This dissertation has been microfilmed exactly as received 67-16,304

MACHEN, Ronald Clement, 1930--
COMPLEXES OF CALCIUM, MAGNESIUM AND STRONTIUM IONS WITH TETRAPHOSPHATE.

The Ohio State University, Ph.D., 1967
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan
COMPLEXES OF CALCIUM, MAGNESIUM AND STRONTIUM IONS WITH TETRAPOHOSPHATE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

RONALD CLEMENT MACHEN, B.S., M.S.

The Ohio State University 1967

Approved by:

Adviser
Department of Chemistry
ACKNOWLEDGMENTS

It is with profound gratitude that I express my appreciation to Dr. James I. Watters for his encouragement, interest and guidance throughout my graduate career.

I am especially indebted to my wife, Myrna, who has given me inspiration when there was despair and helped to prepare this manuscript.

I also wish to express my appreciation to The Ohio State University Chemistry Department.

To my parents, who have helped in numerous ways, thank you.
VITA

July 21, 1930 B. S. N. - Chicago, Illinois
1952 . . . . . B. S., University of Illinois, Urbana, Illinois
1954-1957 . . Research Assistant, Research Foundation,
The Ohio State University, Columbus, Ohio
1957-1966 . . Teaching Assistant, Department of Chemistry,
The Ohio State University, Columbus, Ohio
1963. . . . M. S., The Ohio State University, Columbus, Ohio
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Complexes of Calcium, Magnesium, and Strontium Ions with Tetraphosphate Ions</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Calculations</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Results and Discussion</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Purity Check of Sodium Tetrametaphosphate</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>The Magnesium Tetraphosphate System</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Strontium Tetraphosphate Complexes</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>The Calcium Ion-Exchange Electrode</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>The Calcium Tetraphosphate System</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
<td>50</td>
</tr>
<tr>
<td>II</td>
<td>The Possible Complex Formation of Guanidinium Ion with Pyrophosphate and Tripolyphosphate</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Results and Discussion</td>
<td>58</td>
</tr>
<tr>
<td>III</td>
<td>The Polarographic Study of the Complexes of Cupric Ion with Trimetaphosphate</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Calculations</td>
<td>73</td>
</tr>
<tr>
<td>Chapter</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>III  Results and Discussion</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>List of References</td>
<td>89</td>
<td></td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Activity Coefficient of Hydrogen Ion.</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>Effect of Magnesium Ion on the Acidimetric Titration.</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>Effect of Strontium Ion on the Acidimetric Titration.</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>Effect of Calcium Ion on the Acidimetric Titration.</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>Comparison of Polyphosphate Complexes with Alkaline Earth Metal Ions.</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>Potential Data of the Copper(II) Trimetaphosphate System</td>
<td>84</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Computer Program for Calculating &quot;a&quot; Values</td>
<td>19</td>
</tr>
<tr>
<td>2.</td>
<td>Chromatogram for Qualitative Identification of Ring and Chain Phosphates in Descending Order</td>
<td>22</td>
</tr>
<tr>
<td>3.</td>
<td>The Effect of Various Concentrations of Magnesium Ion on the Titration of Tetraphosphate Ion with Hydrochloric Acid</td>
<td>25</td>
</tr>
<tr>
<td>4.</td>
<td>Graphic Determination of $\beta_{101}$ and $\beta_{201}$ for Magnesium Tetraphosphate Complexes</td>
<td>30</td>
</tr>
<tr>
<td>5.</td>
<td>Graphic Determination of $\beta_{101}$ and $\beta_{201}$ for Strontium Tetraphosphate Complexes</td>
<td>35</td>
</tr>
<tr>
<td>6.</td>
<td>Electrode Potential Behavior vs Solution of pH for Calcium Ion-Exchange Electrode</td>
<td>38</td>
</tr>
<tr>
<td>7.</td>
<td>Calcium Ion Concentration vs Electrode Potential at an Ionic Strength of Unity</td>
<td>41</td>
</tr>
<tr>
<td>8.</td>
<td>The Effect of Various Concentrations of Calcium Ion for the Titration of Tetraphosphate Ion with Hydrochloric Acid</td>
<td>44</td>
</tr>
<tr>
<td>9.</td>
<td>Graphic Determination of $\beta_{101}$ and $\beta_{201}$ for Calcium Tetraphosphate Complexes</td>
<td>49</td>
</tr>
<tr>
<td>10.</td>
<td>The Effect of Various Concentrations of Guanidinium Ion on Curves for the Titration of Sodium Pyrophosphate with Hydrochloric Acid</td>
<td>61</td>
</tr>
<tr>
<td>11.</td>
<td>The Effect of Various Concentrations of Guanidinium Ion on the Titration of Triphosphate Ion with Hydrochloric Acid</td>
<td>63</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>12.</td>
<td>Anodic-Cathodic Polarograms of Copper(II) Ions in Various Concentrations of Trimetaphosphate Ion Using the Dropping Copper Amalgam Electrode.</td>
<td>80</td>
</tr>
<tr>
<td>13.</td>
<td>Slope Analysis of Anodic-Cathodic Polarograms of Copper(II) Ions in Various Concentrations of Trimetaphosphate Ion Using the Dropping Copper Amalgam Electrode</td>
<td>83</td>
</tr>
<tr>
<td>14.</td>
<td>The Plot of $E_{sp}$ Versus SCE Against $-\log C_x$</td>
<td>87</td>
</tr>
</tbody>
</table>
CHAPTER I

Complexes of Calcium, Magnesium, and Strontium Ions with Tetraphosphate Ions

Introduction

The metal ion complexes and basicity of polyphosphates were investigated in this laboratory using polarographic, potentiometric pH and spectrophotometric methods. In the present work, the magnesium, calcium, and strontium tetraphosphate complexes were studied on the basis of pH lowering due to complex formation. The calcium activity was also measured by means of a calcium ion-exchange electrode.

Previously, Lambert and Watters determined the formation constants and complexes of magnesium and calcium pyrophosphate and tripolyphosphate by means of pH measurements.\(^1,^2\) Since it was necessary to keep the calcium ion concentration low to prevent formation of the pyrophosphate and tripolyphosphate precipitates, solid calcium sulfate was equilibrated against sulfate ion added as tetramethylammonium sulfate.


Studies of tetraphosphates have been hindered by the difficulty of obtaining pure crystalline salts, and by the rather rapid rate of hydrolysis of the tetraphosphate to lower phosphates. To prepare the salt, Thilo and Ratz\(^3\) hydrolyzed an aqueous solution of tetrameta-
phosphate with sodium hydroxide at 40°C, but could not obtain the crystalline sodium salt. Quimby was successful in preparing the crystalline guanidinium tetraphosphate monohydrate by precipitation in aqueous formamide solution.4


The soluble crystalline ammonium tetraphosphate has been prepared from ammonium sulfide and lead tetraphosphate hexahydrate.5 The lead tetraphosphate has been formed by the reaction of lead carbonate with 85 percent phosphoric acid heated at temperatures of 150°C to 550°C for 12 hours. Lead tetraphosphate was also prepared by Schulz who evaporated a 3:4 ratio of lead oxide to phosphoric acid mixture and then heating for 90 hours at 400°C.6 This salt was identical to the lead tetraphosphate formed by Osterheld and Langguth by heating lead dihydrogen orthophosphate at 700°C.7


Schulz prepared crystalline bismuth tetraphosphate by heating bismuth oxide and phosphoric acid in a 1:4 ratio at a temperature of 700°C using a procedure similar to that for the preparation of lead tetraphosphate.6 The lead tetraphosphate was insoluble but the bismuth tetraphosphate was slightly soluble in water and nitric acid, and soluble in hydrochloric acid.
Paper chromatography, ion-exchange chromatography, electrophoresis, and thin layer chromatography have been used for the purification and qualitative and quantitative determination of chain and ring polyphosphates. The application of paper chromatography to the separation of inorganic phosphates was first made by Westman and Scott\(^8\),\(^9\) and by Ebel.\(^10\),\(^11\) A method based on descending chromatography\(^8\),\(^9\),\(^12\) and later on ascending chromatography has been used.\(^13\) Ebel employed ascending solvent fronts\(^10\) and then developed a two-dimensional technique\(^11\) for separating ring and chain phosphates into two distinct groups.


In the past decade numerous workers\(^14\),\(^15\),\(^16\) have modified the solvents, developers, papers and techniques. Kolloff has developed modified solvents and a new highly selective chromatographic spray for reducing the tetrapolyphosphomolybic acid complex on high capacity chromatographic paper.\(^17\)


Rieman and co-workers have studied the theory and experimental techniques of ion exchange chromatography for the separation of chain and ring condensed phosphates. The automation of ion-exchange chromatography analysis of condensed phosphate mixtures was accomplished using a Technicon auto analyzer.

Electrophoresis of commercial tripolyphosphate and hexametaphosphate has been used to separate the phosphate, pyro-, tripoly-, trimeta-, and tetrametaphosphate anions. Whatman No. 3 paper held firmly between two glass plates with borax, boric acid, and sodium chloride buffer of pH 8.5 was used. The potential difference was 1000 volts.

A two or three component system of sodium phosphate, pyrophosphate and tripolyphosphate was resolved by thin layer chromatography.
Glass plates were coated with silica gel H. A solvent consisting of trichloroacetic acid, ammonium hydroxide, methyl alcohol and water was used.


Watters and his co-workers studied the acidity of the tetraphosphate ion and the stability of complexes of guanidinium ion with tetraphosphate. Matsumoto determined the stability constants for the complexes of lithium, sodium, and potassium tetraphosphate. The values of the complexity constants for the complexes indicated increasing stability in the order of $K^+ < Na^+ < Li^+$, agreeing with the observation of Schindewolf and Bonhoeffer.


Complexes of these alkali and the alkaline earth metal ions, calcium and magnesium, with pyro- and tripolyphosphate were also investigated in this laboratory, and it was observed, with one exception, that the stability of the (1:1) complexes increased as the number of phosphate tetrahedra increased. The stability constants of lithium tetraphosphate decreased slightly. This tendency was also observed for

stability constants of complexes of adenosine pyro-, tri-, and tetraphosphate with calcium and magnesium\(^{32,33}\) and copper.\(^{34}\)


Polarographic studies of mercurous ion\(^{35}\) and cupric ion with pyro-,\(^{36}\) tri-,\(^{37}\) and tetraphosphate\(^{38}\) were made in this laboratory. It was observed that the stability per PO\(_4\) tetrahedron of the unprotonated complexes decreased as the chain length increased.

(37) P.E. Sturrock, E.D. Loughran, and J.I. Watters, ibid., 1, 547 (1962).
Guanidinium tetraphosphate, \((\text{C}(\text{NH}_3)_4)\text{P}_4\text{O}_{13}\cdot\text{H}_2\text{O})\), was prepared by the hydrolysis of the commercial grade sodium tetrametaphosphate, "Cyclophos," Victor Chemical Works, according to a procedure due to Thilo and Ratz,\(^3\) and the salt was recrystallized according to Quimby's procedure,\(^4\) with minor modifications employed by Matsumoto.\(^27\) A 10 percent solution of sodium tetrametaphosphate was prepared by dissolving 300 grams of \(\text{Na}_4\text{P}_4\text{O}_{12}\cdot\text{H}_2\text{O}\) in 2 liters of water at room temperature and then filtering. Ethanol was added in a steady small stream until precipitation began, after which the rate was reduced so that the remainder of 1 liter of ethanol was added dropwise over a period of at least 1 hour, the solution being stirred vigorously throughout the addition. The solution was filtered on a sintered glass filter and washed twice, first with 300 ml of 50 percent ethanol, then with 300 ml of 35 percent ethanol. The crystals were redissolved and reprecipitated as before with a total of 1 ml of ethanol for each 2 ml of water used.

A 15 percent solution by weight, of \(\text{Na}_4\text{P}_4\text{O}_{12}\cdot\text{H}_2\text{O}\) was prepared and, after cooling, filtered and then mixed with sufficient cold concentrated NaOH to yield a 8.5-10 percent solution of \(\text{Na}_4\text{P}_4\text{O}_{12}\cdot\text{H}_2\text{O}\) and 3 moles NaOH per mole of \(\text{Na}_4\text{P}_4\text{O}_{12}\), without allowing the temperature to exceed 25°C, maximum allowable temperature, 40°C. This solution was stored at room temperature until two moles of NaOH had been consumed, as shown by periodic titrations of the excess NaOH to a pH of about 10. The time required was 17 days.
A more concentrated solution was prepared by mixing an equal volume of ethanol with the above solution of Na₆P₄O₁₃ and allowing it to stand until two liquid layers formed. The upper layer was translucent, while the lower layer was white and viscous in appearance. The lower layer, which contained about 44 percent Na₆P₄O₁₃, was separated by means of a separatory funnel. The syrupy liquid was stored in a freezer. It was found that prolonged storage resulted in a poorer yield in the following steps. Further purification was effected by adding 3 volumes of water to 1 volume of the 44 percent solution, mixing well, then adding 4 volumes of ethanol and separating as before. This procedure was repeated twice.

