

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

A Method of Investigating Complex Equilibria in Mixtures of Ligands Using the Glass Electrode: Copper(II) Ion in Mixtures of Oxalate Ion and Ethylenediamine

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A general experimental procedure and mathematic treatment based on Bjerrum's formation function is presented for solving the complexity constants of all complex species in the presence of mixtures of ligands of different basicities. The new method permits the direct evaluation of the complexity constants of all complex species after determining the consecutive formation or complexity constants of the simple amine complex directly by Bjerrum's method. It is possible to evaluate the consecutive formation constants of the simple complex of a very weakly basic ligand for which Bjerrum's method is not readily applied. In this way the consecutive formation constants of copper(II) oxalate complexes, which have not been previously evaluated, were found to be $10^{6.48}$ and $10^{3.93}$ at 25° and an ionic strength adjusted to 1.1 ± 0.1 with KNO_3 .

Spectrophotometric methods have been used by the author and his co-workers to establish the existence and stabilities of mixed complexes of copper(II) ion with amines and chelating anions.¹⁻³ In these studies stepwise replacement constants were introduced as a means of evaluating the complexity constants of mixed complexes. In another series of papers general expressions were given for the stepwise addition of different species of ligands to form a series of simple and mixed complexes and a procedure based on electrode potentials was presented for solving the equilibrium constants.^{4,5} Previously Fronaeus⁶ had developed a method for evaluating complexity constants in mixed complex systems. His method involved the graphic integration of an expression related to Bjerrum's⁷ formation function. Recently Bennett⁸ has combined spectrophotometric and *pH* measurements to study the stepwise mixed complex formation of copper(II) with ethylenediamine and iminodiacetic acid.

In the present paper a general experimental procedure based on the *pH* titrations and a mathematical treatment based on Bjerrum's formation function⁷ are presented for solving the complexity constants of all complex species in the presence of mixtures of ligands of different basicities. Experimentally the method may consist of the *pH* titration with an acid to remove the more basic ligand from the complex in mixtures containing the less basic ligand and the metal ion in various integral concentration ratios. This experimental procedure is particularly useful in the study of complexes in ligand deficient solutions of oxalate and amines since oxalate precipitates tend to form in these solutions. In this titration procedure the required data usually can be obtained before precipitation occurs.

The complex equilibria of aqueous solutions containing copper(II) ion with oxalate and ethylenediamine may be used to illustrate the method. Since copper(II) is tetracoördinate in most solutions and accepts only two bidentate ligands, the calculations are not particularly involved.

(1) J. I. Watters and E. D. Loughran, *THIS JOURNAL*, **75**, 4819 (1953).

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

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

(4) J. I. Watters and J. G. Mason, *ibid.*, **78**, 285 (1956).

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

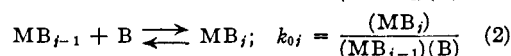
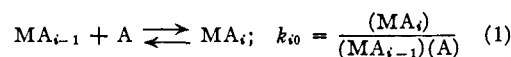
(6) S. Fronaeus, *Acta Chem. Scand.*, **4**, 72 (1950).

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, Denmark, 1941.

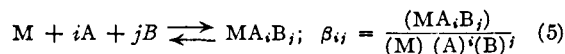
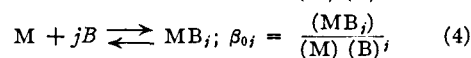
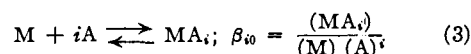
(8) W. E. Bennett, *THIS JOURNAL*, **79**, 1290 (1957).

