

precipitate will quickly form. According to the equations of paper II, the relative amounts of chains having two or three phosphorus atoms apiece becomes quite large in glasses near $5\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5$. When this calculated composition is compared in Fig. 7 with the solubility data, it can be seen that a smooth curve connects the fraction of pyro- and tripolyphosphates theoretically present in the glass with the amounts of these phosphates precipitated from solution. In addition some study was made of the effect of phosphate glasses on the solubility of the crystalline phosphates. Although this work was abandoned because of its complexity, it also indicated that the above ideas are essentially correct. Thus the analytical results reported in Table I as well as the solubility data discussed here are found to agree reasonably well with the tripoly- and pyrophosphate content of the glasses computed from the Poisson distribution.

Acknowledgment.—Thanks are due to the Rumford Control Laboratory for carrying out the phosphorus pentoxide analyses used in this work. I also wish to thank Messrs. Albert Marshall, Raymond Copson and Bernard Starrs for their advice and constructive criticism.

Summary

The methods commonly used in the solubility fractionation of organic polymers have been applied to the separation of fractions from sodium phosphate glasses lying in the range between the meta and pyro compositions. The fractions were analyzed by *pH* titrations to find the ratio of the equivalents of total phosphorus to end-group phosphorus. Assuming that this ratio equals $1/2$ the average chain length of the polyphosphates making up each fraction, a chain length distribution curve could be plotted for each glass fractionated. These curves were found to agree satisfactorily with the chain length distributions discussed in the previous paper of this series.

The dissolution and solubility behavior of the various sodium phosphate glasses in water was also reported. According to the theoretical predictions, a minimum was found in the rate of dissolution near the $\text{Na}_2\text{O} \cdot 2\text{P}_2\text{O}_5$ composition. In addition it was found that precipitates consisting of mixtures of crystalline pyro- and tripolyphosphates were formed immediately upon the dissolution of glasses near the $5\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5$ composition.

RUMFORD, R. I.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RUMFORD CHEMICAL WORKS]

Structure and Properties of the Condensed Phosphates. IV. Complex Ion Formation in Polyphosphate Solutions

By JOHN R. VAN WAZER* AND DORIS A. CAMPANELLA

Very soon after the discovery¹ of the condensed phosphates, it was found that precipitates of metals other than the alkalis would redissolve in an excess of the alkali metal salts of certain condensed phosphoric acids,² which according to the conclusions reached in the earlier papers of this series we shall call polyphosphates. Before the turn of the century this phenomenon was ascribed³ to the formation of a relatively stable, soluble complex between the metal and the phosphate. This concept of complex formation is still in vogue.

Because of experimental difficulties, the complexes between the metals and the polyphosphates have not yet been defined in terms of a chemical formula⁴ and a dissociation constant. As the common cations, except those of the alkali metals, ammonia and the amines, form precipitates with

most of the phosphates, the available range of concentrations is quite restricted and many of the standard methods of studying complexes cannot be applied. Thus the work reported here is limited to two experimental methods based on polarographic and electrometric *pH* techniques, respectively.

Structure of Complexes

From consideration of the structure of chains of interlinked PO_4 tetrahedra, it appears that a chelate ring⁵ might be completed between any two adjacent PO_4 tetrahedra. We shall, therefore, find it convenient to advance the hypothesis that the strong complexing ability of the linear polyphosphates is due to the formation of chelate rings. Although it has been shown⁶ that the formal valence bond structures do not make major contributions to the over-all resonance in simple PO_4 groups, the chelate structures⁷ given

* Present address: Great Lakes Carbon Corporation, Morton Grove, Illinois.

(1) Clark, *Edinburgh J. of Sci.*, **7**, 298 (1827); Graham, *Phil. Trans.*, **123**, 253 (1833).

(2) Persoz, *Ann.*, **65**, 163 (1848); Rose, *Phil. Mag.*, **34**, 321 (1849); Scheerer, *J. prakt. Chem.*, **75**, 113 (1858).

(3) Tammann, *ibid.*, **45**, (Ser. 2), 417 (1892).

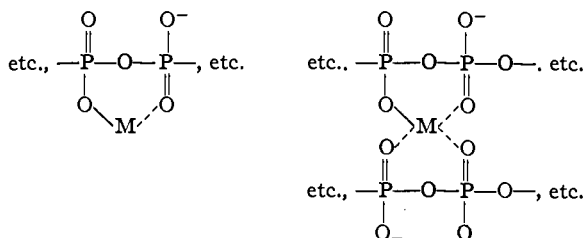
(4) However, some purely empirical formulas have been suggested: e. g., Chwala, "Textilhilfsmittel," Springer, Wien, 1939, p. 78 (reprinted by Edwards Bros., Ann Arbor, in 1943).

(5) Diehl, *Chem. Rev.*, **21**, 39 (1937); also Liebafsky, *J. Chem. Ed.*, **23**, 341 (1946).

(6) Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, pp. 239-250.

(7) As shown in the formula the metal, M, is monovalent; but polyvalent metals can also enter into similar structures. Furthermore, the number of phosphorus pairs connected to each metal atom will be determined by the relative concentrations of metal

below are based on the valence bond picture for the sake of simplicity



Because of the resonance requirements discussed in Paper I of this series, the formation of such a chelate ring at the end of a polyphosphate chain would cause the weak hydrogen atom to become strongly dissociated. This has been observed and forms the basis of a method, used in this paper, of determining the strength of the complex.

Metaphosphate compounds may or may not form a complex depending on the size of the metaphosphate ring. In certain metaphosphate rings it seems reasonable that neighboring PO_4 tetrahedra might be mechanically constrained from forming a chelate structure. This seems to be the case for NaPO_3 I, in which the trimetaphosphate ring⁸ is rather rigid.