To 100 grams of the syrupy liquid, 121 grams of guanidinium chloride, C(NH₂)₃Cl, (Eastman Organic Chemicals) in 121 ml of water was added. The guanidinium chloride solution was filtered before the addition. To the aqueous solution at 25-28°C, formamide was gradually added with vigorous stirring, until the solution became faintly turbid, and further small additions were periodically made until the turbidity persisted. This required about 620-720 ml of formamide. Stirring was continued for one hour after which the crystals were filtered off on a sintered glass filter and washed three times with 50 ml portions of anhydrous ethanol. The crystals were dried under reduced pressure to constant weight at room temperature or air dried if the relative humidity was below 50 percent. All water used in preparing solutions and washing the ion-exchange columns was demineralized, doubly distilled, and purged with nitrogen to remove the dissolved carbon dioxide.
The purity of the sodium tetrametaphosphate was checked qualitatively by paper chromatography according to the method of D.N. Bernhardt and W.B. Chess, using Ebel's modified acid solvents. Molybdate reagent was used to identify phosphates in the paper chromatography procedure. For the preparation of the eluent, 25 ml of a 20 percent trichloroacetic acid solution were mixed with 10 ml of water and 65 ml of acetone. The 20 percent trichloroacetic solution was prepared by dissolving 100 grams of trichloroacetic acid in water, adding 7 ml of concentrated ammonium hydroxide, and diluting to 500 ml with water.

A stock solution of stannous chloride was prepared weekly by dissolving 8 grams of stannous chloride monohydrate in 2 ml of concentrated hydrochloric acid.

To prepare the acid molybdate solution, 10 grams of ammonium paramolybdate were dissolved in 10 ml of concentrated hydrochloric acid and 50 ml of concentrated perchloric acid, then diluted to 1 liter with water.

Twenty microliter aliquots samples of reagent grade or laboratory purified soluble sodium or guanidinium phosphates, 0.25 grams to 100 ml of water were placed evenly, 1.25 inches apart, on a starting line 1 inch from the bottom of 10 x 10 inch square or 16.5 x 12 inch rectangular sheets of Carl Schleicher and Schuell Co., paper 589, orange ribbon. After the paper was dry, it was fastened in a cylindrical position and placed in a 18 x 16 inch diameter cylindrical glass covered jar saturated with the vapors of 100 ml of the eluent, trichloroacetic acid solution. The elution was allowed to proceed for
2 to 3 hours at room temperature or 3 to 12 hours, between 0° to 10°C in a refrigerator.

The paper was removed from the jar and dried for at least 45 minutes in an oven maintained between 80° and 90°C. Both sides of the paper were sprayed with acidic molybdate solution and the paper was dried for 5 to 7 minutes. The spraying and drying procedure was repeated with freshly prepared stannous chloride solution consisting of five drops of stock solution in 100 ml of 0.2N hydrochloric acid. Disintegration of the paper was prevented by drying just until it ceases to be damp.

According to the procedure described in earlier papers on the complexes and acids of pyrophosphate, triphosphate, and tetraphosphate by Watters and co-workers, 26,29,39a,b,c 0.16M guanidinium tetraphosphate solution was converted to tetramethylammonium tetraphosphate stock solutions of concentrations between 0.04M and 0.08M through the use of Dowex 50W-X2, 100-200 mesh, cation exchange resin. The tetramethylammonium tetraphosphate effluent was divided into three 30 ml portions and stored in 2 ounce polyethylene bottles.

Two bottles of solution were frozen until needed, and the third bottle of solution was stored in the tray beneath the freezer compartment of a refrigerator. Periodic titrations of the unfrozen tetraphosphate solution with hydrochloric acid demonstrated that

(39) (a) J.I. Watters, E.D. Loughran, and S.M. Lambert, J. Am. Chem. Soc., 78, 4855 (1956); (b) 79,3651 (1957); (c) 79,4262 (1957).
essentially no hydrolysis occurred in four weeks. The frozen solutions could be stored at least six weeks if kept under a nitrogen atmosphere.

Aqueous stock solutions of the appropriate concentration of magnesium chloride, MgCl$_2$·6H$_2$O, calcium chloride, CaCl$_2$·H$_2$O and strontium chloride, SrCl$_2$·6H$_2$O, all Baker Chemical Co., Reagent Grade, were prepared and then diluted to the desired concentrations in both the solution titrated and the titrant. The stock solutions were standardized by determining the chloride content volumetrically with silver nitrate according to Fajan's chloride method, and/or an ion exchange method. In the latter, a 2.7(dia.) x 17 cm column of Dowex 50W-X2, 100-200 mesh, charged with hydrochloric acid was used to convert the salt to the acid which was then titrated with sodium hydroxide. The flow rate of the effluent was 2 ml per minute.

The general procedure for the titrations and measurements was as follows. The titrants and solutions being titrated had identical concentrations of alkaline metal chlorides and tetramethylammonium tetraphosphate. In the titrations, the concentration of hydrochloric acid was adjusted to require a minimum of 8 ml of titrant for two moles of hydrogen ion to one mole of tetraphosphate ion, $a=2$. For pH measurements at particular points in the titration, each solution was prepared individually. The points of particular interest are those at which the ratio of concentration of added H$^+$ to total P$_4$O$_{13}^-$ are 0.5 and 1.5. The ionic strength of all solutions was adjusted to unity with a 2M solution of Eastman's tetramethylammonium chloride having a pH adjusted to 7.00 with tetramethylammonium hydroxide. The
tetramethylammonium chloride was not recrystallized. All solutions were kept thermostatically at 25.0 ± 0.1° under an atmosphere of nitrogen during measurements.

Except for the study of the electrode potential behavior of the calcium electrode versus pH using a Beckman Research Model pH meter with a Beckman general purpose glass electrode, No. 39000, the pH and millivolt measurements were made with a Corning pH meter, model 12, using a Corning general purpose glass electrode, No. 476022.

The calcium ion-exchange electrode was obtained from Orion Research, Inc., 11 Blackstone Street, Cambridge, Massachusetts 02139. The principle of operation for the electrode in detecting calcium ion is similar to that of the conventional glass pH electrode for detecting hydrogen ion. An electrical potential is developed across a thin layer of water-immiscible liquid ion exchanger held by a thin, porous, inert membrane disc. A liquid ion exchanger, a calcium organophosphate, exhibits a very high selectivity for calcium ion. The internal filling solution, calcium chloride, contacts the inside surface of the membrane disc. The calcium ion in this solution provides a stable potential between the inside of membrane and the filling solution, while the chloride ion maintains a stable potential between the Ag-AgCl reference electrode and the filling solution. Changes in the potential are due only to changes in calcium activity of the sample solution.
Calculations

The calculations for the stability of magnesium, calcium, and strontium tetraphosphate complexes are based on a new mathematical procedure developed by Watters and Matsumoto for the guanidinium tetraphosphate complexes.\(^{27}\) It was observed from the titration curve that the association of tetraphosphate ion with the first and second proton occurred with a barely perceptible break. This break vanished when the tetraphosphate formed a complex with another species. The new method of calculation has eliminated any effect of overlap of the two equilibria.

The symbols and nomenclature used in describing this method is as follows: M represents the central alkaline earth ion; L, the tetraphosphate ion; and H, the proton; brackets indicate concentrations and parentheses indicate activities; ionic charges are omitted for convenience.

The equilibria for complexes of M, L, and H may be shown as follows:

\[
\begin{aligned}
&M + L \rightleftharpoons ML \\
&M + 2L \rightleftharpoons ML_2 \\
&M + H + L \rightleftharpoons MHL \\
&M_i + H_j + L_k \rightleftharpoons M_i H_j L_k
\end{aligned}
\]

The stepwise or overall complexity constants for the preceding equilibria are:

\[
\beta_{101} = \frac{[ML]}{[M][L]} \quad (1)
\]
The scripts $i$, $j$, and $k$ which indicate the number of metal, hydrogen and tetraphosphate ions, respectively, associated in a complex, can take the values from zero to $N$, $N'$, and $N''$, respectively. The subscript $t$ after the symbol for the concentration indicates the total added concentration of a species. The symbol "$a$" expresses the number of moles of acid per mole of tetraphosphate ion.

The method of calculation is related to Bjerrum formation function and is based on the average number of hydrogen ions, $\bar{n}_H$, bound to the ligand, $L$, in any form whether free or in the form of a complex with another species, $M$. The general equation is

$$\bar{n}_H = \Sigma_{i=0}^{N} \Sigma_{j=0}^{N'} \Sigma_{k=1}^{N''} \frac{[M_iH_jL_k]}{[M]^i[H]^j[L]^k}$$

The concentrations of metal ion to ligand were usually in large excess or in the concentration range where polynuclear species such as
ML₂ was improbable. Diprotonated complexes can also be neglected since the acid titration curves of the tetraphosphate ion in the presence or absence of alkaline earth metal ion are nearly identical after the addition of two hydrogen ions per tetraphosphate ion.

The postulated complex species are ML, M₂L, MHL, and M₂HL. Equation (5) can be expressed as

\[ \overline{E_h} = \frac{[HL] + 2[H₂L] + [MHL] + [M₂HL]}{[L] + [HL] + [H₂L] + [ML] + [M₂L] + [MHL] + [M₂HL]} \] (6)

The mean number of bound hydrogen ions can be solved from the known added acid and ligand concentrations and the pH as

\[ \frac{[H^+]_t - [H^+]}{[L]_t} \] (7)

The pH was in the range of 4 to 8 for most of the experimental work. For pH values above 5, the H⁺ concentration could be neglected and below pH values of 5 could be calculated from the pH and the hydrogen ion activity coefficient. Substituting overall formation constant for the species in equation (6) yields

\[ \overline{E_h} + (\overline{E_h} - 1)\beta_{011}(H^+) + (\overline{E_h} - 2)\beta_{021}(H^+)^2 + \\
(\overline{E_h} - 1)\beta_{111}[M](H^+) + (\overline{E_h} - 1)\beta_{211}[M]^2(H^+) + \\
\overline{E_h}\beta_{101}[M] + \overline{E_h}\beta_{201}[M]^2 = 0 \] (8)

Since the acidity constants, \( \beta_{011} \) and \( \beta_{021} \) are known, the simultaneous solution of four equations of this form for four solutions, each favorable to relatively large concentrations of one of the complex species will yield constant values for the constants of all species actually present. When \( a=0.5 \), ML should be the predominant species at
low concentrations of M and ML₂ at high concentrations of M. In the
region of \( a = 1.5 \), MHL and M₂HL are predicted respectively for high and
low concentrations of M. However, simultaneous equations were not
used for the calculations of the stability constants in this work. One
of the attractive features of the new procedure is that graphic
confirmation is possible by rearranging eq. (8) into the following
respective forms when \( \bar{n}_H = 0.5 \) and 1.5.

\[
F_{0.5} = \beta_{101} + \beta_{201}[M] = [M]^{-1}\{\beta_{011}(H^+) + 3\beta_{021}(H^+)^2 + \beta_{111}[M](H^+) + \beta_{211}[M]^2(H^+)^{-1}\}
\]

\[
F_{1.5} = \beta_{111} + \beta_{211}[M] = [M]^{-1}(H^-)^{-1}\{\beta_{021}(H^+)^2 - \beta_{011}(H^+) - 3\beta_{101}[M] - 3\beta_{201}[M]^2 - 3\}
\]

\( F_{0.5} \) and \( F_{1.5} \) can be evaluated from the right side of the above
equations from the known acidity constants, the pH, iterated value for
the complexity constants, and concentration of the free metal ion. As
a first approximation of the free metal ion concentration one can assume
that one metal ion is bound by each tetraphosphate ion present since
the metal ion concentration is usually in sufficient excess.

