METAL COMPLEXING BY PHOSPHATES

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I. INTRODUCTION

The ability of chain phosphates to form soluble complexes with metal ions has been recognized for more than a century. Shortly after the discovery that there were several kinds of phosphates (9, 26, 41), it was found (77, 86, 95) that some of the chain phosphates had the ability to prevent precipitation or to redissolve precipitates of the alkaline earth metals. Towards the end of the nineteenth century, this phenomenon was ascribed (108) to the formation of relatively stable soluble complexes between the metal and the phosphate. The concept of the formation of a soluble complex—whether by strong ion association or covalent bonding—has been used to the present day for interpreting various chemical anomalies found in phosphate solutions. It appears that this representation of the phenomenon will remain popular for many years to come.

The pronounced complexing action of the chain phosphates was an obscure piece of information of little interest to either science or applied technology until the mid 1930's, when Hall (48) applied this effect to the softening of water. After this, considerable emphasis was placed on the study of polyphosphato complexes in a number of industrial laboratories, primarily in the United States and Germany. This led to a resurgence of interest in these complexes in academic circles—a resurgence which has been reinforced during the last few years by the now common knowledge (21) that long-chain phosphates are typical polyelectrolytes.

The phosphate family of compounds is a very large one (114, 119). By definition, the phosphates are those structures in which the anions consist of PO_4 tetrahedra which may be linked together by the sharing of corners. There is a continuous range of phosphates going from the orthophosphate to pure P_2O_5 (which can be considered as a limiting phosphate even though it is not ionized). The simplest phosphate corresponds to the isolated PO_4^{3-} ion, which is called the orthophosphate ion. Then there are the homologous series of chain and ring phosphates in which PO_4 groups are held together through P—O—P linkages. The orthophosphate can be considered to be the first member of the chain series, with the pyro- and tripolyphosphates being the second and third members, respectively. Esters of the chain phosphates play important roles in biology. Perhaps the best known of these esters are the adenosine mono-, di-, tri-, and tetraphosphates, which are derivatives of the ortho-, pyro-, tripoly-, and tetrapolyphosphates, respectively. The homologous series of chain phosphates extends up to members containing as many as a million phosphorus atoms per chain. The long-chain phosphates exhibit the metaphosphate composition.

Ring phosphates also have the metaphosphate composition. Two of these rings are well known and higher members of the ring series have been discovered only recently (121). The two well-known rings are the trimetaphosphate anion, $P_3O_9^{3-}$, which is based on a ring composed of three phosphorus atoms alternating with three oxygen atoms (a six-membered ring), and the tetrametaphosphate, $P_4O_{12}^{4-}$, which exhibits an eight-membered ring. Branched phosphates, which include all structures in which one or more PO_4 groups share oxygen atoms with three neighboring PO_4 groups, are not of much interest in solution chemistry because of their rapid hydrolysis to structures in which there are no branching points (78, 105, 116, 120). Branched phosphates will not be discussed further in this review.

A considerable amount of work on the complexing of metal ions has been carried out with the vitreous sodium phosphates. These sodium phosphate glasses consist of bell-shaped distributions of chain phosphates of varying lengths (122). The average chain length, as measured by the number-average number of phosphorus atoms per chain, ranges from 4.5 to ca. 18 for the commercial phosphate glasses. However, glasses prepared in the laboratory can range from 3 to ca. 300 phosphorus atoms per average chain.

II. EXPERIMENTAL METHODS

The experimental techniques which have been employed for the quantitative study of phosphate complexes are listed below:

1. Determination of the minimum amount of phosphate which will prevent precipitation of an insoluble metal salt (2, 15, 22, 25, 27, 30, 32, 36, 38, 42, 46, 49, 50, 51, 65, 76, 80, 87, 88, 99, 104, 111, 130).
2. Determination of the minimum amount of phosphate which will dissolve a precipitate (6, 28, 54, 73, 80, 99, 111, 134).

3. Determination of the amount of phosphate needed to give a stable soap foam in hard water (48, 51, 62, 70, 112, 130).
4. Bucking one complexing agent against another (58).
5. Acid-base titrations (15, 17, 60, 67, 68, 85, 100, 101, 118, 120, 126, 128).
6. Spectrophotometric measurements (6, 90, 124, 127, 129).
7. Ion-exchange studies (31, 39, 75, 90).
8. Conductivity and transference studies (15, 28, 42, 47, 54, 55, 63, 71, 72, 73, 74, 85, 96, 123, 125).
9. Electromotive force measurements, including polarography (18, 23, 35, 36, 44, 59, 83, 85, 93, 97, 102, 118, 125).
10. Ultracentrifuge measurements (64).
11. Miscellaneous physical measurements, including magnetic susceptibility, electrophoretic, thermometric, cryoscopic, and nuclear magnetic resonance studies (e.g., 19, 20, 47, 106, 133).

In this review, the more interesting work on the complexing action of the phosphates is covered in detail. References are also given to a number of other papers. In Section V an attempt has been made to correlate the reliable information into a set of self-consistent answers as to the stoichiometry, stability, and type of bonding in the complexes of various chain and ring phosphates with divers metals.

It should be noted at the very beginning that the chain phosphates are relatively strong complexing agents, the ring phosphates are much less efficacious, and the orthophosphate is a poor complexing agent. Indeed for the alkaline earth metals, the orthophosphate ion is a good precipitant with negligible complexing ability.

III. Complexing by Orthophosphates

The complexing action of orthophosphate on the transition metals, particularly as applied to analytical chemistry, has been recognized for many years. As early as 1882 the decolorizing action of orthophosphoric acid on the ferric ion was utilized in analytical procedures (82, 132). The role of soluble complexes of iron with orthophosphate in analytical chemistry has been discussed by Kolthoff and Sandell (57).

Orthophosphoric acid is commonly used as an acidulant in food products, such as soft drinks, jams, and jellies. In these applications the orthophosphoric acid not only contributes an enjoyable tart flavor but also complexes traces of iron, thereby preventing dulling of the colors of the naturally occurring vegetable dyes.

Salmon (89) points out that the following evidence exists for the formation of soluble complexes between ferric ion and orthophosphoric acid: (*1*) orthophosphoric acid decolorizes solutions of ferric chloride; (*2*) the oxidation potential of the ferrous–ferric system is lowered in the presence of orthophosphoric acid (24); (*3*) the reversible oxidation of ferrous ion by iodine goes to completion in the presence of orthophosphoric acid (16); and (*4*) orthophosphates interfere in the colorimetric determination of ferric ion by thiocyanates. The movement of iron to the anode in transference measurements on solutions of ferric salts in excess orthophosphoric acid is also strong evidence for the existence of anionic orthophosphato-ferrate complexes (3).

There are several differing views on the exact nature of the complexes formed. Various investigators report that the complexes are $[Fe(PO_4)_2]^{3-}$ and $[Fe(PO_4)_3]^{6-}$ (131), $[FeHPO_4]^+$ (61), $[FeH_2PO_4]^{2+}$ (53), and $[Fe(PO_4)Cl_3]^{3-}$ in the presence of chloride ions (29, 84). On the other hand, Bonner and Romeyn (16) think that the complex (or complexes) can not be stoichiometrically formulated. Salmon (89) found that iron can be removed from ferric orthophosphate solutions by using either cation-exchange or anion-exchange resins. Batch experiments with the orthophosphate form of an anion-exchange resin indicated the presence in solution of a complex containing three orthophosphate groups per iron atom. Banerjee (5) points out that both $[Fe(HPO_4)]^+$ and $[Fe(HPO_4)_2]^-$ are indicated by breaks in the conductometric titration curves of phosphoric acid with ferric chloride. The relative stability of the ferric complexes of orthophosphate as compared with other anions was studied by Thomas and Gantz (110), using spectral measurements.

Several salts of the orthophosphato-ferric acids have been isolated (4, 91, 131) in crystalline form. The anions corresponding to these salts were formulated as $[Fe(PO_4)_2]^{3-}$ and $[Fe(PO_4)_3]^{6-}$. The phase diagram for the system ferric iron–phosphoric acid–water has been worked out in part (4). Like iron, aluminum forms complexes in orthophosphoric acid (24, 53). The dissociation constants of the complexes of aluminum with the orthophosphate ion have been reported in terms of several assumed formulas for the complexes (12).

The probable existence of complexes of orthophosphate with cobalt (34), copper (69), and silver ions (92) have been reported. The thorium (135), plutonium (56), and uranium (33) orthophosphate complexes have also been examined.

Considerable work has been done in recent years on orthophosphate complexes of the alkaline earth metals. The first reliable measurements reported for a magnesium complex having an assumed uncharged 1:1 formula of $MgHPO_4$ gave negative logarithms of the dissociation constant, pK_D, equal to 1.53 (43, 113) and 1.43 (107). Similarly, a pK_D value of 1.89 was found for the calcium complex, $CaHPO_4$ (40, 43). In the latest study (100), orthophosphate complexes of magnesium, calcium, strontium, and manganous ions were also interpreted in terms of an uncharged $MHPO_4$ complex. The pK_D values were 1.88, 1.70, 1.52, and 2.58 for magnesium, calcium, strontium, and manganous ions, respectively, at 25°C. and an ionic strength of 0.2. Under the same conditions, creatine phosphate exhibits pK_D values of 1.30, 1.15, 1.08, and 2.04 for magnesium, calcium, strontium, and manganous ions, respectively. Similar data for adenosine monophosphate complexes are given in table 6. Both creatine phosphate and adenosine monophosphate are orthophosphate derivatives.

Sodium orthophosphate buffers are more acidic than the equivalent potassium orthophosphates under the same conditions. This effect may be as large as one pH unit. The most comprehensive study of this phenomenon has been interpreted in terms of osmotic and activity coefficients (94) rather than as complex formation. In a more recent paper (101), the pK_D values for the 1:1 complexes of the alkali metals by orthophosphate were found to be 0.72, 0.60, and 0.49 for lithium, sodium, and potassium ions, respectively, at 25°C. and an ionic strength of 0.2. Results for adenosine monophosphate (a monoester of orthophosphoric acid) are given in table 6.

IV. Complexing by Chain and Ring Phosphates

A. NEPHELOMETRIC TITRATIONS

1. Calcium sequestration values

Early quantitative studies (2, 25, 27, 32, 38, 46, 49, 50, 65, 76, 87, 88) of the metal complexes of chain phosphates dealt with the "calcium value" or "sequestering[1] ability" of the phosphates, i.e., the weight of the phosphate needed to prevent the precipitation of alkaline earth salts under allegedly practical conditions. One experimental technique commonly used is nephelometric measurement, either by visual or electrical means, of the amount of calcium which will form a barely discernible precipitate upon addition of a soluble calcium salt to a solution of the phosphate. Reports of such studies are still appearing in the scientific literature (e.g., 15), as well as in trade journals.

Extensive nephelometric measurements of the calcium-sequestering ability of a sodium phosphate glass (having an average chain length of ca. five phosphorus atoms) under a number of experimental conditions have been carried out in the laboratories of the Rumford Chemical Works, which manufactures the glassy sodium phosphate called Quadrafos®. Some of this information, obtained by adding a solution of calcium and magnesium ions to a solution of the phosphate, has been put (22) in the form of phase diagrams.

Examples of such diagrams for this phosphate glass in the presence of (A) trisodium orthophosphate and (B) sodium carbonate are reproduced in figure 1. The curved surfaces shown in this figure are the boundaries between turbid (region above surfaces) and clear solutions (region below). The hard water referred to in this figure and in figure 2 is a mixture of 60 moles of calcium chloride and 40 moles of magnesium sulfate in distilled water. The concentration of this synthetic hard water is given in terms of parts per million (or grains per gallon) of equivalent $CaCO_3$—determined by adding together the moles of calcium and magnesium and converting to the weight equivalent of calcium carbonate.