The type of chelate structure suggested here is entirely different from the one advanced by Langmuir and Schaefer.⁹ These authors suggested that the complex formed between calcium and a phosphate glass has the form of a ring made up by attaching each end of a long polyphosphate chain to the calcium. They assumed that only the sodium atoms at the ends of the chain become ionized and predicted that pyrophosphates would not form complexes. These ideas are not in accord with the pH titration curves of phosphate glasses or the known complexing ability of pyrophosphate.

Polarographic Studies

Very soon after its invention, the polarographic method was employed¹⁰ in the study of pyrophosphato-metal complexes. However, because of the novelty and relative lack of knowledge of the method at that time the work was quite incomplete

and phosphate in solution, with the maximum number depending on the ratio of the ionic radius of the metal to that of oxygen. When the number of attached phosphorus pairs is small, the complex will tend to become insoluble and a precipitate may form. When more than one phosphorus pair is connected to a given metal atom, they may come, *a priori*, from the same or different polyphosphate chains. Although recent work [Her, *THIS JOURNAL*, **69**, 724 (1947)] on metallo-organic complexes indicates the preferred structures are those in which a single chain coils around a given metal atom so that several active groups from the one chain enter into the coordination field of the metal, the presence of a negative charge on each PO_4 group tends to keep the polyphosphate chains stretched out and hence inhibits the formation of polydentate structures.

(8) Proof that NaPO_3 I has the trimeta structure is furnished by the X-ray work of Caglioti, Giacomello and Bianchi, *Atti. accad. Italia Rend.*, **3**, Sec. 17, 781 (1942), and the chemical evidence of G. B. Hatch, U. S. Patent 2,365,190.

(9) Langmuir and Schaefer, *THIS JOURNAL*, **59**, 2400 (1937).

(10) Sartori, *Gazz. chim. ital.*, **64**, 3 (1934).

according to present day standards. In two recent papers¹¹ a polarograph was also used in an indirect study of barium phosphate precipitates.

Apparatus.—In all of the studies reported here, a manually adjusted polarograph was used¹² with the dropping electrode described by Lingane and Laitinen.¹³ In most cases a cell with a pool of mercury on the bottom as anode was employed. However, in the study of iron complexes it was necessary to use a cell with an external anode.¹³

The cells were thermostated in a large beaker which was adjusted to $25 \pm 1^\circ$. The potential of the anode pool was measured against a saturated calomel electrode and all reported potentials are corrected for that of the anode. The potential scale, absolute value of the current readings, and the dropping electrode were calibrated according to the procedures recommended by Kolthoff and Lingane,¹⁴ and all potentials are reported with respect to the saturated calomel electrode. Capillaries used for the dropping electrode were chosen so that the time for formation of a drop equaled 4 to 6 sec. under a pressure of *ca.* 20 cm. at zero applied potential.

In this paper we have used the theory of the reversible reduction of a complex metal ion to the amalgam at the dropping mercury cathode presented in Chapt. X of Kolthoff and Lingane.¹⁴ This reference together with the paper on complexes by Stackelberg and Freyhold¹⁵ form the basis of the following interpretation of the experimental data. In accord with the previously postulated hypothesis of complex formation, the concentration of the polyphosphate is measured in terms of pairs of phosphorus atoms regardless of the number of phosphorus atoms per molecule.

Polarography of Barium.—Complex ion formation causes the half-wave potential of a metal to shift to a more negative value. Therefore, complexes of alkali and alkaline earth metals are difficult to study because of the large negative value of their half-wave potential. Except for radium, barium has the least negative half-wave potential of the alkaline earth metals and hence was chosen for this work. In order to avoid the competitive action of sodium ion in forming a phosphate complex and to overcome the difficulties encountered by Campbell,¹¹ sodium ion was removed from the phosphate solutions by use of Amberlite ion-exchange resin. As it is desirable to have a relatively high concentration of complex forming substance, it was necessary to start with a solution that contained several atomic weights of phosphorus per liter and to avoid adding much water during ion exchange. The exchange was accomplished in the following manner:

To the concentrated phosphate solution the hydrogen form of the ion-exchange resin was added until no free liquid could be seen. The mixture was then allowed to stand for several minutes and the solution was filtered from the ion-exchange resin. This process of adding and then removing exchange resin was repeated approximately 20 times to give a solution containing *ca.* $\frac{1}{2}$ atomic weight of phosphorus per liter. The concentration of this solution was determined by titrating a portion after boiling. The acid from the exchange process was then neutralized with concentrated tetramethylammonium hydroxide. Adjustments of pH were made by varying the proportions of hydroxide and acid.

A polarographic experiment was usually carried out as follows. A sample of the tetramethylammonium phosphate solution, as prepared above, was put into the polarographic cell and a plot of current *vs.* voltage obtained. In the optimum case this polarogram would be almost identi-

(11) Campbell and Schenker, *THIS JOURNAL*, **67**, 767 (1945). Campbell, *ibid.*, **69**, 109 (1947).

(12) Fisher Electrode, mfd. by Fisher Scientific Co., Pittsburgh 19, Penna.

(13) Lingane and Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(14) Kolthoff and Lingane, "Polarography," Interscience Publ. Co., New York, N. Y., 1946, Chapters XIV and XV.