A more exact determination of the free metal ion concentration is
obtained as follows. Divide the expression for the total concentration
of the metal ion which is complex bound \([M]_{tc}\) by the total tetra-
phosphate concentration \([Pq]_t\).

\[
\frac{[M]_{tc}}{[Pq]_t} = \frac{[MHPq] + [MPq] + 2[M₂Pq]}{[Pq] + [HPq] + [H₂Pq] + [MPq] + [M₂Pq] + [MHPq]}
\]
Substituting overall formation constants into this expression, factoring out M and cancelling out Pq yields

\[
[M]_{tc} = [Pq]_t \left\{ \frac{\beta_{111}(H)[M] + \beta_{101}[M] + 2\beta_{201}[M]^2}{1 + \beta_{011}(H) + \beta_{021}(H)^2 + \beta_{101}[M] + \beta_{111}[M](H) + \beta_{201}[M]^2} \right\} \tag{12}
\]

Then

\[
[M] = [M]_t - [M]_{tc} \tag{13}
\]

$[M]_{tc}$ is solved using temporary values of $[M]$ in equation (12). Then an improved value of $[M]$ is obtained by substituting $[M]_{tc}$ into equation (13). Then equations (10) and (9) are solved for improved values of the overall formation constants. The entire sequence, (12), (13), (10) and (9), are repeated until $[M]$ and the formation constants reach constant values. The values converge rapidly especially if $[M]_t >> [Pq]_t$.

The temporary constants for $\beta_{111}$ were obtained first by solving $F_{1.5}$ by neglecting the terms containing $\beta_{101}$ and $\beta_{201}$ and assuming $[M]_{tc} = [Pq]_t$. It is possible however, to get preliminary values for $\beta_{101}$ and $\beta_{201}$ from values obtained by determinants since their contributions are relatively small. A plot of $F_{1.5}$ vs $[M]_t$ should finally yield a straight line having an intercept equal to $\beta_{111}$ and a slope equal to $\beta_{211}$. For the complexes studied, the functions were constant and thus confirms the absence of the M$_2$HL complexes.

The solved $\beta_{111}$ value was substituted into eq. (9) and $F_{0.5}$ is solved. A similar plot of $F_{0.5}$ vs $[M]_t$ should finally yield a straight line with the slope equal to $\beta_{201}$ and intercept equal to $\beta_{101}$.
The values of $\beta_{011}$ and $\beta_{021}$ were determined under experimental conditions from pH measurements at a 0.5 and a 1.5.

$$\beta_{011} = K_6^{-1} = \frac{[HP_d]}{(H^+)[P_d]} = 10^{8.350}$$  \hspace{1cm} (14)

$$\beta_{021} = K_5^{-1} \cdot K_6^{-1} = \frac{[H_2P_d]}{(H^+)[P_d]} = 10^{14.988}$$  \hspace{1cm} (15)

$K_5$ and $K_6$ are the last two acid dissociation constants of $H_6P_4O_{13}$.

The calculation of "a" values for the plotting of the titration curve was done on an IBM 7090 computer using Scatran source language at The Ohio State University, Numerical Computation Laboratory. The tetraphosphate ion and metal ion concentrations were identical in both the acidic titrant and solution being titrated.

The equation used for calculating "a" was

$$a = \frac{(M_A)(V_{ADD})}{(M_S)(V_I + V_{ADD})}$$  \hspace{1cm} (16)

The symbols $M_A$ and $M_S$ indicate, respectively, the molarity of the added HCl and the molarity of tetraphosphate salt: $V_I$, $V_{ADD}$, and $V_F$ represent, respectively, the initial volume of the solution titrated, volume of titrant added, and final total volume of solution. $V_{ADD}$ was assigned a value of 0.01 ml to avoid the necessity of making individual data cards for each titration. The total volume, $V_F$, was determined by the volume needed to reach a minimum value of $a = 4$. The following computer program was used for determining "a" for the titrations, Figure 1.
Computer Program for Calculating "a" Values

*** RUN

*** STATEMENT LISTING

*** DUMP LOWER CORE

*** SCATRAN

FLOATING(MA,MS)

FIRST READINPUT,F1,(MA,MS,VIN,VADD,VF)

FF1 (5F10.6)

TVADD = VADD

S1 A = (MA*TVADD)/(MS*VIN)

WRITEOUTPUT,F2,(VIN,A,TVADD)

FF2 (3F10.4)

S2 VIN = VIN + VADD

TVADD = TVADD + VADD

TRANSFerto(S1) PROVIDED(VIN.LE.VF)

CALLSUBROUTINE() = ENDJOB()

ENDPROGRAM(FIRST)

*** DATA

Figure 1
Results and Discussion

Purity Check of Sodium Tetrametaphosphate

The purity of sodium tetrametaphosphate was verified by using paper chromatography. Figure 2 contains chromatograms of various sodium polyphosphate solutions which were run for 5.5 hours and at a temperature of 6°C. Chromatograms 1 and 5 separated in descending order as ortho-, pyro-, tripoly-, trimeta- and tetrametaphosphate. The last three polyphosphate anions, $\text{P}_3\text{O}_{10}^{5-}$, $\text{P}_3\text{O}_9^{3-}$, and $\text{P}_4\text{O}_{12}^{4-}$ were more closely spaced on the chromatogram than the separation of the $\text{P}_2\text{O}_7^{4-}$ and $\text{PO}_4^{3-}$. Chromatogram 3 was of twice recrystallized sodium tetrametaphosphate and chromatograms 2 and 4 of twice recrystallized sodium trimetaphosphate; no polyphosphate impurities were observed.

The techniques of placing the sample on the chromatography paper and spraying with developer and reducing agents were important. Chromatograms 1 and 5 of the same solution shows that chromatogram 5 gave better zone displacement and uniformity than chromatogram 1. This difference may be attributed to the sample placement and spraying techniques. In spotting the sample on the chromatography paper, it is essential to keep the sample spot area small. When the sample solution tends to spread, the solvent is evaporated before applying additional sample solution. Spraying should be uniform and not to the point where the paper is supersaturated with sprayer.

Attempts were made to use an aerosol chromato-sprayer manufactured by Warner-Chilcott Laboratories Instrument Division, Morris Plains, New Jersey, but the background of the chromatograms was too dark.
Whatman 1M paper was used and gave unsatisfactory results. The Schleicher and Schuell Co., paper 589, orange ribbon was most efficient for the separation of the lower polyphosphates.
Figure 2. Chromatogram for Qualitative Identification of Ring and Chain Phosphates in Descending Order

Ortho
Pyro
Triply
Tetrameta

T 6°C
Time of elution  5.5 hours
The Magnesium Tetraphosphate System

In Figure 3, the titration curves of tetraphosphate ion with acid show that the pH lowered appreciably throughout the entire range below a=2 when magnesium ion was present in solution. Curve 1 was obtained in the titration of tetraphosphate ion with hydrochloric acid in the absence of magnesium while curves 2, 3, and 4 were obtained in the presence of increasing concentrations of Mg$^{2+}$. Curves 2, 3, 4, and 5 approach curve 1 shortly after "a" exceeded 2, but do not quite blend with it. This small displacement of curves 2, 3, 4, and 5 from 1 is attributed to the acidity of MgHP$_4$O$_{13}$$^{3-}$. There is also a small activity coefficient effect particularly in curve 5. The data are summarized in Table 2. The points of the titration curves were so numerous that it was not practical to show them.

This effect of acidity was confirmed by calculating $\bar{\text{H}}$. Using eq. (7), $\bar{\text{H}}$ at theoretical value of 1.996 was calculated to be 1.9025 showing that all of the hydrogen ion is not associated as H$_2$P$_4$O$_{13}$$^{4-}$. This calculation was made possible by first experimentally determining the activity coefficient of the hydrogen ion in the concentration range of 0.5mM to 5mM of hydrochloric acid for an ionic strength adjusted to unity with tetramethylammonium chloride at 25°C. The results are tabulated in Table 1. The last two acidity constants of tetraphosphate required in these calculations were recalculated under identical experimental conditions and agreed closely with values reported by previous researchers.$^{26,27}$
Concentrations of tetramethylammonium tetraphosphate and magnesium chloride were identical for titrant and titrated solutions. All titrants contained 0.01305M HCl. The ionic strength of all solutions was adjusted to unity with tetramethylammonium chloride and T = 25°C.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$[\text{MgCl}_2]$ ,mM</th>
<th>$[\left(\text{TMA}\right)<em>{4N}P_4O</em>{13}]$ ,mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.919</td>
</tr>
<tr>
<td>2</td>
<td>3.996</td>
<td>1.919</td>
</tr>
<tr>
<td>3</td>
<td>7.992</td>
<td>1.919</td>
</tr>
<tr>
<td>4</td>
<td>15.984</td>
<td>1.919</td>
</tr>
<tr>
<td>5</td>
<td>99.900</td>
<td>1.919</td>
</tr>
</tbody>
</table>
Table 1. Activity Coefficient of Hydrogen Ion

<table>
<thead>
<tr>
<th>HCl $^a$, mM</th>
<th>Beckman Research pH Meter</th>
<th>Corning pH Meter, Model 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5220</td>
<td>0.701</td>
<td>0.695</td>
</tr>
<tr>
<td>1.044</td>
<td>0.734</td>
<td>0.730</td>
</tr>
<tr>
<td>1.566</td>
<td>0.757</td>
<td>0.748</td>
</tr>
<tr>
<td>2.610</td>
<td>0.766</td>
<td>0.755</td>
</tr>
<tr>
<td>3.654</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>5.220</td>
<td>0.757</td>
<td>0.774</td>
</tr>
<tr>
<td>Average</td>
<td>0.743</td>
<td>0.740</td>
</tr>
</tbody>
</table>

$^a$ Ionic strength of all solutions adjusted to unity with tetramethylammonium chloride.

$^b$ $T = 25 \pm 0.1^\circ C$
From Table 2 it is observed that value of log $F_{1.5}$ converged quickly to $12.087 \pm .153$ with random fluctuation for a substantial range of tetraphosphate ion and magnesium ion concentrations. This proves the presence of only one protonated complex $\text{MgHP}_4\text{O}_{13}^{3-}$ having the following complexity constant

$$
\beta_{111} = \frac{[\text{MgHP}_4\text{O}_{13}^{3-}]}{[\text{Mg}^{2+}](\text{H}^+)[\text{P}_4\text{O}_{13}^{6-}]} \tag{17}
$$

A more meaningful way of expressing this constant in terms of the protonated ligand is done as follows:

$$
\beta_{\text{M.RL}} = \frac{[\text{MgHP}_4\text{O}_{13}^{3-}]}{[\text{Mg}^{2+}][\text{HP}_4\text{O}_{13}^{5-}]} = \frac{\beta_{111}}{\beta_{011}} = 10^{3.737 \pm 0.153} \tag{18}
$$

A plot of values of $F_{0.5}$ vs $[\text{Mg}]_f$ listed in Table 2 gave a straight line having an intercept of $1.10 \times 10^6$ corresponding to $\beta_{101}$ and the slope of $1.69 \times 10^8$ corresponding to $\beta_{201}$, Figure 4. Thus

$$
\beta_{101} = \frac{[\text{MgP}_4\text{O}_{13}^{2-}]}{[\text{Mg}^{2+}][\text{P}_4\text{O}_{13}^{6-}]} = 10^{6.041 \pm 0.200} \tag{19}
$$

$$
\beta_{201} = \frac{[\text{Mg}_2\text{P}_4\text{O}_{13}^{2-}]}{[\text{Mg}^{2+}]^2[\text{P}_4\text{O}_{13}^{6-}]} = 10^{8.228 \pm 0.200} \tag{20}
$$
Table 2. Effect of Magnesium Ion on the Acidimetric Titration