Theoretical

Consider the equilibria between a metal ion M and ligands A and B, the latter being a considerably stronger base in the Brönsted sense. For example, A may indicate oxalate ion and B may indicate ethylenediamine. The following equations for the stepwise addition of ligands and the corresponding stepwise formation constant are sufficient to describe all equilibria of the simple complexes. The subscripts *i* and *j* after the constant indicate the number of A and B ligands in the higher complex. The values of (*i* + *j*) vary from 0 to *N'*, where *N'* is the total number of bound ligands. Parentheses indicate concentrations, brackets indicate activities, and charges are omitted in general expressions. The general expressions for the stepwise equilibria and the corresponding consecutive formation constants, *k*, for the simple complexes, are



In addition the following equations for the overall equilibria and the corresponding consecutive complexity constants, β , may be written for the simple and mixed complexes



For simple complexes containing only one species of ligand, both the formation constants, *k_{ij}*, and the complexity constants, β_{ij} , are convenient to use in various mathematical functions. For the mixed complex species it usually is more convenient to use the complexity constants. Consecutive formation constants for any species of ligand in a mixed complex may have several values depending on the order of addition of the different kinds of ligands. Complexity constants on the other hand, are single values since only a particular complex and the completely dissociated species are involved. As suggested by Bjerrum,⁹ the *N'*'th root of the complexity constant is a better criterion of bond strength than the formation constants. The latter contain a statistical factor in addition to the ligand effect

(9) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

present in both. They vary in magnitude due to the effect of the entrance of additional ligands on the bonding of those already present.

One may write the following general expressions for the formation function for \bar{n}_a and \bar{n}_b , the mean number of ligands, A and B, resp., bound to the metal ion. If other species of ligands are present, additional equations are required.

$$\bar{n}_a = \frac{\sum_{i=0}^{N'} \sum_{j=0}^{N'} i(\text{MA}_i\text{B}_j)}{\sum_{i=0}^{N'} \sum_{j=0}^{N'} (\text{MA}_i\text{B}_j)} = \frac{\sum_{i=0}^{N'} \sum_{j=0}^{N'} i\beta_{ij}(\text{A})^i(\text{B})^j}{\sum_{i=0}^{N'} \sum_{j=0}^{N'} \beta_{ij}(\text{A})^i(\text{B})^j} \quad (6)$$

$$\bar{n}_b = \frac{\sum_{i=0}^{N'} \sum_{j=0}^{N'} j(\text{MA}_i\text{B}_j)}{\sum_{i=0}^{N'} \sum_{j=0}^{N'} (\text{MA}_i\text{B}_j)} = \frac{\sum_{i=0}^{N'} \sum_{j=0}^{N'} j\beta_{ij}(\text{A})^i(\text{B})^j}{\sum_{i=0}^{N'} \sum_{j=0}^{N'} \beta_{ij}(\text{A})^i(\text{B})^j} \quad (7)$$

It is evident that the same equations are valid in the presence of only one species of ligand since the terms containing the second species become zero when its concentration becomes zero.

For a tetracoördinate central species, M, combined with two bidentate ligands the complex species which must be considered are MA, MA₂, MAB, MB and MB₂. Of the 5 unknown complexity constants, the two for the simple B complexes, β_{01} and β_{02} , may be solved by applying Bjerrum's method⁷ to data for solutions containing only M and B. The subscripts after either ligand concentration indicate the values of \bar{n}_a and \bar{n}_b , resp., in a particular solution satisfying these conditions.

In the presence of sufficient ligand A so that in the absence of B only the saturated complex MA₂ is present, the ligand B can enter the complex only through displacement of ligand A. Thus

$$\bar{n}_a = 2 - \bar{n}_b \quad (8)$$

Since unsaturated complexes may be neglected under these conditions, formation functions for $\bar{n}_a = 3/2$ and $\bar{n}_b = 1/2$ may be written for the solution satisfying these conditions.

$$\bar{n}_a = 3/2 = \frac{2\beta_{20}(\text{A})^{3/2}(\text{B})^{1/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2}}{\beta_{02}(\text{B})^{2/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{20}(\text{A})^{3/2}(\text{B})^{1/2}} \quad (9)$$

$$\bar{n}_b = 1/2 = \frac{2\beta_{02}(\text{B})^{2/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2}}{\beta_{02}(\text{B})^{2/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{20}(\text{A})^{3/2}(\text{B})^{1/2}} \quad (10)$$