(15) Stackelberg and Freyhold, *Z. Elektrochem.*, **46** (3), 120 (1940).

cal to that of a supporting electrolyte of carefully purified tetramethylammonium bromide. However, there was usually a small wave, probably due to the presence of a trace of sodium. Then a small volume of barium chloride was added and the current-voltage curve again taken. If the sodium wave did not interfere too markedly with that of the barium, more barium was added to get a family of curves corresponding to a fixed amount of tetramethylammonium phosphate and various amounts of barium (see Fig. 1). When correction was made for the residual current, the diffusion current was always found to be proportional to the amount of barium added. Other families of curves were obtained for supporting electrolytes made of mixtures of the tetramethylammonium phosphate solution with 0.1 *N* tetramethylammonium bromide. Various ratios of bromide to phosphate were used. It is interesting to note that the measured half-wave potential of barium ion in pure 0.1 *N* $(\text{CH}_3)_4\text{NBr}$ was very close to that found by Zlotowski and Kolthoff.¹⁶ However, our polarographic waves for simple barium ion exhibited sharp maxima not reported by these authors.

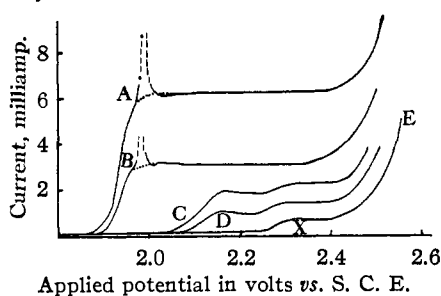


Fig. 1.—Polarographic waves of barium. The higher curves (A and B) are found for barium ion in a supporting electrolyte of 0.1 *N* tetramethylammonium bromide. The lower curves (C and D) are for barium in a supporting electrolyte made by neutralizing the acid corresponding to a sodium phosphate glass for which $\bar{n} = 5.0$ (at a concentration of 0.22 atomic weights of phosphorus per liter) with tetramethylammonium hydroxide to pH 7.0. Curve E is found for the pure tetramethylammonium polyphosphate supporting electrolyte. The wave marked X in curves C, D and E is probably due to a trace of sodium. Curve A, 1.0 millimole of Ba/l.; B, 0.5 millimole Ba/l.; C, 1.0 millimole Ba/l.; D, 0.5 millimole Ba/l.

The first series of measurements was made with the tetramethylammonium salt of the acid corresponding to a sodium phosphate glass¹⁷ having an average chain length of 5.0. Addition of the phosphate caused the diffusion current to decrease and the half-wave potential of the barium wave to shift to a more negative value. When $\log i/(i_d - i)$ ¹⁸ was plotted against $E_{d.e.}$ a straight line with a slope of 0.06 volt resulted. Since the theoretical slope for a reduction involving a two electron transfer is 0.029 v., the electrode reaction cannot be completely reversible. However, a measurement of the effects of temperature on the polarographic waves indicated that the overvoltage is probably not very great. The temperature coefficient of the half-wave potential was

(16) Zlotowski and Kolthoff, *THIS JOURNAL*, **66**, 1431 (1944).

(17) Quadrafos (reg. trade-mark) mfg. by Rumford Chemical Works.

(18) i is the current corresponding to the applied potential $E_{d.e.}$ and i_d is the constant value of the diffusion current obtained at more negative potentials.

found to be -0.9 mv. per deg., and the coefficient for the increase of diffusion current with temperature was *ca.* 2% per deg. Since both of these values are of the magnitude associated with reversible reactions, the data will be treated as if the reaction were reversible. An unquestionable test for reversibility was attempted by using barium amalgam instead of mercury in the dropping electrode. However, reaction of the amalgam with water overshadowed the normal electrode process.

By plotting (see Fig. 2) the half-wave potential as a function of phosphate concentration, the properties of the complex ion can be determined. From the slope of this curve, the coordination number of the most prevalent complex ion in the range of concentration studied is found to be 4, indicating that two phosphorus pairs form chelate rings with barium. Assuming complete reversibility, the dissociation constant for this complex ion is $10^{-9.5}$, based on mole concentrations of barium and pairs of phosphorus atoms. This value may be quite high because overvoltage was not taken into account in the calculation.

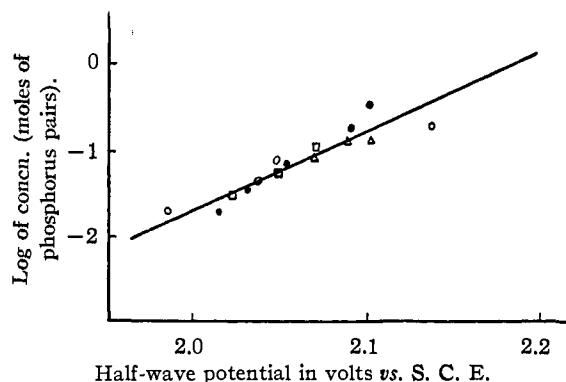


Fig. 2.—Variation of half-wave potential of barium in tetramethylammonium polyphosphate solutions made from a glass for which $\bar{n} = 5.0$. Each type of point in the graph corresponds to a given series of experiments.

Some added support is given to the complex structure in which barium has a coordination number of four by analysis of the diffusion coefficients determined polarographically. The experimental value of the diffusion coefficient of simple barium ion in aqueous solutions checks with that found by Zlotowski and Kolthoff and that calculated from conductivity data.¹⁹ When the phosphate was added to a solution of barium, the polarographic diffusion coefficient of the complex was found to be equal to 5.9×10^{-7} sq. cm./sec. It should be noted that this coefficient corresponds to free diffusion, since the presence of the supporting electrolyte diminished interionic effects. By using the Stokes-Einstein²⁰ equation with variously chosen shape factors²¹

(19) Fergusson and Vogel, *Phil. Mag.*, **4**, 233 (1927).

(20) Einstein, *Ann Physik*, [4] **17**, 549 (1905).

(21) Shape factors estimated from data by Kunkel, *J. Applied Phys.*, **19**, 1056 (1948).

to compute the volume and hence the molecular weight of the diffusing particle, we find that the molecular weight of the solvated complex probably lies between 10^3 and 10^5 . This large value can be accounted for by assuming that a barium links two of the phosphate molecule-ions together and that this takes place many times to form a loosely-knit macromolecule-ion. From the structure of the complex given above, formation of such assemblages appears reasonable.