<table>
<thead>
<tr>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>([\text{PO}_4^{3-}]_t), mM</th>
<th>([\text{Mg}^{2+}]_t), mM</th>
<th>([\text{Mg}^{2+}]_t), mM</th>
<th>log F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.350</td>
<td>1.843</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.938</td>
<td>1.843</td>
<td>7.992</td>
<td>5.797</td>
<td>6.335</td>
<td></td>
</tr>
<tr>
<td>5.944</td>
<td>1.843</td>
<td>7.992</td>
<td>5.793</td>
<td>6.327</td>
<td></td>
</tr>
<tr>
<td>5.676</td>
<td>1.843</td>
<td>15.984</td>
<td>13.57</td>
<td>6.560</td>
<td></td>
</tr>
<tr>
<td>5.682</td>
<td>1.843</td>
<td>15.984</td>
<td>13.57</td>
<td>6.553</td>
<td></td>
</tr>
<tr>
<td>5.335</td>
<td>1.843</td>
<td>39.960</td>
<td>37.36</td>
<td>6.872</td>
<td></td>
</tr>
<tr>
<td>5.046</td>
<td>1.843</td>
<td>79.920</td>
<td>77.26</td>
<td>7.157</td>
<td></td>
</tr>
<tr>
<td>4.949</td>
<td>1.843</td>
<td>99.900</td>
<td>97.23</td>
<td>7.253</td>
<td></td>
</tr>
<tr>
<td>0.434</td>
<td>5.745</td>
<td>3.504</td>
<td>19.980</td>
<td>15.12</td>
<td>6.595</td>
</tr>
<tr>
<td>0.434</td>
<td>5.435</td>
<td>3.504</td>
<td>39.960</td>
<td>34.85</td>
<td>6.869</td>
</tr>
<tr>
<td>0.434</td>
<td>5.260</td>
<td>3.504</td>
<td>59.940</td>
<td>54.75</td>
<td>7.040</td>
</tr>
<tr>
<td>0.433</td>
<td>5.505</td>
<td>7.008</td>
<td>39.960</td>
<td>29.80</td>
<td>6.800</td>
</tr>
<tr>
<td>0.433</td>
<td>5.368</td>
<td>10.512</td>
<td>59.940</td>
<td>44.31</td>
<td>6.930</td>
</tr>
<tr>
<td>0.432</td>
<td>5.310</td>
<td>17.520</td>
<td>79.920</td>
<td>53.50</td>
<td>6.986</td>
</tr>
<tr>
<td>1.5</td>
<td>6.638</td>
<td>1.843</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.697</td>
<td>1.843</td>
<td>7.992</td>
<td>7.405</td>
<td>12.365</td>
<td></td>
</tr>
<tr>
<td>4.700</td>
<td>1.843</td>
<td>7.992</td>
<td>7.402</td>
<td>12.365</td>
<td></td>
</tr>
<tr>
<td>4.531</td>
<td>1.843</td>
<td>15.984</td>
<td>15.23</td>
<td>12.191</td>
<td></td>
</tr>
<tr>
<td>4.278</td>
<td>1.843</td>
<td>39.360</td>
<td>38.96</td>
<td>11.967</td>
<td></td>
</tr>
<tr>
<td>4.042</td>
<td>1.843</td>
<td>79.920</td>
<td>78.86</td>
<td>11.836</td>
<td></td>
</tr>
<tr>
<td>3.956</td>
<td>1.843</td>
<td>99.900</td>
<td>98.81</td>
<td>11.812</td>
<td></td>
</tr>
<tr>
<td>4.053</td>
<td>5.758</td>
<td>59.940</td>
<td>57.20</td>
<td>12.106</td>
<td></td>
</tr>
<tr>
<td>3.851</td>
<td>9.595</td>
<td>99.900</td>
<td>95.20</td>
<td>12.043</td>
<td></td>
</tr>
<tr>
<td>3.510</td>
<td>9.595</td>
<td>199.80</td>
<td>195.30</td>
<td>12.095</td>
<td></td>
</tr>
</tbody>
</table>

av. 12.087 - .153
Figure 4. Graphic Determination of $\beta_{101}$ and $\beta_{201}$ for Magnesium Tetraphosphate Complexes.
Intercept: $\beta_{101} = 1.10 \times 10^6$
Slope: $\beta_{201} = 1.69 \times 10^8$

Figure 4
Strontium Tetraphosphate Complexes

The calculations of $F_{0.5}$ and $F_{1.5}$ for strontium tetraphosphate system was similar to those of the magnesium tetraphosphate system. However, both strontium ion and tetraphosphate ion were smaller due to the tendency of a strontium tetraphosphate precipitate to form. It was often possible to make pH measurements of supersaturated solutions before precipitation occurred. The results are given in Table 3. An attempt was made to measure the free strontium ion by saturating the ligand ion-exchanger of the calcium electrode. Only erratic results were obtained. Similar results have been reported by King and Mukherji.  


It is observed from Table 3 that the log $F_{1.5}$ values fluctuated only in a random manner with concentrations of strontium ion and had an average of $11.826 \pm 0.081$. This proved the presence of only the mono-nuclear protonated complex, $\text{SrHP}_4\text{O}_{13}^{3-}$. The complexity constant, $\beta_{111}$, expressed in a form similar to that of eq. (17) is equal to $10^{11.826} \pm 10^{0.081}$. Converting this constant $\beta_{111}$, into the more meaningful form in terms of the protonated ligand indicated by (18) yields

$$
\beta_{M\cdot HL} = \frac{\beta_{111}}{\beta_{011}} = 10^{3.486} \pm 10^{0.081}
$$

(21)

As shown in Table 3 and Figure 5, $F_{0.5}$ varied in a linear manner as a function of free strontium ion concentration within experimental error of $\pm 10^{0.04}$. The intercept and slope yielded the following values for $\beta_{101}$ and $\beta_{201}$:
\[ \beta_{101} = \frac{[\text{SrP}_40_{13}^{4-}]}{[\text{Sr}^2+][\text{P}_40_{13}^{6-}]} = 10^{4.816 \pm 0.04} \]  \hfill (22)

\[ \beta_{201} = \frac{[\text{Sr}_2\text{P}_40_{13}^{2-}]}{[\text{Sr}^2+]^2[\text{P}_40_{13}^{6-}]} = 10^{8.243 \pm 0.04} \]  \hfill (23)
Table 3. Effect of Strontium Ion on the Acidimetric Titration

<table>
<thead>
<tr>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>$[\text{Pi}<em>4^6^-</em>{13}]_{\text{M}}$</th>
<th>$[\text{Sr}^{2+}]_{\text{M}}$</th>
<th>$[\text{Sr}^{2+}]_{\text{M}}$</th>
<th>log F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.340</td>
<td>2.197</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.864</td>
<td>2.197</td>
<td>1.011</td>
<td>0.108</td>
<td>4.892</td>
</tr>
<tr>
<td></td>
<td>7.310</td>
<td>2.197</td>
<td>2.022</td>
<td>0.191</td>
<td>5.086</td>
</tr>
<tr>
<td></td>
<td>6.946</td>
<td>2.197</td>
<td>3.032</td>
<td>0.547</td>
<td>5.252</td>
</tr>
<tr>
<td></td>
<td>6.695</td>
<td>2.197</td>
<td>4.043</td>
<td>1.134</td>
<td>5.439</td>
</tr>
<tr>
<td></td>
<td>6.475</td>
<td>2.197</td>
<td>5.054</td>
<td>1.986</td>
<td>5.616</td>
</tr>
<tr>
<td></td>
<td>8.320</td>
<td>3.034</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.022</td>
<td>3.034</td>
<td>1.011</td>
<td>0.022</td>
<td>4.836</td>
</tr>
<tr>
<td></td>
<td>7.592</td>
<td>3.034</td>
<td>2.022</td>
<td>0.093</td>
<td>4.941</td>
</tr>
<tr>
<td></td>
<td>7.545</td>
<td>3.034</td>
<td>2.022</td>
<td>0.093</td>
<td>4.991</td>
</tr>
<tr>
<td></td>
<td>7.241</td>
<td>3.034</td>
<td>3.032</td>
<td>0.235</td>
<td>5.074</td>
</tr>
<tr>
<td></td>
<td>6.905</td>
<td>3.034</td>
<td>4.043</td>
<td>0.602</td>
<td>5.305</td>
</tr>
<tr>
<td>1.5</td>
<td>6.630</td>
<td>3.034</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.667</td>
<td>3.034</td>
<td>3.032</td>
<td>1.619</td>
<td>11.805</td>
</tr>
<tr>
<td></td>
<td>5.440</td>
<td>2.197</td>
<td>4.043</td>
<td>2.931</td>
<td>11.770</td>
</tr>
<tr>
<td></td>
<td>5.402</td>
<td>3.034</td>
<td>4.043</td>
<td>2.659</td>
<td>11.969</td>
</tr>
<tr>
<td></td>
<td>5.390</td>
<td>3.034</td>
<td>4.043</td>
<td>2.727</td>
<td>11.972</td>
</tr>
<tr>
<td></td>
<td>5.395</td>
<td>3.034</td>
<td>5.054</td>
<td>3.455</td>
<td>11.719</td>
</tr>
<tr>
<td></td>
<td>5.379</td>
<td>3.034</td>
<td>5.054</td>
<td>3.486</td>
<td>11.757</td>
</tr>
<tr>
<td></td>
<td>5.205</td>
<td>3.034</td>
<td>6.065</td>
<td>4.625</td>
<td>11.903</td>
</tr>
<tr>
<td></td>
<td>5.171</td>
<td>3.034</td>
<td>7.075</td>
<td>5.518</td>
<td>11.809</td>
</tr>
<tr>
<td></td>
<td>5.097</td>
<td>3.034</td>
<td>8.086</td>
<td>6.528</td>
<td>11.730</td>
</tr>
</tbody>
</table>

av. 11.826 ± 0.081
Figure 5. Graphic Determination of $\beta_{101}$ and $\beta_{201}$ for Strontium Tetraphosphate Complexes.
Intercept: $\beta_{101} = 6.70 \times 10^4$
Slope: $\beta_{201} = 1.75 \times 10^8$
The Calcium Ion-Exchange Electrode

The investigation of complexes of calcium and tetraphosphate was based on two kinds of measurements, pH and calcium ion activity. The stability constants were determined by the same method of calculation used for magnesium and strontium tetraphosphate complexes. It was hoped that the calcium ion electrode might serve as an independent method for determining the activity of the free calcium ion. In this event it might be applied to ligands forming a very soluble compound with the calcium ion.

An investigation of the calcium ion-exchange electrode was made to determine its pH dependence and the linearity of the potential versus logarithm of calcium ion concentration for various concentrations of calcium chloride at ionic strength of unity adjusted with tetramethylammonium chloride at 25°C. Figure 6 is a plot of the potential in millivolts vs pH for two solutions of concentrations 10.03 mM Ca\(^{2+}\), curve 1 and 1.003 mM Ca\(^{2+}\), curve 2. The potentials are nearly constant with varied pH for 10.03 mM Ca\(^{2+}\) in the pH range of 4 to 9 and for 1.003 mM Ca\(^{2+}\) in the pH range of 5 to 9. The results indicate that potential readings for both concentration ranges could be extended to pH of 11 by applying a positive millivolt correction for reading the working curve. The sharp dips of curves 1 and 2 obtained at pH values below 4 represent the lower useful pH limit. After the minimum, at pH values close to 3.5, the potential increased presumably due to the effect of H\(^+\) activity.
Figure 6. Electrode Potential Behavior vs Solution pH for Calcium Ion-Exchange Electrode.

Ionic strength adjusted to unity with tetramethylammonium chloride.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Solution Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>10.03mM CaCl$_2$</td>
</tr>
<tr>
<td>Curve 2</td>
<td>1.003mM CaCl$_2$</td>
</tr>
</tbody>
</table>
An examination of Figure 7 in which calcium ion concentration is plotted vs potential on 4 cycle semi-log paper, showed the concentration to vary nearly linear in the concentration range of 0.1000M to 0.001OM and curve toward the potential axis with concentrations less than 0.001M.

A comparison of these figures to similar figures in the Calcium Activity Electrode Manual, Model 92-20, Orion Research, Inc., has shown that the reliability of potential readings for the calcium ion activity is extended to lower pH values at ionic strength of unity used in this study as compared to similar concentrations of Ca$^{2+}$ at ionic strengths of .075 and .0075. Also, the working curve of concentration vs potential is more nearly linear at unity ionic strength for Ca$^{2+}$ concentrations greater than 0.0100M.
Figure 7. Calcium Ion Concentration vs Electrode Potential at an Ionic Strength of Unity.

Ionic strength was adjusted to unity with tetramethylammonium chloride.
Ionic strength adjusted to unity with tetramethylammonium chloride

Calcium Ion Electrode Potential vs. SCE (MV)

* Ionic strength adjusted to unity with tetramethylammonium chloride
The acidimetric titration curves of tetraphosphate ion with hydrochloric acid, Figure 8, show that the presence of calcium ion in solution resulted in a lowering of the pH for the entire range of "a" values below 2. The titration of tetraphosphate ion with hydrochloric acid is shown in curve 1, while curves 2, 3, and 4 show the effect of the presence of calcium ion. At "a" values greater than 2, curves 2 and 3 blend together and curve 4 is slightly lower because of a small activity coefficient effect due to the high calcium ion concentration. The small displacement of curves 2, 3, and 4 from curve 1 just before a=2 is attributed to high acidity of CaHPO$_4$$\cdot$13$^3$-. This acidity was substantiated by using eq. (7) and the previously determined activity coefficient of hydrogen ion to calculate an experimental $\tilde{\alpha}_H$ of 1.960 as compared to theoretical value of 2.003.

