THE INORGANIC PHOSPHATES AS POLYELECTROLYTES

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Received April 19, 1954

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I. INTRODUCTION

About twenty-five years ago it was realized that many completely inorganic compounds exhibit large formula weights and hence may be considered as high polymers.[1] This realization was based primarily on x-ray data (15) which showed the existence of three-dimensional assemblages (e.g., diamond, silica), as well as chains (e.g., the pyroxenes, calcium metaborate), rings (e.g., tremolite, alkali metaborates), and certain more complex arrangements which are present as polyanions in crystals.

In most cases, the inorganic polymers so typified cannot be dissolved in any solvent without complete destruction of the compound. This is exemplified by the silicate minerals, the structures of which were elucidated by the Braggs (5) and their successors. On the other hand, many of the completely inorganic polymers which can be dissolved belong to the class called aggregation polymers, the degree of polymerization of which will increase or decrease with changes in pH, concentration, and temperature. The soluble sodium silicates typify the aggregation polymers. It is well known that these materials polymerize to hydrated silica (a three-dimensional polymer of extremely high molecular weight) upon addition of acid and depolymerize at a moderate rate to the orthosilicate (the SiO_4^{-4} monomeric anion) upon the addition of base. Under intermediate conditions, the silicate anions probably consist of SiO_4 tetrahedra connected by the sharing of oxygen atoms in a manner similar to the way in which the polyanions

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[1] The word "polymer" as used in this paper refers to the members of homologous series as well as to any material the composition of which is an exact multiple of a base composition. For the larger members of a homologous series of compounds, the composition and formula weight approach multiples of the base composition and weight.

are held together in the insoluble silicate minerals.[2] Some other inorganic polymers appear to depolymerize completely to the monomer upon being dissolved. The sodium polyborates offer an example of immediate degradation to the monomer upon dissolution in water (31).

In the case of the condensed phosphates the situation is quite different. These materials contain polyanions which are stable in aqueous solution. Dilute solutions of these salts never polymerize but only slowly undergo degradation, by hydrolysis (56), towards the monomer (orthophosphate) at rates which are comparable to the solvolytic degradation of many organic polymers. As far as is known, the condensed phosphates are unique in this respect among the purely inorganic substances. These phosphates can readily be studied in solution by means of the methods of polymer physics, and the major part of this paper will be devoted to a review of such studies.

The condensed phosphates are made up of units, each of which consists of a tetrahedral grouping of four oxygen atoms around a central phosphorus atom. The evidence for this has been discussed elsewhere (47, 57), and it has also been shown that the phosphates can be conveniently classified into three groups: the chain, the ring, and the branched phosphates (52). Chain phosphates are called polyphosphates and consist of unbranched P—O—P chains formed by the sharing of oxygen atoms between adjacent phosphorus atoms. Ring phosphates are included in the class of metaphosphates and consist of simple rings of interconnected phosphorus and oxygen atoms. At present only the six- and eight-membered rings are known (three phosphorus atoms in the six-membered rings and four in the eight). The branched phosphates or ultraphosphates include all structures in which one or more PO_4 groups share oxygen atoms with three neighboring groups (49). It is believed that immediately upon dissolution such branching PO_4 groups are converted to groups in which no, one, or two oxygen atoms are shared. This means that only orthophosphates, simple rings, or unbranched chains are present in aqueous solution. However, some recent work (37, 42) indicates that cross-linked phosphates may have a transient existence in aqueous solution.

From the viewpoint of polymer physics, the unbranched chains are of particular interest because of the high molecular weights of some of them. Most of the published papers on long-chain phosphates deal with the Kurrol salts (sodium or potassium metaphosphates exhibiting asbestos-like crystals) and Graham's salts (vitreous sodium phosphates having a $(Na_2O + H_2O)/P_2O_5$ mole ratio near unity). The glasses for which $1 \leqslant (Na_2O + H_2O)/P_2O_5 < 1.7$ and $Na_2O \gg H_2O$ have also been studied by high-polymer methods.