As might be expected, the substitution of Graham's salt for the glass containing the short chain polyphosphates did not materially affect the polarographic results. The coordination number of the complex is again 4 and the dissociation constant, assuming complete reversibility, 10^{-10} . The electrode reaction is apparently slightly more irreversible than that found for the shorter chain polyphosphate complex; and the diffusion coefficient corresponds to a molecular weight between 10^3 and 10^7 .

In the alkaline range, variation of the pH was found to have an inappreciable effect on the polarographic waves. Attempts to investigate the effect of pH in the acid range using the compensation method²² for obviating the effects of the hydrogen wave were unsuccessful because of galvanometer oscillation. Very little effort was spent on trying to improve the compensatory circuit, since the ratio of the height of the hydrogen wave to that of the barium complex was impracticably large.

An attempt was made to study the pyrophosphato-barium complex, but the low solubility of both the sodium and barium salts of pyrophosphate as compared with those of the glassy phosphates, coupled with the rather large dilution that occurs during the removal of sodium, made the final solution too dilute for practical work. A precipitate was found to form on the addition of very small amounts of barium and, since the sodium had not been completely removed, the barium wave was overshadowed by that of sodium.

When phosphorus pentoxide or glasses containing more phosphorus than corresponds to the metaphosphate composition were used in the polarograph, a relatively high and misshapen wave concealed the barium wave. This result can probably be attributed to some easily reducible impurity present in the phosphorus pentoxide.

Polarography of Sodium.—The investigation was carried out in a manner identical to that used in studying the phosphato-barium complexes, except that sodium instead of barium was added to the condensed phosphoric acids from the ion-exchange process. The plot of $\log(i/i_a - i)$ vs. $E_{d.e.}$ was a straight line having the theoretical slope of 0.06 v. for the sodium wave in tetramethylammonium phosphate solutions made from the glass for which $\bar{n} = 5.0$, Graham's salt, or

(22) Ref. 14, p. 235.

sodium pyrophosphate. Therefore, the reduction is probably reversible. As would be expected for complex ion formation, the half-wave potential was found to shift to a more negative value as the phosphate concentration was increased. Analysis of the data leads to a coordination number of 2 for the complex and a dissociation constant = *ca.* 10^{-3} (based on mole concentrations of barium and phosphorus pairs). These values are not precise because interference from more easily reducible materials is difficult to avoid at the necessary high potential. Within experimental error the effects of polyphosphate anions from sodium phosphate glasses having average chain lengths of 75 and 5.0, as well as from crystalline sodium pyrophosphate, were the same when compared on the basis of equal phosphorus content.

The diffusion coefficients of the phosphato-sodium complexes are only slightly smaller than that of simple sodium ion.²³ This result is in accord with the concept that each sodium ion is bound to only one polyphosphate molecule-ion at a time, corresponding to a coordination number of 2.

Polarography of Other Metals.—A few preliminary studies were made on the polarographic behavior of some heavy metals in phosphate solutions. Cadmium and cupric copper gave very broad flat waves in solutions containing the sodium phosphate glass for which $\bar{n} = 5.0$, from which the sodium ion had not been removed. Work with these metals was suspended because interpretation in terms of complex ion formation is ostensibly impossible.

The polarographic behavior of iron in solutions of sodium phosphate glasses or sodium pyrophosphate was found to be somewhat similar to the behavior of iron in oxalate medium.²⁴ Sodium was not removed from the solutions as the experiments did not progress beyond the preliminary stage. When the phosphate concentration was increased, the ferric-ferrous wave as well as the ferrous-metallic iron wave moved to a more negative potential. Since the half-wave potential of either the anodic or cathodic waves corresponding to the ferric-ferrous couple in the phosphate solutions was the same, the reduction is reversible. Calculations based on the data indicate that the ferrous complex is considerably less stable than is the ferric complex. Both complexes have the same coordination number. The wave corresponding to the reduction of the ferrous complex to the metal was rather flat and quite irreproducible. Presumably, this reduction is very irreversible.

The most interesting feature of the polarographic study of iron was the fact that, as the pH of the phosphate solution was lowered, the half-wave potential of both reductions became

(23) Zlotowski and Kolthoff, *THIS JOURNAL*, **64**, 1297 (1942).

(24) Lingane, *ibid.*, **66**, 2449 (1946).

less negative. At a pH of 4 or less the polarographic waves in the presence of phosphate were nearly identical to those in the absence of phosphate. This behavior can be ascribed to the breakdown of complexes at the end of the polyphosphate chains due to the weakly ionized hydrogen.

Thallos ion is frequently used as a pilot ion²⁵ to establish the potential scale in polarographic analyses because it displays little tendency toward complex-ion formation. However, in solutions of a tetramethylammonium condensed phosphate, there is an appreciable shift of the half-wave potential to a more negative value. The pilot ion procedure is thus not applicable in the presence of condensed phosphates.

pH Studies

Since there are literature references²⁶ to the pronounced effect of alkaline-earth salts on the pH of polyphosphate solutions, the use of pH measurements as a method of studying complex formation seemed worthy of investigation. In this work the general scheme used by Schwarzenbach, Kampitsch and Steiner²⁷ in their study of the complexes of nitrilo-triacetic acid with metallic ions was followed.

Experimental Procedure.—Acids corresponding to several sodium phosphates were prepared by the use of an ion-exchange column as described in Paper I. Different amounts of standardized solutions of various nitrates or chlorides were then added to different portions of each acid, and electrometric titrations were carried out using 0.1 *N* tetramethylammonium hydroxide as base.