The stability constants of calcium tetraphosphate system were determined by the method employed for the magnesium and strontium tetraphosphate systems which used only pH measurements, procedure A, and secondly using pH measurements and the free calcium ion concentration determined from using the calcium ion-exchange electrode, procedure B. Both sets of calculations used eqs. (9) and (10).

In Table 4, the values of log F$_{1.5}$ converged to 11.876 and 11.649, respectively for both procedures. These two values for $\beta_{1.1.1}$ may be converted to the more frequently used form in terms of the protonated ligand using eq. (18).
Figure 8. The Effect of Various Concentrations of Calcium Ion for the Titration of Tetraphosphate Ion with Hydrochloric Acid.

Titrant contained 0.01305N HCl with the same concentration of calcium as solution being titrated. All solutions adjusted to an ionic strength of unity with tetramethylammonium chloride and $T = 25^\circ C$.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$[\text{CaCl}_2], \text{mM}$</th>
<th>$[\text{([TMA]}_4N)_6\text{P}<em>4\text{O}</em>{13}], \text{mM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>0.0000</td>
<td>1.919</td>
</tr>
<tr>
<td>Curve 2</td>
<td>2.061</td>
<td>2.197</td>
</tr>
<tr>
<td>Curve 3</td>
<td>4.122</td>
<td>2.197</td>
</tr>
<tr>
<td>Curve 4</td>
<td>7.213</td>
<td>2.197</td>
</tr>
</tbody>
</table>
Table 4. Effect of Calcium Ion on the Acidimetric Titration

<table>
<thead>
<tr>
<th>pH</th>
<th>[P_4O_13]^- [Ca^{2+}]</th>
<th>total</th>
<th>measured</th>
<th>calculated</th>
<th>pH &amp; [Ca^{2+}] calculated from meas's.</th>
<th>pH meas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.325</td>
<td>1.919</td>
<td>0.000</td>
<td>0.000</td>
<td>5.682</td>
<td>5.611</td>
</tr>
<tr>
<td></td>
<td>6.890</td>
<td>1.919</td>
<td>2.061</td>
<td>0.281</td>
<td>0.237</td>
<td>5.682</td>
</tr>
<tr>
<td></td>
<td>6.576</td>
<td>1.919</td>
<td>3.091</td>
<td>1.07</td>
<td>0.730</td>
<td>5.841</td>
</tr>
<tr>
<td></td>
<td>6.192</td>
<td>1.919</td>
<td>5.152</td>
<td>3.37</td>
<td>2.316</td>
<td>6.171</td>
</tr>
<tr>
<td></td>
<td>6.340</td>
<td>2.197</td>
<td>0.000</td>
<td>0.000</td>
<td>5.703</td>
<td>5.538</td>
</tr>
<tr>
<td></td>
<td>6.996</td>
<td>2.197</td>
<td>2.061</td>
<td>0.10</td>
<td>0.185</td>
<td>5.570</td>
</tr>
<tr>
<td></td>
<td>6.665</td>
<td>2.197</td>
<td>3.091</td>
<td>0.58</td>
<td>0.546</td>
<td>5.832</td>
</tr>
<tr>
<td></td>
<td>6.429</td>
<td>2.197</td>
<td>4.122</td>
<td>1.32</td>
<td>1.160</td>
<td>5.997</td>
</tr>
<tr>
<td></td>
<td>6.236</td>
<td>2.197</td>
<td>5.152</td>
<td>2.28</td>
<td>1.979</td>
<td>6.167</td>
</tr>
<tr>
<td></td>
<td>5.884</td>
<td>2.197</td>
<td>8.243</td>
<td>4.72</td>
<td>4.861</td>
<td>6.521</td>
</tr>
<tr>
<td></td>
<td>5.693</td>
<td>2.197</td>
<td>10.304</td>
<td>7.50</td>
<td>7.280</td>
<td>6.704</td>
</tr>
<tr>
<td>1.5</td>
<td>6.630</td>
<td>1.919</td>
<td>0.000</td>
<td>0.000</td>
<td>12.187{superscript}a</td>
<td>12.256{superscript}a</td>
</tr>
<tr>
<td></td>
<td>5.436</td>
<td>1.919</td>
<td>2.061</td>
<td>1.32</td>
<td>1.312</td>
<td>12.187{superscript}a</td>
</tr>
<tr>
<td></td>
<td>5.220</td>
<td>1.919</td>
<td>3.091</td>
<td>1.85</td>
<td>2.289</td>
<td>12.230{superscript}a</td>
</tr>
<tr>
<td></td>
<td>5.152</td>
<td>1.919</td>
<td>5.152</td>
<td>3.17</td>
<td>4.055</td>
<td>11.676</td>
</tr>
<tr>
<td></td>
<td>6.643</td>
<td>2.197</td>
<td>0.000</td>
<td>0.000</td>
<td>11.861</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.418</td>
<td>2.197</td>
<td>2.061</td>
<td>.43</td>
<td>1.261</td>
<td>11.317</td>
</tr>
<tr>
<td></td>
<td>5.062</td>
<td>2.197</td>
<td>5.152</td>
<td>2.11</td>
<td>4.070</td>
<td>12.038</td>
</tr>
<tr>
<td></td>
<td>4.860</td>
<td>2.197</td>
<td>10.304</td>
<td>5.45</td>
<td>8.921</td>
<td>11.321</td>
</tr>
</tbody>
</table>

Note: The superscript 'a' indicates additional calculations or notes related to the data.
<table>
<thead>
<tr>
<th>pH</th>
<th>[F$<em>4$O$</em>{13}$] 6$^-$</th>
<th>[Ca$^{2+}$], mM</th>
<th>measured</th>
<th>calculated</th>
<th>log F calculated from pH &amp; [Ca$^{2+}$] meas's.</th>
<th>pH meas.</th>
</tr>
</thead>
</table>

Average of log F$_{1.5}$

11.649 
± 0.200 
± 0.183

*These values were not included in average because of low metal ion concentration.*
A plot of \( F_{0.1} \) vs free calcium ion was linear and had an intercept of \( 2.85 \times 10^5 \) and slope of \( 6.37 \times 10^8 \) for procedure B. The intercept and slope were respectively \( 2.90 \times 10^5 \) and \( 3.44 \times 10^8 \) for procedure A. The intercept and slope yielded the following values for 101 and 201:

\[
\beta_{101} = \frac{[\text{CaP}_{4013}^{4-}]}{[\text{Ca}^{2+}][\text{P}_{4013}^{6-}]} = 10^{5.462} \pm 10^{0.01} \quad (A) \\
\beta_{011} = \frac{10^{3.536} \pm 10^{0.183}}{10^{3.309} \pm 10^{0.200}} \quad (B)
\]

\[
\beta_{201} = \frac{[\text{CaP}_{2013}^{2-}]}{[\text{Ca}^{2+}]^2[\text{P}_{4013}^{6-}]} = 10^{8.536} \pm 10^{0.01} \quad (A) \\
\beta_{011} = \frac{10^{8.804} \pm 10^{0.12}}{10^{9.63} \pm 10^{0.20}} \quad (B)
\]

The values of the stability constants as calculated by procedure A and procedure B have reasonably good agreement considering the method used to calculate free calcium ion from pH measurements as compared to direct measurement.

Calcium ion concentrations on the basis of pH and by means of the calcium ion exchange electrode are listed in Table 4. The agreement is good for values of a=0.5. However, at a=1.5, the difference between the measured and calculated calcium ion concentrations are increased with decreasing pH. It is possible that the accuracy of the calcium ion-exchange electrode was effected at lower pH due to the effect of hydrogen ions on the electrode potential.
Figure 9. Graphic Determination of \( \beta_{101} \) and \( \beta_{201} \) for Calcium Tetraphosphate Complexes.
Figure 9

Intercept: $\beta_{10}$ $2.90 \times 10^5$ $2.85 \times 10^5$
Slope: $\beta_{20}$ $3.44 \times 10^8$ $6.37 \times 10^8$
Conclusions

In Table 5, a comparison of the formation constants of alkaline earth metals with various polyphosphate ions are listed. The stepwise formation constants of ML and MHL were calculated by equations similar to (22) and (23); M²⁺L was determined as follows:

\[ K_{201} = \frac{[M_2\text{P}_4\text{O}_{13}^{2-}]}{[M^{2+}][\text{P}_4\text{O}_{13}^{4-}]} = \frac{8_{201}}{8_{101}} \] (27)

It was observed that the stability of all alkaline earth metal tetraphosphate complexes formed, ML, MHL, and ML₂ increased with the number of phosphate tetrahedra. Part of the increase in stability of the tetraphosphate ion complexes may be attributed to a statistical probability of the metal ion first forming a single bond with any terminal oxygen before going into a chelating position to form a six membered ring consisting of two phosphorus atoms, three oxygen atoms, and the metal ion. For pyro-, tri-, and tetraphosphate, there are, respectively, 6, 8, and 10 positions to form the first bond but only one way to dissociate. Thus, the statistical factor of the first metal ion complex with tetraphosphate ion could account for \(10^{0.10}\) of the increase stability of the tetraphosphate complexes relative to the triphosphate complexes and \(10^{0.22}\) of the increase stability of tetraphosphate complexes relative to the pyrophosphate complexes. Also, the relatively large tetraphosphate ion may coil around the divalent alkaline earth ion to form a stable complex as predicted by Watters and et al.²⁷,²⁸ The higher ionic charge of the tetraphosphate ion may be localized by the divalent ion. The ionic radii of the alkaline earth
ions are $0.65\text{Å}$, $0.99\text{Å}$, $1.13\text{Å}$, respectively, for Mg$^{2+}$, Ca$^{2+}$, and Sr$^{2+}$. The decreasing order of charge density is Mg$^{2+}$ > Ca$^{2+}$ > Sr$^{2+}$. Thus, the strength of the ML complexes should be in this order if only this effect is considered since previous studies indicate that the bonding is largely ionic.$^{33}$ An examination of Table 5 shows this order of stability for the ML complexes. Additional proof of some ionic bonding was the decreased stability of complexes of tetraphosphate ion with the large singly charged quanidinium ion$^{27}$ relative to the divalent alkaline earth ions.

Schwarzenbach and co-workers$^{32}$ have shown that the stability constants of magnesium adenosine tetraphosphate complexes were somewhat more stable than the magnesium adenosine triphosphate complexes.

In studies of cupric and mercurous ions with the polyphosphates, Watters and co-workers$^{35-38}$ found the bond strength per phosphate tetrahedron but not per polyphosphate molecule to decrease with chain length. The same effect is shown in Table 5 for the alkaline earth polyphosphate complexes.
Table 5

Comparison of Polyphosphate Complexes with Alkaline Earth Metal Ions

<table>
<thead>
<tr>
<th>Metal</th>
<th>Complex Form</th>
<th>$\log K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$P_{2O7}^{4-}$</td>
</tr>
<tr>
<td>Mg</td>
<td>ML</td>
<td>5.41&lt;sup&gt;b&lt;/sup&gt; 5.42&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>MHL</td>
<td>3.06 3.05</td>
</tr>
<tr>
<td></td>
<td>ML&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.34 2.33</td>
</tr>
<tr>
<td>Ca</td>
<td>ML</td>
<td>4.95 4.89</td>
</tr>
<tr>
<td></td>
<td>MHL</td>
<td>2.30 4.63</td>
</tr>
<tr>
<td></td>
<td>ML&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.77</td>
</tr>
<tr>
<td>Sr</td>
<td>ML</td>
<td>4.816</td>
</tr>
<tr>
<td></td>
<td>MHL</td>
<td>3.486</td>
</tr>
<tr>
<td></td>
<td>ML&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.427</td>
</tr>
</tbody>
</table>

<sup>a</sup> Stepwise constants in terms of metal ion and protonated or unprotonated free ligand concentrations.

<sup>b</sup> This laboratory<sup>1</sup>,<sup>2</sup>, $u=1$ with tetramethylammonium chloride.

