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DETERMINATION OF STABILITY CONSTANTS AT 25° C FOR THE INTERACTION IN AQUEOUS SOLUTION OF SERINE WITH Co (II), Ni (II), Cd (II), Zn (II), and Cu (II) IONS

A Thesis
Presented to the
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In Partial Fulfillment
of Requirements for the Degree
Master of Science

by
Liak Hwe Ma
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This thesis, by Liak Hwe Ma, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the thesis requirements for the degree Master of Science.

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LIST OF SYMBOLS

The following is a list of symbols that have not been clearly defined in the text. All other symbols are defined when used.

β_n	$K_1 K_2 \ldots K_n$
α^o	the ratio of the concentration of a given complex to the total concentration of metal ion in the solution
M^{2+}	divalent metal ion
HA	serine molecule
ΔH	the enthalpy change
pK	the - log K
[ ]	denotes concentration when enclosed about a single species
( )	denotes activity when enclosed about a single species
μ	ionic strength
γ	activity coefficient

I. INTRODUCTION

Historical Background

The theoretical basis for the determination of stability constants for metal complex formation was laid in the 19th Century by Arrhenius' dissociation theory[1] and Werner's coordination theory.[2] The pioneer investigations in this field were initiated by Abegg, Bodlander, Immerwahr,[3, 4, 5] and others in the period between 1900 and 1920. Most of these early workers were able to determine only the overall stability constants. Morse,[6] however, was able to calculate the first two stability constants, K_1 and K_2, for the mercury (II) chloride system from solubility measurements as early as 1902. From 1920 to 1941, the amount of work done in this field was small. A great deal of work in this area, however, has been done since Bjerrum[7] and Leden[8] introduced in 1941 the general methods for computing stability constants from experimental $\bar{n}$ and α^{o} values. The formation constants reported in the literature up to 1963 have been compiled by Sillen and Martell.[9]

Literature Survey

Since 1941, the number of stability constants reported in the literature has been enormously increased. The studies in this field have included a wide variety of ligands, and metal ions with different theoretical interests and motives. Studies have been done to correlate the stability of the metal chelates in connection with ligand basicity,[10, 11] the effect of the ring size of a chelate,[12] as well as the steric effects from the ligand structure.[13] Other investigators have attempted to determine the entropy changes involved when water molecules of the hydrated metal ions are replaced by the chelating ligand groups.[14] There have been a few attempts to determine the formation constants as a function of temperature.

Few stability constants had been reported for the metal-serine system when this research project was started. The nickel (II)-serine system at 10°, 20°, and 30°C has been investigated in some detail by Pelletier.[15, 16] The overall stability constants, β_2, at 20°C for Cu (II) and Co (II)-serine complexes have been obtained from the formation curves by Albert[17] and from polarographic studies by Li and Doody.[18] Perrin[19, 20] has reported stability constants for 1:1 complexes of serine with ferrous and ferric ions at 20°C. Schubert[21] studied Co^{2+} and Sr^{2+} complexes of serine using an ion exchange technique and radioisotopes. Calcium (II) was studied using an ionic exchange method by Schubert[21] and from solubility measurements by Davies et al.[22] Morrell[23] determined the formation constants for 1:2 complexes of serine with Hg (II), Zn (II), Cd (II), Ag (I), and In (III) at 10°, 20°, 30°, and 40°C. Recently Sharma[24] has reported stability constants for the metal-serine system for Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Pb^{2+} at 37°C from pH titration data. With the exception of the copper (II)-serine complex previously studied at 25°C by Li and Doody, formation constants at 25°C for the 1:3 complexes of serine with the metal ions Co^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+} have not been reported.

Purpose of Study

The purpose of my determination of the equilibrium constants for the stepwise interactions of serine with Ni (II), Co (II), Cd (II), Zn (II), and Cu (II) was three-fold. First, a quantitative study of these formation constants, except in the case of Cu (II) at 25°C has not been reported. My present study, thus, provides experimental data for metal-serine systems.

Second, equilibrium formation constants for the metal-serine complexes usually have been reported for only the first two steps. It was hoped from this study to make equilibrium constants for the third step interaction of metal-serine complexes available.

Third, equilibrium constants for metal-serine complex formation were determined in low ionic strength solutions in this study. These values are essential for later ΔH determinations.

II. EXPERIMENTAL

Reagent Preparation and Standardization

1. Buffer solutions

Buffer solutions of pH 6.865 (prepared with KH_2PO_4 and Na_2HPO_4, NBS sample no. 186-I-b and 186-II-b, respectively) and pH 9.180 (prepared with borax, NBS sample no. 187a) were used as reference solutions in pH titrations. Buffer solutions were prepared according to instructions provided by the National Bureau of Standards and were stored under a nitrogen atmosphere.

2. Ligand solution

The ligand studied was D, L-serine (A grade, CalBiochem Lot. 33229). Its purity, as assayed by titrating it with a standard NaOH solution in a solution of formaldehyde in water, was 99.86%.

A 0.4 molar sodium serinate solution was then prepared using the calculated amount of serine and an equivalent amount of standard NaOH solution. Boiled, doubly distilled water was used to prepare and dilute the solution until the desired concentration was obtained. The sodium serinate solution was stored under a nitrogen atmosphere and kept in a refrigerator when not in use.

3. Metal ion solutions

Reagent grade $NiCO_3$ (Baker 'Analyzed'), $CoCO_3$ (Baker 'Analyzed'), CdO (Matheson, Coleman and Bell 'Reagent Powder'), ZnO (Merk 'Reagent'), Cu wire (Baker 'Analyzed'), freshly boiled, doubly-distilled water, and standard $HClO_4$ were used in the preparation of metal ion solutions.

Standard stock solutions of the metal perchlorates were prepared (1) from the metal oxide or elemental metal by dissolving a weighed amount of the oxide or metal in a slight excess of $HClO_4$ solution, and (2) from the metal carbonates by refluxing excess metal carbonate with a solution containing a known amount of $HClO_4$ until the pH of the solution was greater than 6. The solution was then cooled, the excess carbonate was filtered off, and enough standard $HClO_4$ solution was added to suppress hydrolysis of the metal ion.

Each solution was standardized for metal ion by titrating with standard EDTA (Baker 'Analyzed') using Erichrome Black T as indicator.

4. Volumetric reagents

The NaOH (Baker 'Analyzed') and $HClO_4$ (Baker and Adamson 'Reagent') solutions were prepared and standardized against potassium hydrogen phthalate (National Bureau of Standards) and tris (hydroxymethyl) aminomethane (THAM) (Baker 'Analyzed'), respectively.

Apparatus

All pH measurements were made using a Beckman Research pH meter or Orion Research digital pH meter ('Ionalyzer' model 801).

Beckman glass and saturated calomel electrodes were used in the determination. Both pH meters could be read within ± 0.001 pH unit.

The pH titrations were made using a calibrated 5-ml microburet equipped with a reservoir and a 3-way teflon stopcock. The buret could be read within ± 0.001 ml. Calibrated pipets of appropriate volumes were used to deliver the metal ion solution or boiled, doubly-distilled water into a round-bottom titration vessel having four side necks and one center neck. The four side necks were used to hold two electrodes, a tube for nitrogen inlet, and a glass stirring rod which was turned by a small electric motor.

During a titration, the titration vessel was placed in a 20-liter waterbath in which the temperature was controlled by a mercury thermo regulator. A 500-watt heating unit and a copper coil, cooled by a constant stream of 15° tap water, were used as the temperature regulating apparatus. The bath was stirred vigorously and its temperature was maintained constant at $25.00 \pm 0.05^{\circ}C$.

Experimental Procedure

All titrations were performed in aqueous solution, and measurements were made at three different ionic strengths for each metal ion-serine system. The titration at each ionic strength was repeated at least three times except in the case of Cd (II) which was repeated twice. Each titration was performed under a nitrogen atmosphere. The titrations were carried out as follows.

A 50 ml. aliquot of 0.008 molar metal perchlorate solution was pipetted into a titration vessel. The vessel was then placed in a constant temperature waterbath and was allowed to come to thermal equilibrium. A 0.4 molar sodium serinate solution was added incrementally from the microburet, and a pH measurement was made at each point. The solution was stirred constantly and chemical equilibrium was established (as shown by no drift in the pH reading) after each addition of the titrate. The electrodes were standardized against the pH 6.865 buffer before and after the titration. If the value for the buffer differed by more than 0.005 pH unit, the titration was discarded. For measurements at the other two ionic strengths, the same procedure as described above was followed, except that 200 ml or 400 ml of water was added.

