\text{X}]$ at each value of $[\text{X}]$, then a plot of this F_{10} function versus $[\text{X}]$ represents a quadratic function whose intercept is B and whose limiting slope is C , *i.e.*

$$F_{10} = \frac{F_{00} - A}{[\text{X}]} = B + C[\text{X}] + D[\text{X}]^2 \quad (12)$$

Continuing this procedure, the F_{20} function is seen to be linear with slope C , and F_{30} is equal to the constant D , the F_{30} vs. $[\text{X}]$ plot being horizontal to the $[\text{X}]$ axis. In actual practice, least squares intercepts and slopes, calculated from the F_{ij} data with an IBM 650 electronic computer, as described previously,²⁴ were used to guide the graphical extrapolations in order to obtain more accurate intercepts, and ligand concentrations at constant ionic strength were used in place of activities.

Equations 10 and 11 show that D is equal to K_{30} , the over-all complexity constant of the simple system containing the metal ion with X alone. The value of C is equal to $K_{20} + K_{21}[\text{Y}]$ and allows the value of K_{21} to be calculated directly if K_{20} is known for the simple system. The expression for B contains two unknown constants, K_{11} and K_{12} , in addition to K_{10} , which can be known from the simple system; thus B must be measured at a minimum of two different values of $[\text{Y}]$ to evaluate the two unknown constants.

(24) D. L. McMasters and W. B. Schaap, *Proc. Indiana Acad. Sci.*, **67**, 111 (1958).

Some judgment must be exercised in choosing the Y concentration range over which the various constants are evaluated. The concentrations should be chosen so that the corresponding complexes are present in solution in appreciable amounts. At concentrations far removed from these regions, the F_{ij} values may vary widely and become meaningless.

Experimental

Chemicals.—All chemicals were of reagent grade and were not purified further except the Eastman Kodak (white label) ethylenediamine, which was distilled twice under nitrogen from sodium at reduced pressure. Standard solutions of copper(II) sulfate, ethylenediamine, nitric acid and potassium oxalate were prepared and standardized according to generally accepted procedures.

Apparatus.—All polarograms were recorded with a Sargent Model XXI Visible Recording Polarograph at a sensitivity of 0.020 microamp. mm.⁻¹ with no electrical damping. The effects from the very slight non-linearity in the slide-wire were cancelled out, or minimized, by recording every polarogram over the same portion of the slidewire. Potential measurements were made before and after the wave to the nearest 0.01 mv. with a potentiometer. Potentials at various points along the wave were obtained by interpolation. Voltages were corrected for iR drop arising from the resistance of the cell and the measuring resistor of the Polarograph.

The dropping mercury electrode, when inserted into a solution containing 1.0 M NaNO_3 , had a drop time of 4.36 sec. per drop and a flow rate of 1.78 mg. sec.⁻¹ of mercury at a column height of 49.0 cm. and at the potential of the saturated calomel electrode. The H-type electrolysis cell and the water-jacketed s.c.e. reference electrode were kept at a constant temperature of $25.0 \pm 0.05^\circ$.

The current and voltage data obtained from the recorded polarograms were analyzed for the least-squares-best $E_{1/2}$ values and slopes using an IBM 650 computer program described previously.²⁵

Measurement of pK_a Values of the Ligands.—The ionization constants of oxalic acid and the acid form of ethylenediamine were measured at several different concentrations in solutions of ionic strength 1.0, adjusted with sodium nitrate, so that these constants would be known under conditions corresponding as closely as possible to those employed in the mixed complex studies. To obtain the two pK_a values for each ligand, the calculated amount of sodium nitrate was added so that the ionic strength would be 1.0 at the $1/4$ - or at the $3/4$ -point of the total titration curve. Thus, two titrations were required at each concentration of ligand employed. The basic forms of the ligands were titrated at $25 \pm 0.1^\circ$ with a standard nitric acid solution. The pH measurements were made with a Beckman Model G pH meter. The pK_a values read from the titration curves are given in Table I.

TABLE I
IONIZATION CONSTANTS OF THE ACID FORMS OF ETHYLENEDIAMINE AND OXALATE ION

Concn., M	pK_1	pK_2
Ethylenediamine: ($\mu = 1.0$)		
0.002	7.38	10.10
.02	7.38	10.06
.2	7.31	9.85
Potassium oxalate: ($\mu = 1.0$)		
0.002	2.77	3.60
.02	1.90	3.43
.2	(Ppt.)	(Ppt.)

Formation Constants of Single-Ligand Complexes of Copper.—The formation constants of the complexes of copper (and cadmium) with ethylenediamine and with oxalate were measured separately prior to the study of the mixed-

(25) D. L. McMasters and W. B. Schaap, *ibid.*, **67**, 117 (1958).

ligand system. The conditions used corresponded as closely as possible to those planned for the mixed system, *i.e.*, $\mu = 1.0$, adjusted with sodium nitrate. The values obtained for the single-ligand system are needed in the calculation of the formation constants of the mixed-ligand complexes or may be compared with the results of the mixed system.