From the results of a number of such nephelometric measurements (e.g., 15) and from information obtained in practical field evaluations, operating curves have been developed (see, e.g., 14 and 103) to show the amount of chain

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[1] The term "sequestration" was introduced by Hall (48) to describe the process whereby ions such as Ca^{++} could remain *in solution* and yet act as if they were not there (or as if they were there in considerably lesser concentrations). Later extensions of the concept have tacitly broadened the term "sequestration" so that it now includes the combined complexing and dispersing action of the chain phosphates in practical water-softening and related applications.

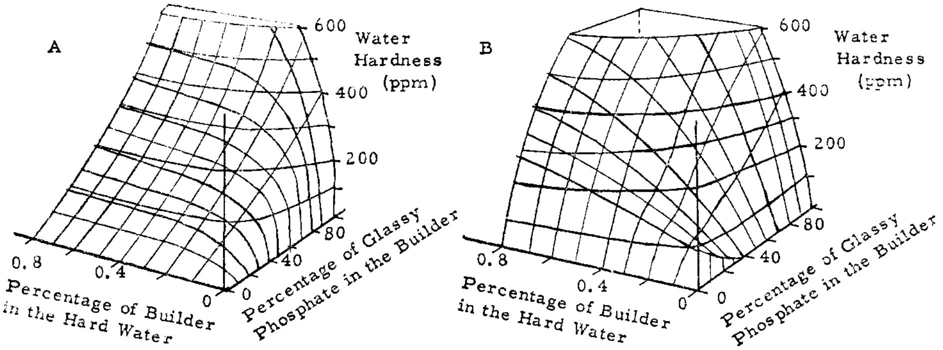

FIG. 1. Builder–hard water phase diagrams. In diagram A the builder is a mixture of a sodium phosphate glass, having an average chain length of five, with trisodium orthophosphate dodecahydrate (TSP), $Na_3PO_4 \cdot$ca. $0.2NaOH \cdot$ca. $12H_2O$. In diagram B the builder is a mixture of the same sodium phosphate glass with soda ash, Na_2CO_3.

phosphates needed to hold the calcium and magnesium in the hard water in soluble form, even in the presence of commonly used additives (such as soda ash) which normally would form precipitates. In figure 2, typical operating curves give the amounts of chain phosphates usually employed in softening hard waters at room temperature. The phosphate levels recommended in these curves are somewhat higher than the actual amounts determined from most of the nephelometric measurements, since it is desirable not to operate on the ragged edge of precipitate formation.[2]

Indiscriminate comparison of "calcium values" has led in the past to conflicting claims and practical recommendations, but careful checking of the data and procedures has pointed up the complexity of the systems involved. A number of variables including (*1*) the presence and the concentration of precipitating anions other than the chain phosphates, (*2*) the precipitable metal ions present, (*3*) the particular chain phosphate used and its concentration, (*4*) the pH, and (*5*) the concentration of neutral salts such as sodium chloride need to be carefully controlled. A thorough study of the calcium titration of phosphate solutions (22) has shown that there are also experimental problems in obtaining reproducible nephelometric endpoints. No matter how a solution

[2] It should be noted that such factors as the relative rate of dissolution of the components in a built detergent or water-softening composition may necessitate the use of more sequestrant than indicated by figures 1 and 2, or allow less to be used. In one case, a product which was formulated so as to give a clear solution in 300 p.p.m. water was found to produce unwanted precipitation in 200 p.p.m. water. This was finally traced to the too rapid dissolution of finely powdered trisodium orthophosphate and silicate which formed a slowly dissolving, gummy precipitate with the hard water before the sequestering phosphate had time to dissolve. The problem was solved by blending together more uniform granulations and using 10 per cent more of a more rapidly dissolving chain phosphate in the manufacture of the product.

Appreciable concentrations of anions (such as fluoride or oxalate) which form very insoluble precipitates with calcium or magnesium ions (see table 3) demand the use of more phosphate than indicated in figure 2.

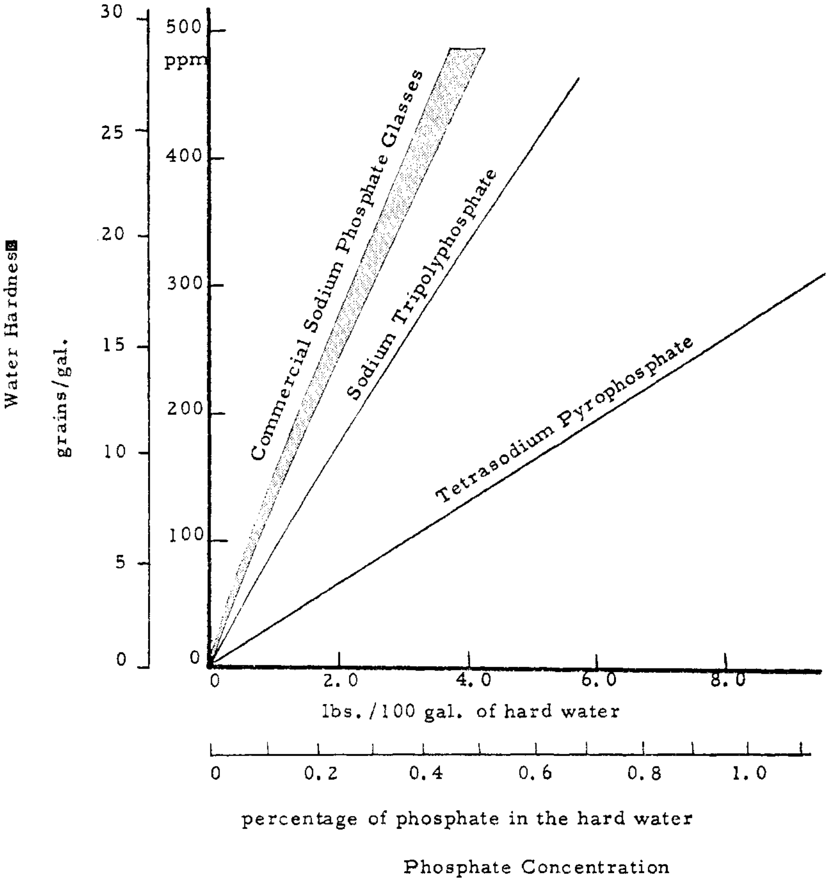

FIG. 2. Practical amounts of commercially available chain phosphates used in softening of hard water at room temperature.

of a calcium salt is added to the phosphate, a small amount of precipitate forms because of local excess concentrations. This precipitate dissolves rapidly at the beginning of the experiment but much more slowly as the endpoint is reached. In addition, the particle size of the suspended precipitate may undergo continual change; indeed it has been observed (22) that the intensity of scattered light, following the formation of a small amount of calcium phosphate precipitate, changes slowly and continuously with time—increasing under some conditions and decreasing under other conditions.

2. Sequestration of metal ions other than calcium

Because of the use of the condensed phosphates in water softening, there has been some work on comparing the sequestration of calcium ion with that of magnesium ion. Generally the chain phosphates are many times more effective in sequestering magnesium ion than calcium ion. Also, the pyrophosphate

TABLE 1

Sequestration data from titration to a turbidimetric endpoint
No adjustment of pH and no added precipitant (15)

	Moles of Metal Ion Sequestered by 100 Moles of Phosphate			
	Mg^{++}	Ca^{++}	Cr^{+++}	Ba^{++}
Pyrophosphate	52	11	3.6	ca. 0
Tripolyphosphate	No precipitate	29	32	5.1

anion is said to be more effective than the tripolyphosphate which, in turn, is more effective than the glassy phosphates in magnesium sequestration (104). This alleged order of effectiveness is reversed in the case of calcium ion. Although only those tests in which the sequestering phosphate was the precipitatng agent or soap foams were used as indicator have been employed in comparing magnesium ion with calcium ion, it is usually assumed that about five to ten times the amount of magnesium as compared to calcium will be sequestered by a given phosphate. An example of the type of data obtained by comparing the various alkaline earth metal ions is shown in table 1 (15), in which it should be noted that higher "sequestering values" are obtained for the tripolyphosphate as compared to the pyrophosphate, in opposition to the statement made in the Westvaco bulletin (104).

There have been several studies (e.g., 99, 104, 111) of sequestration of iron by the chain phosphates. The data are difficult to interpret because of the extremely good peptizing action of the chain phosphates on precipitates of hydrated ferric oxide. However, it appears that the chain phosphates are at least several times less effective in holding iron in solution than in holding calcium in solution. In practice, when waters having high iron content are treated with chain phosphates, the resulting finely divided precipitates are well peptized and hence are usually completely harmless and "sequestered" in the practical sense. The inability of the chain phosphates to prevent precipitation of hydrated ferric oxide in basic media is probably attributable to the great insolubility of the precipitate rather than to weakness of the soluble complex. The existence of a polyphosphato-ferric complex is simply demonstrated by chain-phosphate decolorization of ferric chloride solutions and by the prevention or dissolution of the blue color (Turnbull's or Prussian blue) obtained by combining ferric with ferrocyanide ions or ferrous with ferricyanide ions.

3. Interpretation of sequestration data

Some typical calcium values, both with and without an added precipitating anion, are shown in table 2 (22). The values obtained with only the phosphate in the solution vary considerably from one phosphate to another. Such values obviously depend on two quantities: (*1*) the complexing ability of the phosphate, working against (*2*) the insolubility of its precipitate. A much more logical test for comparing the sequestering abilities of the phosphates consists in determining the amount of calcium ion necessary to form a barely discernible precipitate in a solution in which (*1*) there is a given excess of an anion forming

TABLE 2

*Typical calcium values for various phosphates obtained from titrations with 0.1 M calcium chloride to a barely discernible precipitate**

Phosphate (0.01 to 0.05 *M* in Phosphorus)	Calcium Values in Moles of Calcium Ion Per 100 Moles of Phosphorus at pH = 8.0†	
	Condensed phosphate alone	Orthophosphate present (0.10 to 0.15 *M*)
Trimetaphosphate (ring compound)	>400	<1
Pyrophosphate	2.2 ± 0.5	2.8 ± 0.5
Tripolyphosphate	23 ± 1	12 ± 1
Sodium phosphate glass having an average chain length of 5	30 ± 4	16 ± 1
Sodium phosphate glass having an average chain length of 14	34 ± 4	13 ± 1
Sodium phosphate glass having an average chain length of ca. 75	33 ± 4	11 ± 3

* This information was obtained at the Rumford Chemical Works, Providence, Rhode Island.

† The pH was continuously controlled to ± 0.05 pH unit throughout the titrations by addition of small amounts of sodium hydroxide or hydrochloric acid as needed.

a more insoluble calcium precipitate than any of the phosphates, and (*2*) the pH and the concentration of the phosphate are fixed at a given value. The figures in the second column of table 2 represent such studies in which orthophosphate at pH 8 is the precipitating anion. Since the presence of orthophosphate in the pyrophosphate solutions did not lower the calcium value, it appears that the calcium precipitate with the pyrophosphate is more insoluble than the calcium precipitate with orthophosphate. The variations in calcium value with the size of the chain phosphates in the presence of orthophosphate are not large and indicate that, to a first approximation, the complexing ability is dependent on the number of moles of phosphorus present and is not a function of chain length. Furthermore, the data show that the variation in calcium values of the various phosphates as measured without another added precipitant is primarily due to differences in the solubilities of the calcium precipitates of the phosphates. It is also apparent that the trimetaphosphate anion does not appreciably prevent the precipitation of the calcium orthophosphate which forms at pH 8 (presumably $CaHPO_4 \cdot 2H_2O$) under the conditions of the test. That is to say, it is a poor sequestering agent.