III. CALCULATIONS

Activity Coefficients

Activity coefficients at each point on the titration curve were calculated using the classical Debye-Hückel equation[25]

$$\log \gamma_{\pm} = - \frac{Az^2\sqrt{\mu}}{1 + B\,\overset{o}{a}\sqrt{\mu}} \qquad (1)$$

where γ is the activity coefficient, z is the ionic charge, A and B are constants with the numerical values of 0.5091 and 0.3286, respectively, and $\overset{o}{a}$ represents the effective radius of the ion. A value for $\overset{o}{a}$ of 4.4 Å was used in this calculation. The ionic strength, μ, is defined as

$$\mu = \tfrac{1}{2}\Sigma\, C_i Z_i^2 \qquad (2)$$

where C is the molar concnetration and Z is the charge of each ion in solution. It was assumed that the γ values were the same for all species of the same charge type and the activity coefficient for a neutral species was unity. These assumptions would be expected to be valid in the low ionic strength solutions ($\simeq 5 \times 10^{-3}$) used in this study. Activities thus obtained were used to convert the pH, the Kw (ion product of water), and the pK_2 of serine to the corresponding concentration quantities at each experimental point. This was done so that the quantities used in the equations for the calculation of $\bar{n}$ and the concentration quotient would be concentration terms and not a mixture of concentration and activity terms. Since μ was not constant during a titration, it was calculated at each experimental point. This required a series of successive approximations since the concentrations of all charged species were not known prior to the calculation of the equilibrium constants being determined. The computer program was written such that recycling continued until successive approximations of μ agreed within 0.1%.

Dissociation Constants of Serine

No attempt was made to determine the first dissociation constant, K_1, of protonated serine, H_2A^+. This is justified by the fact that the first dissociation constant of H_2A^+, reported by Morrell,[26] is of the order of 10^{-2}. Since the first $\bar{n}$ value was not calculated until the pH of the metal ion solution was 5 or higher, the concentration of H_2A^+ and H^+ as represented by the reaction $H_2A^+ = H^+ + HA$ could be neglected for the $\bar{n}$ calculations without introducing significant errors.

The second dissociation constant of serine was calculated from pH data obtained by titrating a sodium serinate solution with a standardized perchloric acid solution. The reaction $A^- + H^+ = HA$ was assumed to take place and pK_2 was calculated from the equation

$$pK_2 = pH + \log\left\{\left[\frac{A_T}{B - (OH)} - 1\right] (\gamma)^{-1}\right\} \qquad (3)$$

where A_T is the total amount of serine added to the solution and B is the meq-of base per ml. of solution at the time of measurement. Equation (3) may be derived from the following equations:

$$K_2 = \frac{[A^-][H^+]}{[HA]} \tag{4}$$

$$A_T = [HA] + [A^-] \tag{5}$$

$$B = [A^-] + [OH^-] \tag{6}$$

Equations (5) and (6) are true only if the concentrations of the species H^+ and H_2A^+ are negligible.

Thermodynamic Stability Constants

The technique used in this study for the calculation of stepwise formation constants has been described by Rossotti and Rossotti.[27] The equilibrium reactions used for the calculation of formation constants are discussed below.

The maximum number of serine molecules that can chelate with Cu (II) is two. Therefore, reactions for the Cu (II)-serine stepwise interactions become

$$M^{2+} + A^- = MA^+$$

$$\frac{[MA^+]}{[M^{2+}][A^-]} = Q_1 \tag{7}$$

$$MA^+ + A^- = MA_2$$

$$\frac{[MA_2]}{[MA^+][A^-]} = Q_2 \tag{8}$$

However, for the rest of the metal ions used in this study, the number of serine molecules that chelate with each metal ion is three. Thus the reaction for the third step of metal-serine interaction should include

$$MA_2 + A^- = MA_3^-$$

$$\frac{[MA_3^-]}{[MA_2]\,[A^-]} = Q_3 \qquad (9)$$

Transition metal ions hydrolyze in aqueous solution unless the pH is kept sufficiently low. The reactions for divalent metal-ion hydrolysis are assumed to be as given in (10) and (11).

$$M^{2+} + H_2O = M[OH]^+ + H^+$$

$$\frac{[H^+]\,[M(OH)]}{[M^{2+}]} = k_1 \qquad (10)$$

$$M[OH]^+ + H_2O = M[OH]_2\ (aq) + H^+$$

$$\frac{[H^+]\,[M(OH)_2]}{[M(OH)^+]} = k_2 \qquad (11)$$

Hydrolysis constants for each metal ion used in this study were obtained from the literature (see Table 7). The value of 1.008 x 10^{-14} was used for the ion product of water at 25°C. The value of pK_2 = 9.227 for serine (see Table 8) was used in the calculation.

Values of $\bar{n}$, which is defined as the average number of ligands bound per metal ion, may be calculated by first defining the quantities A_B, A_T, and M_T where

A_B = the concentration of ligands bound to a metal ion

A_T = the total ligand concentration

M_T = the total metal ion concentration

The mass balance equations for A_B, A_T, and M_T are as follows:

$$A_B = MA + 2\,MA_2 + 3\,MA_3 \qquad (12)$$

$$A_T = A + HA + MA + 2\,MA_2 + 2\,MA_3 \qquad (13)$$

$$M_T = M + MA + MA_2 + MA_3 + M[OH] + M[OH]_2 \qquad (14)$$

Equation (13) is valid only if the concentration of the species H_2A^+ is negligible, i. e. when the pH of the solution is equal to or greater than 5. From the definition of $\bar{n}$

$$\bar{n} = \frac{A_B}{M_T} \tag{15}$$

$$\bar{n} = \frac{MA + 2MA_2 + 3MA_3}{M + MA + MA_2 + MA_3 + M(OH)^+ + M(OH)_2} \tag{16}$$

Using equations (4), (8), (9), (10), and (11)

$$\bar{n} = \frac{Q_1M(A) + 2\,Q_1Q_2M(A)^2 + 3Q_1Q_2Q_3M(A)^3}{M + Q_1M(A) + Q_1Q_2M(A)^2 + Q_1Q_2Q_3M(A)^3 + C(M)} \tag{17}$$

where C(M) is the correction for the hydrolysis of a metal ion in solution. C(M) can be derived from equations (10) and (11) where

$$C = \frac{k_1}{H} + \frac{k_1k_2}{(H)^2} \tag{18}$$

Rearranging with $\beta_1 = Q_1$, $\beta_2 = Q_1Q_2$, and $\beta_3 = Q_1Q_2Q_3$ equation (17) can be simplified to

$$\bar{n} = [(A = \bar{n}A)\beta_1 + (2A - \bar{n}A^2)\beta_2 + (3A - \bar{n}A^3)\beta_3]\frac{1}{1 + C} \tag{19}$$

The unknown βi values are obtained by taking n points on the titration curve, obtaining n equations of the form (19) and solving them simultaneously for the βi values. The calculations were done by an IBM 7040 computer.*

In equations (12) to (19), no account was taken of the fact that the activity of each species should be written as the product of its concentration

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* Computer programs for the calculation of log K can be found in Dee Johnston, Ph. D. Thesis, Brigham Young University, 1968.

and its activity coefficient. Charges on the species have been omitted for clarity.

Equation (19) is the general equation used for the calculation of $\bar{n}$ values in the systems where the number of ligands which combine with a metal ion is 3. However, if we let $\beta_3 = 0$, it can also be applied to the systems where the number of ligands which combine with the metal ion is 2.

In using equation (19), values of $\bar{n}$ and A were determined for each equilibrium reaction being considered. Points on the titration curve were selected so that the $\bar{n}_1$ value lies between 0.25 and 0.75, the $\bar{n}_2$ value between 1.25 and 1.75, and the $\bar{n}_3$ value between 2.25 and 2.75.

Determination of the βi values in equation (19) is made possible by the fact that $\bar{n}_i$ and A_i values are functions of known quantities, i.e., M_T, A_T, and A_B.

M_T and A_T can be calculated from the following relationships:

$$M_T = \frac{[M]_o V_m}{V_T} \tag{20}$$

$$A_T = \frac{[HA]_o V_A}{V_T} \tag{21}$$

where $[M]_o$ = the initial metal ion concentration

V_m = the initial volume of metal ion solution

$[HA]_o$ = the initial serine concentration in the titrant

V_A = the total volume of serine solution added at the time of measurement

V_T = the total volume of solution involved at the time of measurement

Because chelation of each serine molecule with a metal ion released a proton into the solution, the number of ligands bound to the metal ion can be calculated from the concentration of hydrogen ion and certain other reactions. Therefore, the equation which balances the $[H^+]$ should equate the final $[H^+]$ to the initial $[H^+]$, plus H^+ produced from the dissociation of HA and the dissociation of H_2O, plus the H^+ released due to the hydrolysis reactions (19) and (11), plus the H^+ released from the ligand when it becomes bound to the metal ion, less the amount of H^+ which reacts with the NaOH titrant. A_B at each instance thus can be calculated from the pH, at each point the moles of NaOH and serine added, and the concentration and the volume of the metal ion solution. After a value of A_B has been determined A and $\overline{n}$ can easily be calculated using equation (19).