In the studies with ethylenediamine, all solutions contained $4.8 \times 10^{-4} M$ Cu^{+2} and 0.001% "Triton X-100" as maximum suppressor. The pH was adjusted with HNO_3 and sufficient $NaNO_3$ was added to make the ionic strength equal to 1.0. The concentration of "free" ethylenediamine, $[en]$, was calculated from the pH and the total amount present, using the appropriate pK values from Table I. The experimental data and the $F_j(X)$ values for the single-ligand systems will not be included here, only the results.

In the oxalate system, the same concentration of Cu^{+2} was used, but no maximum suppressor was needed. The concentration of the divalent oxalate anion, $[ox]$, was varied either by varying the total concentration of potassium oxalate ($pH > 5$) or by decreasing the pH below 5 and calculating $[ox]$ using the ionization constants in Table I.

The half-wave potential of the simple cupric ion, $(E^{1/2})_s$, measured to ± 0.1 mv. in 1 M $NaNO_3$ at the time of each series of polarograms was run, varied between $+0.025$ to $+0.029$ v. *vs.* s.c.e. for the various series on which the calculations are based.

The average of the experimental values of $F_2(en)$, which is equal to the over-all formation constant, K_2 , for $[Cu(en)_2]^{+2}$, is $3.06 \pm 0.34 \times 10^{20}$, where the range is the observed standard deviation of the mean ($\log K_2 = 20.49 \pm 0.1$).²⁶ This value agrees well with values measured under somewhat similar conditions listed by Bjerrum, Schwarzenbach and Sillén.²⁷ Because of the great stability of the bis-(ethylenediamine) complex, insufficient data were obtained in the region where the mono-(ethylenediamine) complex exists to allow K_1 to be evaluated from the data. However, the constant for this complex has been measured many times, and an average of these literature values,²⁷ 5.63×10^{10} ($\log K_1 = 10.75 \pm 0.1$), will be assumed for K_1 . No evidence for $[Cu(en)_3]^{+2}$ was observed in the concentration range studied.

The data from the oxalate studies allow both consecutive formation constants to be evaluated. The intercept of the plot of $F_1(ox)$ versus oxalate concentration, obtained graphically and by least squares calculation, is 5.00×10^6 and is equal to K_1 ($\log K_1 = 5.70 \pm 0.1$). The average of the values of $F_2(ox)$ in the region of higher oxalate concentration, where the bis-(oxalate) complex predominates, gives $K_2 = 1.66 \pm 0.10 \times 10^9$, where the range is the observed standard deviation of the mean ($\log K_2 = 9.22 \pm 0.1$).

The value for K_2 falls within the range of values listed for this complex by Bjerrum, *et al.*²⁷ These authors list no value for K_1 , but Watters¹⁸ recently reported the values $\log K_1 = 5.43$ and $\log K_2 = 9.36$, measured under similar conditions, which agree quite closely with the values found in this study.

Formation Constants of Single-Ligand Complexes of Cadmium.—The complexes of cadmium with ethylenediamine and with oxalate were also investigated separately in order to obtain data under conditions similar to those used in the mixed complex studies.

In the studies involving ethylenediamine as ligand, the same general procedure was followed as described for the copper studies. The solutions contained $5.3 \times 10^{-4} Cd^{+2}$, 0.001% "Triton X-100" as maximum suppressor and 0.21 M added ethylenediamine. The pH was adjusted with nitric acid and $[en]$ was calculated from the pH and the appropriate pK_a value from Table I. The ionic strength was ad-

justed to 1.0 with sodium nitrate. The $(E^{1/2})_s$ of Cd^{+2} in 1 M $NaNO_3$ was measured accurately at the time of running each series of solutions and ranged between -0.571 and -0.575 v. *vs.* the s.c.e.

No maximum suppressor was needed in the investigation of the oxalate complexes of cadmium. The pH was held above 5.0, so that the total concentration of $K_2C_2O_4$ present served as a measure of $[ox]$. As before, $NaNO_3$ was added to adjust the ionic strength to 1.0. Data from the initial set of experiments gave an abnormally high value for K_3 , the last stepwise formation constant, probably because of an undetected temporary malfunctioning of a reference electrode in use at that time. The measurements were repeated later with improved results. Data and results from these latter measurements²⁸ are used in these calculations.