II. METHODS USED FOR CHARACTERIZING THE PHOSPHATES

The various methods of high-polymer physics that have been used to characterize and determine the size of the phosphate polymers include (*1*) end-group titration (38, 57), (*2*) cryoscopy (39, 44), (*3*) light scattering (42), (*4*) dialysis

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[2] This statement is based upon qualitative but convincing evidence observed in industrial practice and has been made with knowledge of the work of Debye and Nauman (10).

and diffusion (27, 32, 34), (*5*) ultracentrifugation (32, 34), (*6*) flow birefringence (55), (*7*) relative and intrinsic viscosity in salt solutions (41, 42, 51), and (*8*) solubility fractionation (50). All of these methods are standard procedures for characterizing polymeric materials. Although the theory of several of the methods has been developed rationally only for unionized materials, the use of swamping electrolytes has allowed these techniques to be extended to polyelectrolytes, including the high-molecular-weight phosphates.

pH titration (57) is probably the most useful method of analysis for the phosphates, because the end-groups can be determined independently by a direct titration between the end-points neaı pH 4.5 and 9. However, the sensitivity of the method is low for the large molecule-ions, and for these materials it is necessary to resort to other determinations. The degree of polymerization (or the number-average number of phosphorus atoms per chain), $\bar{n}$, is determined as follows:

Let

w = the number of equivalents of base used to titrate 1 g. of the total phosphate between the pH 4.5 and 9 end-points = moles of end-groups per gram of total phosphate,
s = the gram-atomic weight of phosphorus per gram of total phosphate,
o = the moles of orthophosphate per gram of total phosphate,

and

r = the gram-atomic weight of ring phosphorus per gram of total phosphate.

Then

$$\bar{n} = \frac{2(s - r - o)}{(w - o)} \tag{1}$$

Cryoscopic measurements in pure water cannot be readily interpreted (48), since the quantitative degree of ionization is unknown and there is a very large interionic attraction. Satisfactory cryoscopic measurements apparently have been made (39) using the transition point of sodium sulfate decahydrate, under conditions where the amount of ionized sodium accompanying the phosphate molecule-ions becomes inconsequential. For this operation, a small amount of the sodium phosphate is mixed with the solid sodium sulfate decahydrate, the mixture is melted, and the lowering of the transition point at which the sulfate solidifies is measured. The cryoscopic constant for this solvent (melted hydrate) is 33.7°C./mole. In such measurements, care must be taken to assure that all of the polymer dissolves, and that none of it is being salted out at the higher concentrations, i.e., above ca. 1 weight per cent (18). Later, in this paper, the degrees of polymerization (for a number of samples) measured in this way will be compared with those obtained from end-group titrations.

Strauss and coworkers (42) have shown that light-scattering techniques can be used to determine the degree of polymerization of sodium polyphosphates.

These authors found that the relation between light-scattering data and molecular weight given by Debye (9) and Doty (11), i.e.,

$$Hc/\tau = \frac{1}{M} + 2Bc \tag{2}$$

for non-ionic polymers whose molecules are isotropic and small compared to the wave length of light is applicable to sodium polyphosphates in sodium bromide solutions, even though it does not apply to polyelectrolytes under all conditions. In equation 2, τ is the excess turbidity of the solution over that of the solvent, c is the concentration of polymer in grams per milliliter of solution, and

$$H = \frac{32\pi^3 n_0^2}{3N_0\lambda^4}\left(\frac{n - n_0}{c}\right)^2$$

where N_0 is Avogadro's number, λ is the wave length of the light, and n_0 and n are the refractive indices of solvent and solution, respectively. M is the molecular weight, and B is a constant which depends on the interaction of the polymer molecules with one another. The results that Strauss *et al.* obtained for one sample of Graham's salt are shown in figure 1. The lines all have a common intercept, which is the reciprocal of the molecular weight of the sample.