IV. RESULTS

Log K values for the stepwise interaction of serine with Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} are given in Table 1.1 Table1.1 contains the average values valid at zero ionic strength for all runs for all ionic strengths used.

Results of a representative titration for each metal ion studied at each ionic strength used are included in Tables 2.1 to 6.3. Each of these tables contains (1) the log K values determined for the particular ionic strength used, (2) the experimental $\bar{n}$ values which were calculated at each point from the pH titration data, (3) the $\bar{n}$ values calculated using the log K values, (4) the per cent of difference between the experimental and calculated values, (5) the ml. of titrant, and (6) the pH at each point.

Tables 7 and 8 (8.1 to 8.3) contain the values of pK_2 for serine and the hydrolysis constants for each metal studied, respectively.

The uncertainties in log K and pK_2, in all cases, are given as standard deviations.

TABLE 1.1

EQUILIBRIUM CONSTANTS (± STANDARD DEVIATION) VALID AT ZERO IONIC STRENGTH FOR THE STEPWISE FORMATION OF METAL ION-SERINE COMPLEXES AT 25 DEGREES C.

Metal Ion	log K_1	log K_2	log K_3	log β_2	log β_3	No. of Runs
Cu^{2+}	8.16 ± .02	6.78 ± .02	—	14.94	—	10
Zn^{2+}	5.07 ± .02	4.14 ± .03	2.52 ± .17	9.21	11.73	9
Cd^{2+}	4.28 ± .02	3.50 ± .03	2.16 ± .08	7.78	9.94	8
Ni^{2+}	5.71 ± .02	4.60 ± .02	2.93 ± .06	10.32	13.24	12
Co^{2+}	4.74 ± .02	3.71 ± .02	2.42 ± .05	8.45	10.87	10

TABLE 1.2

EQUILIBRIUM CONSTANTS (± STANDARD DEVIATION) REPORTED BY JOHNSTON,[37] VALID AT ZERO IONIC STRENGTH FOR THE STEPWISE FORMATION OF METAL ION-GLYCINE COMPLEXES AT 25 DEGREES C.

Metal Ion	log K_1	log K_2	log K_3	log β_2	log β_3
Cu^{2+}	8.57 ± .02	7.26 ± .02	—	15.83	—
Zn^{2+}	5.36 ± .02	4.43 ± .02	2.52 ± .15	9.81	12.30
Cd^{2+}	4.69 ± .01	3.71 ± .01	2.28 ± .05	8.41	10.60
Ni^{2+}	6.13 ± .01	4.92 ± .01	3.18 ± .03	11.05	14.23
Co^{2+}	5.07 ± .01	4.02 ± .01	2.54 ± .04	9.09	11.62

TABLE 1.3

PERTINENT LITERATURE VALUES OF EQUILIBRIUM CONSTANTS FOR THE FORMATION OF METAL ION-SERINE COMPLEXES

Metal Ion	T°C	log K_1	log K_2	log K_3	log β_2	log β_3	reference
Cu^{2+}	25	—	—	—	14.54	—	18
	20	—	—	—	14.60	—	17
	37	7.56	6.45	—	14.01	—	24
Zn^{2+}	37	4.47	3.84	2.25	8.31	10.56	24
Ni^{2+}	20	5.44	4.38	—	9.82	—	15,16
	30	5.27	—	—	9.57	—	15,16
	37	5.21	4.38	2.90	9.59	12.49	24
Co^{2+}	20	—	—	—	8.0	—	17
	37	4.20	3.36	2.25	7.56	9.81	24

TABLE 2. 1

TITRATION OF 74.99 ml 0.008056 MOLAR COPPER (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.007936 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 8.13 \pm 0.03$

$\log K_2 = 6.80 \pm 0.01$

$\log \beta_2 = 14.94 \pm 0.03$

(Ionic Strength Varies Between 0.02275 and 0.02751)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.438	0.460	-5.15	2.042	3.313
0.578	0.577	0.27	2.286	3.469
0.727	0.708	2.71	2.535	3.636
0.943	0.935	0.82	2.885	3.923
1.043	1.017	2.47	3.042	4.028
1.195	1.186	0.75	3.280	4.245
1.358	1.355	0.19	3.531	4.467
1.523	1.523	-0.04	3.783	4.702
1.685	1.687	-0.12	4.031	4.973
1.855	1.849	0.30	4.288	5.364

Notes:

$\bar{n}$ (exp.) represents the experimental $\bar{n}$ which was calculated at each point from the pH titration data from Tables 2.1 to 6.3. $\bar{n}$ (calc.) represents the $\bar{n}$ values calculated using the log K values. The difference between the values of $\bar{n}$ (exp.) and $\bar{n}$ (calc.) at each point in a titration curve is experssed as the % error.

TABLE 2.2

TITRATION OF 274.56 ml 0.002200 MOLAR COPPER (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.002168 MOLAR) WITH 0.4000 SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 8.17$

$\log K_2 = 6.77$

$\log \beta_2 = 14.95$

(Ionic Strength Varies Between 0.006468 and 0.007737)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.437	0.448	-2.54	2.013	3.746
0.569	0.570	-0.02	2.256	3.913
0.711	0.700	1.48	2.500	4.088
0.855	0.847	0.88	2.740	4.287
1.010	1.003	0.75	2.990	4.503
1.169	1.163	0.56	3.240	4.728
1.328	1.326	0.15	3.485	4.956
1.486	1.486	0.02	3.728	5.186
1.644	1.646	-0.13	3.968	5.442
1.809	1.812	-0.14	4.220	5.800

TABLE 2.3

TITRATION OF 474.01 ml 0.001274 MOLAR COPPER (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.001255 MOLAR) WITH SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 8.18 \pm 0.02$

$\log K_2 = 6.75 \pm 0.01$

$\log \beta_2 = 14.93 \pm 0.02$

(Ionic Strength Varies Between 0.00377 and 0.004808)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.327	0.342	-4.69	1.781	3.803
0.445	0.446	-0.36	2.019	3.959
0.578	0.573	0.89	2.267	4.135
0.723	0.710	1.75	2.519	4.323
0.871	0.863	0.96	2.766	4.536
1.028	1.021	0.68	3.018	4.765
1.179	1.176	0.30	3.255	4.990
1.344	1.339	0.39	3.510	5.225
1.499	1.501	-0.11	3.747	5.462
1.661	1.664	-0.21	3.993	5.731
1.826	1.829	-0.20	4.244	6.107

TABLE 3.1

TITRATION OF 49.88 ml 0.007497 MOLAR CADMIUM (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.007461 MOLAR) WITH 0.4000 SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 4.30 \pm 0.01$

$\log K_2 = 3.46 \pm 0.01$

$\log K_3 = 2.15 \pm 0.03$

$\log \beta_2 = 7.76 \pm 0.02$

$\log \beta_3 = 9.90 \pm 0.03$

(Ionic Strength Varies Between 0.02264 and 0.03623)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.340	0.337	0.96	1.254	6.888
0.544	0.548	-0.67	1.450	7.166
0.808	0.799	1.15	1.704	7.420
1.054	1.051	0.25	1.945	7.647
1.285	1.299	-1.09	2.179	7.866
1.535	1.529	0.44	2.443	8.081
1.702	1.695	0.44	2.634	8.249
1.887	1.896	-0.50	2.882	8.473
2.003	2.020	-0.84	3.066	8.620
2.131	2.155	-1.11	3.311	8.788
2.250	2.265	-0.69	3.572	8.929
2.330	2.355	-1.06	3.815	9.046
2.417	2.422	-0.21	4.066	9.138
2.476	2.470	0.23	4.269	9.205
2.522	2.522	-0.00	4.508	9.280
2.571	2.555	0.65	4.706	9.330
2.616	2.592	0.93	4.951	9.389

TABLE 3.2

TITRATION OF 249.53 ml 0.001499 MOLAR CADMIUM (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.0014917 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 4.25 \pm 0.01$

$\log K_2 = 3.38 \pm 0.01$

$\log K_3 = 2.21 \pm 0.01$

$\log \beta_2 = 7.63 \pm 0.01$

$\log \beta_3 = 9.84 \pm 0.01$

(Ionic Strength Varies Between 0.004998 and 0.008006)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.417	0.418	-0.36	1.355	7.662
0.659	0.657	0.25	1.610	7.950
0.831	0.821	1.21	1.797	8.117
1.040	1.034	0.56	2.040	8.320
1.278	1.265	1.07	2.343	8.534
1.433	1.433	-0.01	2.577	8.692
1.571	1.583	-0.73	2.825	8.838
1.698	1.701	-0.13	3.075	8.957
1.785	1.808	-1.30	3.318	9.069
1.862	1.896	-1.85	3.566	9.164
1.932	1.965	-1.69	3.805	9.240
1.976	2.034	-2.95	4.056	9.317
2.049	2.083	-1.65	4.305	9.373
2.090	2.132	-2.02	4.549	9.429
2.130	2.175	-2.07	4.792	9.478
2.200	2.200	-0.00	4.966	9.508