The data obtained from the cadmium-ethylenediamine system allow the three successive formation constants to be evaluated. Plots of the $F_j(en)$ data, supplemented by least squares calculations, give the following results: $K_1 = 4.0 \times 10^6$ ($\log K_1 = 5.60 \pm 0.1$), $K_2 = 4.3 \times 10^{10}$ ($\log K_2 = 10.63 \pm 0.1$) and $K_3 = 1.2 \pm 0.2 \times 10^{12}$ ($\log K_3 = 12.1 \pm 0.1$). These values are in close agreement with the results of several other workers.²⁷

Results for the successive formation constants of the cadmium oxalate complexes, also obtained by supplementing the plots of $F_j(ox)$ data with least squares calculations, are as follows: $K_1 = 4.10 \times 10^2$ ($\log K_1 = 2.61 \pm 0.1$), $K_2 = 1.37 \times 10^4$ ($\log K_2 = 4.14 \pm 0.1$) and $K_3 = 1.09 \pm 0.1 \times 10^6$ ($\log K_3 = 5.04 \pm 0.1$). No other data are available at or near an ionic strength of 1.0 with which to compare these results. Values reported at very low ionic strengths for K_1 and K_2 do not correspond closely to those obtained in this study. No previous value for K_3 has been reported.

Results and Discussion

The Copper(II)-ethylenediamine-oxalate Mixed Complex System.—The copper(II)-ethylenediamine-oxalate system was chosen for the initial study because of its simplicity (only one mixed complex exists, $[Cu(en)(ox)]$) and because independent results are available for comparison. Prior to this study DeWitt and Watters⁶ obtained a mean value of $\log K_{11} = 15.44 \pm 0.14$ for the mixed complex using spectrophotometric measurements. Subsequent to this study, Watters¹⁸ reported a value of $\log K_{11} = 15.39$ obtained on the basis of analysis of pH titration curves.

Because it is experimentally much easier to hold the oxalate concentration constant and vary the ethylenediamine concentration (by changing the pH) than *vice versa*, the F_{00} function will be written as a function of $[en]$, assuming $[ox]$ is constant. Because only two bidentate ligands can add to copper(II) ion, the function is

$$F_{00} = A + B[en] + C[en]^2$$

where $A = K_{00} + K_{01}[ox] + K_{02}[ox]^2$; $B = K_{10} + K_{11}[ox]$ and $C = K_{20}$. (Note: The first subscript refers to the number of ethylenediamine ligands present in the complex and the second subscript to the number of oxalate anion ligands.)

The value of A can be obtained by extrapolating the plot of F_{00} values to $[en] = 0$, or it can be calculated for each given oxalate ion concentration using the already determined consecutive formation constants of the copper-oxalate complexes. The value of C is known from the formation constant of $[Cu(en)_2]^{+2}$. The intercept of the F_{10} plot gives the value of B . If K_{10} for $[Cu(en)]^{+2}$ is known, then the value of K_{11} can be calculated directly.

(28) Private communication from D. L. McMasters, J. C. Di-Raimondo and R. Philip Lindley, Beloit College, Beloit, Wis.

(26) The observed standard deviations of the mean are calculated from the values included in the mean. In some instances these values are selected in the sense that negative values of $(F_j(X) - K_j)$ must be omitted and that values from only appropriate concentration ranges are included, as mentioned at the end of the Theoretical section. We have chosen to make the uncertainties given with the $\log K$ values more realistic by rounding off to the next higher one-tenth log unit. For simple complexes these uncertainties are usually ± 0.1 at most, but for the mixed complexes they should be greater because their constants are calculated from the constants of simple complexes plus additional data.

(27) J. Bjerrum, G. Schwarzenbach and L. Sillén, "Stability Constants, Part I: Organic Ligands," The Chemical Society London, Burlington House, 1957.