Data and Interpretation.—As is shown in Figs. 3 and 4, the shape of the pH titration curves of the polyphosphoric acids is greatly altered by the addition of a neutral salt. This observed strengthening of the weak acid function cannot, of course, be attributed to free acid in the added salt as this would cause a shift in one or both of the neutralization points. Since nearly identical titration curves were obtained upon the addition to a given phosphoric acid of equivalent amounts of salts of the same positive ion with different highly ionized anions (*e. g.*, curves C and D of Fig. 3), the effect also cannot be ascribed to the anion of the added salt. Rather it is caused by complex formation between the added metal ion and the phosphate, as is seen qualitatively in the curves of Fig. 5. As all of the titration curves were quite similar to those given in Figs. 3 and 4, data for the various metals can be intercompared in the simple graph of Fig. 5. It should be noted that some of the titration curves (*viz.*, ammonium and ferric ions) for which points are given were found to prematurely flatten off in the

(25) Ref. 14, p. 266.

(26) *E. g.*, Frankenthal, *THIS JOURNAL*, **66**, 2124 (1944).

(27) Schwarzenbach, Kampitsch and Steiner, *Helv. Chim. Acta*, **28**, 828 (1945).

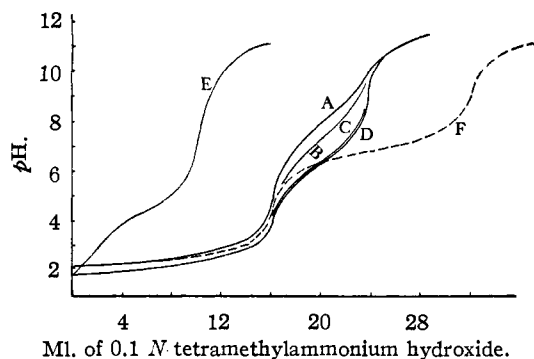


Fig. 3.—Effect of sodium ions on the titration curve of a dilute polyphosphoric acid made from a sodium phosphate glass for which $\bar{n} = 5.0$. Curve A resulted from titration of a pure acid. Curves B and D correspond to the addition of 5×10^{-3} and 4×10^{-2} mole of sodium chloride, while curve C corresponds to 4×10^{-2} mole of sodium nitrate. Curve E was found when the solution was saturated with sodium chloride so that some of the phosphate was salted out. Curve F resulted from titration of the orthophosphoric acid from complete hydrolysis of A.

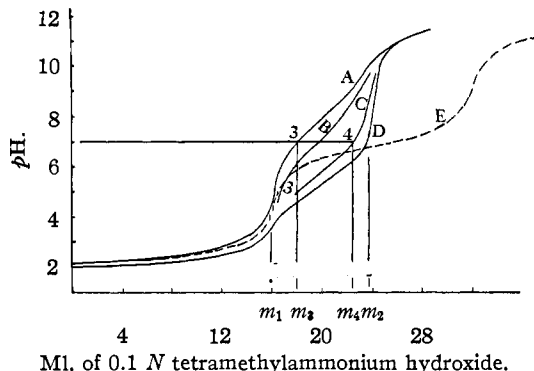


Fig. 4.—Effect of calcium on the titration curve of a dilute polyphosphoric acid made from a sodium phosphate glass for which $\bar{n} = 5.0$: Curve A corresponds to the pure acid and curves B, C and D to the addition of 1×10^{-4} , 6×10^{-4} and 1×10^{-3} mole of calcium chloride. Curve E is given for the hydrolyzed acid. (Lower 3 = 3'.)

high pH range either because of the weak basicity of the added cation or because of precipitate formation. When it appeared that this premature flattening extended back to the region where the weak acid was half neutralized and thus would affect the value of ΔpH , an arrow was appended to the appropriate point in Fig. 5 to indicate that the point is probably placed too high.

For the metal ions, the curves in Fig. 5 are S shaped as would be expected for a variable directly dependent on an equilibrium process. For the quaternary ammonium salts, which are not known or expected to form complexes, the slight slope of the curve can be attributed to a change in activity due to the interaction between charges.²⁸ From the curves of Fig. 5 it appears that the cations can be divided into three main

(28) Scatchard, *Chem. Rev.*, **19**, 309 (1936).