TABLE 4.1

TITRATION OF 39.94 ml 0.007855 MOLAR COBALT (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.008778 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 4.76 \pm 0.01$

$\log K_2 = 3.74 \pm 0.01$

$\log K_3 = 2.42 \pm 0.03$

$\log \beta_2 = 8.50 \pm 0.01$

$\log \beta_3 = 10.92 \pm 0.03$

(Ionic Strength Varies Between 0.02421 and 0.04305)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.448	0.448	0.00	1.230	6.559
0.765	0.771	-0.78	1.482	6.938
1.138	1.136	0.20	1.781	7.305
1.439	1.438	0.03	2.029	7.608
1.778	1.784	-0.32	2.328	7.983
2.029	2.039	-0.48	2.584	8.291
2.220	2.250	-1.35	2.834	8.560
2.447	2.475	-1.15	3.234	8.864
2.581	2.581	-0.01	3.537	9.024
2.727	2.676	1.89	3.944	9.186

TABLE 4.2

TITRATION OF 239.68 ml 0.001309 MOLAR COBALT (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.001463 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 4.74 \pm 0.01$

$\log K_2 = 3.72 \pm 0.01$

$\log K_3 = 2.44 \pm 0.03$

$\log \beta_2 = 8.47 \pm 0.01$

$\log \beta_3 = 10.91 \pm 0.03$

(Ionic Strength Varies Between 0.004324 and 0.007576)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.408	0.404	0.99	1.205	7.179
0.703	0.707	-0.56	1.449	7.567
0.989	0.989	-0.00	1.694	7.873
1.252	1.250	0.12	1.937	8.146
1.489	1.488	0.11	2.185	8.397
1.686	1.689	-0.17	2.434	8.620
1.851	1.850	0.09	2.693	8.809
1.963	1.972	-0.44	2.933	8.959
2.056	2.072	-0.76	3.181	9.084
2.137	2.152	-0.69	3.432	9.186
2.203	2.221	-0.82	3.686	9.274
2.244	2.286	-1.06	3.883	9.334
2.325	2.314	0.44	4.137	9.394
2.383	2.359	1.03	4.396	0.452
2.405	2.392	0.53	4.596	9.496

TABLE 4.3

TITRATION OF 439.76 ml 0.0007134 MOLAR COBALT (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.0007973 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 4.75 \pm 0.01$

$\log K_2 = 3.70 \pm 0.01$

$\log K_3 = 2.56 \pm 0.02$

$\log \beta_2 = 8.46 \pm 0.01$

$\log \beta_3 = 11.02 \pm 0.01$

(Ionic Strength Varies Between 0.002420 and 0.004293)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.337	0.333	1.22	1.152	7.301
0.628	0.633	-0.74	1.399	7.722
0.962	0.961	0.05	1.700	8.092
1.206	1.202	0.30	1.947	8.347
1.417	1.414	0.20	2.195	8.567
1.621	1.623	-0.16	2.492	8.786
1.755	1.765	-0.58	2.744	8.938
1.858	1.879	-1.14	2.990	9.062
1.943	1.971	-1.45	3.235	9.164
2.021	2.047	-1.31	3.485	9.250
2.080	2.113	-1.55	3.729	9.324
2.142	2.167	-1.15	3.973	9.386
2.205	2.216	-0.47	4.227	9.442
2.254	2.257	-0.13	4.465	9.490
2.309	2.295	0.63	4.714	0.534

TABLE 5.1

TITRATION OF 49.90 ml 0.007694 MOLAR NICKEL (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.008390 MOLAR) WITH 0.400 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 5.74 \pm 0.00$

$\log K_2 = 4.62 \pm 0.01$

$\log K_3 = 2.97 \pm 0.03$

$\log \beta_2 = 10.36 \pm 0.01$

$\log \beta_3 = 13.33 \pm 0.03$

(Ionic Strength Varies Between 0.02305 and 0.03272)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.419	0.421	-0.32	1.449	5.564
0.731	0.730	0.18	1.749	5.956
0.994	0.992	0.21	2.002	6.247
1.260	1.256	0.27	2.258	6.536
1.573	1.576	-0.23	2.562	6.910
1.820	1.821	-0.06	2.806	7.247
2.129	2.116	0.59	3.128	7.726
2.335	2.324	0.45	3.370	8.058
2.517	2.495	0.86	3.614	8.322
2.669	2.660	0.34	3.896	8.599
2.734	2.766	-1.16	4.151	8.820
2.789	2.821	-1.18	4.397	8.966

TABLE 5.2

TITRATION OF 249.53 ml 0.001538 MOLAR NICKEL (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.001676 MOLAR) WITH 0.400 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 5.71 \pm 0.00$

$\log K_2 = 4.63 \pm 0.01$

$\log K_3 = 2.96 \pm 0.02$

$\log \beta_2 = 10.34 \pm 0.01$

$\log \beta_3 = 13.30 \pm 0.02$

(Ionic Strength Varies Between 0.004815 and 0.007783)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.223	0.240	-7.86	1.260	5.865
0.463	0.465	-0.40	1.492	6.250
0.706	0.704	0.25	1.726	6.554
0.937	0.951	-1.57	1.950	6.837
1.145	1.139	0.58	2.153	7.046
1.328	1.331	-0.26	2.333	7.264
1.555	1.554	0.05	2.562	7.533
1.735	1.732	0.15	2.752	7.776
1.893	1.889	0.19	2.935	8.024
2.064	2.050	0.68	3.165	8.305
2.289	2.270	0.80	3.571	8.680
2.463	2.456	0.28	4.056	8.971
2.514	2.506	0.32	4.234	9.049
2.560	2.559	0.02	4.451	9.135
2.609	2.616	-0.28	4.735	9.230
2.625	2.651	-0.99	4.937	9.292

TABLE 5.3

TITRATION OF 449.17 ml 0.0008546 MOLAR NICKEL (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.0009319 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 5.71 \pm 0.02$

$\log K_2 = 4.61 \pm 0.01$

$\log K_3 = 2.89 \pm 0.01$

$\log \beta_2 = 10.42 \pm 0.01$

$\log \beta_3 = 13.31 \pm 0.01$

(Ionic Strength Varies Between 0.002700 and 0.003974)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.220	0.234	-6.48	1.257	6.092
0.366	0.375	-2.51	1.399	6.359
0.522	0.526	-0.66	1.550	6.578
0.736	0.724	1.67	1.757	6.826
0.880	0.873	0.82	1.898	7.001
1.077	1.074	0.27	2.091	7.230
1.281	1.278	0.21	2.295	7.464
1.472	1.474	-0.15	2.493	7.699
1.656	1.656	-0.05	2.694	7.939
1.818	1.815	0.18	2.894	8.181
1.980	1.974	0.31	3.144	8.463
2.060	2.073	-0.63	3.324	8.646
2.194	2.190	0.16	3.645	8.858
2.271	2.269	0.08	3.899	8.991
2.331	2.335	-0.17	4.144	9.096
2.393	2.391	0.08	4.402	9.184

TABLE 6.1

TITRATION OF 49.89 ml 0.007477 MOLAR ZINC (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.007936 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 5.11 \pm 0.08$

$\log K_2 = 4.14 \pm 0.02$

$\log K_3 = 2.34 \pm 0.07$

$\log \beta_2 = 9.25 \pm 0.06$

$\log \beta_3 = 11.60 \pm 0.09$

(Ionic Strength Varies Between 0.02308 and 0.03624)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.521	0.475	8.88	1.587	6.228
0.713	0.756	-6.08	1.767	6.548
0.979	1.016	-3.83	2.017	6.810
1.303	1.313	-0.79	2.324	7.110
1.486	1.483	0.19	2.500	7.297
1.729	1.724	0.31	2.742	7.607
1.949	1.954	-0.22	2.990	7.990
2.119	2.146	-1.28	3.242	8.350
2.244	2.288	-1.93	3.488	8.597
2.361	2.392	-1.30	3.740	8.767
2.444	2.475	-1.26	3.976	8.900
2.528	2.541	-0.51	4.225	9.008
2.600	2.592	0.29	4.464	9.095
2.669	2.634	1.31	4.709	9.170
2.736	2.669	2.43	4.958	9.236

TABLE 6.2

TITRATION OF 249.53 ml 0.001495 MOLAR ZINC (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.001763 MOLAR) WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 5.05 \pm 0.01$

$\log K_2 = 4.16 \pm 0.01$

$\log K_3 = 2.56 \pm 0.04$

$\log \beta_2 = 9.21 \pm 0.01$

$\log \beta_3 = 11.77 \pm 0.04$

(Ionic Strength Varies Between 0.004909 and 0.007620)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.441	0.439	0.47	1.516	6.826
0.714	0.717	-0.28	1.777	7.154
0.962	0.977	-1.55	2.016	7.416
1.215	1.227	-1.02	2.266	7.662
1.456	1.462	-0.42	2.515	7.906
1.720	1.715	0.32	2.819	8.210
1.892	1.893	-0.04	3.072	8.467
2.010	2.029	-0.95	3.319	8.686
2.104	2.134	-1.41	3.572	8.856
2.185	2.214	-1.32	3.826	8.984
2.250	2.280	-1.35	4.074	9.087
2.325	2.333	-0.37	4.327	9.168
2.389	2.380	0.41	4.577	9.238
2.454	2.419	1.41	4.827	9.298

TABLE 6.3

TITRATION OF 449.17 ml 0.0008304 MOLAR ZINC (II) PERCHLORATE SOLUTION (PERCHLORIC ACID CONC. 0.0009792 MOLAR WITH 0.4000 MOLAR SODIUM SERINATE SOLUTION AT 25 DEGREES C.