<sup>c</sup> Irani and co-workers<sup>40</sup>,<sup>41</sup>, $u=1$ with tetramethylammonium bromide.

<sup>d</sup> Constants calculated using $Ca^{2+}$ measured by ion-exchange electrode.

<sup>(41)</sup> (a) R.R. Irani and C.F. Callis, J. Phys. Chem., 64, 1398 (1960); (b) R.R. Irani, <i>ibid.</i>, 65, 1463 (1961).
CHAPTER II

The Possible Complex Formation of Guanidinium Ion with Pyrophosphate and Tripolyphosphate

Introduction

The studies of guanidinium ion as a possible central ion for pyrophosphate and tripolyphosphate complexes was prompted by the formation of crystalline guanidinium pyro-, tripoly and tetraphosphates, and the identification of guanidinium tetraphosphate complexes by Watters and Matsumoto. Stability constants were evaluated for the following guanidinium tetraphosphate complexes: $ML, ML_2,$ and $MHL$ on the basis of pH lowering due to complex formation. The stability of these complexes is quite similar to that of the alkali metal ions with other polyphosphates and is probably due to at least three hydrogen bonds between amine nitrogen and phosphate oxygen atoms. It was postulated that the complex formation was due to multiple hydrogen bonding between the coiled tetraphosphate ion with adjacent guanidinium ions.

Since derivatives of guanidine and polyphosphates are present in most living matter, the biological and physiological importance of complexes of this type could be of great significance. The unique characteristic of guanidinium ion, $C(NH_2)_3^+$, is that it contains one carbon bonded to three equivalent $NH_2$ groups. Resonance considerations indicate that a positive charge must be shared equally by the three equivalent $NH_2$ groups in a planar structure and that the proton would
be strongly bound. This structure has been confirmed by nmr\textsuperscript{42}, infrared\textsuperscript{43}, Raman\textsuperscript{44}, and X-ray studies.\textsuperscript{45} The salts of guanidinium ion with anions of strong acids are essentially neutral and the solution of guanidine in water is a strong base; all characteristics possessed by alkali metal ions. The acid dissociation constant is exceedingly small\textsuperscript{46}, amounting to only $10^{-13.65}$.

\begin{itemize}
  \item \textsuperscript{(44)} J. Gupta, \textit{J. Indian Chem. Soc.}, \textbf{13}, 575 (1936).
  \item \textsuperscript{(45)} W. Theilacker, \textit{Z. Krist}, \textbf{76}, 303 (1931); \textit{90A}, 51, 256 (1934).
\end{itemize}

On the basis of the above evidence, the possibility of guanidinium ion complexing with pyro- and tripolyphosphate is indicated.
Experimental

Stock solutions of 0.02M pyrophosphate and 0.20M tripolyphosphate were prepared from \( \text{Na}_4\text{P}_2\text{O}_7\cdot10\text{H}_2\text{O} \), Baker Chemical Company, Reagent Grade, and \( \text{Na}_5\text{P}_3\text{O}_{10}\cdot6\text{H}_2\text{O} \). The sodium tripolyphosphate was prepared from anhydrous sodium tripolyphosphate, Monsanto Technical Grade, by recrystallizing four times to yield a 99.5 percent pure product by a procedure developed by P.G. Arvan in the Monsanto Laboratory and described in previous papers from this laboratory.

(47) R.A. Ruerwin, private communication, Monsanto Chemical Co., Dayton, Ohio.

Eight hundred and forty grams of the salt was dissolved in 3.8 liters of water. The solution was filtered through a sintered glass filter and then precipitated with 1.4 liters of methanol with vigorous stirring. The crystalline \( \text{Na}_3\text{P}_3\text{O}_{10}\cdot6\text{H}_2\text{O} \) was collected on a filter, sucked as dry as possible, and then allowed to air dry overnight. The precipitate was dissolved in sufficient water to give a 13 percent solution on a dry weight basis. The solution was filtered and the filtrate was treated with methanol in a volume 25 to 30 percent of the filtrate volume. The procedure of filtration and drying was repeated. Four hundred and forty grams of crystalline product was leached by being thoroughly stirred with 200 ml of water, filtered, and the filtrate discarded. Another crystallization, a leaching and a final crystallization were made using the same procedure and the same proportions as in the last steps. According to Quimby, the commercial 85 to 94 percent anhydrous salt can be made 99 percent pure by 3 to 5 recrystallizations from water with
ethanol added to the extent of 25 percent by volume. The total yield from the four recrystallizations was 55.6 percent. All water used for solutions and purification was doubly distilled, demineralized and purged with nitrogen.


The sodium pyrophosphate and tripolyphosphate were converted to the tetramethylammonium salt by using a Dowex 50W-X12,X2 ion exchange resin. The acidic form of the resin was charged with 15 percent tetramethylammonium chloride using the procedure of previous researchers in this laboratory. A negative test for H⁺ with pH paper or Na⁺ using a Beckman D.U. Flame Photometer indicated that the resin was completely charged with tetramethylammonium ion. In the flame test, hydrogen and oxygen pressures of 8 lbs./in² and 6 lbs./in², respectively, were used. The Beckman D.U. settings were 1/2 to 1 turn from maximum sensitivity, slits of 0.01 to 0.04 mm, and wavelength of 589 m. The column was finally washed with water until the effluent gave a negative test for chloride ion with acidic silver nitrate.

For the preparation of the tetramethylammonium pyro- or tripolyphosphate, a sodium salt solution of twice the desired concentration was placed on the column and eluted with water. The movement of the polyphosphate ion on the column was observed by the movement of a greyish orange zone. When the effluent became basic, a volume equal to 5 percent of the original volume of the sodium pyro- or tripolyphosphate solution was discarded. The next fraction, approximately 85 percent of the original volume, was collected in a polyethylene bottle
under a nitrogen atmosphere. Tests for Na⁺ breakthrough were made continuously during the elution.

Hydrolysis of tripolyphosphate ion was prevented by constantly circulating ice water through a 4 cm, in diameter, Pyrex water jacket fitted around the 2x90 cm ion exchange column. This was not necessary for pyrophosphate solutions.

The tetramethylammonium chloride, Eastman Chemical or Matheson Coleman Bell, was recrystallized by dissolving 30 grams of the salt in 300 ml of hot 25 percent methanol in aceton, filtered; and 330 ml of acetone were slowly added dropwise with continuous stirring.⁴⁹

---


If the solution was chilled and filtered immediately, the yield was 55 percent. However, upon standing overnight and then chilling, the yield increased to 66 percent.

A stock solution of 1.775M guanidinium hydrochloric Eastman Chemicals, acid was standardized gravimetric by precipitating the chloride ion as silver chloride. The hydrochloric acid was standardized against National Bureau of Standards potassium hydrogen phthalate. Potassium hydrogen phthalate, borax, disodium phosphate-potassium dihydrogen phosphate buffers were prepared from NBS or Reagent Grade Chemicals.

A Beckman Model G pH meter with a general purpose glass electrode and Corning pH meter, model 12, using a general purpose glass electrode, No. 476022 were used for pH measurements.
Results and Discussion

Figure 10 shows the pH lowering effect of the guanidinium ion on the titrations curves of pyrophosphate with acid is negligible throughout the range of $a=0$ to $a=4$. Within experimental error, curves 1, 2, 3, and 4 are identical.

Curve 1 was obtained in the titration of pyrophosphate with hydrochloric acid in the absence of guanidinium ion, and curves 2, 3, and 4 for concentration ratios of guanidinium ion to pyrophosphate of $44:1$ to $220:1$. If any complexes of guanidinium ion with pyrophosphate were to be formed, they should be present under the above concentration ratios. Thus, it is concluded that guanidinium ion does not complex with pyrophosphate ion, for the experimental conditions used.

In Figure 11, the titration curves of triphosphate ion with hydrochloric acid indicate that guanidinium ion does not have any effect on the acidimetric titration curves for solutions containing 1M tetramethylammonium chloride. Curves 2, 3, and 4 were obtained in the presence of increasing guanidinium ion while curve 1 was obtained in the absence of guanidinium ion. Curves 1, 2, 3, and 4 are identical and therefore, prove the absence of guanidinium ion and triphosphate ion complexes.

Since the stability of alkali metal polyphosphates complexes are similar to guanidinium tetraphosphate complexes, the finding of no complexes of guanidinium ion with pyro- and triphosphosphate ions was surprising. The absence of complexing may be attributed to stereo-effects. The geometry of the guanidinium ion, which is large in size,
is such that a sufficient number of its amine hydrogen do not come into close proximity of the pyro- and tripolyphosphate tetrahedra, $\text{PO}_4^-$.
Figure 10. The Effect of Various Concentrations of Guanidinium Ion on Curves for the Titrations of Sodium Pyrophosphate with Hydrochloric Acid.

Concentrations of sodium triphosphate and guanidinium hydrochloride were identical for titrant and titrated solution. The ionic strength was adjusted to unity with tetramethylammonium chloride for all solutions, $T=25^\circ C$.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$[\text{Na}_4\text{P}_2\text{O}_7],\text{mM}$</th>
<th>$[\text{C(\text{NH}_2)}_3\text{Cl}],\text{mM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>2.006</td>
<td>0.000</td>
</tr>
<tr>
<td>Curve 2</td>
<td>2.006</td>
<td>88.75</td>
</tr>
<tr>
<td>Curve 3</td>
<td>2.006</td>
<td>177.5</td>
</tr>
<tr>
<td>Curve 4</td>
<td>2.006</td>
<td>443.8</td>
</tr>
</tbody>
</table>
Figure 11. The Effect of Various Concentrations of Guanidinium Ion on the Titration of Triphosphate Ion with Hydrochloric Acid.

Concentrations of tetramethylammonium triphosphate and guanidinium hydrochloride were the same in the titrated solution and titrant. All solutions were 1M in tetramethylammonium chloride at $T=25^\circ C$.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$[(\text{TMA})<em>6\text{P}</em>{3\text{O}}<em>{10}]</em>{\text{mM}}$</th>
<th>$[\text{C(NH}_2)<em>3\text{Cl}]</em>{\text{mM}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.608</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>4.608</td>
<td>106.5</td>
</tr>
<tr>
<td>3</td>
<td>4.608</td>
<td>213.0</td>
</tr>
<tr>
<td>4</td>
<td>4.608</td>
<td>355.0</td>
</tr>
</tbody>
</table>
CHAPTER III

The Polarographic Study of the Complexes of Cupric Ion
with Trimetaphosph ate

Introduction

One of the earliest studies of the complexes and acidity of trimeta- and tetrametaphosphate was done by Monk and co-workers\(^5^0\), who had determined the dissociation constants for the acids and a number of metal complexes of tri- and tetrametaphosphate by a conductometric procedure.


Gross and Gryder investigated complexes of sodium, nickel, and cupric ions with tetrametaphosphate using a potentiometric method with the copper amalgam electrode.\(^5^1\) Their results for sodium, nickel and cupric trimetaphosphate complexes were not in complete agreement with those of Monk, et al. The difference in the configuration of the species and association constants could be attributed to one or more of the following reasons: (1) impurities in the metaphosphate used by Monk, et al., (2) incorrect assumption of species and mobilities of the ions present which is required for the conductometric method, (3) the
activity coefficients are such that the thermodynamic constant and the concentration constant differ by a large factor.

Indelli,\(^{52}\) using the procedure of Gross and Gryder, determined the stability constants of \(\text{NaP}_3\text{O}_9^{2-}\) and \(\text{Na}_2\text{P}_3\text{O}_9^{1-}\) and found the complexity constant of \(\text{NaP}_3\text{O}_9^{2-}\) to be a higher but of the same order of magnitude as previous workers. The log of the complexity constant for \(\text{CuP}_3\text{O}_9^-\) was 1.55 and there was some evidence for \(\text{Cu}_2\text{P}_3\text{O}_9\) existing in solution.