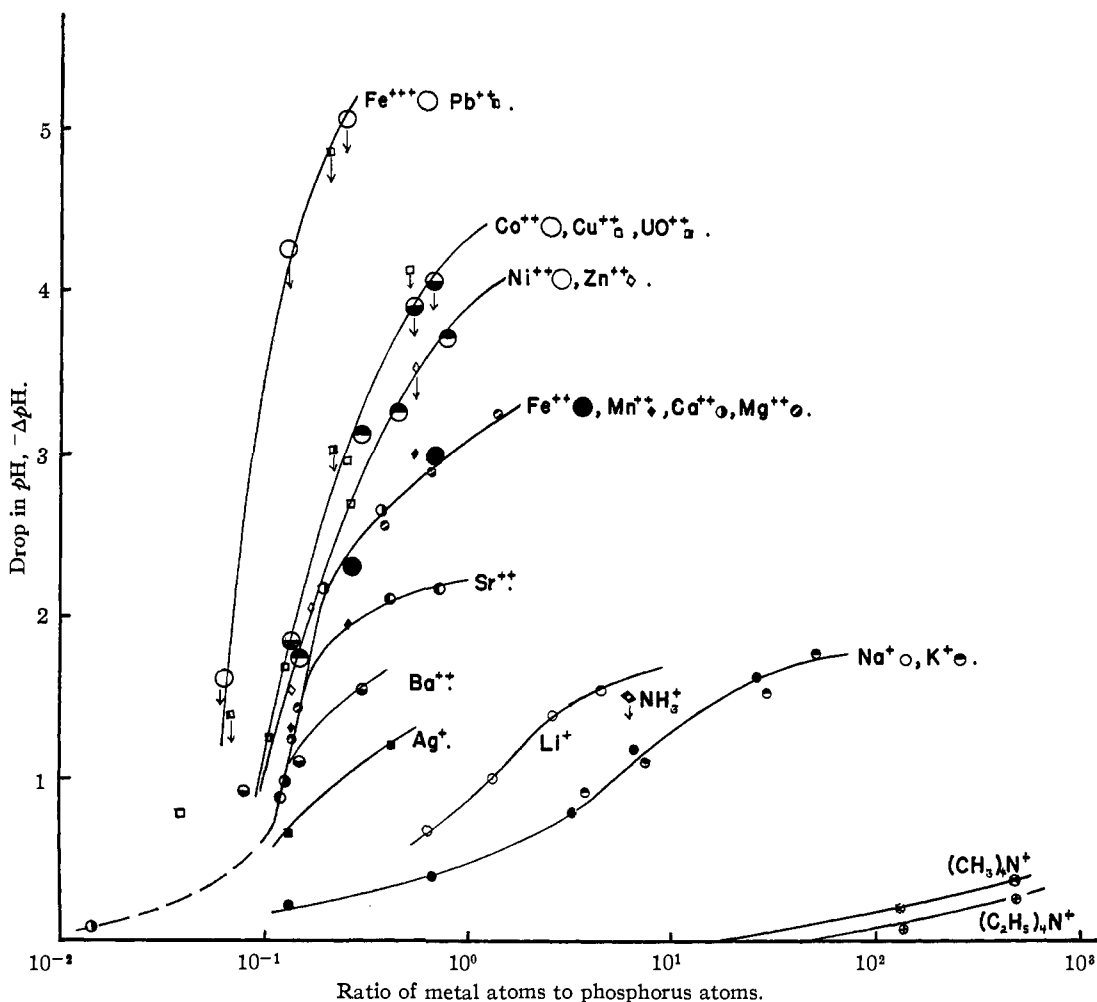


Fig. 5.—The effect of various salts on the pH of a polyphosphoric acid (from a sodium phosphate glass for which $\bar{n} = 5.0$) with the weak acid half neutralized and at a concentration of 15×10^{-4} atomic weights of phosphorus per liter.

classes: quaternary ammonium ions which form no complexes, alkali metals which form weak complexes, and the other metals, including the alkaline earth metals, which are strongly bound in phosphate complexes.

TABLE I
DISSOCIATION CONSTANTS FOR POLYPHOSPHATO-BARIUM
COMPLEXES FOR A COÖRDINATION NUMBER OF FOUR

Source of polyphosphate	Neg. log of dissocn. consts.
Sodium pyrophosphate	4.5
Sodium tripolyphosphate	4.5
Sodium phosphate glass for which $\bar{n} = 5.0$	5.5
Sodium phosphate glass for which $\bar{n} = 8.5$	6.0
Sodium phosphate glass for which $\bar{n} = 75$	6.5

As is shown in the Appendix, an equation relating the observed strengthening of the weak acid function to the dissociation constant of the complex can be derived with the use of several simplifying assumptions. This equation has been

applied to the data obtained by adding barium to solutions of various phosphates and it is found (see Table I) that the calculated dissociation constants do not depend much on the chain length of the polyphosphates although, of course, the relative amounts of base needed to go to the first and second neutralization points, respectively, and hence the general appearance of the titration curves is appreciably affected by chain length. In Table II the same data that were presented in Fig. 5 are given in terms of dissociation constants calculated on the assumption of a coördination number of 2, 4 and 6. The constants which were found to be practically independent of the concentration of the added salt over the available pH range have been underlined. These constants and the accompanying coördination numbers are presumably the correct values. When it was impossible to decide which constant was the least variable, more than one value is underlined. It should be noted that the logarithms of the

TABLE II
DISSOCIATION CONSTANTS OF THE COMPLEXES FORMED
BETWEEN VARIOUS METALS AND A POLYPHOSPHATE FOR
WHICH $\bar{n} = 5.0^a$

Metal (M)	Negative logarithm of dissoen. consts. assuming several coordination numbers		
	$p = 2$	$p = 4$	$p = 6$
Li	1.5	4.3	7.4
Na	1.3	4.0	6.6
K	0.7	3.5	6.0
NH ₄	1.0	3.5	6.5
Mg	3.2	6.0	9.5
Ca	3.0	6.0	9.0
Sr	2.8	4.5	8.5
Ba	3.0	5.5	8.5
Cu(II)	3.5	5.5	9.0
Ag	3.5	5.0	8.0
Zn	2.5	6.0	9.5
Pb(II)	3.0	5.5	10.0
Mn(II)	2.5	5.5	9.0
Fe(III)	3.5	6.5	10.0
Fe(II)	3.0	6.0	9.5
Co(II)	3.0	6.0	9.0
Ni(II)	3.0	6.5	10
UO ₂ (II)	3.0	6.0	9.5

^a Made from a sodium phosphate glass, Quadrafos (reg. trademark), mfg. by Rumford Chemical Works.

constants calculated for barium and sodium are approximately twice as large as the logarithms of the constants obtained polarographically. Although part of the difference in the case of barium is undoubtedly due to the polarographic overvoltage, probably the major source of error is to be found in the derivation of equation 8. The polarographic and *pH* methods are, however, in agreement as to the value of the coordination number.

Additional Notes

The work done in this Laboratory offers the first proof of the existence of phosphato-sodium complexes. The formation of a phosphato-sodium complex based on the interpretation of conductivity data using the Ostwald-Bredig rule was reported by Pascal.²⁹ However, this interpretation was based on the hexameta formulation of the sodium metaphosphate glass. According to our present knowledge of structure, the Ostwald-Bredig rule cannot be readily applied because of the complexity of the system. It is also worth noting that this rule is quite empirical and has fallen into disuse.