The amount of calcium ion needed to form a barely discernible precipitate in a calcium titration must be dependent upon two competing equilibria, as shown below:

$$\begin{aligned} &\mathrm{Ca^{++}} + \text{chain phosphate molecule-anion} \\ &\qquad\qquad \rightleftharpoons \text{calcium complex of chain phosphate} \quad (1) \end{aligned}$$

$$\mathrm{Ca^{++}} + \text{precipitating anion}^{3} \rightleftharpoons \text{calcium precipitate} \quad (2)$$

Such a theory is based upon the assumptions that (*1*) the experimental methods minimize the dispersing action and colloid stabilization found in phosphate solutions and (*2*) the effects of counter-ions (such as sodium ion and chloride

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[3] The precipitating anion may be the chain phosphate molecule-anion and/or another anion which is a more effective precipitant.

TABLE 3

*Action of various anions on the calcium values of sodium phosphate glass**
(0.16 weight per cent solution of the glassy phosphate, having an average chain length of five phosphorus atoms)

Precipitating Anion Added as Sodium Salt	Controlled Value of pH	Assumed Composition of Precipitate	Solubility Product Used in the Calculations	Calculated Calcium-Ion Concentration in 1/10 *M* Anion Solution Over Precipitate ($\times 10^7$)	Calcium Value in Milliliters of Calcium Per 100 ml. P in the Presence of 1/10 *M* Anion
Fluoride	10.0	CaF_2	3.9×10^{-11}	0.04	1
Orthophosphate	11.5	$Ca_5(PO_4)_3(OH)$	1×10^{-25}	0.2	3
Oxalate	10.0	CaC_2O_4	2.27×10^{-9}	0.3	4
Carbonate	12.0	$CaCO_3$	4.82×10^{-9}	0.5	25
Metasilicate	12.0	$CaSiO_3$	6.6×10^{-7}	66	15
Orthophosphate	8.0	$CaHPO_4$	ca. 5×10^{-6}	500	20
Polyphosphate glass with Na_2O/P_2O_5 = ca. 1.3	10.0	Amorphous	—	(2000)	37
Sulfate	10.0	$CaSO_4$	2.4×10^{-5}	2400	42

* Information obtained from the Rumford Chemical Works, Providence, Rhode Island (22).

ion) are negligible. The latter assumption is, of course, only a rough approximation. This is shown by the fact that, when the measurements of table 2 were repeated in a system where all the sodium ion was substituted by tetramethylammonium ion, the observed values for calcium ion were considerably higher (22).

One would expect that calcium values would be reduced as precipitating anions forming more insoluble calcium salts are used, since equation 2 above would be shifted to the right. The effect of an excess of various anions which form insoluble salts with calcium on the calcium value of a sodium phosphate glass is shown in table 3. It is seen that, in every case except the carbonate, the observed calcium value increases in the expected manner with increasing calcium-ion concentration calculated from the solubility constants of the assumed precipitate. Presumably the real precipitate formed in the presence of carbonate is not calcium carbonate but is a more soluble mixed carbonate-phosphate corresponding to a calcium-ion concentration of ca. 1×10^{-4} moles per liter instead of the 5×10^{-8} moles per liter calculated for calcium carbonate under the experimental conditions. In a more thorough study of this type, the precipitates themselves should be examined chemically and by x-ray.

It is interesting to note that the calcium values are as much as severalfold higher when only a very small amount of the added precipitating anions is present and drop back to the expected values at the higher concentrations. This exhilaration of the calcium value is probably attributable to inhibition of crystal nucleation by the small amount of added anion so that the phenomenon is related to threshold treatment (115).

Spectrographic analyses and x-ray diffraction studies on precipitates formed in dilute systems containing calcium chloride and sodium tripolyphosphate have been reported (42). The boundary between homogeneous and heterogeneous regions at 60°C. for this system is shown in the graph of their data

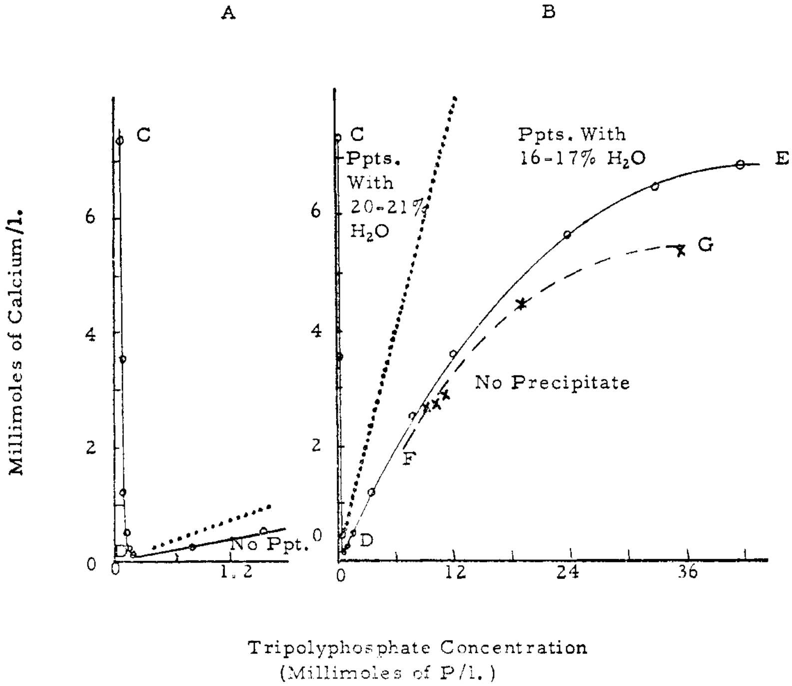


Fig. 3. Homogeneous and heterogeneous regions at 60°C. for the calcium tripolyphosphate system (42). The solid curve *CDE* was determined turbidimetrically; the dashed curve *FG* represents saturated solutions obtained from compositions in the heterogeneous region to right of the dotted line.

given in figure 3. The heterogeneous region is very wide and comes close to the calcium axis; so close, in fact, that this very narrow area of clear solution is generally overlooked in titrations of calcium with the phosphate. Semiquantitative spectrographic analyses of some of the precipitates along the right boundary of the heterogeneous region verified the presence of sodium. Most precipitates from compositions to the left of the dotted line in figure 3 were found to be amorphous to x-rays and in air-dried form to contain 20–21 per cent water, while those from compositions to the right of this line were crystalline and in air-dried form had 16–17 per cent water. Considerable variation was found in the composition of the precipitates in both regions, and it was found to be impossible to completely define the equilibrium phases. The calcium values corresponding to the right boundary of the heterogeneous region range from 33 moles of calcium per 100 moles of phosphorus near the origin to 16 moles of calcium per 100 moles of phosphorus at the highest concentrations studied. A calcium value of 33 corresponds to one tripolyphosphate molecule-ion per calcium ion.

An estimate of the dissociation constant of a soluble complex can be obtained from measurements of the solubility of a salt in a solution of the complexing anion. The concentration of free metal ion is obtained from the solubility product of the salt in pure water, and the calculation is based upon an assumption as to the ratio of metal to anion in the complex ion. The dissociation constant of the tripolyphosphato-calcium complex has been estimated in this way (42) from measurements of the clarification of calcium oxalate suspensions. Assuming a 1:1 calcium to tripolyphosphate complex as the species in solution, the negative logarithms of the dissociation constants, pK_D, were calculated to be 6.68 at 60°C. and 6.51 at 30°C. A similar treatment of the nephelometric data given in tables 2 and 3 is presented later in this paper.

Davies and Monk (28, 54, 73) estimated the dissociation constants of calcium and strontium complexes of trimeta- and tetrametaphosphate from measurements of the solubility of the respective metal iodates in the phosphate solution and in pure water. By assuming formulas for the complex, and calculating the concentration of free metal ion from the solubility of the iodate in pure water, dissociation constants for the assumed complexes were obtained. In these calculations (134), corrections were applied for association of ions other than the complex under study and theoretical activity coefficients were used. The average pK_D for the $(CaP_3O_9)^-$ complex was thus calculated to be 3.48 at concentrations of total metal ion of 9–13 $\times$ 10^{-3} moles per liter and for mole ratios of total phosphorus to total metal ranging from 1 to 5. The average value estimated for the $(SrP_3O_9)^-$ complex was 3.35 for similar concentrations. The pK_D's of $(CaP_4O_{12})^{2-}$ and $(SrP_4O_{12})^{2-}$ were estimated to be 5.32 and 5.15, respectively, also at concentrations and phosphorus-to-metal ratios in the range given above for the trimetaphosphate.

The existence of a pyrophosphato-copper complex has been inferred from the unusually high solubility of the salt $Na_6Cu(P_2O_7)_2 \cdot 16H_2O$ (6). The dark blue, well-formed crystals of this salt dissolve congruently to give a saturated solution containing 37 g. of $Na_6Cu(P_2O_7)_2$ per 100 g. of solution at 25°C. Most copper pyrophosphates (with or without alkali metals) are very light colored and essentially insoluble.

4. Soap tests

Other extensively used tests for the calcium-sequestering ability of the phosphates are: (*1*) titration of a calcium soap with the phosphate, using foam as the indicator (sometimes referred to as a calcium repression test) and (*2*) titration with a standard soap solution of water of known hardness treated with the phosphate. Again the appearance of a stable foam is the endpoint indicator (e.g., 48). This latter test, which is a modification of the American Public Health Association (APHA) water-hardness test (112), is particularly sensitive to elapsed times in the titration and to variation in pH (62). As with the calcium values measured in turbidity tests, the results have direct practical significance only to field conditions essentially identical with those of the test. This restriction holds true because of the importance of the relative rates of dissolution and the order of addition of the various components commonly used in combination with the chain phosphates in sequestering applications (136).

The modified APHA test mentioned above has been employed (62) to deter-

TABLE 4

Calcium-sequestering ability of sodium phosphates from soap tests at room temperature (62)*

	Moles of Calcium Sequestered by 100 Moles of Phosphorus		
	Initial water hardness = 75	150	300
	(Standard 60/40 Ca/Mg water)		
Chain phosphate:			
Tetrasodium pyrophosphate	3.6	3.8	4.2
Sodium tripolyphosphate	11.8	8.1	8.2
Sodium phosphate glass with an average chain length of 6	23.0	20.0	17.3

* The test is carried out as follows: Various amounts of the water-softening agent are added to 100-ml. portions of water of the desired hardness and temperature, followed by immediate titration with standard soap solution until a foam stable for 5 min. is obtained.

The amount of soap is plotted on the vertical axis of a graph in which the amount of softening agent is plotted horizontally. The intersection of this curve with a horizontal line representing the sum of the soap requirements for 1 grain per gallon hardness plus the "lather factor" of the soap gives the "sequestering value." The "lather factor" is the small amount of soap needed to give a stable foam in 100 ml. of distilled water.

mine the quantities of chain phosphates needed to soften water to an approximate "residual hardness" of one grain per gallon or 17 p.p.m. calcium carbonate (see table 4). Additional data obtained at 60°C. show the phosphates to be slightly more effective at the higher temperature. No pH control was used in these tests, however.