In support of the ring structure of trimetaphosphate, X-ray studies have shown that sodium trimetaphosphate hexahydrate to be a six membered ring with alternate phosphorus and oxygen atoms.\(^{53}\) The titration curves of the acid with sodium hydroxide were practically indistinguishable from the titration curve of a strong acid with the same equivalent concentration.\(^{54}\) This indicated that the three protons came from different \(\text{OPO}_3\text{H}\) groups and is consistent with the cyclic structure. The nuclear magnetic resonance spectrum of phosphorus in solutions of sodium trimetaphosphate has shown only the resonance peak corresponding to middle groups.\(^{55}\) Numerous reviews have given additional structural features of the trimeta, tetrameta and polyphosphates.\(^{56-58}\)


(57) E. Thilo, Angew. Chem. internat. Edit., 4, 1061 (1965)

The present study was undertaken to investigate the feasibility of determining metal complexes of trimetaphosphate by polarography using the copper amalgam electrode with cupric ion as an indicating ion.
Experimental

The commercial sodium trimetaphosphate, Victor Division, Stauffer Chemical Co., was purified by two different procedures of recrystallization. From the graph of solubility of Na$_3$P$_3$O$_9$ in water (Ref. 53, p. 688), the amount of Na$_3$P$_3$O$_9$ needed to prepare a saturated solution at 25°C was determined. Fifty-four grams of Na$_3$P$_3$O$_9$ were dissolved in 200 ml of water, the solution filtered, and the filtrate transferred to a 400 ml beaker which was placed in a water bath maintained at 25°C ± 0.1°C. A watch glass was used as a canopy.

After a period of 24 days, crystallization had proceeded to the extent where it was feasible to remove the crystals from the supernatant liquid. The crystals were filtered on a sintered glass filter and washed with ethanol. The sodium trimetaphosphate prepared was pure, but the time requirement was a disadvantage.

The second procedure was as follows: 150 grams of commercial Na$_3$P$_3$O$_9$ was dissolved in 600 ml of water at room temperature, filtered on a sintered glass funnel to remove undissolved particles. To the filtrate, 400 ml ethanol were added with constant stirring at 2 to 3°C. At this temperature the hexahydrate should be crystallized.

Sodium trimetaphosphate was also prepared from heating NaH$_2$PO$_4$·H$_2$O for 6 hours at 550°C and then grinding the cooled melt, dissolving in water and recrystallizing with ethanol as above.

The purity of the sodium trimetaphosphate was checked by a precipitation reaction, examination of the pH titration curve of the acid with a strong base, and paper chromatography. A few drops of
1.4M \( \text{BaCl}_2 \) added to a few grains of sodium polyphosphates dissolved in water gave precipitates for ortho-, pyro, tri, tetraphosphate but not with trimetaphosphate.

(59) Inorganic Syn Thesis, 3, p. 104 (19\).


The pH titration curve of trimetaphosphoric acid with tetramethylammonium hydroxide or sodium hydroxide showed only one break. The chromatogram of two sodium trimetaphosphate samples in Figure 1 had no other phosphates present.

Sodium trimetaphosphate was converted to its acid or the tetramethylammonium salt through the use of Dowex 50\( W \)-X2, 200 to 400 mesh, ion exchange resin. For the preparation of the acid, a glass column 25x2.7 cm in diameter, with a resin bed height of 17.3 cm was charged with 3N hydrochloric acid. The column was washed with water until the effluent was neutral to pH paper. A dilute, ca 0.01M, sodium trimetaphosphate solution was placed on the column and eluted with water until the effluent was neutral.

The column for converting the sodium salt to the tetramethylammonium salt, 61x2.5 cm in diameter, was charged with 10 percent tetramethylammonium chloride. A few drops of 0.1M uranyl nitrate added to portions of the effluent converted any trimetaphosphate ions present almost instantaneously to tripolyphosphate ions. Uranyl nitrate precipitates tripolyphosphate quantitatively.
The Beckman D.U. Flame spectrophotometer was used to test for the presence of sodium ion in the effluent. This procedure was described in Chapter 2.


\[ \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O and CuSO}_4 \cdot 5\text{H}_2\text{O, Baker Reagent Grade, were used to prepare 0.1M copper stock solution and copper amalgam, respectively. The 0.1M copper nitrate stock solution was diluted to 0.01M and standardized volumetrically with EDTA, using the following procedure.} \text{\[62\]}

Twenty-five ml of 0.01M Cu(NO_3) solution were pipetted into a 250 ml erlenmeyer flask and 1M KH\textsubscript{2}OH added dropwise until the appearance of the deep blue Cu(NH\textsubscript{3})\textsuperscript{4+} complex. At this point 10 ml of 1M NH\textsubscript{4}Cl and 10 drops of a freshly saturated solution murexide, the ammonium salt of purpuric acid, were added. The solution was titrated to its medium violet endpoint with EDTA. A half drop before the endpoint the solution was light mustard in color.

\[ \text{(62) G. Schwarzenbach, Complexometric Titrations, Interscience Publishers, Inc., New York, (1957).} \]

A 0.0005 percent copper amalgam was prepared by electrically reducing a known amount of copper into a known weight of triply distilled mercury. The electrolytic solution contained a few drops of nitric acid and ethylenediamine. A flag shaped anode and cathode of platinum wire were used as electrodes. Two 1.5 volt dry cells in series were connected to the electrodes and the electrolysis was allowed to proceed over night with slow rate of bubbling of nitrogen through the
solution. The next day the violet color of the copper ethylenediamine complex had disappeared. The amalgam was washed with water and acetone under a nitrogen atmosphere and transferred to the reservoir of the electrode assembly. The amalgam was covered with a thin layer of Nujol and kept under a nitrogen atmosphere.

The anodic diffusion current agreed very closely with the results of Matsumoto, Schupp, and Sturrock.


(64) P.E. Sturrock, ibid., (1960).

The dropping amalgam electrode was an all glass assembly which Schupp found necessary to prevent oxidation of copper in the amalgam. It was possible to effectively adjust the amalgam column height of the electrode assembly by a mercury manometer connected to the side stopcock of the reservoir. The manometer was flushed with nitrogen. The drop time and capillary characteristics were respectively 3.12 seconds and $2.272 \frac{mg^{2/3}}{sec^{-1/2}}$ at an amalgam height of 60.1 cm and a potential zero volts versus the SCE for most experiments.

The supporting electrolyte, tetramethylammonium nitrate, was prepared by neutralizing tetramethylammonium hydroxide with 1:1 nitric acid that had been prepared from freshly boiled concentrated acid. The tetramethylammonium hydroxide, (TMAOH), Eastman or Matheson Coleman Bell, was available as a 10 percent aqueous solution or 25 percent methanol solution. The following procedure yielded 97.6 percent
tetramethylammonium nitrate, TMANO₃, of the theoretical yield and was applicable to either aqueous or methanol TMAOH solutions.

Five-hundred grams of 24 percent TMAOH was neutralized to a pH of 6.99 with cooled 1:1 HNO₃ prepared from freshly boiled concentrated acid. As the reaction is exothermic, care should be taken to avoid splattering. A precipitate formed with the first addition of the 1:1 nitric acid but disappeared as neutralization proceeded. The final volume of 900 ml was evaporated very slowly to a volume of 500 ml. The TMANO₃ solution was transferred to a 1 liter round bottom flask, connected to a rotary drier, and evaporated under a partial vacuum with steam heat. When a thick slurry formed, it was dissolved in a hot solution of 400 ml methanol and 100 ml water. The solution was chilled and 200 ml acetone added with vigorous stirring. The precipitate was allowed to stand two days, chilled and tested for completeness of precipitation with acetone. The crystals were filtered on a sintered glass funnel, washed with cold acetone and air dried; 66 percent yield. The filtrate of 800 ml was evaporated to 400 ml in a beaker and finally to near dryness in the rotary drier. Only 10 ml of water was used with 400 ml methanol to dissolve the precipitate and the above mentioned crystallization procedure was repeated. The yield was 31.6 percent.

An attempt to make TMANO₃ using Bio-Rad AG1-X8, 200-400 mesh, anion exchange resin charged with nitrate ion was unsuccessful due to chloride ion breakthrough.

Agar salt bridges of 1M tetramethylammonium chloride and saturated potassium chloride were prepared in 1.5 cm, o.d., tubing with a height of 14 cm. The pH equipment and buffers were discussed in the
experimental of Chapter 1 and 2. All water used for purification and solutions was doubly distilled, demineralized and outgassed with nitrogen. Potentials were measured with a Rubicon model 2780 potentiometer in combination with a manual polarograph designed by Watters. 65

---


---

A Leeds and Northrup Electro-Chemograph Type E Polarograph was used for survey polarograms.
Calculations

The polarographic method can be used to study complex metal ions by observing the shift of potential, $\Delta E$, at any point on the complex wave from the corresponding point on the wave for the complex free solution containing the same metal ion and amalgam concentration, or it may be the shift in the half-wave potential regardless of the metal ion or amalgam concentration. Deford and Hume\(^{66}\) have derived equations for Leden's function\(^{67}\) in terms of conventional polarographic data with excess ligand present while Ringbom and Eriksson\(^{68}\) have derived equations applicable to polarographic data obtained in the presence of relatively low ligand concentrations. Watters and Mason\(^{69}\) have applied Leden's equations to systems of mixed complexes.


In the present studies, it was decided that an expression similar to one derived by Lingane\(^{70}\) be used for calculating the formula and formation constant, $K_f$, of complex metal ions using the shift of the half-wave potential due to the formation of metal ion complex.

\(^{70}\) J. Lingane, Chem. Revs., 29, 1 (1941).
The electrode reaction for the reduction of an aquo metal ion to the metallic state (amalgam) is

\[ M^{n+} + ne \rightleftharpoons M_{\text{am}} \quad (1) \]

Assuming the amalgam concentrations to be so dilute that the activity of free mercury is unchanged, the Nernst equation can be written in the form

\[ E = E_0 + S \log \frac{[M]_s f_m}{[M_{\text{am}}]_s f_{\text{am}}} \quad (2) \]

where \( E \) is the measured potential versus the standard hydrogen potential, \( E_0 \) is the standard potential for the electrode reaction of the aquo metal ion, \( S \) indicates 2.303 \( RT/nF \), \( f_m \) and \( f_{\text{am}} \) are the activity coefficient of the aquo metal ion in solution and free metal in the amalgam. Brackets indicate concentration. The subscripts \( s \) and \( b \) after the brackets indicate concentrations at the electrode surface and in the bulk of the solution or the bulk of the amalgam drop respectively. The subscript \( t \) as in \([M_t]\) indicates the total concentration of the metal in all forms.

For all solutions, measured at constant ionic strength, equation (2) can be modified to

\[ E = E'_0 + S \log \frac{[M]_s}{[M_{\text{am}}]_s} \quad (3) \]

where \( E'_0 = E_0 + S \log \frac{f_m}{f_{\text{am}}} \). If the concentration of the metal dissolved
in the amalgam remains constant, equation (3) can be reduced to

\[ E = E''_0 + S \log [M]_s \]  

(4)

where \( E''_0 = E'_0 + S \log [M_{am}]_s \).

The general expression for the equilibrium of the aquo metal ion with the trimetaphosphate ion, assuming only mononuclear complexes are formed, is

\[ M + iL \overset{\rightleftharpoons}{\longrightarrow} ML_i \]  

(5)

and the stepwise or overall complexity constant for the reaction is

\[ \beta_p = \frac{[ML_i]}{[M][L]} \]  

(6)

Considering all species containing metal, the conservation of metal may be expressed as

\[ [M_t]_s = \sum_{i=0}^{N} [ML_i]_s \]  

(7)

Substituting in complexity constants and factoring out \([M]_s\)

\[ [M_t]_s = [M]_s \sum_{i=0}^{N} \beta_i [L]^i \]  

(8)

Solving for \([M]_s\) in equation (8) and substituting for it in equation (4) yields

\[ E_c = E_o + S \log [M_t]_s - S \log \sum_{i=0}^{N} \beta_i [L]^i \]  

(9)
For a corresponding aquo solution with no complexing agents present

\[ E_a = E_o + S \log [M_i] \]  

Subtracting equation (9) from equation (10) gives

\[ \Delta E = (E_a - E_c) = S \log \frac{\sum_{i=0}^{N} \beta_i [L]^i}{[L]^i} \]  

If spontaneous potentials are measured, the current is zero. Then the concentrations of ligand at the surface of the drop and in the bulk of solution are equal.

\[ [L]_S = [L]_b \]  

Solving for S at 25°C and one atmosphere of pressure, and assuming [L]_b equals total ligand concentration, C_x, for excess ligand, equation (13) is obtained,

\[ \Delta E = \frac{0.0591}{n} \log \beta_p + p \frac{0.0591}{n} \log C_x \]  

where i equals p the number of ligands per central metal ion.