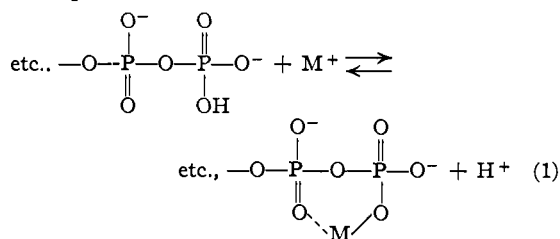
Both the polarographic and *pH* studies indicate that the complexing ability of a condensed phosphate is proportional to the total number of phosphorus atoms in the polyphosphates, regardless of chain length. This conclusion means that the segments of a polyphosphate chain can be treated independently. It may also be interpreted as a partial confirmation of the chelate-ring structure for the polyphosphato complexes advanced at the beginning of this paper.

(29) Pascal. *Compt. rend.*, **194**, 762 (1932).

This paper is only concerned with the formation of complexes in phosphate solutions. Therefore, the results reported here will usually not be directly applicable to industrial problems involving the use of the complex-forming phosphates. In most applications, the solubility of the precipitates formed between the polyvalent metals and the complex-forming phosphates as well as the dispersing action of the phosphates play an important rôle. In order to properly choose a phosphate for a given use, all of these interrelated properties must be considered.

Appendix

Derivation of *pH* Equation.—Since the weakly acid hydrogen comes from the terminal PO₄ groups of polyphosphate molecules, the only type of complex formation that can affect the strength of the weak acid function must involve these terminal groups. Using formal valence bond structures, we can set up the following chemical equation for this process. In the example shown in equation 1 the coordination number of the metal is 2; naturally, it can be a multiple of this number.



If we let θ stand for terminal pairs of adjoining PO₄ groups, the dissociation constant of the complex shown in equation 1 is

$$K_0 = \frac{(A_\theta)^{p/2} A_{M^{n+}}}{A_{\text{complex}}} \quad \text{for } p/2 \leq n \quad (2)$$

where p is the coordination number of the metal M, which has a positive valence equal to n . A is the symbol for activities.

In addition we must remember that there is an ionization constant for the end-group hydrogen

$$K_1 = A_{\text{H}^+} A_\theta / A_{\text{H}\theta} \quad (3)$$

Now let us assume that the pure polyphosphoric acid was titrated to, let us say, point 3 on curve A of Fig. 4. Then let enough Mⁿ⁺ ion be added to lower the *pH* to point 3' on curve C and follow this with an addition of base sufficient to raise the *pH* to its original value (point 4 on curve C). At points 3 and 4, A_{H⁺} is fixed and thus, according to equation 3, A_{Hθ}/A_θ is a constant which we shall designate by κ . From the titration curve of the pure acid, we find that

$$\kappa \approx \frac{m_2 - m_3}{m_3 - m_1}$$

And at point 4 of Fig. 4

$$A_\theta \approx [\theta] = \frac{m_2 - m_4}{V\kappa} = \frac{1}{V} \left(\frac{m_2 - m_4}{m_2 - m_3} \right) (m_3 - m_1) \quad (4)$$

where m_x is the total number of moles of base added to the solution to go to point X on the titration curve, and V is the volume of the solution. As other more serious approximations appear in this derivation, concentrations³⁰ are used in place of activities.

The amount of θ used up to form the complexes at the ends of the polyphosphate chains is therefore

$$1/V \left\{ (m_3 - m_1) - \frac{m_2 - m_4}{m_2 - m_3} (m_3 - m_1) \right\}$$

Thus, generalizing for any coördination number, p , this becomes

$$[\text{End complexes}] = (2/pV)(m_3 - m_1) \left(1 - \frac{m_2 - m_4}{m_2 - m_3} \right) \quad (5)$$

For purposes of discussion, the amount of M that is involved in complex formation can be divided into two classes, that releasing hydrogen ion and thus on an end of a chain, and that in the middle of a polyphosphate chain. By definition, we shall let m_M be the total number of moles of M , both free and complexed. Moreover, m_1 = the total number of moles of phosphorus atoms; and $m_2 - m_1$ = the total number of terminal phosphorus atoms. The average chain length is thus $2m_1/(m_2 - m_1)$. The number of positions along the chain where a metal ion can form a complex are one less than the chain length. Moreover, only the formation of a complex at the two end positions results in hydrogen ion liberation. Therefore, the fraction of the metal held in complexes which result in hydrogen ion liberation is

$$\frac{2}{(\text{chain length}) - 1} = 2 \left(\frac{m_2 - m_1}{3m_1 - m_2} \right)$$

Now we can say that, since m_M is the sum of the simple metal ion plus the metal held in complexes both at the middle and the ends of the chain

$$\frac{m_M}{V} = [M^{n+}] + \frac{[\text{End complexes}]}{2 \left(\frac{m_2 - m_1}{3m_1 - m_2} \right)} \quad (6)$$

From equations 5 and 6 we see that

$$[M^{n+}] = \left\{ m_M - \frac{1}{2n} \left(\frac{3m_1 - m_2}{m_2 - m_1} \right) (m_3 - m_1) \left(1 - \frac{m_2 - m_4}{m_2 - m_3} \right) \right\} \frac{1}{V} \quad (7)$$

Substitution from equations 4, 5 and 7 in equation 2 gives an expression for the dissociation constant for complexes formed at the ends of polyphosphate chains. Assuming that the same dissociation constant can be used for complexes at the middle or ends of a chain, this equation is a general statement of the dissociation constant

(30) The usual formality of denoting concentration of a substance by enclosing the name or symbol of the substance in square brackets is followed here.

in terms of the experimental variables measured in a titration curve.