It is significant to note here that Huber (51), Hall (48), Partridge (76), and Campanella, Deckey, and Van Wazer (22, see table 2) report that sodium trimetaphosphate, the ring compound, is ineffective as a sequestrant in either a soap test or against precipitation of calcium ion by other anions. Because of these results, the ring phosphates have not been considered as sequestering agents. Since ring phosphates form relatively soluble salts with most of the cations which precipitate with the other phosphates, calcium values cannot be obtained for these substances without the use of another anion which will precipitate with calcium ion. They give calcium values close to zero in most sequestration tests.

B. TITRATIONS WITH ORGANIC CHELATING AGENTS

It is possible, in principle, to determine the dissociation constant of one complexing agent by pitting it against another complexing agent and measuring the relative amounts of metal ion complexed by each. A preliminary approach along these lines has been made by Kubias (58), who described a study in which the amount of hydrogen ion liberated by the reaction of an organic chelating agent, disodium nitrilotriacetate, $Na_2H[(OCOCH_2)_3N]$, with a solution containing calcium and a glassy chain phosphate was measured.

C. ACID-BASE TITRATIONS

There are two important inflection points in the pH titration curves of phosphates (120). One point lies near pH 4.5, and the other near pH 9.5. Titration of phosphoric acids to the endpoint near pH 4.5 gives the total number of phos-

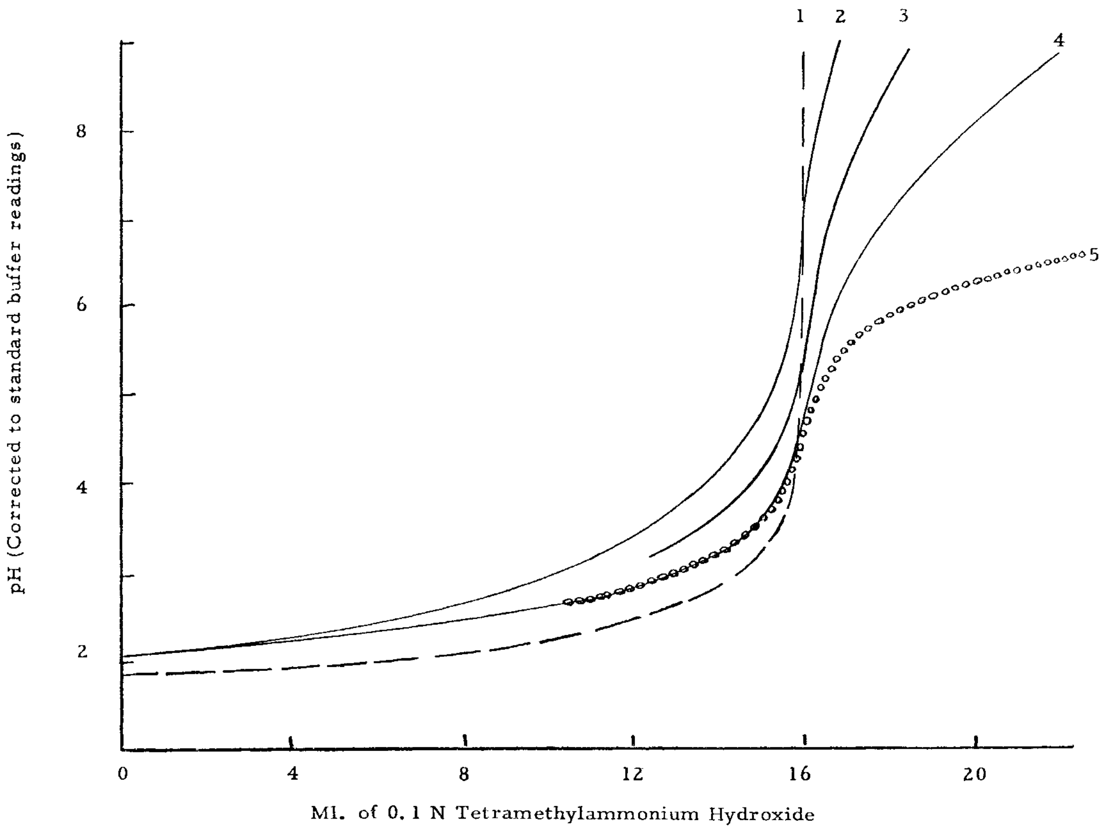


Fig. 4. pH titration curves of various condensed phosphoric acids. The acids corresponding to these curves are enumerated in the text.

phorus atoms, since there is one reasonably strong hydrogen for each phosphorus atom, whether the phosphorus is in a ring or a chain or in the isolated PO_4^{3-} (orthophosphate) ion. Titration between the endpoint pH 4.5 and 9.5 is a measure of the number of end groups present in chain phosphates plus the number of orthophosphates. There is a relatively weak hydrogen at each end of a phosphate chain, but middle PO_4 groups in either chains or rings do not have such weak hydrogens. The orthophosphate has a third replaceable hydrogen which is so very weak that an inflection point corresponding to it does not show up in a pH titration curve.

pH measurements have been very valuable in studying complexes of the chain and ring phosphates. pH titration curves of fresh solutions of various phosphoric acids are presented in figure 4 (120). The acids were made from sodium trimetaphosphate (curve 1) and from anhydrous sodium phosphate glasses having chain lengths of 20, 8.7, and 4 phosphorus atoms per chain (curves 2, 3, and 4, respectively). Curve 5 corresponds to orthophosphoric acid as formed by complete hydrolysis of the chain or ring. A comparison of the titration curve of trimetaphosphoric acid (ring compound) with that of acid from the metaphosphate glass (long-chain compound) exhibiting the same proximate analysis shows that molecular arrangement rather than chemical analysis determines the exact strength of the strong acid function. The longer the chain, the weaker is the strong acid function. It should be noted, however, that the curve (No. 2 in figure 4) for the longest-chain glass is not like that for a typical weak acid, since the line in the region near pH 2 is straight like that for a strong acid but in the pH 4–6 region it is highly curved like that for a weak acid. This can be interpreted by saying that the hydrogen atoms in the pure acid are not more firmly bound than they would be in relatively strong acids ($pK \approx 2$) such as $H(H_2PO_4)$ but that in the neutral pH range the hydrogens are bound about as firmly as in an acid for which pK is ca. 6. This kind of titration curve is to be expected for a polyelectrolyte for which the individual acid functions are reasonably strong. The usual weak-acid titration curve corresponds to an equilibrium between the ionized hydrogen and covalently bonded hydrogen, whereas the titration of a long-chain phosphate corresponds to hydrogens which are weak because they are held in the counter-ion atmosphere of the long-chain anions.

Van Wazer and Campanella (118) used the general method of Schwarzenbach, Kampitsch, and Steiner (98) in studying the titration of a commercial phosphate glass (average chain length of five) with tetramethylammonium hydroxide in the presence of various metal ions. The effect of sodium ions is reproduced in figure 5. Similar curves are obtained when calcium or other ions are introduced as their salts. From the pH changes observed in these experiments, it was possible to divide the metal ions into the three following general groups depending upon their ability to form complexes with the chain phosphates: (*1*) quarternary ammonium ions, which form no complexes, (*2*) alkali metal and similar cations, which form weak complexes, and (*3*) the other metal ions which form relatively strong complexes. Estimates of the dissociation

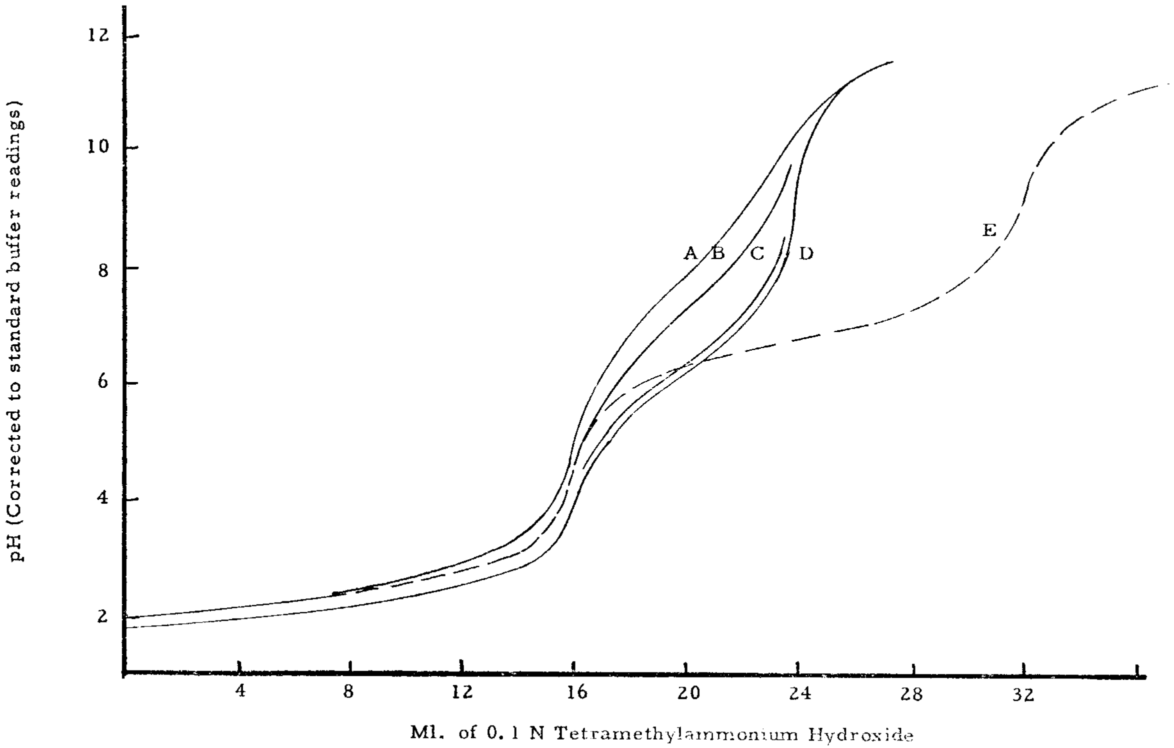


FIG. 5. Effect of sodium ions on the titration of the acid corresponding to a commercial sodium phosphate glass (average chain length of five) (118). The curves were obtained for (A) pure acid from glass of chain length five; (B) this acid plus 5×10^{-3} M sodium chloride; (C) this acid plus 4×10^{-2} M sodium nitrate; (D) this acid plus 4×10^{-2} M sodium chloride; (E) orthophosphoric acid from complete hydrolysis of A.

TABLE 5

Pyro- and tripolyphosphate complexes of the alkali metals

Complexes	pK_D at 25°C. and $\mu = 1$		
	Li^+	Na^+	K^+
Pyrophosphate complexes:			
$(MP_2O_7)^{3-}$	2.39	1.00	0.80
$(MHP_2O_7)^{2-}$	1.03	—	—
Tripolyphosphate complexes:			
$(MP_3O_{10})^{4-}$	2.87	1.64	1.39
$(MHP_3O_{10})^{3-}$	0.88	0.77	—

constants of the barium complexes of a series of chain phosphates were made (118) from such pH data, assuming fourfold coördination of the barium by two pairs of neighboring PO_4 groups in the chain phosphate. These pK_D values increase from 4.5 for pyrophosphate and tripolyphosphate to 5.5, 6.0, and 6.5 for glasses having average chain lengths of 5.0, 8.5, and 75, respectively. The problem here of how to apply the Law of Mass Action in computing a dissociation constant for a long-chain polyelectrolyte will be more fully considered later in this paper.