TABLE II
 DATA AND RESULTS FOR COPPER-ETHYLENEDIAMINE-OXALATE SYSTEM

pH	$\frac{[En]}{M}$	$\frac{(E_{1/2})_s - (E_{1/2})_0}{V}$	I_M/I_0	F_{00}	F_{10}	F_{20}
Series I: $[ox^{-2}] = 2.43 \times 10^{-3} M$; En (added) = 0.205 M ; $A = 1.134 \times 10^4$ (calcd.); $(E_{1/2})_s = 0.0283$ v.						
5.48	6.089×10^{-8}	0.1804	1.004	12.6×10^5	2.05×10^{13}	2.22×10^{20}
5.42	4.625×10^{-8}	.1789	0.984	11.0×10^5	2.36×10^{13}	3.58×10^{20}
5.38	3.852×10^{-8}	.1739	.980	7.42×10^5	1.90×10^{13}	3.11×10^{20}
5.22	1.849×10^{-8}	.1596	.957	2.38×10^5	1.23×10^{13}	2.86×10^{20}
5.18	1.539×10^{-8}	.1578	.958	2.07×10^5	1.27×10^{13}	3.73×10^{20}
5.04	0.809×10^{-8}	.1468	.957	0.879×10^5	0.947×10^{13}	3.05×10^{20}
				$B = 7.00 \times 10^{12}$ $C_{av.} = 3.09 \times 10^{20}$		
				$K_{11} = 2.88 \times 10^{15}$		
Series II: $[ox^{-2}] = 0.247 M$; En (added) = 0.205 M ; $A = 1.030 \times 10^8$ (calcd.); $(E_{1/2})_s = 0.0283$ v.						
6.72	15.27×10^6	0.3033	0.931	16.7×10^9	10.9×10^{14}	0.43×10^{20}
6.64	10.90×10^6	.2983	.930	11.3×10^9	10.3×10^{14}	$.55 \times 10^{20}$
6.48	5.474×10^6	.2824	.937	3.30×10^9	5.85×10^{14}	$.28 \times 10^{20}$
6.30	2.484×10^6	.2724	.933	1.51×10^9	5.68×10^{14}	$.56 \times 10^{20}$
6.18	1.457×10^6	.2622	.939	0.687×10^9	4.00×10^{14}	..
5.92	0.452×10^6	.2528	.955	0.336×10^9	5.15×10^{14}	1.88×10^{20}
				$B = 4.30 \times 10^{14}$ $C_{av.} = 0.74 \times 10^{20}$		
				$K_{11} = 1.74 \times 10^{15}$		
Series III: $[ox^{-2}] = 0.247 M$; En (added) = 0.0205 M ; $A = 1.030 \times 10^8$ (calcd.); $(E_{1/2})_s = 0.0284$ v.						
7.08	7.134×10^{-6}	0.2922	0.943	7.12×10^9	9.84×10^{14}	0.34×10^{20}
6.92	3.807×10^{-6}	.2833	.932	3.52×10^9	8.98×10^{14}	0.42×10^{20}
6.82	2.537×10^{-6}	.2769	.943	1.45×10^9	5.22×10^{14}	..
6.72	1.675×10^{-6}	.2717	.912	2.09×10^9	11.9×10^{14}	2.67×10^{20}
6.66	1.301×10^{-6}	.2673	.924	1.01×10^9	6.99×10^{14}	..
6.50	0.655×10^{-6}	.2616	.952	0.665×10^9	8.55×10^{14}	1.76×10^{20}
				$B = 7.4 \times 10^{14}$ $C_{av.} = 1.30 \times 10^{20}$		
				$K_{11} = 3.0 \times 10^{16}$		

The ratio of ligand concentrations at which the mixed complex will be present in maximum amounts can be estimated from the formation constants of either the two mono- or bis-ligand complexes. The ratio $[ox]/[en]$ for which $K_{01}[ox] = K_{10}[en]$ or $K_{02}[ox]^2 = K_{20}[en]^2$ falls in the range $10^{5.1}$ to $10^{5.6}$. At equal analytical concentrations of the ligands, this ratio of the actual complexing species is achieved around pH 6. At the analytical ratio of ethylenediamine to potassium oxalate actually used, about 100 to 1, the desired ligand ratio occurs at about pH 5. Above about pH 5, the divalent oxalate anion is essentially completely dissociated.

Data from three different series of runs carried out at two widely different concentrations of oxalate ion, and the calculated F_{ij} values, are shown in Table II. The pH was adjusted with nitric acid and sodium nitrate was used to adjust the ionic strength to 1.0.

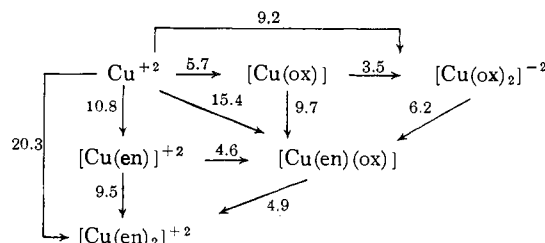
In spite of the considerable differences in composition of the solutions, the results of the three series agree rather well. The average value found for K_{11} of the mixed complex, $[Cu(en)(ox)]$, is $2.54 \pm 0.4 \times 10^{15}$ ($\log K_{11} = 15.40 \pm 0.15$).²⁶ Because activity coefficients are absorbed in the formation constants, some differences in K_{ij} values may be expected.

The conditions employed in Series I correspond closely to the conditions used by DeWitt and Watters⁶ and by Watters,¹³ and the value of $\log K_{11}$ obtained in Series I is well within experimental

error of the results obtained by these investigators. The average value of K_{20} from all results is $1.83 \pm 0.34 \times 10^{20}$ ($\log K_{20} = 20.26 \pm 0.1$) which corresponds favorably to the value obtained in the simple system for the bis-(ethylenediamine) complex and to values reported by other investigators.²⁷

It is significant that the polarographic method gives essentially the same results as spectrophotometric and pH measurements. The latter methods involve measurements made essentially at equilibrium, whereas polarographic half-wave potentials are measured under dynamic diffusion conditions in which changes in pH and in ligand concentration at the electrode surface have been assumed to be negligible.

The results of this present study are conveniently summarized in the diagram, where the numerical values shown are the logarithms of the equilibrium constants for the reactions indicated.



