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Study of Metal-1,10-Phenanthroline Complex Equilibria
by Potentiometric Measurement¹

MASTER

By John M. Dale² and Charles V. Banks

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- (1) Abstracted from dissertation submitted by John M. Dale to graduate faculty of Iowa State University in partial fulfillment of requirements for the degree of doctor of philosophy, 1962.
- (2) Present address: Oak Ridge National Laboratory, Oak Ridge, Tennessee.
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Abstract

The silver-1,10-phenanthroline system has been studied and the stability constants determined for the 1:1 and 2:1 complexes using the silver electrode. This known system was then used to study the complexes of 1,10-phenanthroline with other metals. The $\log \beta_n$ values found for the over-all stoichiometric stability constants are as follows: Ag, 5.02, 12.07; Mn, 3.88, 7.04, 10.11; Cd, 5.93, 10.52, 14.30; Zn, 6.83, 12.05, 16.92. The stoichiometric stability constants determined for copper are $\log k_2 = 6.42$ and $\log k_2 k_3 = 11.05$.

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Introduction

The silver electrode has been used in the past to study complexes of metal ions by competitive means.^{3,4} The 1:1

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- (3) I. Leden, Acta Chem. Scand., 6, 971 (1952).
- (4) S. Cabani and E. Scrocco, Ann. chim. (Rome), 48, 99 (1958).
-

complexes of some transition metals with 1,10-phenanthroline have been investigated using the mercury electrode.⁵

- (5) G. Anderegg, Helv. Chim. Acta, 42, 344 (1959).
-

The purpose of the present work was to investigate the complexes of silver with 1,10-phenanthroline using the silver electrode and to apply this known system to the study of complexes of 1,10-phenanthroline with some transition metals. The method depends upon the competition between the ions of silver and of a second metal to form complexes with 1,10-phenanthroline. The theory of competitive systems has been previously discussed.⁶

- (6) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1961.
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Sullivan et al.⁷ have developed a program for the least

- (7) J. C. Sullivan, J. Rydberg, and W. F. Miller, Acta Chem. Scand., 13, 2023 (1959).
-

squares treatment of potentiometric titration data using the IBM 704 electronic computer. This program was used to evaluate the stability constants and their standard deviations for the transition metals investigated in this work.

Experimental

Titration were performed in a three-compartment cell. The center compartment, containing a saturated solution of potassium sulfate, was separated from the outer compartments by ultra-fine porosity pyrex disks. Salt diffusion through the pyrex disks was shown to be negligible compared to that already in the solution by a conductometric time study. The construction of the cell permitted thorough cleaning of the frits after each titration. During the titrations, the potential difference between two Beckman silver billet electrodes in each of the outer two compartments was followed. Potentiometric measurements were made with a Leeds and Northrup No. 7552 Type K-2 potentiometer coupled with a No. 2430-C Type E galvanometer having a sensitivity of $0.005 \mu\text{a/mm}$. The temperature was controlled at $25 \pm 0.05^\circ\text{C}$.

At the beginning of each titration, the two outer compartments of the cell contained identical solutions. One solution which was not altered served as a reference while the other solution was titrated. The titrant, except for the 1,10-phenanthroline concentration, was identical to the solution to be titrated with respect to ionic strength and total concentrations of sulfate, acetate, acetic acid, and metal ions. Thus, the over-all composition of the solution to be titrated was not altered during titration except for the addition of the 1,10-phenanthroline. Metal sulfates were used in this work because nitrate and perchlorate ions form insoluble salts with the $\text{bis}(1,10\text{-phenanthroline})\text{Ag(I)}$ complex ion.

After each addition of titrant, the system came to equilibrium in approximately 3 to 5 minutes in most cases. Equilibrium was assumed to have been attained when two consecutive readings, one minute apart, did not differ by more than 0.01 or 0.02 of a millivolt. Equilibrium was very slowly established in the titration of nickel, an hour being required for certain experimental points.

Evaluation of the System

In order to evaluate the response of the concentration cell, potentiometric measurements were made for several dilute solutions of silver. The ionic strength in both the reference and experimental solutions was 0.1 and the pH was 4.80. The concentrations of silver were calculated from the emf's of the concentration cell and compared to the concentration of silver known to be present.