For the solution in which $\bar{n}_a = 1/2$ and $\bar{n}_b = 3/2$ the formation equations become

$$\bar{n}_a = 1/2 = \frac{2\beta_{20}(\text{A})^{3/2}(\text{B})^{1/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2}}{\beta_{02}(\text{B})^{2/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{20}(\text{A})^{3/2}(\text{B})^{1/2}} \quad (11)$$

$$\bar{n}_b = 3/2 = \frac{2\beta_{02}(\text{B})^{2/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2}}{\beta_{02}(\text{B})^{2/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{20}(\text{A})^{3/2}(\text{B})^{1/2}} \quad (12)$$

The above equations for \bar{n}_a and \bar{n}_b of a particular solution are equivalent. Combining equation 9 or 10 and equation 11 or 12 with the elimination of β_{11}

$$\beta_{20} = \beta_{02} \frac{\left(\frac{(\text{B})^{1/2}(\text{A})^{1/2}}{(\text{A})^{1/2}(\text{B})^{1/2}} + \frac{3(\text{B})^{1/2}(\text{A})^{1/2}}{(\text{A})^{1/2}(\text{B})^{1/2}} \right)}{\left(\frac{(\text{A})^{1/2}(\text{B})^{1/2}}{(\text{B})^{1/2}(\text{A})^{1/2}} + \frac{3(\text{A})^{1/2}(\text{B})^{1/2}}{(\text{B})^{1/2}(\text{A})^{1/2}} \right)} \quad (13)$$

It is evident that one can solve the complexity constant β_{20} directly from the previously solved value of β_{02} and the readily calculated values of (A) and (B) for the solutions in which $\bar{n}_a = 3/2$, $\bar{n}_b = 1/2$ and $\bar{n}_a = 1/2$, $\bar{n}_b = 3/2$, resp. Solving the pair of equations in which $\bar{n}_a = 3/2$ and $\bar{n}_b = 1/2$ for β_{11} yields

$$\beta_{11} = \beta_{20} \frac{(\text{A})^{1/2}(\text{B})^{1/2}}{(\text{B})^{1/2}(\text{A})^{1/2}} - 3\beta_{02} \frac{(\text{B})^{1/2}(\text{A})^{1/2}}{(\text{A})^{1/2}(\text{B})^{1/2}} \quad (14)$$

Likewise solving the pair of equations in which $\bar{n}_a = 1/2$, $\bar{n}_b = 3/2$ for β_{11} yields an equivalent equation

$$\beta_{11} = \beta_{02} \frac{(\text{B})^{1/2}(\text{A})^{1/2}}{(\text{A})^{1/2}(\text{B})^{1/2}} - 3\beta_{20} \frac{(\text{A})^{1/2}(\text{B})^{1/2}}{(\text{B})^{1/2}(\text{A})^{1/2}} \quad (15)$$

The remaining equilibrium constant β_{10} for the unsaturated complex MA can be solved from data for the solution in which $\bar{n}_a = 1$ and $\bar{n}_b = 1/2$.

$$\bar{n}_a = 1 = \frac{\beta_{10}(\text{A})^{1/2} + 2\beta_{20}(\text{A})^{3/2}(\text{B})^{1/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2}}{1 + \beta_{10}(\text{A})^{1/2} + \beta_{20}(\text{A})^{3/2}(\text{B})^{1/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{01}(\text{B})^{1/2} + \beta_{02}(\text{B})^{2/2}} \quad (16)$$

$$\bar{n}_b = 1/2 = \frac{\beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{01}(\text{B})^{1/2} + 2\beta_{02}(\text{B})^{2/2}}{1 + \beta_{10}(\text{A})^{1/2} + \beta_{20}(\text{A})^{3/2}(\text{B})^{1/2} + \beta_{11}(\text{A})^{1/2}(\text{B})^{1/2} + \beta_{01}(\text{B})^{1/2} + \beta_{02}(\text{B})^{2/2}} \quad (17)$$