A number of interesting observations can be made from these data. First, the tendency for

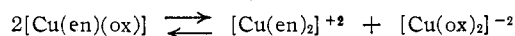
TABLE III
 DATA AND RESULTS FOR CADMIUM-ETHYLENEDIAMINE-OXALATE SYSTEM

pH	[En] M	$(E_{1/2})_s - (E_{1/2})_e$ v.	I_M/I_0	F_{00}	F_{10}	F_{20}	F_{30}
Series I: [ox ⁻²] = 0.020 M; A = 1541 (calcd.); $(E_{1/2})_s = -0.5720$ v.							
11.60	2.061×10^{-1}	0.3117	1.091	3.76×10^{10}	1.82×10^{11}	8.85×10^{11}	3.81×10^{12}
10.78	1.804×10^{-1}	.3039	1.055	1.98×10^{10}	1.10×10^{11}	6.09×10^{11}	2.82×10^{12}
10.36	1.464×10^{-1}	.2943	1.042	9.27×10^9	6.33×10^{10}	4.32×10^{11}	2.27×10^{12}
10.03	9.662×10^{-2}	.2807	1.072	3.31×10^9	3.43×10^{10}	3.54×10^{11}	2.63×10^{12}
9.64	5.395×10^{-2}	.2618	1.068	7.57×10^8	1.40×10^{10}	2.60×10^{11}	2.96×10^{12}
9.02	1.582×10^{-2}	.2239	1.026	3.81×10^7	2.41×10^9	1.49×10^{11}	3.12×10^{12}
8.28	2.790×10^{-3}	.1755	1.075	9.22×10^5	3.30×10^8	1.03×10^{11}	..
7.87	9.319×10^{-4}	.1470	1.053	9.81×10^4	1.04×10^8	0.662×10^{11}	..
7.52	3.204×10^{-4}	.1269	1.075	2.10×10^4	6.06×10^7	$.581 \times 10^{11}$..
7.16	9.079×10^{-5}	.1099	1.071	5.56×10^3	4.43×10^7	$.245 \times 10^{11}$..
6.54	7.318×10^{-6}	.0963	1.124	2.02×10^3	6.60×10^7
$B = 4.2 \times 10^7$ $C = 1.0 \times 10^{11}$ $D_{av.} = 2.94 \times 10^{12}$							
Series II: [ox ⁻²] = 0.0101 M; A = 6.65 (calcd.); $(E_{1/2})_s = -0.5720$ v.							
10.88	1.859×10^{-2}	0.2178	1.015	2.34×10^7	1.26×10^9	6.77×10^{10}	3.10×10^{12}
10.50	1.598×10^{-2}	.2123	1.015	1.53×10^7	9.55×10^8	5.97×10^{10}	3.11×10^{12}
10.16	1.243×10^{-2}	.2023	1.010	6.97×10^6	5.61×10^8	4.50×10^{10}	2.82×10^{12}
9.86	8.124×10^{-3}	.1906	1.010	2.81×10^6	3.45×10^8	4.24×10^{10}	..
9.40	3.747×10^{-3}	.1730	1.026	7.24×10^5	1.93×10^8	5.13×10^{10}	..
8.70	8.414×10^{-4}	.1358	1.025	4.00×10^4	4.75×10^7
7.90	1.112×10^{-4}	.0852	0.990	7.52×10^2	6.70×10^6
7.52	3.514×10^{-5}	.0599	1.015	1.08×10^3	2.87×10^6
7.23	1.289×10^{-5}	.0425	1.014	2.77×10^1	1.63×10^6
6.90	3.621×10^{-6}	.0309	1.017	1.13×10^1	1.28×10^6
6.38	3.998×10^{-7}	.0237	1.031	6.52
$B = 1.2 \times 10^6$ $C = 1.0 \times 10^{10}$ $D_{av.} = 3.0 \times 10^{12}$							

an oxalate anion to add as the second ligand to [Cu(ox)] and to [Cu(en)]⁺² can be compared. The log *K* values are 3.5 and 4.6, respectively. Because the statistical factor is only 2, in favor of the mixed complex, the largest part of the difference in log *K* must be attributed to the neutralization of charge accompanying the latter reaction. In addition to coulombic effects, such a neutralization of charge would be expected to be accompanied by a positive entropy change due to a decreased orientation of the solvent molecules.

The tendency to add an uncharged ethylenediamine molecule as the second ligand to [Cu(ox)] and to [Cu(en)]⁺² can also be compared. In this case a strong charge neutralization effect would not be expected and, indeed, is not observed. Log *K* values of 9.7 and 9.5 show that the mixed complex is slightly favored by an amount corresponding closely to that predicted by the statistical factor.

Finally, the constant for the disproportionation reaction is 0.05, *i.e.*, log *K* = -1.3. Again the



mixed complex is preferred. The statistical factor of 1/4 for this reaction accounts for only part of the stability of the mixed complex and in this case the effects of charge neutralization, including entropy changes, are again apparent.

The Cadmium-ethylenediamine-oxalate Mixed Complex System.—The cadmium mixed complex system with ethylenediamine and oxalate has not been studied previously. Because the maximum coordination number of cadmium is 6, three different mixed complexes are possible with the

two different bidentate ligands. These are [Cd(en)(ox)], [Cd(en)₂(ox)] and [Cd(en)(ox)₂]⁻².