The same general method has been used recently (60, 126) to study the pyro- and tripolyphosphate complexes with the alkali metals. Since these chain phosphates are small, the usual mass action calculations were employed. The data are summarized in table 5.

These authors also measured the ionization constants of pyro- (60) and tripolyphosphoric (128) acids. For pyrophosphoric acid, $H_4P_2O_7$, the pK_D values for the four hydrogens were found to be 0.82, 1.81, 6.13, and 8.93 at 25°C. and unit ionic strength. For tripolyphosphoric acid, $H_5P_3O_{10}$, the five pK_D values were <0.8, 1.06, 2.11, 5.83, and 8.81 under the same conditions.

Titrations of pyrophosphate with copper, zinc, cadmium, magnesium, nickel, cobalt, aluminum, lead, and iron were followed by pH measurements in a study reported by Rogers and Reynolds (85). Similar titrations of pyrophosphate and tripolyphosphate with calcium, strontium, barium, and magnesium are

TABLE 6

Values of pK_D for 1:1 metal complexes of the adenosine phosphates at 25°C. and 0.2 ionic strength

Ion	Adenosine Monophosphate	Adenosine Diphosphate	Adenosine Triphosphate	Adenosine Tetraphosphate
Li^+	0.61	1.15	1.58	1.91
Na^+	0.46	0.83	1.16	1.43
K^+	0.21	0.74	1.06	1.29
Mg^{++}	1.69	3.00 (1.45)*	3.47 (1.49)*	—
Ca^{++}	1.43	2.81 (1.52)	3.29 (1.61)	—
Sr^{++}	1.32	2.50 (1.34)	3.03 (1.48)	—
Mn^{++}	2.19	3.54 (1.49)	3.98 (1.59)	—

* Values in parentheses correspond to a 1:1:1 complex of the metal, hydrogen, and adenosine phosphate ions. All other values correspond to hydrogen-free complexes.

described by Bobtelsky and Kertes (15). The observed changes in pH are closely tied in with precipitate formation but are not directly interpretable in terms of the formation of soluble complex ions.

The technique of interpreting pH titrations on the assumption that the quaternary ammonium ion is essentially uncomplexed, as used by Van Wazer (118) and Watters (60, 126), has also been applied to the adenosine phosphates. Smith and Alberty investigated complexing of the ions of the alkali (101) and alkaline earth (100) metals in considerable detail. Their data are reported in table 6. It should be noted that similar results were given for the sodium and potassium complexes in an earlier report (68). Titrations with sodium hydroxide have also been used to study the adenosine phosphate complexes of ions of the alkaline earth metals (17, 67).

D. SPECTROPHOTOMETRIC MEASUREMENTS

Watters and Aaron (124, 127) have published an extensive spectrophotometric investigation of the copper complexes of pyrophosphate, including studies in the presence of other complexing agents such as ethylenediamine and ammonia. The concentration range of the metal ions studied was considerably higher (generally an order of magnitude) than that used by Laitinen and Onstott (59) in the polarographic investigation, discussed in a later section, of this same system. The reactions are dependent on hydrogen-ion concentration; and, whereas Laitinen and Onstott could not interpret their data for pH values above 5 because of the irreversible character of the electrode processes, Watters and Aaron ran into difficulty with precipitate formation at pH values less than 5. Verification of the existence of several soluble species is based upon the shifts observed in the absorption maxima with different wavelengths, using the now well-known method of continuous variations. Evidence for 1:2 and 1:1 complexes of metal to pyrophosphate in the pH range of 5 to 10 is presented, and for 2:1 and 4:1 complexes in much more dilute solutions. The equilibrium constant for the dissociation of the complex ion $[Cu(P_2O_7)_2]^{6-}$ into $(CuP_2O_7)^{2-}$ and $P_2O_7^{4-}$ was determined from the observed variations in the ratio of the extinction coefficient at two different wavelengths for differing ratios of metal to pyrophosphate. The constant for the dissociation of the $(CuP_2O_7)^{2-}$ ion was determined indirectly from equilibration experiments with copper ferrocyanide. The reported pK_D values are 3.77 for the 1:2 complex and 8.80 for the 1:1 complex.

Spectrophotometric measurements in the visible range do not find wide applicability in the study of phosphate complexes because many of the commercially important salts are colorless. It is interesting to note that the intense blue color of the soluble copper pyrophosphate complexes has been observed (6) to persist in only one crystal, the soluble crystalline $Na_6Cu(P_2O_7)_2 \cdot 16H_2O$. Bassett, Bedwell, and Hutchinson (6) cite this color and the high solubility of the salt as evidence that the copper ions in this crystal are complexed. Samuelson (90) studied the absorption of solutions of Graham's salt (long-chain phosphate) and ferric ions in the ultraviolet region.

E. ION-EXCHANGE STUDIES

The equilibrium technique of ion exchange has been used (39) to compare the calcium-complexing abilities of the ring and chain phosphates. Linear relationships between the molar concentration of phosphorus and the reciprocal of the distribution coefficient of the metal between resin and solution at very low concentrations of phosphorus are cited as evidence for the formation of 1:1 complexes. Significant deviations from linearity were noted at higher concentrations of phosphorus. Tracer techniques with radioactive calcium were employed in measuring the distribution ratios of the calcium ion between the cation-exchange resin (Dowex 50) and the solution. The pK_D values for the dissociation of the 1:1 calcium-to-phosphate complex ions calculated from this data are 1.79 for orthophosphate, 3.47 for pyrophosphate, 4.32 for tripolyphosphate, 2.50 for trimetaphosphate, and 3.36 for tetrametaphosphate. Data are also given for "hexametaphosphate," which is presumably a phosphate glass with an average chain length of six (based on titration data given in the paper) and not the "sodium hexametaphosphate" of commerce (103), which has an average chain length of fourteen phosphorus atoms. With this chain phosphate, the reciprocal of the distribution coefficient is proportional to the square of the phosphorus concentration, but the concentration range is lower by a factor of ten.

A similar study of the complexing ability of Graham's salt (long-chain phosphate) for ferric ions was carried out by Samuelson (90), using a sulfonated polystyrene cation-exchange resin. By comparing the behavior of solutions containing the chain-phosphate molecule-ions with those containing noncomplexing anions, it was concluded that the complex was dissociated to less than 1 per cent under the conditions used.

Dissociation constants for the calcium complexes of the adenosine phosphates were calculated from data obtained in tracer studies with radiocalcium and cation-exchange resins (31). Adenosine triphosphate was found to be a stronger complex-forming agent than adenosine diphosphate with pK_D values of 4.06 and 3.74, respectively, at 37°C., pH equal to 7.4, and an ionic strength of 0.1.

A recent paper, based on the use of the anion-exchange resin Dowex 1, presented a very thorough picture of the complexing of magnesium and calcium ions by the adenosine phosphates (75). The dissociation constants of the complexes were found to vary with pH, ionic strength, and temperature. The complex between adenosine triphosphate and magnesium ion was tenfold stronger in alkaline than in acid media. On the other hand, the calcium complex is essentially unaffected by pH. The pK_D for the magnesium complex was found to increase by a factor of 1.4 when going from zero ionic strength to a value of $\mu = 0.3$ at pH 8.8.

At 25°C. and $\mu = 0.1$, the 1:1 complexes exhibit pK_D values of 3.61 and 3.14 for magnesium and calcium ions with adenosine triphosphate (the complex has a double negative charge) and pK_D values of 3.04 and 2.84 for magnesium and calcium ions with adenosine diphosphate (the complex has a single negative charge). For adenosine triphosphato-magnesium, the free energy of formation from the magnesium and adenosine triphosphate ions was found to be −4.5 kcal., the heat of the reaction was +4.1 kcal., and the entropy change was +29 units. For adenosine triphosphato-calcium, these values were −4.0 kcal., +4.6 kcal., and +29 units, respectively.

F. CONDUCTIVITY AND TRANSFERENCE STUDIES

Using conductivity data, Monk and coworkers (54, 55, 71, 72, 73, 74) have made extensive calculations of the dissociation constants of the hydrogen, sodium, calcium, barium, magnesium, manganese, nickel, strontium, lanthanum, and some complexed cobalt complexes of trimeta- and tetrametaphosphate (ring phosphates), and of the hydrogen and sodium complexes of pyro- and tripolyphosphate. The calculations for the hydrogen and sodium complexes were based upon the conductivity of dilute (1 to 25×10^{-4} *M*) solutions of relatively pure compounds. In all cases, theoretical activity coefficients were applied and simple assumptions were made as to the species present.

The pK_D values reported for the dissociation of the complexes assuming a 1:1 ratio of hydrogen to ring phosphate are 2.05 for trimetaphosphate and 2.74 for tetrametaphosphate. The comparable values for sodium ion are 1.17 and 2.05, respectively. The pK_D values (71) for the dissociation of the four hydrogens of pyrophosphoric acid, $H_4P_2O_7$, are 1.0, 2.0, 6.57, and 9.6. These should be compared with the values for the same equilibrium constants given in Section IV,C of this review and with the ionization constants (7, 8, 11) of the three hydrogens of orthophosphoric acid, H_3PO_4: viz. 2.148, 7.20, and 12.3. The pK_D values for the complexes (1:1 ratio of sodium ion to phosphate chain) of pyro- and tripolyphosphate are given by Monk (71) as 2.35 and 2.52.

The measurements with the divalent metal complexes were made upon solutions containing varying proportions of the metal chloride and the sodium phosphate. Allowances were made for the assumed presence of $(NaP_3O_9)^{2-}$ in the trimetaphosphate solutions and of $(NaP_4O_{12})^{3-}$, $(M_2P_4O_{12})$, and $(NaMP_4O_{12})^{-}$ in the tetrametaphosphate solutions. The pK_D values for the complexes (1:1 ratio of divalent metal to trimetaphosphate) ranged from 3.22 for nickel ion to 3.56 for manganous ion at concentrations of total metal ion in the range of 5 to 15×10^{-4} moles per liter and for mole ratios of total phosphorus to total metal of the order of 0.5 to 2.0. The comparable tetrametaphosphate complexes (1:1) were found to have pK_D values ranging from 4.95 for nickel ion to 5.74 for manganous ion. In the experiments with trivalent cations (73), corrections were made for $(NaP_3O_9)^{2-}$ and $(MCl)^{2+}$. The pK_D values for dissociation of the 1:1 lanthanum complexes of trimeta- and tetrametaphosphate are 5.70 and 6.67, respectively, and for the comparable complexes of the hexamine-cobaltic ion, 6.44 and 7.56.

Gray and Lemmerman (42) found conductometric evidence consistent with the existence of a soluble complex exhibiting a 1:1 ratio of calcium to tripolyphosphate, using Job's method of continuous variations. Very low concentrations were deliberately chosen in order to avoid precipitate formation at any mole ratio whatsoever of calcium ion to phosphorus. The available range

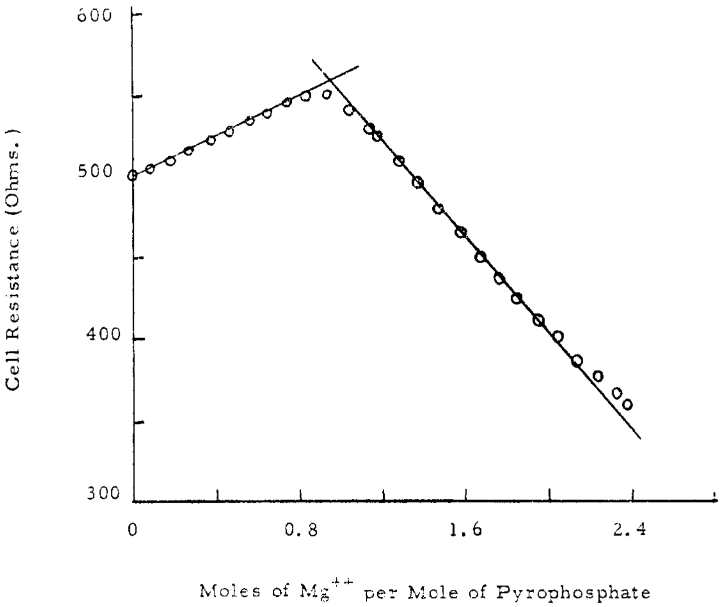


FIG. 6. Conductometric titration of pyrophosphate with magnesium (85)

of concentrations that can be used in a study of phosphate complexes by the method of continuous variations is quite restricted because of precipitation with the common cations. In the system studied by Gray and Lemmerman, the measurements were made below the minimum denoted by *D* in the curve of figure 3.