Karbe and Jander (27) measured dialysis coefficients of solutions of the polyphosphate polymers, and used the following relationship for approximating the degree of polymerization:

$$M_1 = \left(\frac{\delta_2}{\delta_1}\right)^2 M_2 \tag{3}$$

where M_2 is the molecular weight and δ_2 is the dialysis coefficient of a reference material. Sodium trimetaphosphate was used as the reference material in this comparison. Their work clearly demonstrated the high-polymeric nature of the glassy phosphate erroneously named hexametaphosphate.

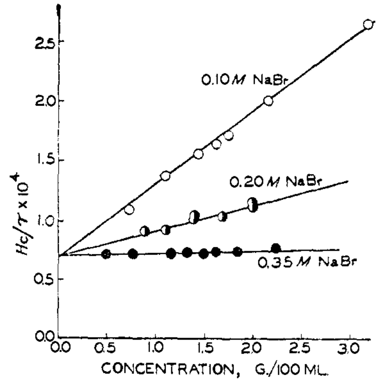

FIG. 1

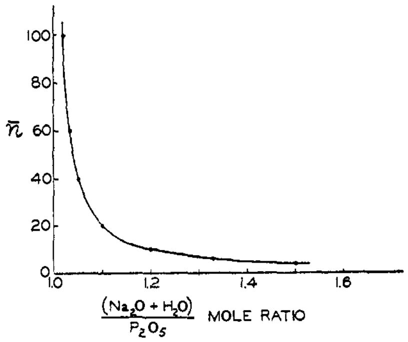

FIG. 2

FIG. 1. Light-scattering data for a sodium polyphosphate (Graham's salt) (42)
FIG. 2. Theoretical chain lengths of the polyphosphate glasses *versus* composition

Diffusion measurements using Lamm's scale method (28) can be combined with measurements of the sedimentation rate in the ultracentrifuge (43) to give the molecular weight of a polymer. In this sedimentation velocity method, the molecular weight is calculated from Svedberg's formula,

$$M = \frac{s}{D} \cdot \frac{RT}{1 - V\rho} \tag{4}$$

where s is the sedimentation constant, D is the free diffusion coefficient, V is the specific volume of the added salt, and ρ is the density of the solution. Malmgren (32) applied this technique in studying the degree of polymerization of potassium Kurrol salts.

Flow birefringence studies (55) have also been used to characterize the type of molecule-ions present in solutions of glassy sodium polyphosphates and solubilized potassium polyphosphates. The equation for the rotary diffusion constant of a prolate ellipsoid in terms of the major and minor semiaxes was manipulated to give a relation between the number-average chain length and the rotary diffusion constant. By assuming a geometrical model for the polyphosphate, the experimental data were then shown to fit the theoretical equation.

A number of investigators (e.g., Baker, Fuller, and Heiss (2)) have demonstrated that the intrinsic viscosity, $[\eta]$, is related to the viscosity-average molecular weight, $\bar{M}_v$, in the range of molecular weights below about 6000 by the equation

$$[\eta] = K_i \bar{M}_v + K_0 \tag{5}$$

in which K_i and K_0 are two characteristic constants. Van Wazer (51) found that the above relationship was valid for solutions of Graham's salt in 10 per cent tetramethylammonium bromide. Malmgren (32) investigated the effects of ionic strength and type of swamping electrolyte on the viscosity of solutions of solubilized potassium Kurrol salts. The results of this work emphasize the fact that in using viscosity for comparisons of unknown polymers, it is imperative that the solutions contain the same concentration of the same electrolyte.

Perhaps the most revealing evidence concerning the nature of the polyphosphate glasses was obtained from an acetone solubility fractionation study (50). Each of the various fractions separated from the original solution by successive additions of acetone (7) was analyzed by pH titration.

The significant results of this work and that of the other studies mentioned, as well as their contribution to a consistent overall picture of the phosphate polymers, will now be considered.