$\log K_1 = 5.08 \pm 0.02$

$\log K_2 = 4.10 \pm 0.01$

$\log K_3 = 2.58 \pm 0.02$

$\log \beta_2 = 9.19 \pm 0.02$

$\log \beta_3 = 11.77 \pm 0.03$

(Ionic Strength Varies Between 0.002779 and 0.0042203)

$\bar{n}$ (exp.)	$\bar{n}$ (calc.)	% error	ml titrant	pH
0.274	0.263	4.30	1.360	6.747
0.527	0.542	-2.92	1.603	7.179
0.757	0.794	-4.89	1.828	7.470
0.978	0.999	-2.14	2.048	7.688
1.255	1.253	0.18	2.335	7.954
1.466	1.462	0.23	2.575	8.183
1.642	1.647	-0.34	2.810	8.404
1.779	1.798	-1.07	3.042	8.604
1.875	1.919	-2.36	3.275	8.781
1.955	2.011	-2.83	3.516	8.922
2.028	2.081	-2.60	3.756	9.031
2.090	2.139	-2.34	3.991	9.120
2.141	2.192	-2.36	4.234	9.200
2.222	2.232	-0.44	4.483	9.260
2.284	2.274	0.46	4.749	9.322

TABLE 7

LITERATURE VALUES FOR HYDROLYSIS CONSTANTS, k_1 AND k_{12}, AT 25 DEGREES C. AND ZERO IONIC STRENGTH USED IN THE CALCULATION OF LOG K VALUES FOR METAL ION-SERINE SYSTEMS

$$k_1 = \frac{[M(OH)^+]}{[M^{2+}]\,[OH^-]}$$

$$k_{12} = \frac{[M(OH)_2]}{[M^{2+}]\,[OH^-]^2}$$

M^{2+}	k_1	k_{12}	references
Cu^{2+}	6.37	7.00	31, 32
Ni^{2+}	3.20	5.00	33
Zn^{2+}	4.64	5.00	34
Co^{2+}	2.90	3.10	35
Cd^{2+}	4.51	5.00	36

TABLE 8.1

DETERMINATION OF pK_2 AT 25 DEGREES C. FOR SERINE BY TITRATING SODIUM SERINATE SOLUTION WITH 0.4021 F $HClO_4$

Run 1. Solution Titrated:

Volume = 25.02 mls.
NaOH conc. = 0.1081 F
Serine conc. = 0.1085 F
H_2O added = 49.93 mls.

ml	pH	$\overline{n}$	pK_2	$\sqrt{\mu}$
1.769	9.603	0.267	9.228	0.0353
2.007	9.529	0.304	9.229	0.0351
2.298	9.444	0.345	9.229	0.0350
2.526	9.377	0.378	9.226	0.0349
2.724	9.324	0.408	9.226	0.0348
2.932	9.271	0.438	9.228	0.0347
3.413	9.143	0.509	9.224	0.0345
3.607	9.093	0.538	9.224	0.0344
3.758	9.052	0.561	9.222	0.0344
4.355	8.897	0.649	9.228	0.0341
4.519	8.850	0.673	9.228	0.0340
4.697	8.798	0.699	9.229	0.0340
4.849	8.750	0.722	9.228	0.0339
4.999	8.700	0.744	9.228	0.0338

Average $pK_2 = 9.228 \pm .003$

TABLE 8.2

DETERMINATION OF pK_2 AT 25 DEGREES C. FOR SERINE BY TITRATING SODIUM SERINATE SOLUTION WITH 0.4021 F $HClO_4$

Run 2. Solution Titrated:

Volume = 25.02 mls.
NaOH conc. = 0.1081 F

Serine conc. = 0.1085 F
H_2O added = 49.93 mls.

ml	pH	$\bar{n}$	pK_2	$\sqrt{\mu}$
2.253	9.460	0.338	9.233	0.0350
2.460	9.400	0.369	9.231	0.0349
2.617	9.358	0.392	9.231	0.0349
2.799	9.308	0.419	9.230	0.0348
3.125	9.220	0.467	9.227	0.0346
3.285	9.180	0.491	9.228	0.0346
3.437	9.140	0.513	9.227	0.0345
3.571	9.103	0.533	9.224	0.0344
3.707	9.065	0.553	9.221	0.0344
3.835	9.032	0.572	9.222	0.0343
3.967	8.993	0.591	9.218	0.0343
4.123	8.955	0.615	9.222	0.0342
4.269	8.914	0.636	9.221	0.0341

Average pK_2 = 9.226 ± .005

TABLE 8.3

DETERMINATION OF pK_2 AT 25 DEGREES C. FOR SERINE BY TITRATING SODIUM SERINATE SOLUTION WITH 0.4021 F $HClO_4$

Run 3. Solution Titrated:

Volume = 25.02 mls.	Serine conc. = 0.1085 F
NaOH conc. = 0.1081 F	H_2O added = 199.80 mls.

ml	pH	$\bar{n}$	pK_2	$\sqrt{\mu}$
2.255	9.476	0.340	9.233	0.0119
2.423	9.428	0.365	9.232	0.0119
2.609	9.378	0.392	9.232	0.0119
2.787	9.330	0.418	9.231	0.0119
3.172	9.230	0.475	9.231	0.0119
3.385	9.173	0.506	9.228	0.0119
3.567	9.125	0.533	9.227	0.0118
3.905	9.040	0.583	9.230	0.0118
4.045	8.995	0.604	9.222	0.0118
4.188	8.960	0.625	9.226	0.0118
4.321	8.922	0.644	9.224	0.0118
4.454	8.884	0.664	9.224	0.0118
4.799	8.780	0.715	9.224	0.0118
4.996	8.715	0.744	9.233	0.0118

Average pK_2 = 9.227 ± .004

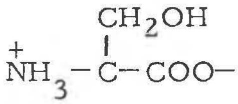
V. CONCLUSIONS

Discussion of Results

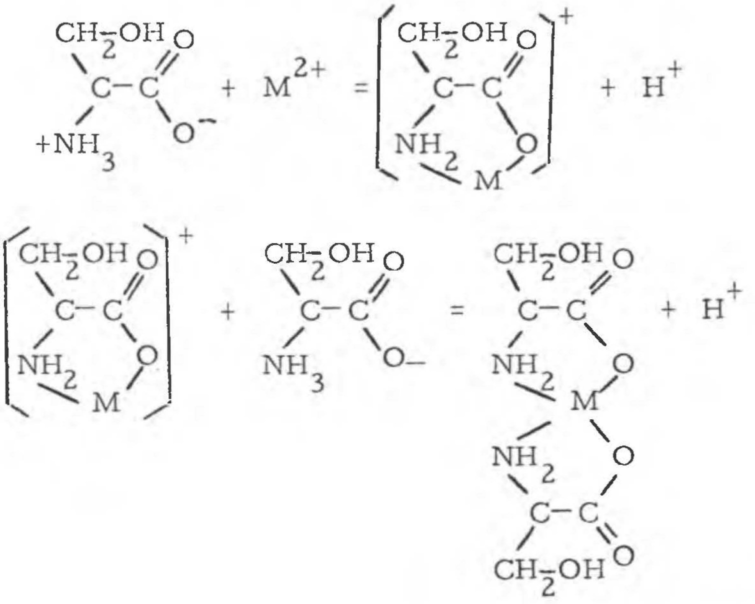
Values for the equilibrium constants valid at zero ionic strength for the metal ion-serine systems studied at 25°C are reported in Table 1.1. Literature values pertaining to this study are included in Table 1.3. No stability constants valid at zero ionic strength and 25°C have been previously reported for the complexation of serine with the metal ions studied. Small differences were found in correlating the log K values for the metal ion-serine systems in this work with values reported earlier. These differences are due to the different value of pK_2 for serine used in the calculation and also probably due to the different experimental conditions employed by different workers.