Rogers and Reynolds (85) report conductometric titrations of 4×10^{-4} *M* solutions of sodium pyrophosphate with 0.1 *M* solutions of such metal ions as calcium, cobalt, nickel, magnesium, aluminum, ferric iron, copper, and zinc. The data obtained for magnesium ion are reproduced in figure 6. The maximum resistance for solutions of the divalent metal ions all occurred at molar ratios of metal to pyrophosphate ranging from 0.93 to 0.97; and, except for cadmium ion, precipitation was said not to occur until after the resistance peak was passed. The resistance peak shifted with concentration in the case of copper so that, at high concentrations, the peak corresponded to two pyrophosphates complexing the copper ion, and at low concentrations one pyrophosphate per copper ion. A shift of resistance peak with concentration was also observed for zinc ion. Three inflection points were observed with ferric iron and with aluminum corresponding to mole ratios of pyrophosphate to metal ion of 2:1, 1:1, and 0.75:1 (noticeable precipitation at this point). A similar study involving thermometric and transference studies as well as conductometric titrations was made (47) on pyrophosphato-copper complexes. The conclusions reached in this work are in agreement with those of Rogers and Reynolds.

Conductometric titrations of 0.025 to 0.125 *M* solutions are reported (15) for pyrophosphate and tripolyphosphate with calcium, barium, and magnesium

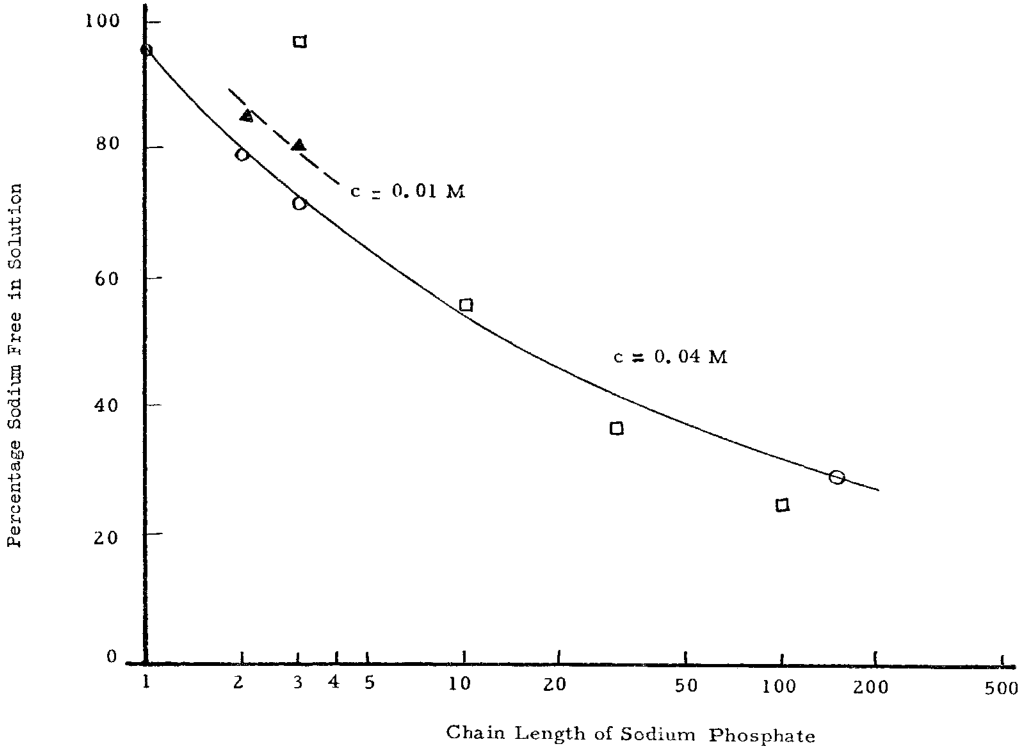


FIG. 7. Degree of dissociation of chain phosphates from electrolytic conductance and transference measurements. ○, Wall and Doremus (123); $c = 0.04\ M$ in sodium. ▲, Wall and Doremus; $c = 0.01\ M$ in sodium. □, Schindewolf (96); $c = 0.01\ M$ in sodium.

ions. Unfortunately, in this work the relative effects of precipitation and of the formation of soluble ions are not clearly differentiated.

Data on the degree of dissociation of the sodium salts of chain phosphates from electrolytic conductance and transference measurements have been given by both Wall and Doremus (123) and Schindewolf (96). Results are in fair agreement for the longer chain lengths (see figure 7), although Schindewolf's value for the degree of dissociation of the tripolyphosphate is much higher than Wall's value, or the value determined by Schindewolf and Bonhoeffer (97) from membrane electrode measurements. The discrepancy is probably a consequence of the analytical uncertainty in determining the increase in phosphate concentration in the electrode compartment (mentioned by Schindewolf), since, for the short chain lengths, the degree of dissociation naturally becomes more sensitive to errors in the difference between two numbers which are approaching equality. Wall's data, on the other hand, are less subject to this source of error, because the results are based upon measurements of the amount of radioactive sodium ion diffusing into the compartment containing nonradioactive sodium ion.

G. ELECTROMOTIVE FORCE MEASUREMENTS, INCLUDING POLAROGRAPHY

The chain phosphates of the alkaline earths have been investigated with the polarograph (18, 23, 93, 118), but considerable difficulty is encountered because of the large negative values of the half-wave potentials. Barium ion, which has the least negative half-wave potential of all the alkaline earth metals, was studied by Van Wazer and Campanella (118). In order to overcome interference from sodium ion, this ion was removed by ion exchange prior to the experiment. As shown in figure 8, addition of the phosphate causes the diffusion current to decrease and the half-wave potential to shift to a more negative value. The higher curves (A and B) in figure 8 are for barium ion in 0.1 *M*

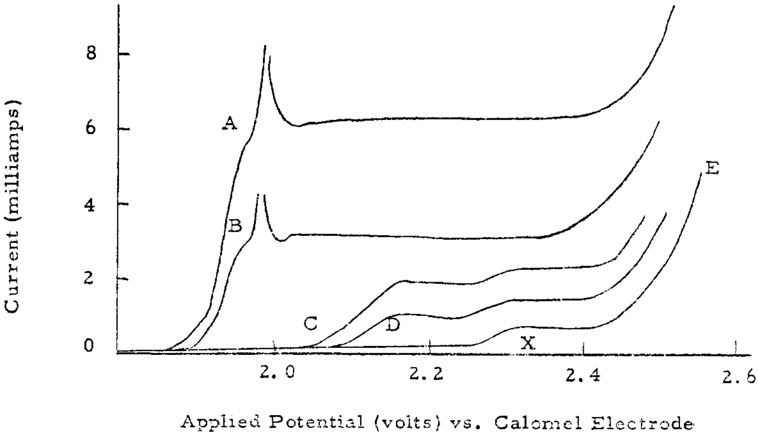


FIG. 8. Polarographic waves of barium in solutions of tetramethylammonium salts. The wave marked X in curves *C*, *D*, and *E* is probably due to a trace of sodium. Other lettered curves are explained in the text.

tetramethylammonium bromide. The concentration of barium ion ranges from 0.5 to 1.0 millimole per liter. The lower curves (C and D) are for barium in a supporting electrolyte made by neutralizing with tetramethylammonium hydroxide to pH 7.0 the acid corresponding to a sodium phosphate glass having an average chain length of five phosphorus atoms. The electrode reaction was found to be not completely reversible; but, because of the magnitude of the temperature coefficient of the half-wave potential, the data were treated as if the reaction were reversible. In this investigation, the concentration of the chain phosphate was measured in terms of pairs of phosphorus atoms. Analysis of the data led to a coördination number of four for the most prevalent complex, a pK_D equal to 9.5, and a molecular weight of the migrating species ranging from 10^3 to 10^5. The results for Graham's salt (a long-chain phosphate) were substantially the same. A similar investigation using sodium ion instead of barium ion indicated that the diffusion coefficients of the phosphate-sodium complexes are only slightly smaller than that of the simple sodium ion, and that the pK_D for the complex is ca. 3. Both the barium and sodium complexes studied here are the ones stable in the presence of large excesses of the chain phosphate. Presumably, the diffusion coefficients indicate that the barium ion ties different phosphate chains together into a large aggregation, whereas the sodium ions are each held by only one phosphate chain.

Rogers and Reynolds (85) observed that the cuprous, plumbous, and ferric reductions were reversible in sodium pyrophosphate solution. The two polarographic reduction waves attributed to the stepwise reduction of the cupric ion were later shown by Laitinen and Onstott (59) to be due to the presence of two complexes of cupric ion, the 2:1 and the 1:1 pyrophosphate-to-metal species. The pK_D's for the dissociation of the $[Cu(HP_2O_7)_2]^{4-}$ and the $(CuHP_2O_7)^-$ ions to the free metal ion plus anion were given as 10.0 and 6.40, respectively.

The manganese pyrophosphate system has been studied polarographically by Kolthoff and Watters (125), who presented evidence for a 3:1 pyrophosphate-to-metal complex stable at pH values of 4.3 and below. The molecular weight of the complex ion was estimated by application of Jander's expression (52) to the polarographically determined diffusion coefficients.

Gross and Gryder (44) calculated the dissociation constants of the sodium, copper, and nickel complexes of tetrametaphosphate from potentiometric measurements in a copper amalgam concentration cell. In the experiments involving copper and sodium tetrametaphosphate, the best fit of the data was obtained by assuming the presence of the species $(NaP_4O_{12})^{3-}$, $(CuP_4O_{12})^{2-}$, and $[Cu(P_4O_{12})_2]^{6-}$, and the absence of appreciable amounts of $Na_2(P_4O_{12})^{2-}$, $NaCuP_4O_{12}^-$, or $Cu_2P_4O_{12}$. The pK_D values for the dissociation of $(NaP_4O_{12})^{3-}$, $(CuP_4O_{12})^{2-}$, and $[Cu(P_4O_{12})_2]^{6-}$ were found to be 0.81, 3.18, and 4.64, respectively. The constants for the nickel complexes were determined by a procedure involving the displacement of copper in the copper amalgam concentration cell. The pK_D values reported for the $(NiP_4O_{12})^{2-}$ and $[Ni(P_4O_{12})_2]^{6-}$ complex ions are 2.63 and 3.48.