The procedure employed for the cadmium mixed complex study is similar to that used for the copper system. Because of experimental advantages, oxalate concentration was held at several different fixed values, allowing the *F*₀₀ function to be evaluated as a function of ethylenediamine concentration, which varied with pH. Under these conditions, for the cadmium system, the *F*₀₀ function may be written

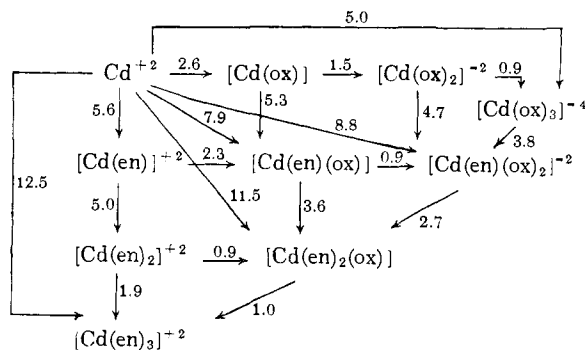
$$F_{00} = A + B[\text{en}] + C[\text{en}]^2 + D[\text{en}]^3$$

where now $A = 1 + K_{01}[\text{ox}] + K_{02}[\text{ox}]^2 + K_{03}[\text{ox}]^3$; $B = K_{10} + K_{11}[\text{ox}] + K_{12}[\text{ox}]^2$; $C = K_{20} + K_{21}[\text{ox}]$; and $D = K_{30}$. As before, the values of *A* and *D* are known from studies of the simple systems. Values of *B* and *C* can be obtained graphically as discussed above. The mixed complex constant, *K*₂₁, can be evaluated once *C* is known, but *B* must be evaluated at least at two different appropriate oxalate ion concentrations before the other two mixed constants, *K*₁₁ and *K*₁₂, can be calculated. The two oxalate ion concentrations used were approximately 0.01 and 0.2 *M* (as *K*₂C₂O₄), at which values the initial predominant species should be [Cd(ox)] and [Cd(ox)₂]⁻², respectively. Nitric acid was used to adjust the pH to desired values and the ionic strength was adjusted to the value 1.0 with sodium nitrate. Data and calculated *F*_{ij} values are given in Table III.

From plots of the *F*₁₀ data versus ethylenediamine concentration over wide ranges of concentration, the following intercept values were evaluated:

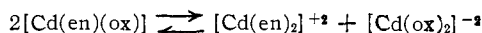
For Series I, $B = 4.2 \times 10^7$, $C = 1.00 \times 10^{11}$ and $D = 2.94 \times 10^{12}$; for Series II, $B = 1.22 \times 10^8$, $C = 1.0 \times 10^{10}$ and $D = 3.0 \times 10^{12}$. Values for A for both series were calculated using constants obtained from the simple system, but each can be shown to agree well with the intercept of the plot of the F_{00} values versus ethylenediamine concentration. The average value of $D(K_{30})$ from both series is $2.96 \pm 0.14 \times 10^{12}$, where the range represents the standard deviation of the mean of the results given in Table III ($\log K_{30} = 12.47 \pm 0.1$). This agrees reasonably well with the value $\log K_3 = 12.1$ evaluated for the complex $[\text{Cd}(\text{en})_3]^{+2}$ from the simple system containing no oxalate.

The over-all formation constants evaluated for the mixed complexes from the intercept data are $K_{11} = 7.5 \times 10^7$, $K_{12} = 6.5 \times 10^8$ and $K_{21} = 2.8 \times 10^{11}$. Log K values for all the complexes present in the system and for the equilibria between them are summarized below. (We estimate that the log K values for the simple complexes are reproducible to ± 0.1 , that log K_{21} , which depends on one other constant, is uncertain within ± 0.15 , while log K_{11} and log K_{12} are reproducible to ± 0.2).²⁶



The tendency of $[\text{Cd}(\text{ox})]$ and $[\text{Cd}(\text{en})]^{+2}$ to add a second ligand can be compared, as was done in the case of the copper complexes. For the addition of an oxalate anion, the log K values are, respectively, 1.5 and 2.3. Again, the difference is much larger than the statistical factor of 2 would predict, showing the effects of charge neutralization. Addition of an uncharged ethylenediamine ligand to each of the above complexes gives rise to log K values of 5.3 and 5.0, respectively, a difference equal to that predicted by the statistical factor.

The disproportionation reaction



has a value of $\log K = -1.1$ in the direction written, which corresponds closely to the value of $\log K (-1.3)$ observed for the corresponding reaction in the copper system. Equilibrium constants for other disproportionation reactions can be calculated, all of which show the mixed complexes to be favored.

Rather startling results are obtained upon comparison of the equilibrium constants for the addition of oxalate ion or ethylenediamine to the various bis-ligand complexes. With oxalate anions, the log K values for the addition of ox^{-2} to $[\text{Cd}(\text{en})_2]^{-2}$, $[\text{Cd}(\text{en})(\text{ox})]$ and $[\text{Cd}(\text{en})_3]^{+2}$ are all 0.9 and equal. The strong effect on K of the relative charges of the combining species observed with the mono-ligand complexes is now absent.