Examination of Table 1.1 indicates that the values of stability constants for the metal ions used, except in the case of Cd^{2+}, fall in the usual Irving-Williams[28] order--$Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. The values of log K for each step of metal serine interaction in all cases increases in the order $K_1 > K_2 > K_3$. Two important factors are believed to cause this observation. The first is associated with a statistical factor which is based on the number of bonding sites on the metal ion available for each coordinating ligand molecule. Thus the first ligand molecule can coordinate with the metal ion by replacing any one of the water molecules on a hydrated metal ion. Consequently, the probability for the second ligand to replace another water molecule on the same metal ion will be decreased. The second factor is a result of the work done in bringing a ligand molecule from infinity to its equilibrium position against the repulsive force exerted by the already bonded ligand (or ligands).[29, 30]

It is interesting to note that the values of the stability constants for the metal ion-glycine systems (see Table 1.2), studied by Johnston[37] under similar experimental conditions to those of this work, are generally higher than those of the corresponding complexes of serine. Since the structure of serine differs from that of glycine in that the α hydrogen on the glycine is substituted for the $-CH_2OH$ group, the lower stability may be attributed to the steric interference resulting from the interactions of the relatively bulky $-CH_2OH$ group of the serine molecule.

Since the calculated $\bar{n}$ values agree well with those $\bar{n}$ values obtained from experimental data, it can be concluded that the possible ionization of the hydroxyl group of $-CH_2OH$ in  $\overset{+}{N}H_3-\overset{\overset{CH_2OH}{|}}{C}-COO-$ is not likely in the pH region where the data were taken. It was assumed that in the metal complexes of serine, the coordination occurs only through the amino nitrogen and the carboxyl oxygen.

Copper (II) formed only MA^+ and MA_2 complexes, demonstrating the well known reluctance of Cu (II) to acquire a coordination number greater than four. It is assumed that the Cu (II)-serine complex is a square planar arrangement. The reactions for the stepwise interaction of Cu (II) ion with serine are assumed to be as follows:



For the rest of the metal ions studied, formation of MA_3^- complexes has been obtained. This suggests the octahedral structure of the complex. The assumption of the MA_3^- octahedral arrangement at least holds true for the conditions in the pH region studied since the calculated and experimental $\bar{n}$ values agree well and the experimental $\bar{n}$ values do not rise above three.

Suggested Future Work

There are at least three areas in which the work described in this thesis might be extended. First, values for the formation constants of serine with the metal ions used could be determined at more than two temperatures so that the enthalpy and entropy changes for the reactions studied could be calculated.

Second, calorimetric determination of ΔH values for each metal ion-serine system is desirable. Since the log K values obtained in low ionic strength solution are best understood in terms of ΔH, which is a measure of the bonding of the complex and the difference in the heat of formation of the reactants and the products, a knowledge of these values is important for an understanding of factors causing complex formation.

Third, structural identifications of metal-serine complexes in aqueous solution of different pH values might be profitable, since a knowledge of the correct species present in solution is essential for the calculation of stability constants.

APPENDIX

DATA

A. Titrations of Zn^{2+} with sodium serinate solution at 25°C.

Run 1

Solution Titrated:
Volume = 49.89 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.300	5.802	3.364	8.518
1.543	6.297	3.606	8.720
1.780	6.607	3.854	8.870
2.077	6.914	4.106	8.982
2.334	7.165	4.357	9.077
2.575	7.446	4.591	9.154
2.834	7.787	4.942	9.250
3.108	8.218		

Run 2

Solution Titrated:
Volume = 49.89 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.537	6.238	3.259	8.371
1.776	6.552	3.513	8.618
2.026	6.813	3.756	8.787
2.274	7.062	4.005	8.918
2.515	7.323	4.313	9.040
2.763	7.642	4.556	9.124
3.015	8.027	4.796	9.195

Run 3

Solution Titrated:
Volume = 49.89 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.587	6.228	3.242	8.350
1.767	6.548	3.488	8.597
2.017	6.810	3.740	8.767
2.324	7.110	3.976	8.900
2.500	7.297	4.225	9.008
2.742	7.607	4.464	9.095
2.990	7.990		

Run 4

Solution Titrated
Volume = 49.93 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.319	6.367	3.362	8.695
1.615	6.942	3.614	8.859
1.865	7.236	3.864	8.984
2.117	7.492	4.116	9.085
2.369	7.732	4.370	9.166
2.610	7.968	4.625	9.236
2.863	8.225	4.929	9.304
3.113	8.480		

Run 5

Solution Titrated:
Volume = 49.93 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.477	6.745	3.197	8.583
1.717	7.091	3.403	8.744
1.963	7.358	3.657	8.898
2.202	7.596	3.903	9.016
2.458	7.840	4.151	9.109
2.697	8.086	4.457	9.203
2.944	8.343	4.708	9.268

Run 6

Solution Titrated:
Volume = 49.93 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.376	6.556	3.364	8.728
1.620	6.979	3.592	8.869
1.882	7.273	3.814	8.984
2.120	7.523	4.066	9.085
2.374	7.766	4.312	9.167
2.620	8.012	4.562	9.238
2.863	8.266	4.814	9.295
3.113	8.516		

Run 7

Solution Titrated:	Titrant:
Volume = 49.93 mls.	Serine Conc. = 0.4000 F
$Zn(ClO_4)_2$ conc. = 0.007477 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.008816 F	
H_2O added = 199.80 mls.	

ml titrant	pH	ml titrant	pH
1.516	6.826	3.319	8.686
1.777	7.154	3.573	8.856
2.016	7.416	3.826	8.984
2.266	7.662	4.074	9.087
2.515	7.906	4.327	9.168
2.819	8.210	4.577	9.238
3.072	8.467	4.827	9.298

Run 8

Solution Titrated:	Titrant:
Volume = 49.93 mls.	Serine conc. = 0.4000 F
$Zn(ClO_4)_2$ conc. = 0.007477 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.008816 F	
H_2O added = 399.62 mls.	

ml titrant	pH	ml titrant	pH
1.533	7.070	3.275	8.749
1.779	7.385	3.531	8.903
2.027	7.645	3.775	9.018
2.279	7.887	4.023	9.116
2.522	8.122	4.277	9.198
2.779	8.346	4.522	9.262
3.025	8.562	4.777	9.289

Run 9

Solution Titrated:
Volume = 49.93 mls.
$Zn(ClO_4)_2$ conc. = 0.007477 F
$HClO_4$ conc. = 0.008816 F
H_2O added = 399.62 mls.

Titrant:
Serinc conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.360	6.747	3.275	8.781
1.603	7.179	3.516	8.922
1.828	7.470	3.756	9.031
2.048	7.688	3.991	9.120
2.335	7.954	4.234	9.200
2.575	8.183	4.483	9.260
2.810	8.404	4.749	9.322
3.042	8.604		

B. Titrations of Co^{2+} with sodium serinate solution.

Run 1

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.189	6.497	2.529	8.246
1.382	6.825	2.733	8.477
1.583	7.090	2.981	8.704
1.781	7.334	3.220	8.876
1.976	7.573	3.481	9.012
2.281	7.944	3.726	9.118

Run 2

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.287	6.666	2.668	8.388
1.578	7.060	2.908	8.631
1.869	7.417	3.104	8.777
2.113	7.716	3.354	8.934
2.411	8.086	3.555	9.036

Run 3

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.247	6.599	2.494	8.194
1.494	6.957	2.742	8.479
1.739	7.272	2.994	8.693
1.987	7.574	3.248	8.878
2.247	7.876	3.496	9.019

Run 4

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.095	6.293	2.359	8.031
1.351	6.774	2.657	8.386
1.602	7.114	2.901	8.632
1.854	7.421	3.164	8.820
2.103	7.722	3.413	8.964

Run 5

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.196	7.168	2.906	8.949
1.439	7.557	3.155	9.077
1.680	7.863	3.405	9.180
1.924	8.136	3.646	9.267
2.162	8.377	3.896	9.342
2.415	8.604	4.139	9.403
2.661	8.795	4.337	9.448

Run 6

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.205	7.179	2.933	8.959
1.449	7.567	3.181	9.084
1.694	7.873	3.432	9.186
1.937	8.146	3.686	9.274
2.185	8.397	3.883	9.334
2.434	8.620	4.137	9.394
2.693	8.809	4.396	9.452

Run 7

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.143	7.099	2.998	9.002
1.387	7.509	3.208	9.100
1.569	7.742	3.456	9.200
1.767	7.976	3.705	9.278
2.013	8.240	3.996	9.348
2.263	8.486	4.114	9.390
2.513	8.698	4.337	9.441
2.772	8.866		

Run 8

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.149	7.087	2.890	8.940
1.397	7.506	3.132	9.068
1.647	7.824	3.391	9.174
1.946	8.106	3.643	9.264
2.141	8.360	3.891	9.338
2.387	8.586	4.142	9.402
2.635	8.781	4.398	9.457