Values for the degree of dissociation of alkali polyphosphates were determined by Schindewolf and Bonhoeffer (97) from membrane electrode measurements. Since activity coefficients are not known, and no attempt was made to introduce theoretical coefficients, the values reported represent the electrochemical activity of the cations in the phosphate solution as compared to that of an equally concentrated chloride solution. The degree of dissociation of the sodium salts decreases from 100 per cent with orthophosphate to 22 per cent for a chain phosphate of 150 phosphorus atoms. The potassium phosphates appear to dissociate to a greater extent, and the lithium to a lesser extent than sodium. Evidence for incomplete dissociation of the alkali metal salts of the long-chain phosphates was also discussed by Snell (102). His data were obtained from potentiometric measurements in a cell with liquid junction and incorporating a semipermeable cation-exchange membrane. In this study, only slight differences between sodium ion and potassium ion were noted.

H. MISCELLANEOUS STUDIES

From an ultracentrifuge study of the behavior of 0.5 per cent solutions of long-chain potassium phosphates (Kurrol's salts) in 0.4 *M* sodium chloride, Malmgren (64) has outlined the steps necessary to calculate the effective charge of the phosphate molecule-anion. The ratio of the effective charge to the total number of phosphorus atoms per chain gives the percentage of the sodium ions free in solution. This is predicated upon the assumption that the potassium ions along the chain are replaced by sodium ions and that the molar frictional constant for the molecule-anion has the same value in sedimentation as in electrophoretic motion (see reference 64 for details). The values of the percentage of free sodium ion in solution calculated in this way decrease from 1 per cent at a chain length of 2400 phosphorus atoms to 0.4 per cent for a chain length of 19,000 phosphorus atoms. Thermometric, magnetic, and cryoscopic measurements of the pyrophosphate complexes of nickel and cobalt have been reported (47) in saturated solutions of sodium sulfate. The behavior of these two metals is similar to that of copper. The magnetic measurements gave 3.281 and 4.937 Bohr magnetons for the nickel and cobalt complexes, respectively, and were interpreted to indicate ionic bonding. Studies of the lead, beryllium, and zinc systems are also reported (47). The beryllium appears in complexes exhibiting 2:1 and 1:1 ratios of pyrophosphate to beryllium.

In an unpublished study (20) presented at the Symposium on Chelation held at Brooklyn Polytechnic Institute in 1955, some data were obtained on the nuclear magnetic resonance spectra of Na^{23} in solutions of sodium phosphates, including the orthophosphate, pyrophosphate, tripolyphosphate, and a long-chain phosphate as well as the trimetaphosphate and tetrametaphosphate rings. The most interesting finding in this work was that the resonance line widths increased greatly with increasing size of the chain phosphates. The ring phosphates gave a line width about the same as that found for the orthophosphate. The authors speculated that the observed broadening is related to a rigid binding (19) of the sodium ion by the phosphates, with the proportion of bound sodium ion increasing with increasing chain length of the phosphate. A subsequent note from another laboratory (133) bears out the observed phenomenon and shows that a similar line broadening is found at very high concentrations for poorer sodium-complexing agents than the chain phosphates. The line broadening of the sodium in this other group of salts was attributed to ion association at the high concentrations.

An exploratory study based on electrophoresis, intrinsic viscosity, and salting-out measurements shows a qualitative difference between the tetramethylammonium and the alkali metal ions as counter-ions to chain phosphates (106). The quaternary ammonium ion is apparently held by general electrostatic interaction, whereas the data support the idea of specific site-binding for the alkali metal ions. According to these results, the relative binding is as follows: $Li^+ > Na^+ > K^+ \gg (CH_3)_4N^+$.

V. CONCLUSIONS AND SUMMARY

A. ORTHOPHOSPHATES

The orthophosphate complexes of the alkali and alkaline earth metals are considerably weaker than the equivalent complexes by chain or ring phosphates, as can be seen by comparing tables 7, 8, 9, and 10. This same relationship holds for the adenosine phosphates, as shown in table 6.

Orthophosphate complexes of the transition metals are much more stable than those of the alkali and alkaline earth metals. As shown in table 7, the pK_D for the orthophosphato-manganous complex is 2.58, as determined from acid-base titration. Presumably the ferric-ion complex is even more associated, having a pK_D perhaps several units higher than that measured for the manganous-ion complex. Reliable quantitative studies of the orthophosphato-ferric complex are needed in order to obtain a trustworthy value of the dissociation constant. The problem here is to avoid the confusion introduced by peptized precipitates which are stabilized by the presence of either orthophosphate or the chain and ring phosphates.

The low values of pK_D obtained for the orthophosphate complexes of the alkali and alkaline earth metals probably indicate that these complexes are

TABLE 7

Negative logarithm of dissociation constants at 25°C. and 0.2 ionic strength of various 1:1 orthophosphate complexes

Metal Ion	pK_D by Acid-Base Titration	Reference	Comments
Li^+	0.72	(101)	$(C_3H_7)_4N^+$ assumed not to complex
Na^+	0.60	(101)	Value of 0.52 calculated from transference number data (123)
K^+	0.49	(101)	
Mg^{++}	1.88	(100)	$(C_3H_7)_4N^+$ assumed not to complex; $MHPO_4$ formula assumed; other values are 1.53 (43, 113) and 1.43 (107)
Ca^{++}	1.70	(100)	Other value is 1.89 (40, 44); $MHPO_4$ formula assumed in all cases
Sr^{++}	1.52	(100)	$MHPO_4$ formula assumed
Mn^{++}	2.58	(100)	$MHPO_4$ formula assumed

TABLE 8

Negative logarithm of dissociation constants of various 1:1 ring phosphate complexes

Metal Ion	Trimetaphosphate		Tetrametaphosphate	
	pK_D	References and comments	pK_D	References and comments
Na^+	1.17	(28)	2.05	(28)
Mg^{++}	3.31	(55)	5.17	(54)
Ca^{++}	3.41	(54, 55); other value is 2.5 by ion exchange (39) and calcium value (22)	5.4	(28, 54); other value is 3.36 by ion exchange (39); for the $(Ca_2P_4O_{12}) = Ca^{++} + (CaP_4O_{12})^{2-}$ equilibrium, $pK_D = 2.66$ (28)
Sr^{++}	3.35	(72)	5.1	(72)
Ba^{++}	3.35	(55)	4.99	(54)
Mn^{++}	3.56	(55)	5.74	(54)
Ni^{++}	3.22	(55)	4.95	(54); value of 2.63 from potentiometric study (44) at higher concentrations, ignoring activities

held together by electrostatic attraction. However, it is quite possible that the iron complexes may involve iron–oxygen bonds exhibiting appreciable covalent character. Since the complexes for which pK_D values are presented in table 7 probably represent ion association, treatment of the data in terms of a 1:1 complex is very arbitrary and may be an unrealistic idealization. On the other hand, the assumption of negligible association of the tetramethylammonium ion with orthophosphate is probably a very minor source of error in the values given in table 7.

B. RING PHOSPHATES

The dissociation constants for the trimeta- and tetrametaphosphate complexes of sodium, the alkaline earth metals, manganese, and nickel are presented in table 8. All of these values were obtained by Monk and associates from electrical conductivity and solubility studies. Several generalities are apparent from this table. First, it can be seen that the ratio of the tetrametaphosphate pK_D's to the trimetaphosphate pK_D's for the various metals is about 1.6. Furthermore, the pK_D values for the calcium complex of either of the ring phosphates are roughly 2.8 times greater than the respective values for the sodium complex.

It is quite possible that the pK_D values given in table 8 are too large, and are thus not comparable with the data of tables 7, 9, 10, and 11. This conclusion is based upon the fact that the pK_D value for the first hydrogen of the ring acids, as determined by Monk from conductivity data, was between 2 and 3, although the titration curves of trimeta- and tetrametaphosphoric acids indicate that these acids are much stronger. Furthermore, the pK_D values for the calcium complexes obtained from conductivity and solubility measurements are greater than those obtained from ion-exchange measurements. However, this is not a serious criticism, since in all of the measurements presented in this review the ion-exchange values were found to be low. Although the ring phosphates are not known to be sequestering agents, the pK_D values reported

TABLE 9

Negative logarithm of dissociation constants at 25°C. of various metal complexes of pyrophosphate

Metal Ion	pK_D	Complex	Method	Comments
K^+........	0.80	$(KP_2O_7)^{3-}$	Acid-base titration (60)	
Na^+.......	1.0	$(NaP_2O_7)^{3-}$	Acid-base titration (60)	From conductivity (71), pK_D = 2.35; and calculated from transference numbers (123), pK_D = 0.92, assuming 1:1 complex
Li^+........	2.39	$(LiP_2O_7)^{3-}$	Acid-base titration (60)	
Ca^{++}.......	(4–5)	$(CaP_2O_7)^{2-}$	"Guesstimated"	From uncorrected solubility data (22), pK_D = 3.0; by ion exchange (39), pK_D = 3.5
Cu^{++}......	6.40	$Cu(HP_2O_7)_2{}^{4-}$	Polarography (59)	pH 3.5 to 5
	10.0	$Cu(HP_2O_7)^-$	Polarography (59)	pH 3.5 to 5
	8.8	$(CuP_2O_7)^{2-}$	Solubility (63, 125)	pH 7 to 10
	12.57	$Cu(P_2O_7)_2$	Spectrophotometry (63, 125)	pH 7 to 10

in table 8 indicate that these compounds should dissolve moderately soluble calcium precipitates, such as calcium sulfate (see figure 10).

The work of Monk and associates was criticized in a recent paper (44). In this paper, lower pK_D values were found; however, activities were ignored. Working at a lower concentration, Monk was able to apply theoretical activity coefficients to his data which, in this respect, should be superior to the more recent work.

C. CHAIN PHOSPHATES

The chain phosphates are the only phosphates which exhibit sufficiently stable complexes with all ions (except those of the alkali metals and quaternary ammonium salts) to be considered as complexing agents of general utility. Indeed, hundreds of millions of pounds of chain phosphates are consumed each year in applications where this complexing ability, especially with alkaline earth metals, plays the major role.

The dissociation constants for the better established pyrophosphate and tripolyphosphate complexes are given in tables 9 and 10. In the case of the

TABLE 10

Negative logarithm of dissociation constants at 25°C. of various metal complexes of tripolyphosphate

Metal Ion	pK_D	Complex	Method	Comments
K^+........	1.39	$(KP_3O_{10})^{4-}$	Acid-base titration (126)	
Na^+.......	1.64	$(NaP_3O_{10})^{4-}$	Acid-base titration (126)	Conductivity (71) gave pK_D = 2.5 and transference numbers (123) gave pK_D = 1.2 at 0.04 *M* concentration
	0.77	$(NaHP_3O_{10})^{3-}$		
Li^+........	2.87	$(LiP_3O_{10})^{4-}$	Acid-base titration (126)	
	0.88	$(LiHP_3O_{10})^{3-}$		
Ca^{++}......	6.5	$(CaP_3O_{10})^{3-}$	Solubility oxalate (42)	Temperature 30°C.; values of 4.3 by ion exchange (39) and 4.0 by solubility of $CaHPO_4$ (22)

alkali metals, it is apparent from these tables that lithium ion is more strongly bound than sodium ion which, in turn, is more strongly bound than potassium ion. As shown in table 7, this order is also true for the orthophosphate complexes.

For the alkali metals, the tripolyphosphate complexes are stronger than the pyrophosphate complexes. The ratio of the pK_D values for tripolyphosphate/pyrophosphate is about the same as for the tetrametaphosphate/trimetaphosphate. Furthermore, the pK_D values for the alkali metal complexes of the ring phosphates are not very different from those of the chain phosphates having the same ionic charge. This indicates that the complexing is primarily electrostatic in nature. The fact that there is a big difference (four to five orders of magnitude) between the dissociation constants of the alkali metal and alkaline earth metal complexes of the chain phosphates may mean that the ions of the alkaline earth metals are partially covalently bonded in the complexes or, at least, are held at specific sites. The much smaller difference (one to two orders of magnitude) between the alkali metal and alkaline earth metal complexes of the ring phosphates gives some support to the idea that all of these complexes are held together by simple electrostatic attraction.