Solving the former equation for $(\text{A})^{1/2}$ yields

$$(\text{A})^{1/2} = \sqrt{\frac{1 + \beta_{01}(\text{B})^{1/2} + \beta_{02}(\text{B})^{2/2}}{\beta_{20}}} \quad (18)$$

Solving equation 17 for β_{10} yields

$$\beta_{10} = \beta_{01} \frac{(\text{B})^{1/2}}{(\text{A})^{1/2}} + 3\beta_{02} \frac{(\text{B})^{2/2}}{(\text{A})^{1/2}} + \beta_{11}(\text{B})^{1/2} - \beta_{20}(\text{A})^{1/2} - (\text{A})^{-1/2} \quad (19)$$

The condition that \bar{n}_b be $1/2$ or a half integral less than N' is experimentally obtained at specific points during titration. The condition that \bar{n}_a be an integral less than N' in ligand deficient solutions can be achieved readily only if the consecutive formation constants of ligand A are sufficiently large, *i.e.*, in the order of 10^2 , so that it is quantitatively bound in ligand deficient solutions. Since a complexity constant of $10^{9.70}$ has been reported⁸ for $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$, it is evident that the oxalate ligand fulfills this requirement. While equations 13, 14, 18 and 19 have been applied to cases in which i and j have half integral or integral values this condition is not absolutely essential. Equations having the forms of 9 to 12, 16 and 17 but with different n_a and n_b values can be solved simultaneously particularly when the n_a and n_b values approach these half integrals or integrals. In this case temporary stepwise constants for simple or mixed complexes are first used to evaluate temporary complexity constants and (A) in the general \bar{n}_a equation 6 with alternate reevaluations of \bar{n}_a .

Experimental

The titrations were performed by adding 2.372 N HNO₃ from a microburet to 50 ml. of the solution containing various ratios of $(\text{Cu}^{2+}):(\text{C}_2\text{O}_4^{2-}):(\text{en})$. The titrated solutions contained 0.10 M ethylenediamine, the ionic strength was adjusted to unity with KNO₃ and the solutions were kept at 25° in a thermostat. Nitrogen was bubbled through the solution during the titration. A Beckman Model G pH meter equipped with the general purpose glass electrode was used. The standardization of the various reagents has been described already.^{2,3}