Run 9

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.117	7.218	2.944	9.038
1.363	7.668	3.243	9.162
1.612	7.990	3.492	9.245
1.806	8.205	3.741	9.318
2.065	8.449	4.035	9.392
2.310	8.652	4.285	9.445
2.552	8.824	4.539	9.494
2.746	8.940	4.784	9.536

Run 10

Solution Titrated:
Volume = 39.94 mls.
$Co(ClO_4)_2$ conc. = 0.007855 F
$HClO_4$ conc. = 0.008778 F
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.152	7.301	3.235	9.164
1.399	7.722	3.485	9.250
1.700	8.092	3.729	9.324
1.947	8.347	3.973	9.386
2.195	8.567	4.227	9.442
2.492	8.786	4.465	9.490
2.733	8.938	4.714	9.534
2.990	9.062		

C. Titration of Cd^{2+} with sodium serinate solution at 25°C.

Run 1

Solution Titrated:
Volume = 49.89 mls.
$Cd(ClO_4)_2$ conc. = 0.007497 F
$HClO_4$ conc. = 0.007461 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.283	6.892	3.516	8.843
1.528	7.223	3.667	8.924
1.832	7.520	3.814	8.996
2.075	7.735	3.962	9.060
2.457	7.952	4.112	9.116
2.696	8.196	4.261	9.170
2.888	8.374	4.457	9.233
3.333	8.727		

Run 2

Solution Titrated:
Volume = 49.89 mls.
$Cd(ClO_4)_2$ conc. = 0.007497 F
$HClO_4$ conc. = 0.007461 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.252	6.898	3.032	8.552
1.450	7.170	3.279	8.734
1.623	7.350	3.529	8.888
1.867	7.532	3.774	9.008
2.063	7.706	4.019	9.110
2.259	7.876	4.273	9.194
2.562	8.139	4.523	9.272
2.811	8.365		

Run 3

Solution Titrated:
Volume 49.89 mls.
$Cd(ClO_4)_2$ conc. = 0.007497 F
$HClO_4$ conc. = 0.007461

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.261	6.875	3.432	8.854
1.554	7.273	3.807	9.040
1.798	7.513	4.067	9.138
1.991	7.682	4.267	9.206
2.272	7.930	4.512	9.278
2.666	8.272	4.752	9.343
2.904	8.490	4.953	9.388
3.211	8.722		

Run 4

Solution Titrated:
Volume 49.89 mls.
$Cd(ClO_4)_2$ conc. = 0.007497 F
$HClO_4$ conc. = 0.007461

Titrant:
Serine conc.= 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.254	6.888	2.882	8.473
1.450	7.166	3.066	8.620
1.704	7.420	3.311	8.788
1.945	7.647	3.572	8.929
2.179	7.866	3.815	9.046
2.443	8.081	4.066	9.138
2.634	8.249	4.269	9.205

Run 5

Solution Titrated:	Titrant:
Volume = 49.89 mls.	Serine conc. = 0.4000 F
$Cd(ClO_4)_2$ conc. = 0.007497 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.007461 F	
H_2O added = 199.80 mls.	

ml titrant	pH	ml titrant	pH
1.350	7.648	3.352	9.094
1.648	7.988	3.597	9.180
1.888	8.200	3.882	9.278
2.142	8.395	4.106	9.344
2.390	8.562	4.343	9.398
2.632	8.719	4.589	9.448
2.883	8.865	4.836	9.500
3.115	8.985		

Run 6

Solution Titrated:	Titrant:
Volume = 49.89 mls.	Serine conc. = 0.4000 F
$Cd(ClO_4)_2$ conc. = 0.007497 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.007461 F	
H_2O added = 199.80 mls.	

ml titrant	pH	ml titrant	pH
1.204	7.385	3.174	8.993
1.448	7.766	3.421	9.100
1.696	8.017	3.671	9.186
1.945	8.228	3.918	9.270
2.187	8.416	4.163	9.336
2.443	8.582	4.409	9.376
2.679	8.736	4.667	9.449
2.928	8.872	4.904	9.498

Run 7

Solution Titrated:
Volume = 49.89 mls.
$Cd(ClO_4)_2$ conc. = 0.007497 F
$HClO_4$ conc. = 0.007461 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.355	7.662	3.318	9.069
1.610	7.950	3.566	9.164
1.797	8.117	3.805	9.240
2.040	8.320	4.056	9.317
2.343	8.534	4.305	9.373
2.577	8.692	4.549	9.429
2.825	8.838	4.792	9.478
3.075	8.957	4.996	9.508

Run 8

Solution Titrated:
Volume = 49.89 mls.
$Cd(ClO_4)_2$ conc. = 0.007497 F
$HClO_4$ conc. = 0.007461 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

m titrant	pH	ml titrant	pH
1.252	7.504	3.235	9.032
1.489	7.833	3.475	9.132
1.743	8.070	3.732	9.218
1.867	8.187	3.979	9.292
2.130	8.373	4.232	9.353
2.444	8.590	4.474	9.413
2.739	8.776	4.717	9.463
2.983	8.920	5.011	9.514

D. Titrations of Ni^{2+} with sodium serinate solution at 25°C.

Run 1

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.007694 F
$HClO_4$ conc. = 0.008390 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.453	5.568	3.227	7.902
1.696	5.893	3.524	8.256
1.898	6.130	3.829	8.553
2.147	6.413	4.072	8.748
2.397	6.704	4.327	8.912
2.699	7.114	4.682	9.088
2.953	7.492		

Run 2

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.007694 F
$HClO_4$ conc. = 0.008390 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.453	5.568	3.135	7.752
1.696	5.893	3.387	8.078
1.898	6.130	3.690	8.407
2.147	6.413	3.943	8.637
2.397	6.704	4.196	8.823
2.652	7.020	4.439	8.972
2.890	7.378	4.841	9.148

Run 3

Solution Titrated:	Titrant:
Volume = 49.90 mls.	Serine conc. = 0.4000 F
$Ni(ClO_4)_2$ conc. = 0.007694 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.008390 F	

ml titrant	pH	ml titrant	pH
1.449	5.564	3.128	7.726
1.749	5.956	3.370	8.058
2.002	6.247	3.614	8.322
2.258	6.536	3.896	8.599
2.562	6.910	4.151	8.820
2.806	7.247	4.397	8.966

Run 4

Solution Titrated:	Titrant:
Volume = 49.90 mls.	Serine conc. = 0.4000 F
$Ni(ClO_4)_2$ conc. = 0.007694 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.008390 F	

ml titrant	pH	ml titrant	pH
1.321	5.360	2.959	7.475
1.621	5.790	3.186	7.807
1.873	6.094	3.448	8.124
2.117	6.382	3.690	8.398
2.415	6.732	3.941	8.631
2.676	7.040		

Run 5

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.007694 F
$HClO_4$ conc. = 0.008390 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.260	5.865	2.935	8.024
1.492	6.250	3.165	8.305
1.726	6.554	3.571	8.680
1.950	6.837	4.056	8.971
2.153	7.046	4.234	9.049
2.333	7.264	4.451	9.135
2.562	7.533	4.735	9.230
2.752	7.776	4.937	9.292

Run 6

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.007694 F
$HClO_4$ conc. = 0.008390 F
H_2O added = 199.80

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.298	5.927	3.057	8.188
1.468	6.215	3.264	8.424
1.638	6.446	3.551	8.666
1.858	6.714	3.786	8.830
2.396	7.344	4.006	8.940
2.672	7.680	4.325	9.081
2.887	7.967		

Run 7

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.007694 F
$HClO_4$ conc. = 0.008390 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.460	6.233	3.414	8.613
1.755	6.624	3.715	8.825
2.051	6.965	3.957	8.963
2.330	7.305	4.349	9.128
2.629	7.679	4.601	9.213
2.921	8.077	4.999	9.324
3.169	8.381	5.822	9.506

Run 8

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.007694 F
$HClO_4$ conc. = 0.008390 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.289	5.935	3.293	8.499
1.537	6.330	3.543	8.705
1.788	6.646	3.836	8.900
2.027	6.943	4.154	9.048
2.259	7.215	4.444	9.168
2.517	7.516	4.903	9.300
2.750	7.836	5.204	9.377
3.001	8.162	5.494	9.440
		5.783	9.493

Run 9

Solution Titrated:	Titrant:
Volume = 49.90 mls.	Serine conc. = 0.4000 F
$Ni(ClO_4)_2$ conc. = 0.008546 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.009319 F	
H_2O added = 399.60 mls.	

ml titrant	pH	ml titrant	pH
1.351	6.272	2.782	8.051
1.550	6.576	3.027	8.346
1.695	6.762	3.275	8.596
1.845	6.944	3.530	8.788
2.085	7.228	3.781	8.938
2.331	7.517	4.030	9.053
2.531	7.746	4.285	9.153
		4.527	9.232