The emf of the working electrode with respect to the reference electrode may be expressed as

$$E = - \frac{RT}{F} \ln \frac{[Ag']_r}{[Ag']_x} \quad (1)$$

where the subscripts r and x refer to the reference and experimental solutions, respectively. The term, $[Ag']$, represents the total concentration of silver not bound to 1,10-phenanthroline. Because the ionic strength in both half-cells was held constant, the activity coefficients of silver cancel. In a like manner, it can be shown that the consideration of the sulfate and acetate complexes of silver introduces a constant term which also cancels

in the ratio of the silver concentrations. Table 1 shows the comparison of the silver concentration known to be present and that calculated from equation (1).

Table 1
Potential Measurements of Dilute Silver Solutions^a

E millivolts	pAg' _x		E millivolts	pAg' _x	
	Taken	emf		Taken	emf
-17.8	2.90	2.90	-94.8	4.20	4.20
-28.2	3.08	3.08	-118.0	4.60	4.60
-35.8	3.20	3.21	-135.5	4.90	4.89
-59.1	3.60	3.60	-145.6	5.08	5.06
-76.8	3.90	3.90	-152.6	5.20	5.18
-87.2	4.08	4.08			

^a Reference solution: $\text{Ag}_2\text{SO}_4 = 1.25 \times 10^{-3} \text{ M}$; $\text{K}_2\text{SO}_4 = 2.21 \times 10^{-2} \text{ M}$; $\text{KOAc} = 3.00 \times 10^{-2} \text{ M}$; $\text{HOAc} = 3.01 \times 10^{-2} \text{ M}$.

Experimental solution: $\text{Ag}_2\text{SO}_4 < 1.25 \times 10^{-3} \text{ M}$; $\text{K}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4 = 2.34 \times 10^{-2} \text{ M}$; $\text{KOAc} = 3.00 \times 10^{-2} \text{ M}$; $\text{HOAc} = 3.01 \times 10^{-2} \text{ M}$.

A comparison at lower concentrations of silver was made by means of a titration with chloride. At the beginning of the titration, the reference and experimental solutions were both 1.0×10^{-3} molar in total silver. The sodium chloride titrant contained the same amounts of sulfate, acetate, and acetic acid as the reference solution, and as the experimental solution to be titrated. Due to the increasing amount of sodium chloride,

the ionic strength of the solution being titrated varied from 0.1 to approximately 0.14 during the titration. The concentrations of silver calculated from the emf measurements were compared to those calculated from the known concentrations of chloride and the solubility product constant of silver chloride.⁸ Even though the ionic strength was not exactly 0.1

(8) J. H. Jonte and D. S. Martin, Jr., J. Am. Chem. Soc., 74, 2052 (1952).

throughout the titration, the solubility product constant was adjusted for $\mu = 0.1$, using the ion activity coefficients of Kielland.⁹ Because only the free silver ion is involved in the

(9) J. Kielland, J. Am. Chem. Soc., 59, 1675 (1937).

solubility product constant, it was necessary, in this case, to account for the sulfate¹⁰ and acetate¹¹ complexes of silver. The

(10) E. C. Righellato and C. W. Davies, Trans. Faraday Soc., 26, 592 (1930).

(11) F. H. MacDougall and L. E. Topol, J. Phys. Chem., 56, 1090 (1952).

values of the formation constants for these complexes were also adjusted for $\mu = 0.1$. All potentiometric measurements were taken beyond the equivalence point. It was shown that a negligible amount of the excess chloride ion was present as AgCl_2^- .⁸

Table 2 shows the results from the titration with chloride.

Table 2

Potential Measurements of Silver Solutions^a Containing Chloride

$[\text{Cl}^-]$ $\times 10^3$	E millivolts	Calc. K_{sp}	pAg_x emf	$[\text{Cl}^-]$ $\times 10^3$	E millivolts	Calc. K_{sp}	pAg_x emf
2.885	-230.0	6.97	6.99	18.56	-277.4	7.78	7.79
4.720	-242.3	7.18	7.20	22.32	-282.1	7.86	7.88
8.186	-256.2	7.42	7.44	27.87	-287.8	7.95	7.97
11.41	-264.8	7.57	7.58	36.89	-295.0	8.08	8.09
15.84	-273.3	7.71	7.73	43.91	-299.6	8.15	8.17

^a Reference solution: $\text{Ag}_2\text{SO}_4 = 5.00 \times 10^{-4} \text{ M}$; $\text{K}_2\text{SO}_4 = 2.28 \times 10^{-2} \text{ M}$; $\text{KOAc} = 3.00 \times 10^{-2} \text{ M}$; $\text{HOAc} = 3.01 \times 10^{-2} \text{ M}$.

In view of the assumptions and adjustments made in order to make the comparisons in Table 2, it was felt that the results were satisfactory. Equation (1) was therefore used for the calculation of silver concentrations from emf data in the titrations with 1,10-phenanthroline.