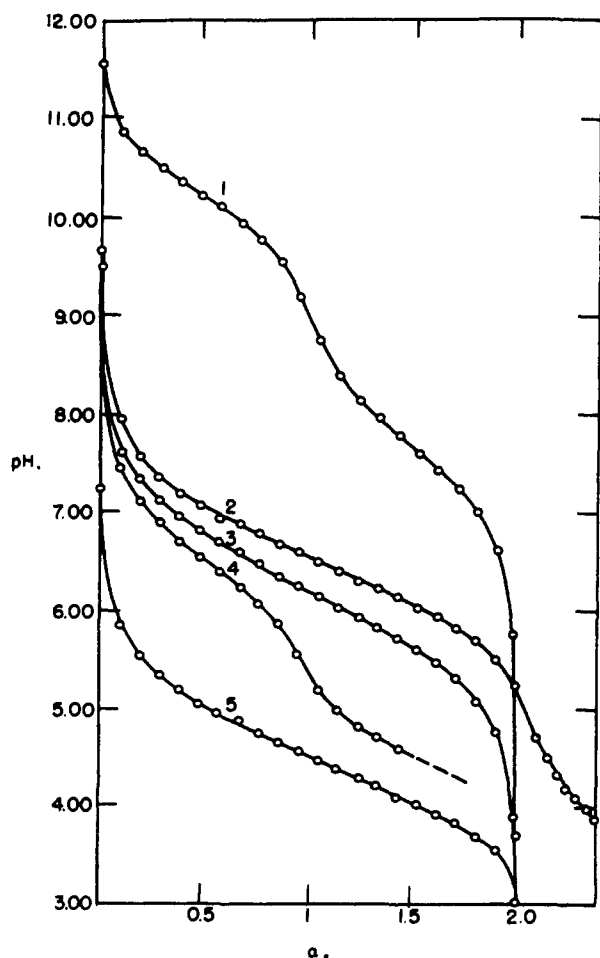


Fig. 1.—Titration curves: curve 1, 50 ml. of the solution titrated contained 0.1 *M* ethylenediamine with KNO_3 added to adjust the ionic strength to unity at 25°. Nitric acid, 2.372 *M*, was added from a microburet; curve 2, like 1 except the solution titrated also contained 0.05 *M* $\text{Cu}(\text{NO}_3)_2$ and 0.20 *M* $\text{K}_2\text{C}_2\text{O}_4$; curve 3, like 1 except the solution titrated also contained 0.05 *M* $\text{Cu}(\text{NO}_3)_2$ and 0.10 *M* $\text{K}_2\text{C}_2\text{O}_4$; curve 4, like 1 except the solution titrated also contained 0.05 *M* $\text{Cu}(\text{NO}_3)_2$ and 0.05 *M* $\text{K}_2\text{C}_2\text{O}_4$; curve 5, like 1 except the solution titrated also contained 0.05 *M* $\text{Cu}(\text{NO}_3)_2$ and no $\text{K}_2\text{C}_2\text{O}_4$.

Results and Discussion

In Fig. 1 are shown the curves for the titration of 0.1000 *N* en in the presence of various concentrations of copper(II) and oxalate ions. A comparison of curves 2 and 3 with curve 5 shows that the inflection after the addition of two moles of hydrogen ion per mole of en persists in the presence of oxalate. This verifies that the added hydrogen ion reacts essentially quantitatively with the bound en before reacting with the less basic oxalate ion, whether bound or free. This effect, which could be predicted by calculations based on the various equilibria, is interesting because the bonding of en with copper(II) is stronger than that with most of the metal ions.

The most pertinent titration data along with the calculated equilibrium concentrations of the H_2en^{2+} and ethylenediamine and n_{en} are given in Table I. All concentrations are given for the original 50-ml.

TABLE I
TITRATION DATA AND CALCULATIONS

Fifty ml. of the solution titrated contained 0.1 *M* ethylenediamine, 0.05 *M* Cu^{2+} and varied concentrations $\text{C}_2\text{O}_4^{2-}$ ion, with KNO_3 added to produce an ionic strength of unity at 25°. Nitric acid, 2.372 *N*, was added from a 10-ml. microburet. The total concentration of nitric acid in 50 ml. of solution is indicated under the heading C_a .

C_a	pH	(H_2en^{2+})	$p(\text{en})$	\bar{n}_{en}
A. Oxalate ion absent				
0.00949	7.24	0.0047	8.40	1.904
.04744	5.18	.02368	9.30	1.535
.05693	5.04	.02843	9.44	1.430
.09488	4.65	.04741	9.80	1.051
.1044	4.56	.05217	9.94	0.955
.1423	4.20	.07115	10.53	.577
.1518	4.10	.07589	10.70	.482
.1993	3.56	.09962	11.66	.007
B. 0.05 <i>M</i> oxalate ion present				
0.00949	7.44	0.00349	5.40	1.880
.04744	6.55	.02262	6.35	1.504
.05693	6.40	.02755	6.58	1.413
.09488	3.37	.0472	8.07	1.047
.1328	4.70	.0664	9.61	0.670
.1423	4.59	.0711	9.80	0.576
C. 0.20 <i>M</i> oxalate ion present				
0.00949	7.93	0.00029	4.42	1.816
.03795	7.18	.0158	5.32	1.558
.04744	7.06	.0207	5.46	1.446
.09488	6.59	.0454	6.10	1.010
.1423	6.14	.0701	6.83	0.556
.1518	6.04	.0751	7.00	.462
.1993	5.23	.0994	8.50	.009