Run 10

Solution Titrated:	Titrant:
Volume = 49.90 mls.	Serine conc. = 0.4000 F
$Ni(ClO_4)_2$ conc. = 0.008546 F	NaOH conc. = 0.4000 F
$HClO_4$ conc. = 0.009319 F	
H_2O added = 399.60 mls.	

ml titrant	pH	ml titrant	pH
1.356	6.278	2.889	8.194
1.551	6.581	3.141	8.467
1.697	6.771	3.381	8.694
1.847	6.954	3.625	8.865
2.047	7.187	3.822	8.973
2.278	7.420	4.056	9.083
2.444	7.651	4.251	9.159
2.437	7.889		

Run 11

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.008546 F
$HClO_4$ conc. = 0.009319 F
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.310	6.204	2.852	8.133
1.462	6.452	3.053	8.371
1.608	6.657	3.255	8.572
1.810	6.903	3.491	8.759
2.056	7.194	3.746	8.916
2.259	7.424	3.991	9.035
2.454	7.656	4.242	9.132
2.653	7.886	4.492	9.218

Run 12

Solution Titrated:
Volume = 49.90 mls.
$Ni(ClO_4)_2$ conc. = 0.008546 F
$HClO_4$ conc. = 0.009319 F
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.257	6.092	2.694	7.939
1.399	6.359	2.894	8.181
1.550	6.578	3.144	8.463
1.757	6.826	3.324	8.646
1.898	7.001	3.645	8.858
2.091	7.230	3.899	8.991
2.295	7.464	4.144	9.096
2.493	7.699	4.402	9.184

E. Titrations of Cu^{2+} with sodium serinate solution.

Run 1

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.767	3.153	3.008	4.018
2.021	3.302	3.258	4.233
2.316	3.492	3.507	4.451
2.515	3.625	3.751	4.680
2.757	3.812	4.009	4.944

Run 2

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056
$HClO_4$ conc. = 0.007936

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
2.136	3.368	3.240	4.203
2.304	3.480	3.450	4.440
2.550	3.648	3.675	4.603
2.855	3.886	3.900	4.818
3.050	4.047		

Run 3

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
2.053	3.323	3.282	4.250
2.290	3.480	3.540	4.476
2.538	3.650	3.770	4.697
2.784	3.832	4.013	4.957
3.035	4.041	4.268	5.327

Run 4

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.988	3.719	3.589	5.048
2.224	3.885	3.834	5.288
2.505	4.092	4.081	5.578
2.755	4.291	4.331	6.025
3.056	4.550		
3.348	4.822		

Run 5

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.917	3.672	3.142	4.629
2.163	3.832	3.388	4.855
2.408	3.998	3.634	5.080
2.693	4.230	3.878	5.324
2.948	4.448	4.099	5.583

Run 6

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.984	3.724	3.223	4.710
2.234	3.886	3.477	4.942
2.484	4.066	3.700	5.153
2.726	4.263	3.950	5.408
2.978	4.486		

Run 7

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F
H_2O added = 199.80 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.776	3.592	3.240	4.729
2.013	3.742	3.485	4.956
2.256	3.906	3.728	5.186
2.500	4.084	3.968	5.442
2.740	4.281	4.220	5.800
2.990	4.503		

Run 8

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.781	3.804	3.255	4.990
2.019	3.959	3.510	5.225
2.267	4.135	3.747	5.462
2.519	4.323	3.993	5.731
2.766	4.536	4.244	6.107
3.018	4.765		

Run 9

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.735	3.778	3.220	4.958
1.947	3.936	3.463	5.192
2.228	4.107	3.718	5.430
2.469	4.290	3.962	5.696
2.719	4.498	4.258	6.148
2.970	4.723		

Run 10

Solution Titrated:
Volume = 74.99 mls.
$Cu(ClO_4)_2$ conc. = 0.008056 F
$HClO_4$ conc. = 0.007936 F
H_2O added = 399.60 mls.

Titrant:
Serine conc. = 0.4000 F
NaOH conc. = 0.4000 F

ml titrant	pH	ml titrant	pH
1.659	3.735	3.121	4.874
1.900	3.890	3.366	5.105
2.144	4.045	3.617	5.339
2.385	4.229	3.863	5.591
2.635	4.430	4.035	5.799
2.929	4.694	4.285	6.228

REFERENCES

1. S. Arrhenius, Z. Physik. Chem. Leipzig, 1, 631 (1887).
2. A. Werner, Z. Anorg. Chem., 3, 267 (1893).
3. R. Abegg and O. Bodlander, Z. Anorg. Chem., 20, 453 (1899).
4. R. Abegg and Immerwahr, Z. Physik. Chem., 32, 142 (1900).
5. R. Abegg, Z. Anorg. Chem., 39, 330 (1904).
6. H. Morse, Z. Physik. Chem., 41, 709 (1902).
7. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen (1941).
8. Z. Leden, Z. Physik. Chem. Leipzig, 188A, 160 (1941).
9. L. G. Sillen and A. E. Martell, Eds., "Stability Constants of Metal-ion Complexes", Chemical Society, London (1964).
10. R. Bruehman and F. H. Verhoek, J. Am. Chem. Soc., 70, 1401 (1948).
11. J. Bjerrum, Chem. Revs., 46, 381 (1950).
12. G. Schwarzenbach and H. Ackerman, Helv. Chem. Acta., 31, 1029 (1948).
13. F. Basolo and R. K. Murmann, J. Am. Soc., 74, 5234 (1952).
14. C. G. Spike and R. W. Parry, Ibid., 75, 3770 (1953).
15. S. Pelletier, J. Curchod, and M. Quintin, Compt. Rend., 243, 1868 (1956).
16. S. Pelletier, Ibid., 245, 160 (1957).
17. A. Albert, Biochem. J., 47, 531 (1950).

18. N. C. Li and E. Doody, J. Am. Soc., 74, 4184 (1952).

19. D. D. Perrin, J. Am. Chem. Soc., 3125 (1958).

20. D. D. Perrin, J. Am. Chem. Soc., 290 (1959).

21. J. Schubert, J. Am. Chem. Soc., 76, 3442 (1954).

22. C. W. Davies and G. M. Waind, J. Chem. Soc., 301 (1950).

23. L. Morrell, Master Thesis, Brigham Young University, 1960.

24. V. S. Sharma, Biochem. Biophys. Acta., 148, 37 (1967).

25. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd Ed., Reinhold Pub. Corp., New York, N. Y., 1958, Chapter 5.

26. L. Morrell, op. cit., p. 64.

27. F. J. Rossotti and H. Rossotti, "The Determination of Stability Constants", McGraw-Hill Book Co., New York, N. Y., 1961, p. 355.

28. H. Irving and R.J.P. Williams, J. Chem. Soc., 3192 (1953).

29. P. G. Manning, Canad. J. Chem., 43, 2911 (1965).

30. Bjerrum, op. cit.

31. T. V. Arden, J. Chem. Soc., 350 (1951).

32. C. R. Fuget, Ph. D. Thesis, Pennsylvania State University, 1956.

33. F. Achenza, Ann. Chim. (Italy), 49, 624, 848 (1959).

34. J. Besson and W. Eckert, Bull. Soc. Chim. France, 10, 1676 (1959).

35. J. A. Bolzan and A. J. Arvia, Electrochim. Acta., 7, 589 (1962).

36. G. Biedermann and L. Ciavatta, Acta. Chem. Scand., 16, 2221 (1962).

37. H. Dee Johnston, Ph. D. Thesis, Brigham Young University, 1968.

DETERMINATION OF STABILITY CONSTANTS AT 25° C FOR THE INTERACTION IN AQUEOUS SOLUTION OF SERINE WITH Co (II), Ni (II), Cd (II), Zn (II), and Cu (II) IONS

An Abstract of a Thesis
Presented to the
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Brigham Young University

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of Requirements for the Degree
Master of Science

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ABSTRACT

Values of thermodynamic stability constants at 25°C for the complexes of serine with the metal ions, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} were obtained from pH titration data.

All measurements were made in aqueous solution, and data were obtained at three different ionic strengths for each metal ion studied. It was assumed that the activity of the zwitterion is unity. The effect of metal ion hydrolysis upon the log K values was taken into account for the calculations.

For all the metal ions studied, stability constants for MA^+, MA_2, and MA_3^- were reported with the exception of copper (II) which formed only MA^+ and MA_2 complexes.

The stabilities of the complexes studied follow the sequence: $Cd^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+}$. The value of log K for each step of metal serine interaction, in all cases, increases in the order, $K_3 < K_2 < K_1$.

Under the conditions studied, it was assumed that the metal ion coordinates through the amino nitrogen and the carboxyl oxygen of the serine only. There was no evidence that the hydroxyl group of serine took part in coordination with the metal ions.

All calculations of stability constants were carried out using an IBM 7040 computer.