$$K_s = \frac{\left\{ m_M - \left(\frac{m_3 - m_1}{p} \right) \left(\frac{3m_1 - m_2}{m_2 - m_1} \right) \left(1 - \frac{m_2 - m_4}{m_2 - m_3} \right) \right\} \left\{ (m_3 - m_1) \left(\frac{m_2 - m_4}{m_2 - m_3} \right) \right\}^{p/2}}{\left\{ V^{p/2} (2/p) (m_3 - m_1) \left(1 - \frac{m_2 - m_4}{m_2 - m_3} \right) \right\}} \quad (8)$$

The above calculations are based on several assumptions: (a) that concentrations can be used in place of activities; (b) that complexes have an equal probability of forming anywhere along a polyphosphate chain; (c) that a complex at one part of a chain is unaffected by complexes at other parts of the same chain; (d) that both ends of the chain are equivalent; and (e) that the chains are sufficiently long so that the ends and middles can be treated separately. When we consider that, in addition to these serious simplifications, complexes with different coördination numbers will exist simultaneously and that mixtures of polyphosphoric acids are obtained from sodium phosphate glasses, it is apparent that the values of dissociation constants calculated from equation 8 will be very rough approximations. In using equation 8, it is necessary to try various values of the coördination number, p , and hope that the constancy of the calculated dissociation constants will indicate the correct value of p .

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Summary

A concept of the structure of complex ions formed with metals in solutions of condensed phosphates is presented, and the results of the experimental investigations of phosphato-complexes are interpreted according to it.

Polarographic studies were made on solutions of some metal ions in a supporting electrolyte containing the tetramethylammonium salt of the acids obtained from several condensed phosphates. From this work it is shown that the coördination number of barium is 4 and that of sodium is 2 in the complexes formed with polyphosphates at the concentrations studied. Dissociation constants for the complexes were also evaluated and were found to be quite independent of the polyphosphate chain length. The sodium reduction appeared to be completely reversible, but the barium reduction was somewhat irreversible. Hence the dissociation constant for the barium complex may be larger than calculated.

In addition, the effect of metal ions on the pH titration curves of the polyphosphoric acids was discussed and it was shown that the cations could be divided into the following groups based on their

ability to form complexes with the polyphosphates (1) quaternary ammonium ions, which form no complexes; (2) alkali metal and similar cations, which form weak complexes; and (3) the other

metal ions which form strong complexes. The pH titration data was also discussed in terms of dissociation constants.

RUMFORD, R. I.

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Polarography in Liquid Ammonia. III. The Mercury Pool Anode¹

BY H. A. LAITINEN AND C. E. SHOEMAKER²

In the first and second papers³ of this series, a mercury pool anode in a saturated solution of tetrabutylammonium iodide in liquid ammonia was used as the reference electrode for polarographic measurements. The potential of the anode was measured against a lead electrode in 0.1 *N* lead nitrate. Using the data of Pleskov and Monosson⁴ for the potential of the lead electrode with reference to the standard hydrogen electrode, it was possible to relate the polarographic data to the hydrogen electrode.

It is well known that in polarographic work in aqueous solution, the mercury pool anode potential is markedly affected by the nature and concentration of substances which form insoluble salts or stable complex ions with mercurous or mercuric ions.⁵ In the absence of such depolarizing substances, the anode potential is determined by the concentration of mercurous ion formed as the oxidation product of mercury at the anode surface. It was of interest to determine whether mercurous or mercuric salts are formed by anodic dissolution of mercury in liquid ammonia, and to investigate various anions as possible anodic depolarizers.

There is some evidence that mercurous ions disproportionate in liquid ammonia to give mercury and mercuric ions. For example, mercurous chloride,^{6a} iodide^{6b} and nitrite^{6c} have been reported to react and darken in liquid ammonia. Various mercuric salts, such as the iodide,^{7a} bromide,^{7b,c} nitrate,^{7d} cyanide,^{6c} cyanate^{7e} and thiocyanate^{7e} are soluble while the sulfate,^{7d}

metaborate^{7f} and various base salts^{7b,c,d} are insoluble. The fact that ammonobasic salts are generally precipitated in solutions containing amide ion is concordant with the large shift of anode potential previously observed upon the addition of sodamide.⁸ Of the common anions, only the sulfate ion would appear to be useful as an anodic depolarizer for polarographic work. Unfortunately, its use is precluded by the insolubility of all of its common salts, including even ammonium sulfate.

To determine whether a reversible oxidation of mercury occurs at a dropping mercury anode, a determination of the slope of the anodic current-voltage curve would be desirable. Thus Koltzoff and Miller⁸ showed that in water solution mercurous ions are reversibly produced at the anode in the absence of depolarizing ions. In the present work, it was found that a reliable value for the slope of the anodic curve could not be obtained using a single compartment cell with saturated tetrabutylammonium iodide as the electrolyte, because of the absence of a cathodic depolarizer for the mercury pool.

Therefore, the anodic oxidation product of mercury was prepared by electrolysis in a divided cell, and identified by chemical tests to be the mercuric ion. A cathodic current-voltage curve of the solution in the anode compartment established the reversible behavior of the mercury-mercuric ion electrode.

To determine variations in the potential of a mercury pool anode, it was convenient to employ the thallos ion as a "pilot ion" as is commonly done in aqueous solution.⁹ The reduction of thallos ion was shown to be reversible, and therefore its half-wave potential served as a convenient reference point for potential measurements.

Experimental

The apparatus differed in several details from that described previously.³ A drawing of the single-compartment cell is shown in Fig. 1. A side arm attached to the top part of the cell provided space for open sample capsules with sealed-in pieces of soft iron wire. The capsules, supported by means of Alnico magnets, could be added in sequence to the sealed cells by removing the magnets.

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