volume of the solution titrated. This eliminates the application of the same dilution factors to all concentrations since these cancel out in the n expressions. The equilibrium concentration of (B) was calculated on the basis of an expression for the conversion of added hydrogen ion combined with expressions for the first and second acidity constants of H_2en^{2+} . Under the conditions of the titration with oxalate ion absent the acidity constants of H_2en^{2+} were

$$K_1 = \frac{[\text{H}^+](\text{Hen}^+)}{(\text{H}_2\text{en}^{2+})} = 10^{-7.56} \quad (20)$$

$$K_2 = \frac{[\text{H}^+](\text{en})}{(\text{Hen}^+)} = 10^{-10.22} \quad (21)$$

When the ionic strength of unity was obtained by 0.2 *M* $\text{K}_2\text{C}_2\text{O}_4$ and 0.4 *M* KNO_3 , the values of K_1 and K_2 became $10^{-7.66}$ and $10^{-10.30}$.

Solving the stepwise constants k_{01} and k_{02} by Bjerrum's⁷ method using data from Table IA and curve 5, Fig. 1 for solutions containing no oxalate yielded the values which agree well with the values

$$k_{01} = \frac{(\text{Cu}(\text{en})_2^{2+})}{(\text{Cu}^{2+})(\text{en})} = 10^{10.81 \pm 0.10} = \beta_{01} \quad (22)$$

$$k_{02} = \frac{(\text{Cu}(\text{en})(\text{en})^{2+})}{(\text{Cu}(\text{en})(\text{en}))} = 10^{9.41 \pm 0.10}; \beta_{02} = 10^{20.02 \pm 0.14} \quad (23)$$

$10^{10.75}$ and $10^{9.32}$ obtained by Bjerrum and Nielson.¹⁰

These constants along with the data from Table IC and curve 2, Fig. 1 for the solution containing

(10) J. Bjerrum and E. N. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

0.20 *M* oxalate, and excess, were substituted into equation 13 to solve β_{20} . The concentration, (B), was calculated in the usual way while (A) was calculated by subtracting bound oxalate from the total oxalate concentration.

$$\beta_{20} = \frac{(\text{Cu}(\text{C}_2\text{O}_4)_2^{2-})}{(\text{Cu}^{2+})(\text{C}_2\text{O}_4^{2-})^2} = 10^{9.36 \pm 0.14} \quad (24)$$

This may be compared to the value $10^{9.70}$ obtained on the basis of polarographic half-wave potentials.³ Substituting the same data into equations 14 or 15 yielded the value of β_{11} .

$$\beta_{11} = \frac{(\text{Cu}(\text{C}_2\text{O}_4)\text{en}^0)}{(\text{Cu}^{2+})(\text{C}_2\text{O}_4^{2-})(\text{en})} = 10^{15.39} \quad (25)$$

This value compares favorably with the mean value $10^{15.44 + 0.14}$ reported previously³ on the basis of spectrophotometric data.

To calculate β_{10} the data for solutions containing $(\text{Cu}^{2+}):(\text{C}_2\text{O}_4^{2-})$ in a 1:1 ratio shown in curve 4, Fig. 1 and summarized in Table IB were used. The

concentration of $(\text{A})_{1/2}$ in the solution for which $\bar{n}_a = 1$ and $\bar{n}_b = 1/2$ was first calculated by equation 18. A small extrapolation from $\bar{n}_b = 0.576$ was used since precipitation occurred beyond this point. Substituting into equation 19 yielded a value for β_{10} .

$$\beta_{10} = \frac{(\text{CuC}_2\text{O}_4^0)}{(\text{Cu}^{2+})(\text{C}_2\text{O}_4^{2-})} = 10^{8.42 \pm 0.14} \quad (26)$$

Combining with the value $10^{9.36}$ for β_{20} yields the value for k_{20} .

$$k_{20} = \frac{(\text{Cu}(\text{C}_2\text{O}_4)_2^{2-})}{(\text{CuC}_2\text{O}_4^0)(\text{C}_2\text{O}_4^{2-})} = 10^{3.93 \pm 0.14} \quad (27)$$

The stepwise constants of this complex and many other oxalato complexes, as well, have not been reported previously due to the experimental difficulties associated with the low solubility of oxalates in oxalate deficient solutions.