The potential of dropping amalgam electrode in equilibrium with the complex metal ion may also be expressed as

\[ E_c = E_o - S \log \beta_p - p \frac{0.0591}{n} \log C_x \]  

A plot of E_c versus log C_x should give a straight line with a slope equal to \(-p \frac{0.0591}{n}\). The value of p follows immediately from a knowledge of the number of electrons, n, involved in the electrode reaction. Plots of \(\log \frac{i_{de}}{i_{da}}\) versus E, the potential of the dropping
amalgam electrode at any point along the polarogram where the current is "i", should have a reciprocal slope of 0.0591/n if the electrode reaction is reversible.
Results and Discussion

In Figure 12 is shown typical anodic-cathodic polarograms of copper(II) in the solution containing no trimetaphosphate ion, at a pH of 3, and in solutions containing trimetaphosphate ion with a pH 5.2 ± 0.2. Polarograms of more acidic solutions of identical concentrations of copper(II) and trimetaphosphate have less potential shift in the polarographic waves due to complex formation. It is observed in Figure 12 that the entire waves are essentially reversible in acidic solutions having a pH less than 5.5. In the presence of a large excess of ligand, curves 5 and 6, the potential shift of the polarograms to more negative potentials due to complex formation, is small. The observed small potential shifts of the polarograms of solutions containing trimetaphosphate ion and copper(II) when compared with the polarogram for a solution containing only aquocopper(II) is an indication that the complexity constant is small.

A plot of \[ \log \frac{i_{dc} - i}{i - i_{da}} \] versus E in Figure 13 for polarograms 1, 3, 5, and 6 of Figure 12 gave reciprocal slopes of 0.032, 0.033, 0.035, and 0.036 volts respectively for curves 1, 2, 3, and 4. These reciprocal slope values agree reasonably well with the theoretical reciprocal slope values of 0.030 ± 0.001 volts for a two electron reaction at a dropping amalgam electrode. A half-wave potential of 0.025 versus SCE was in good agreement with the value of 0.022 volts obtained by Sturrock.64

An investigation of the influence of pH on the spontaneous potential of the dropping amalgam electrode in an aquocopper(II) solution
Figure 12. Anodic-Cathodic Polarograms of Copper (II) Ions in Various Concentrations of Trimetaphosphate Ion Using the Dropping Copper Amalgam Electrode.

Ionic strength of all solutions was adjusted to unity with tetramethylammonium nitrate at T=25 ± 1°C. Nitric acid and tetramethylammonium nitrate were used for pH adjustments.

\[ \text{Cu} = 2.082 \text{mM} \]

Methyl Red = 0.001%

Amalgam = 0.0005%

<table>
<thead>
<tr>
<th>Polarogram</th>
<th>[(\text{TMA})_3\text{P}_3\text{O}_9] mM</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarogram 1</td>
<td>0.000</td>
<td>3.040</td>
</tr>
<tr>
<td>Polarogram 2</td>
<td>1.226</td>
<td>5.510</td>
</tr>
<tr>
<td>Polarogram 3</td>
<td>1.635</td>
<td>5.427</td>
</tr>
<tr>
<td>Polarogram 4</td>
<td>2.044</td>
<td>5.347</td>
</tr>
<tr>
<td>Polarogram 5</td>
<td>8.008</td>
<td>5.139</td>
</tr>
<tr>
<td>Polarogram 6</td>
<td>24.02</td>
<td>5.160</td>
</tr>
</tbody>
</table>
had shown that the potential is nearly constant, ± 0.0002 volts in the pH interval of 2.9 to 3.2 and in agreement with earlier workers.\textsuperscript{63,64} Spontaneous potential measurement of the aquocopper(II) solutions were made in the above mentioned pH range. In more acidic solutions the potential became more negative due to the spontaneous solution of copper in the amalgam. At more alkaline pH's, the copper amalgam electrode is unstable in the absence of complexing agents due to the formation of deposits of cupric oxide on its surface.

In Table 6, the spontaneous potentials and concentrations of copper(II) and trimetaphosphate ion are listed with related data. The same amalgam was used for potential measurements given in parts A and B, but a different amalgam for potential measurements in part C. The spontaneous potentials of identical aquocopper(II) solutions listed in parts A and B and measured three days apart were in excellent agreement, ± 0.00006 volts. However, the spontaneous potential listed in part C of a third identical aquocopper(II) solution with a second amalgam differed by approximately 0.005 volts. This difference can be attributed to slightly different copper concentrations in the two amalgams.

It was observed that the spontaneous potential was nearly constant, ± 0.1 mV, for the aquocopper(II) solution for a period of 24 minutes during frequent measurements and the potential then decreased steadily.

In Figure 14, the plots of \(E_{sp}\) versus \(\log C_x\) are shown. Curves 1, 2, and 3 correspond respectively to the potential and concentration data for parts A, B, and C in Table 6. From equation (14), the slope of this plot is \(-p0.0591/n\). Since \(n\) is 2, \(p\), the number of trimetaphosphate ions per copper(II), was determined to be 1.
Figure 13. Slope Analysis of Anodic-Cathodic Polarograms of Copper (II) Ions in Various Concentrations of Trimetaphosphate Ion Using the Dropping Copper Amalgam Electrode.

The ionic strength of all solutions was maintained at unity with tetramethylammonium nitrate at $T=25 \pm 0.1^\circ C$. Tetramethylammonium hydroxide and nitric acid were used to adjust the pH.

$$CCu = 2.082 mM$$
$$\text{Methyl Red} = 0.001\%$$
$$\text{Amalgam} = 0.0005\%$$

<table>
<thead>
<tr>
<th>[(TMA)$_3$P$_3$O$_9$], mM</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve 1</td>
<td>0.000</td>
</tr>
<tr>
<td>Curve 2</td>
<td>1.635</td>
</tr>
<tr>
<td>Curve 3</td>
<td>8.008</td>
</tr>
<tr>
<td>Curve 4</td>
<td>24.02</td>
</tr>
</tbody>
</table>
Table 6. Potential Data of the Copper(II) Trimetaphosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>[Cu$^{2+}$]$_t$, mM</th>
<th>[(TMA)$_3$P$_3$O$_9$]$_t$, mM</th>
<th>$E_{sp}$ volts</th>
<th>ΔE volts</th>
<th>log C$_x$</th>
<th>log β$_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.867</td>
<td>0.832</td>
<td>0.00</td>
<td>.9782</td>
<td>0.1867</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.117</td>
<td>0.832</td>
<td>19.20</td>
<td>.9771</td>
<td>0.0944</td>
<td>0.00923</td>
<td>-1.7167</td>
</tr>
<tr>
<td>3.010</td>
<td>0.832</td>
<td>48.00</td>
<td>.9780</td>
<td>-0.00247</td>
<td>0.02114</td>
<td>-1.3188</td>
</tr>
<tr>
<td>3.125</td>
<td>0.832</td>
<td>96.00</td>
<td>.9784</td>
<td>-0.01150</td>
<td>0.03017</td>
<td>-1.0177</td>
</tr>
<tr>
<td>2.850</td>
<td>0.832</td>
<td>144.00</td>
<td>.9781</td>
<td>-0.02043</td>
<td>0.03910</td>
<td>-0.8416</td>
</tr>
</tbody>
</table>

Part B$^c$

<table>
<thead>
<tr>
<th>pH</th>
<th>[Cu$^{2+}$]$_t$, mM</th>
<th>[(TMA)$_3$P$_3$O$_9$]$_t$, mM</th>
<th>$E_{sp}$ volts</th>
<th>ΔE volts</th>
<th>log C$_x$</th>
<th>log β$_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.950</td>
<td>0.832</td>
<td>0.00</td>
<td>1.0000</td>
<td>0.01859</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.130</td>
<td>0.832</td>
<td>9.60</td>
<td>0.01484</td>
<td>0.00375</td>
<td>-2.0177</td>
<td>2.1444</td>
</tr>
<tr>
<td>3.225</td>
<td>0.832</td>
<td>28.80</td>
<td>0.00935</td>
<td>0.00924</td>
<td>-1.5406</td>
<td>1.8528</td>
</tr>
<tr>
<td>3.232</td>
<td>0.832</td>
<td>38.40</td>
<td>0.00556</td>
<td>0.01303</td>
<td>-1.4157</td>
<td>1.8559</td>
</tr>
<tr>
<td>3.091</td>
<td>0.832</td>
<td>60.20</td>
<td>-0.00067</td>
<td>0.01926</td>
<td>-1.2204</td>
<td>1.8711</td>
</tr>
</tbody>
</table>
Table 6. (cont'd)

<table>
<thead>
<tr>
<th>pH&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$[\text{Cu}^{2+}]_t$&lt;sup&gt;mM&lt;/sup&gt;</th>
<th>$[(\text{TMA})_3\text{P}_2\text{O}_9]_t$&lt;sup&gt;mM&lt;/sup&gt;</th>
<th>b</th>
<th>$E_{sp}$&lt;sup&gt;volts&lt;/sup&gt;</th>
<th>$\Delta E$&lt;sup&gt;volts&lt;/sup&gt;</th>
<th>log $C_x$</th>
<th>log $\beta_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.013</td>
<td>0.832</td>
<td>0.00</td>
<td>1.0000</td>
<td>0.01380&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.970</td>
<td>0.832</td>
<td>7.932</td>
<td>0.01034</td>
<td>0.00346</td>
<td>-2.1015</td>
<td>2.2176</td>
<td></td>
</tr>
<tr>
<td>2.991</td>
<td>0.832</td>
<td>15.86</td>
<td>0.00923</td>
<td>0.00457</td>
<td>-1.7996</td>
<td>1.9537</td>
<td></td>
</tr>
<tr>
<td>3.045</td>
<td>0.832</td>
<td>23.80</td>
<td>0.00598</td>
<td>0.00782</td>
<td>-1.6234</td>
<td>1.8875</td>
<td></td>
</tr>
<tr>
<td>3.075</td>
<td>0.832</td>
<td>31.73</td>
<td>0.00368</td>
<td>0.01012</td>
<td>-1.4985</td>
<td>1.8405</td>
<td></td>
</tr>
<tr>
<td>3.036</td>
<td>0.832</td>
<td>39.66</td>
<td>0.00194</td>
<td>0.01186</td>
<td>-1.4016</td>
<td>1.8024</td>
<td></td>
</tr>
<tr>
<td>3.004</td>
<td>0.832</td>
<td>47.59</td>
<td>-0.00016</td>
<td>0.01364</td>
<td>-1.3225</td>
<td>1.7834</td>
<td></td>
</tr>
<tr>
<td>3.037</td>
<td>0.832</td>
<td>55.52</td>
<td>-0.00199</td>
<td>0.01579</td>
<td>-1.2555</td>
<td>1.7885</td>
<td></td>
</tr>
<tr>
<td>3.055</td>
<td>0.832</td>
<td>79.32</td>
<td>-0.00725</td>
<td>0.02105</td>
<td>-1.1005</td>
<td>1.8115</td>
<td></td>
</tr>
</tbody>
</table>

av. = 1.939 ± .120

<sup>a</sup> pH adjusted with 2M nitric acid.

<sup>b</sup> Ionic strength, $\mu$, adjusted with tetramethylammonium nitrate.

<sup>c</sup> Same amalgam used for parts A and B, with new amalgam prepared for part C. Amalgam concentration for parts A, B, and C = 0.0005% C.
Figure 14. The Plot of $E_{sp}$ Versus SCE Against $- \log C_X$.

- Curve 1: Data listed in part A, Table 6.
- Curve 2: Data listed in part B, Table 6.
- Curve 3: Data listed in part C, Table 6.
Figure 14

Curves and slopes:

<table>
<thead>
<tr>
<th>Curve</th>
<th>Slope</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.0300</td>
<td>1.014</td>
</tr>
<tr>
<td>2</td>
<td>-0.0314</td>
<td>1.061</td>
</tr>
<tr>
<td>3</td>
<td>-0.0295</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Slope = \(-\frac{0.059l_p}{n}\)
The log of the complexity constant was calculated using equation (13). It was found to be $1.939 \pm 0.120$, and is in reasonable agreement with Indelli's value of $1.55^{52}$.

Even though the copper trimetaphosphate complex is weak, it could be used as an indicator ion for polarographic study of other metal ion complexes with trimetaphosphate ion.
List of References

List of References (cont'd)

23. Technicon Instrument Corp., Chauncey, N.Y.
List of References (cont'd)


45. Theilacker, W., Z. Krist., 76, 303 (1931); 90A, 51, 256 (1934).


47. Ruerwin, R.A., private communication, Monsanto Chemical Co., Dayton, Ohio.


List of References (cont'd)