Silver(I)-1,10-Phenanthroline System

Titration of silver with 1,10-phenanthroline were performed as described previously. The ionic strength was controlled at 0.1 and the pH at 4.80. The composition of the reference solution was the same as that indicated by the footnote to Table 2. The titration curve is shown in Fig. 1.

Values for the logarithm of the over-all conditional formation constant, $\log \beta_2'$, were calculated from the measured

silver concentration, $[Ag']$, and the known concentration of the excess 1,10-phenanthroline, $[P']$, for several experimental points beyond the stoichiometric point. The term, $[P']$, represents the total concentration of 1,10-phenanthroline not bound to a metal. The average value of $\log \beta_2'$ and the standard deviation are given in Table 3.

Once β_2' is known, it is possible to calculate β_1' using experimental points prior to the end point. Equation (2) results from subtracting the expression for the total concentration of silver, Ag_T , from that representing the total concentration of 1,10-phenanthroline, P_T , and substituting for $[AgP_2]$.

$$[Ag']\beta_2'[P']^2 + [P'] + Ag_T - [Ag'] - P_T = 0 \quad (2)$$

The values of $[P']$ may be determined from equation (2) using the values of $[Ag']$ calculated from the experimental emf's. The concentration of AgP_2 may now be calculated and the concentration of AgP found by difference. All quantities necessary for the calculation of β_1' are now known and the average value is given in Table 3.

Table 3

Over-all Conditional Formation Constants^a

Metal	$\log \beta_1'$	$\log \beta_2'$	$\log \beta_3'$
Ag	4.525 ± 0.027	11.186 ± 0.018	
Mn	3.230 ± 0.011	6.004 ± 0.031	8.685 ± 0.031
Cd	5.028 ± 0.016	9.225 ± 0.024	12.624 ± 0.033
Zn	6.081 ± 0.036	10.906 ± 0.036	15.388 ± 0.036
Cu		6.030 ± 0.024^b	10.274 ± 0.030^c

^a Values not corrected for acetate and sulfate complexes or for the presence of phenanthroline ion, $\mu = 0.1$ and $t = 25^\circ \pm 0.05^\circ\text{C}$.

^{b,c} Values reported are $\log k_2'$ and $\log k_2'k_3'$, respectively, where k_n' indicates the step-wise conditional formation constant.

Using the values for β_1' and β_2' the concentration of total 1,10-phenanthroline, P_T , was calculated for each experimental point. The calculated values are plotted in Fig. 1 as a comparison to the experimental curve.

Metal(II)-1,10-Phenanthroline Systems

In this study, titrations were performed which were identical to those with silver alone except that a known amount of a second metal was present. As before, the reference solution, the solution to be titrated, and the titrant were of identical composition except for the 1,10-phenanthroline in the titrant.

The metals studied were cadmium(II), zinc(II), copper(II), nickel(II), and manganese(II). No attempt was made to study iron because iron(II) reduced silver(I) in the initial solutions.

An attempt was made to study cobalt(II) with no success. This was due to the reduction of the free silver by the cobalt(II) complex.

Fig. 2 illustrates the titration data obtained for manganese, cadmium, zinc, copper, and nickel. The curve for silver is also included for comparison. In each case the total silver concentration was $1.000 \times 10^{-3} \text{ M}$ while the total concentration of the second metal was as follows: manganese, $1.004 \times 10^{-3} \text{ M}$; cadmium, $1.004 \times 10^{-3} \text{ M}$; zinc, $1.062 \times 10^{-3} \text{ M}$; copper, $1.003 \times 10^{-3} \text{ M}$; nickel, $1.003 \times 10^{-3} \text{ M}$. Because the concentrations of the second metal were almost the same, comparison of the titration curves gives an indication of the relative strength of the complexes which, in general, increases from left to right.

The values of β_1' and β_2' for the silver-1,10-phenanthroline complexes combined with the measured silver concentration, $[\text{Ag}']$, permitted the calculation of the concentration of the uncomplexed 1,10-phenanthroline, $[\text{P}']$, for each experimental point on these titration curves.

The logarithm of the conditional stability constants, $\log \beta_n'$, obtained from the least squares treatment of the data are shown in Table 3. The adjusted constants wherein the concentrations of the sulfate¹² and acetate¹³ complexes of the metals and the

(12) J. C. James, Thesis, London, 1947; C. W. Davies, J. Chem. Soc., 1938, 2093; P. A. H. Wyatt, Trans. Faraday Soc., 47, 656 (1951).