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[CONTRIBUTION FROM THE STEELE CHEMISTRY LABORATORY, DARTMOUTH COLLEGE]

The Polarography of Hg(II)EDTA in the Presence of Other Metallic Ions

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The equilibrium $\text{Hg}(\text{EDTA}) + \text{M}^{++} = \text{M}(\text{EDTA}) + \text{Hg}^{++}$ has been studied polarographically for various metal ions in 0.6 *M* acetate solution. It is shown that by such measurements the *p*Hg method for determining metal concentrations in complexing media can be extended to those media which compete successfully for mercury with EDTA. A polarographic method for determining metal chelate association rates is described, which requires the existence of a stable chelate that is reversibly reduced to the metal at the dropping mercury electrode.

The mercury(II) complex of ethylenediaminetetraacetate ion (EDTA) rapidly establishes a reversible potential at a mercury electrode. The dissociation constant for this chelate is therefore easily measured potentiometrically, and has been used by several authors^{1,2} as the reference standard for evaluating the stability of other EDTA complexes. The complex is also reduced reversibly at the dropping mercury electrode,^{3,4} a property which among the bivalent metal complexes is shared only by the cupric complex⁵ and that to an inferior degree. The mercury complex is by far the stablest of the common bivalent metal complexes (*p*K = 21.8). This combination of reversibility and stability satisfies, in principle, the requirements of a novel polarographic method for the determination of rates of metal-chelate formation. Preliminary experiments showed, however, that the HgY^- , Hg couple did not possess the degree of reversibility required for this purpose. Nevertheless, the observations made on mixtures of HgY^- and other metallic ions in the course of these experiments were of sufficient interest to

warrant further investigation and form the main subject of this paper. Since the proposed method for determining metal-chelate association rates may find application in systems with the requisite reversibility, an account of the theory is given in the last section of the article.

Results

Polarograms of millimolar HgY^- solutions were obtained in the presence of varying amounts of zinc, manganese, lead and cadmium ions.

In the *p*H range 4–9 the half-wave potential of HgY^- is related to the acidity by the expression

$$E_{1/2} = \text{constant} + \frac{RT}{nF} \ln (1 + (\text{H}^+)/K_4 + (\text{H}^+)^2/K_3K_4)$$

where K_3 and K_4 are dissociation constants of H_2Y^- . It is seen that the wave shifts to more positive potentials as the hydrogen ion concentration increases, until in weakly acid solutions the half-wave potential lies inconveniently near the mercury dissolution potential. In an investigation of the effect of metal ions on the wave, it is desirable to buffer the solution at as high a *p*H as feasible, in order to allow space for positive shifts. A 1:50 HOAc–OAc buffer (*p*H 6.35) was used in most of the experiments.

The effects of adding increasing amounts of zinc ion (*p*K of EDTA complex = 16.5) to a 1 *mM* HgY^- solution in this medium is shown in Fig. 1. As the zinc concentration increases, a preliminary wave extending to the dissolution

(1) R. W. Schmid and C. N. Reilly, *THIS JOURNAL*, **78**, 5513 (1956).

(2) (a) G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **40**, 1773 (1957); (b) G. Schwarzenbach, R. Gut and G. Anderegg, *ibid.*, **37**, 937 (1954).

(3) J. Goffert, G. Michel and G. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

(4) J. Watters, J. Mason and D. Schupp, *THIS JOURNAL*, **78**, 5782 (1956).

(5) R. L. Pecsok, *Anal. Chem.*, **25**, 561 (1953).