A problem of how to apply the Law of Mass Action comes up in interpreting the data obtained on complexes of the long-chain phosphates. This problem involves the question of what effect the formation of a complex at one end of a long chain will have on the stability of a complex formed at the other end of the chain. To a first approximation, distant segments of a chain can be considered as independent units strung together; but, antithetically, neighboring segments are strongly coupled so that the Law of Mass Action must apply in its classical form. This interaction or coupling presumably diminishes with distances between the sites for complexing on a given chain. As a first approximation, where there was an excess of long-chain phosphate as compared to the metal ion being complexed, Van Wazer and Campanella (118) treated each

TABLE 11

*1:1 Metal complexes of the adenosine phosphates**

Comparison of negative logarithm of dissociation constants by independent methods; temperature, 25°C.; ionic strength, 0.1 to 0.2

Metal Ion	Phosphate	pK_D	Method	Comments
Mg^{++}	Adenosine triphosphate	3.47	Acid-base titration (100)	A preliminary value of 4.30 reported (66) by titration; noncomplexing ion not employed as in reference 100
		3.61	Basic ion exchange (75)	
		3.40	Acid-base titration (17)	
Ca^{++}	Adenosine triphosphate	3.29	Acid-base titration (100)	Preliminary values of 4.08 (66) and 4.36 (31), both by acid-base titration, are high
		3.14	Basic ion exchange (75)	
Mg^{++}	Adenosine diphosphate	3.00	Acid-base titration (100)	
		3.03	Basic ion exchange (75)	
Mg^{++}	Adenosine monophosphate	1.69	Acid-base titration (100)	
		2.00	Basic ion exchange (75)	

* Data obtained on lithium, sodium, potassium, strontium, and manganous complexes by acid-base titration are given in table 6.

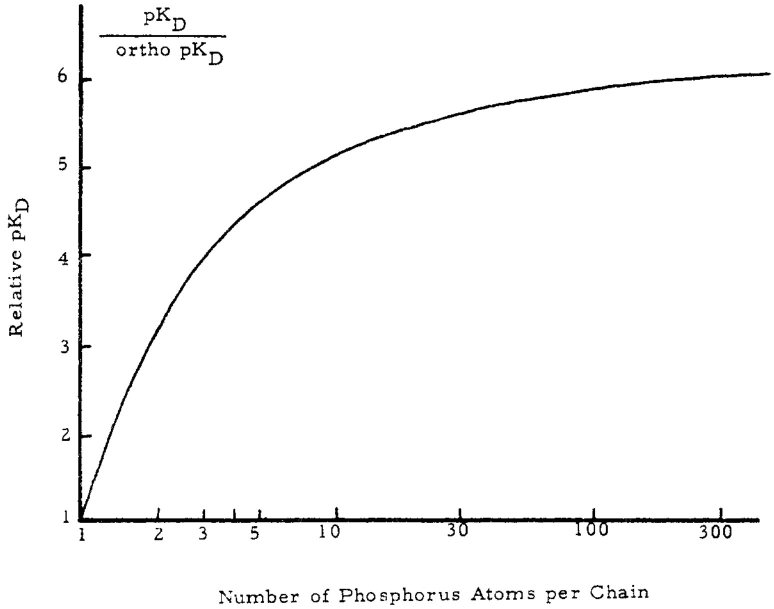


FIG. 9. Estimated increase in pK_D of the calcium complexes with increasing length of the chain phosphates.

P—O—P segment in the chain as being completely independent sites for complexing. On this assumption, it was found that complexes with barium ion increased in stability with increasing chain length, tending to level out at a chain length of ca. 10. Thus, the pK_D calculated in this manner for the barium pyrophosphate complex was 4.5 and the value for the complex with a long-chain phosphate, averaging 75 atoms per chain, was 6.5. From this study, the work of Strauss (106), and other data reviewed herein, the variation of pK_D with chain length can be estimated, as shown in figure 9.

Because of their importance in biology, a considerable amount of reliable work has been carried out on the alkaline earth complexes of adenosine triphosphate. An idea of the consistency obtained in such measurements is given in table 11.

The dissociation constants for ortho-, pyro- and tripolyphosphoric acids are given in table 12. It is interesting to note that (*1*) the two terminal hydro-

TABLE 12

Negative logarithm of thermodynamic dissociation constants at 25°C. for the ortho-, pyro-, and tripolyphosphoric acids

Acid	Hydrogen					References
	1	2	3	4	5	
H_3PO_4	2.15	7.20	12.44	—	—	(1, 7, 8, 11)
$H_4P_2O_7$	Small	2.64	6.76	9.42	—	(60)
$H_5P_3O_{10}$	Small	Small	2.30	6.50	9.24	(60)

gens in either pyro- or tripolyphosphoric acid can be easily distinguished in a pH titration and (*2*) the third hydrogen on orthophosphoric acid is so strongly bound that an inflection point in the titration curve is not observed for it.

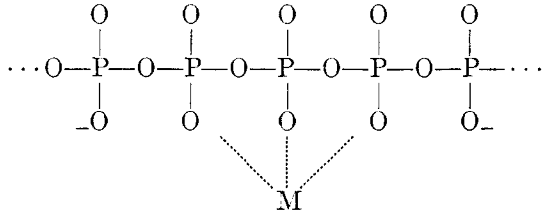
D. GENERALITIES

In almost all of the work reported in this review, the formula of the complex has been assumed. In the few cases where the formula was established (as by the method of continuous variations), the dissociation constants were not confirmed by the measurements of different authors using various experimental procedures on solutions at the same temperature, concentration, and ionic strength.

The question of whether or not any of the phosphates form some complexes exhibiting a significant amount of covalent bonding to the metal is not answered as yet. The classical method of proving covalent bonding in coördination complexes—the resolution of optical antipodes—has not been applied to the phosphates. Furthermore, magnetic data (47) have been interpreted in the traditional manner to indicate ionic bonding in the nickel and cobalt complexes of pyrophosphate. Bjerrum radii (10) have often been used as a criterion for covalent bonding. The rule of the thumb on this matter says that covalent bonding exists if the calculated Bjerrum radius is 2 A. or less (37). Calculation of these radii from the dissociation constants of the calcium tri- and tetrametaphosphate complexes gives 4.2 and 3.5 A., respectively. For the copper pyrophosphate complex, the calculated Bjerrum radius is 2.1 A., which makes this a borderline case. For the calcium tripolyphosphate complex, the Bjerrum radius is calculated to be 3.7 A. so that the bonding would be ionic by this criterion. It should be noted that the Bjerrum radius is obtained from the dissociation constant of the complex and, hence, is sensitive to every assumption made in obtaining this constant. By changing the assumption on which the constant is calculated, it is possible to effect large variations in the Bjerrum radius.

Much of the evidence against simple electrostatic attraction willy-nilly holding the phosphate anions close to the "complexed" cations has been obtained for the alkali metal complexes and, hence, has been interpreted in terms of "specific site-binding" rather than covalent bonding. For the long-chain phosphates, this evidence is the shape of electrophoresis curves and salting-out behavior (106). In addition, site-binding offers a ready explanation of the large increase in pK_D and decrease in diffusion constant when going from the alkali metal to the alkaline earth metal complexes of the chain phosphates (118). It should be noted here that all polyelectrolyte ions, including the long-chain phosphate anions, have a strongly bound counter-ion atmosphere. In addition there may also be binding at specific sites. In this latter case, the Bjerrum radii ought to be calculated for the site-bound complex, from which the interference of the tightly held counter-ion atmosphere is removed. It is believed that different methods of measurement will dig down into the counter-ion atmosphere by various amounts (117), so that a differentiation between site-binding and ionic-atmosphere complexing can be made physically.

The geometry of the chain phosphates is such that an oxygen atom from each of three neighboring PO_4 groups making up the chain can be brought into close proximity with a metal atom. This has led several authors (68, 126) to propose the following structure for site-binding in the metal complexes with the chain phosphates:



This is a very reasonable structure, which may explain why the chain phosphates form far more stable complexes with the multiply charged cations than do the ring phosphates, since the latter are sterically hindered from assuming all possible configurations. This structure implies that there should be a considerable difference in the complexing ability of the boat and chair forms (45) of the ring phosphates.

As previously pointed out, a "sequestering agent" is a substance exhibiting a complexing anion which is sufficiently strong to dissolve common precipitates of the metal ion being complexed. This means that for practical purposes, the complexing ability of a sequestering agent must be compared with the insolu-

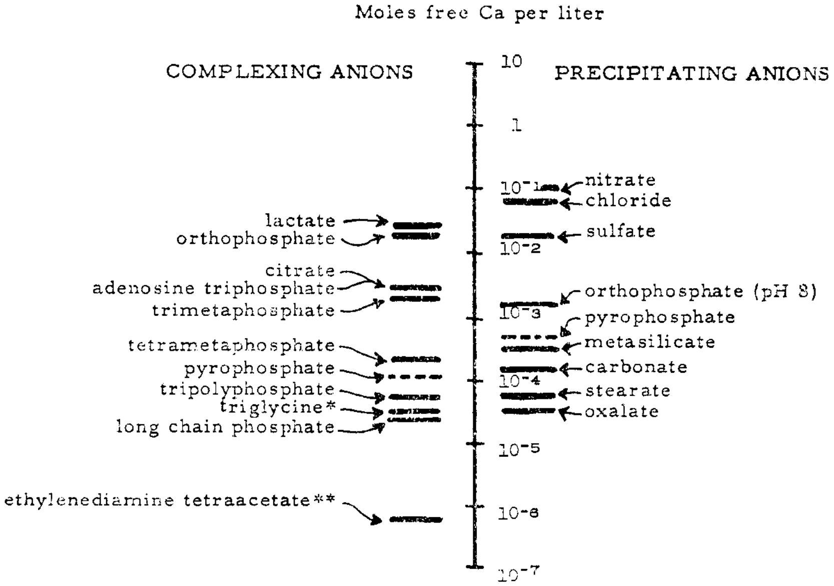


FIG. 10. Comparison of complexing agents with precipitating agents for calcium. The free calcium for the complexing agent is computed for the dissociation of a 0.01 *M* solution of the 1:1 calcium complex. *Triglycine is also called ammonia triacetate or Trilon A. **A well-known trade name for ethylenediamine tetraacetate (EDTA) is Versene.

bility of the precipitates being sequestered. This is readily done on the basis of free metal ion in equilibrium with either the complex or the precipitate. If the value of the free metal ion is lower for the complex than for the precipitate, the precipitate will of course dissolve, so that the complexing agent is then a sequestrant under this experimental condition. In figure 10, the calcium in equilibrium with a 0.01 *M* solution of a number of sequestering agents (66) is compared with the calcium ion in equilibrium with various precipitated calcium salts. Any complexing agent shown in this chart will dissolve all of the precipitates situated higher on the scale. Since the tripolyphosphate and longer-chain phosphates lie lower on the scale than all of the usual "insoluble" calcium salts, these phosphates are capable of dissolving these salts. It should be noted that ethylenediamine tetraacetate lies considerably below the chain phosphates, which means that it is a much stronger complexing agent for calcium ion. However, this added strength is not necessary in most practical situations where the cheaper phosphates are sufficiently strong to do the job.

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