(13) R. S. Kolat and J. E. Powell, Inorg. Chem., 1, 293 (1962); S. K. Siddhanta and S. N. Banerjee, J. Indian Chem. Soc., 35, 419 (1958).

phenanthrolium¹⁴ ion have been taken into account are given in

(14) T. S. Lee, I. M. Kolthoff, and D. L. Leussing,
J. Am. Chem. Soc., 70, 2348 (1948).

Table 4. These values are compared to those obtained by other workers.

Table 4
Stoichiometric Formation Constants^a

Metal	log k_1	log k_2	log k_3	log β_3
Ag	5.02	7.05		
Mn	3.88 4.8 ¹⁵	3.16 4.1 ¹⁵	3.07 5.4 ¹⁵	10.11 14.3 ¹⁵ 7.35 ¹⁶
Cd	5.93 5.17 ¹⁵ 5.75 ¹⁷ 6.01 ⁵	4.59 4.83 ¹⁵ 5.09 ¹⁷	3.78 4.26 ¹⁵ 3.07 ¹⁷ 2.04 ¹⁸	14.30 14.26 ¹⁵ 13.91 ¹⁷ 15.19 ¹⁸
Zn	6.83 6.5 ¹⁹ 6.4 ¹⁵ 6.36 ²⁰ 6.6 ²¹ 6.31 ¹⁷ 6.47 ²² 6.40 ⁵	5.22 5.45 ¹⁹ 5.63 ¹⁵ 5.64 ²⁰ 5.72 ²¹ 6.09 ¹⁷ 5.53 ²²	4.87 5.10 ¹⁹ 4.97 ¹⁵ 5.00 ²⁰ 4.85 ²¹ 4.77 ¹⁷ 1.1 ²²	16.92 17.05 ¹⁹ 17.00 ¹⁵ 17.00 ²⁰ 17.17 ²¹ 17.17 ¹⁷ 13.1 ²²
Cu		6.42 6.57 ¹⁵ 6.65 ²⁰ 6.15 ²³ 6.07 ¹⁷ 6.84 ⁵	4.63 5.02 ¹⁵ 5.25 ²⁰ 5.50 ²³ 5.00 ¹⁷	
	8.82 ¹⁵ 9.15 ²⁰ 6.3 ²³ 7.53 ¹⁷ 9.30 ⁵			20.41 ¹⁵ 21.05 ²⁰ 17.95 ²³ 18.60 ¹⁷

^a Values stated without reference are from this work in which $\mu = 0.1$ and $t = 25^\circ \pm 0.05^\circ\text{C}$.

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- (15) H. Irving and D. H. Mellor, private communication.
- (16) R. R. Miller and W. W. Brandt, J. Am. Chem. Soc., 77, 1384 (1955).
- (17) R. Fullerton, Ph.D. Thesis, Iowa State University, 1959.
- (18) B. E. Douglas, H. A. Laitinen, and J. C. Bailar, J. Am. Chem. Soc., 72, 2484 (1950).
- (19) H. Irving and D. H. Mellor, J. Chem. Soc., 1955, 3457.
- (20) C. V. Banks and R. I. Lystroff, J. Am. Chem. Soc., 81, 6153 (1959).
- (21) I. M. Kolthoff, D. L. Leussing, and T. S. Lee, J. Am. Chem. Soc., 73, 390 (1951).
- (22) J. H. McClure, Ph.D. Thesis, Iowa State University, 1951.
- (23) R. T. Pflaum and W. W. Brandt, J. Am. Chem. Soc., 76, 6215 (1954).
-

The stabilities of the nickel complexes were too large for silver to be an effective competitor and no constants could be calculated for this system. This was also true for the 1:1 complex of copper.

Fig. 3 compares the experimentally determined formation function for each metal with values of $\bar{n}$ calculated from experimental values of $[P']$ and the over-all conditional formation constants.

Acknowledgment

The authors wish to express their thanks to Dr. J. C. Sullivan of Argonne National Laboratory for providing the IBM 704 program for the least squares treatment of potentiometric titration data.

Fig. 1. Titration of Silver with 1,10-Phenanthroline.

Fig. 2 - Titration of Metal Solutions with 1,10-Phenanthroline. I, Silver; II, Manganese + Silver; III, Cadmium + Silver; IV, Zinc + Silver; V, Copper + Silver; VI, Nickel + Silver.

Fig. 3. - Formation Functions I, Copper; II, Zinc; III, Cadmium; IV, Manganese

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