On the other hand, the log K values for the addition of uncharged ethylenediamine as the third ligand to $[\text{Cd}(\text{ox})_2]^{-2}$, $[\text{Cd}(\text{en})(\text{ox})]$ and $[\text{Cd}(\text{en})_2]^{+2}$ are, respectively, 4.7, 3.6 and 1.8. Where small differences were observed previously with the mono-ligand complexes of both copper and cadmium upon addition of ethylenediamine, very large differences now appear.

These trends may be understood if it is assumed, in accord with much evidence which need not be cited here, that the N→metal bond is appreciably more covalent than the O→metal bond with these ligands. The ethylenediamine complexes would then be more strongly influenced by the stereochemistry of the hybridized sp^3 orbitals of cadmium than would the more ionic oxalate complexes and have a correspondingly greater tendency to be tetrahedral. Addition of either an ethylenediamine molecule or an oxalate anion to $[\text{Cd}(\text{en})_2]^{+2}$ would be hindered, despite the opposite charges of the latter two species, while addition of either ligand to $[\text{Cd}(\text{ox})_2]^{-2}$ would proceed more readily, offsetting the repulsion of the like charges in the case of oxalate addition.²⁹

Watters and DeWitt¹⁹ made interesting comparisons between observed formation constants of mixed-ligand complexes of nickel and constants calculated from average constants, i.e., $k_{\text{av.}} = \beta_{\text{N}}^{1/\text{N}}$, of the simple complexes adjusted for statistical factors. Similar calculations for the saturated mixed complexes of cadmium give for $[\text{Cd}(\text{en})(\text{ox})_2]^{-2}$, $K_{12} = 3K_{30}^{1/2}K_{03}^{3/2} = 10^{8.0}$ and for $[\text{Cd}(\text{en})_2(\text{ox})]$, $K_{21} = 3K_{30}^{2/3}K_{03}^{1/3} = 10^{10.5}$. These values are less than the observed values by amounts of $10^{0.8}$ and $10^{1.0}$, respectively. For the unsaturated mixed complex, $[\text{Cd}(\text{en})(\text{ox})]$, $K_{11} = 2 \times 3 K_{30}^{1/2}K_{03}^{1/2} = 10^{6.6}$ which is less than the observed constant by $10^{1.3}$.³⁰

With both cadmium and nickel, comparison of the experimental stepwise constants of the simple complexes with the average constant adjusted for statistical factors, i.e., $k_1 = 3k_{\text{av.}}$, $k_2 = k_{\text{av.}}$ and $k_3 = 1/3 k_{\text{av.}}$, shows that the observed k_1 exceeds the calculated constant by a large factor (usually about 10) in every case, that k_2 is always the closest to the calculated constant and that k_3 is less than

(29) Alternatively, it appears possible to explain the observed trends on the assumption that the negativity charged oxalate anions, each with four oxygen atoms, repel and loosen the coordinated water molecules to a greater extent than do ethylenediamine molecules. Then, $[\text{Cd}(\text{ox})_2]^{-2}$ would be weakly solvated whereas the bis-amine complex would be more strongly solvated and better represented $[\text{Cd}(\text{en})_2(\text{H}_2\text{O})_2]^{+2}$. Addition of a third ligand to the latter would require elimination of the two solvent molecules at a cost of appreciable energy. The charge of the oxalate anion relative to that of the three bis-ligand complexes would tend to compensate for the changing extent of solvation and equalize the constants.

This explanation is in apparent conflict with the conclusion of Davis, Singer and Straveley, *J. Chem. Soc.*, 2304 (1954), based on entropy measurements, that $[\text{Cd}(\text{en})_3]^{+2}$ is essentially not hydrated in aqueous solution. For this reason we prefer the other explanation at present.

(30) The value calculated by Watters and DeWitt for K_{11} of $[\text{Ni}(\text{en})(\text{ox})]$ appears to be in error. Using their data we calculated $K_{11} = 2 \times 3\beta_{\text{en}}^{1/2}\beta_{\text{ox}}^{1/2} = 10^{7.78}$, corresponding to an enhancement of $10^{1.88}$ rather than $10^{0.8}$ as reported. This recalculated enhancement is near what we find for the unsaturated cadmium complex.

the calculated value by a large factor which again averages about 10. (Note: the sum of the logarithms of the deviations of the experimental from the calculated k_i values for each series of simple complexes must equal zero because $(k_1 k_2 k_3)^{1/3} = k_{av.}$) It may therefore be expected that the unsaturated mixed complex, MX_Y , will include the deviations involving k_1 and k_2 of the simple complexes and will show considerable positive deviations, or "enhancements." The saturated complexes, MX_2Y and MX_Y_2 , will include the negative deviation associated with k_3 and should exhibit

net deviations or enhancements considerably smaller, by about a factor of 10, than the unsaturated complex. The data for the mixed complexes of nickel support these predictions almost quantitatively,^{19,30} and the data for cadmium are in qualitative agreement.

Acknowledgments.—The authors wish to thank Mr. Joseph DiRaimondo and R. Philip Lindley of Beloit College for their help in checking certain experimental measurements and the Research Corporation for a grant in partial support of this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK]

Polarographic Characteristics of Osmium. II. The +6 and +4 States

BY RICHARD E. COVER¹ AND LOUIS MEITES

RECEIVED MAY 31, 1961

Information is presented regarding the oxidation-reduction behaviors of +6 and +4 osmium in sodium hydroxide media and of +6 osmium in mineral acid solutions, both at dropping mercury electrodes and at large stirred mercury electrodes.

Introduction

Very little information has been available regarding the polarographic behaviors of the lower oxidation states of osmium. Crowell, Heyrovsky and Engelkemeir² reported that +6 osmium gave a double wave in a saturated calcium hydroxide medium and ascribed this to the reduction scheme $VI \rightarrow IV \rightarrow III$. Willis,³ Ruis and Molera⁴ and Meites⁵ studied the behaviors of +6, +3, and +2 osmium in cyanide media.

The work described here was undertaken in order to supplement this scanty information, to obtain further data bearing on the question of the possible existence of +5 osmium in alkaline media, which had been inferred from previous experiments,⁵ and to provide a basis for the design of electroanalytical methods for the determination of osmium.

Experimental

The apparatus and techniques employed were described in the first paper of this series.³

Solutions of osmium tetroxide were assayed by coulometry at controlled potential, employing the previously described four-electron reduction on the plateau of the total double wave in a cyanide supporting electrolyte. Solutions of +6 osmium were prepared by the quantitative electroreduction of osmium tetroxide in dilute sodium hydroxide media at a mercury cathode whose potential was maintained at -0.35 v. vs. s.c.e. Solutions of +4 osmium were prepared similarly but at a working-electrode potential of -1.00 v. vs. s.c.e.

Although a silver-silver chloride reference electrode⁶ occasionally was used in carrying out controlled-potential electrolyses, all potentials are referred to the usual saturated calomel electrode. All diffusion current constants

are given in $\mu\text{amp./mmole/l./mg.}^{2/3}\text{ sec.}^{-1/2}$ and are calculated from the difference between the total current on the plateau of the wave in question and the separately measured residual current at the same potential.

Results and Discussion

+6 Osmium in Sodium Hydroxide Media.—Polarograms of +6 osmium in solutions containing more than about 0.5 *F* sodium hydroxide consist of two waves, as shown by Fig. 1. Their half-wave potentials are constant and equal to -0.596 ± 0.009 v. and -1.521 ± 0.015 v. at sodium hydroxide concentrations varying from 0.1 to 9.4 *F*. These values are in good agreement with those (-0.61 ± 0.01 v. and -1.51 ± 0.02 v.) previously reported for the second and third waves of +8 osmium in similar media. In the absence of a maximum suppressor, there is also an anomalous wave at about -1.3 v., which is displaced to -1.7 v. by the addition of 0.002% Triton X-100 (*cf.* Fig. 1). The total diffusion current constants of the waves at various sodium hydroxide concentrations are given in Table I.

TABLE I
DIFFUSION CURRENT CONSTANTS OF +6 OSMIUM IN SODIUM HYDROXIDE MEDIA

[NaOH] <i>F</i>	I_1	I_2	$I_{17^{1/2}}$	I_2/I_1
0.098	2.83 ± 0.05^a	6.79 ± 0.13	8.6	2.40
0.25	$2.65 \pm .11^a$	$5.2 \pm .1$	8.1	1.96
1.0	$2.69 \pm .05$	$4.85 \pm .09$	8.9	1.80
3.8	$2.05 \pm .04$	$3.41 \pm .06$	10.2	1.66
9.4	$1.06 \pm .02$	$1.45 \pm .09$	9.8	1.37

Mean 9.1 ± 0.7

^a Total diffusion current constant for a poorly resolved doublet wave.

The decrease of the diffusion current constant of the first wave with increasing sodium hydroxide concentration is due to the increasing viscosity of the solution, as is shown by the near constancy of the product $I_{17^{1/2}}$. The variation of the ratio I_2/I_1 ,

(1) This paper is based on a thesis submitted by Richard E. Cover to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the M.S. degree in June, 1960.

(2) W. R. Crowell, J. Heyrovsky and D. W. Engelkemeir, *J. Am. Chem. Soc.*, **63**, 2888 (1941).

(3) J. B. Willis, *ibid.*, **67**, 547 (1945).

(4) A. Ruis and M. J. Molera, *Anales real soc. espan. fis. y quim. (Madrid)*, **45B**, 1151 (1949).

(5) L. Meites, *J. Am. Chem. Soc.*, **79**, 4631 (1957).

(6) L. Meites and S. A. Moros, *Anal. Chem.*, **31**, 23 (1959).