III. STRUCTURES OF THE CONDENSED PHOSPHATE POLYMERS IN SOLUTION, AS PICTURED FROM THE AVAILABLE DATA

A. Polyphosphate glasses with Na_2O/P_2O_5 *mole ratios greater than one*

The glasses in this category are prepared by rapidly quenching sodium oxide–phosphorus pentoxide melts in the composition range $1 < Na_2O/P_2O_5 < 1.67$. Van Wazer and Holst (57) have theorized that assemblages in which three of the four oxygens of a PO_4 tetrahedron are shared with other PO_4 tetrahedra will be unstable in any environment such as aqueous solution in which solvolytic degradation is possible. Experimentally they found that for solutions of these glasses, the same amount of base was needed to reach the first neutralization end-point before and after hydrolysis to the orthophosphate. This means that there is exactly one strongly ionized acid function for each phosphorus atom, and that in solution there are essentially no PO_4 groups in which three oxygen atoms are shared, and hence no branching. The molecular weight of a linear polymer is a first-order function of the Na_2O/P_2O_5 mole ratio; i.e., theoretically,

$$\frac{(Na_2O + H_2O)}{P_2O_5} = \frac{\bar{n} + 2}{\bar{n}} \tag{6}$$

where $Na_2O \gg H_2O$ and $\bar{n}$ is the degree of polymerization, identical with the $\bar{n}$ used in equation 1. This relationship between chain length and composition is shown graphically in figure 2.

Solubility fractionation studies (50), mentioned earlier, have demonstrated that in solution these polyphosphate glasses exhibit a size distribution of molecule-ions, since they can be roughly separated with acetone into fractions having different ratios of end-group to total phosphorus. A molecular weight obtained for a glassy phosphate is thus an average for the mixture, this average being dependent upon the composition as given in equation 6.

B. Graham's salt

Graham's salt, prepared by rapidly quenching sodium phosphate melts having a Na_2O/P_2O_5 mole ratio of 1, has been of paramount interest for a number of years. These glasses represent the limiting case for both the branched and the linear polymer regions. It can be seen from equation 6 that, if the polymers are linear and the $(Na_2O + H_2O)/P_2O_5$ mole ratio is exactly 1, then the chain length, $\bar{n}$, should be infinite. In practice it is found difficult to volatilize the last trace of water from a melt in which the Na_2O/P_2O_5 ratio is exactly 1. This means that infinity is never reached; and average chain lengths greater than 250 are rarely achieved. In addition there are some rings (apparently nearly all trimetaphosphate) mixed with the long chains. The proportion of rings is found to increase as the average chain length becomes larger, so that about 9 per cent of the total phosphorus is present as rings in a glass having a number-average chain length of 200. The formation of rings appears to be another mechanism for avoiding infinite or extremely long chains. Nature abhors infinity—and a vacuum is just a special case of this!

Strauss and coworkers (42) recently reported that the pH and viscosity of freshly prepared solutions of Graham's salt decreased over the first 12-hr. period after dissolution. They interpreted this decrease in these properties as indicating the presence of a small amount of unstable branching points in the glasses. The total decrease in the intrinsic viscosity amounted to 10–15 per cent of its initial value. However, after the solution (0.35 *M* in sodium bromide) attained a stable condition, measurements of the viscosimetric root-mean-square end-to-end dis-

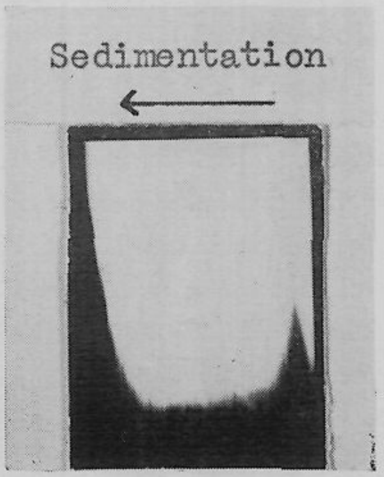

FIG. 3. Sedimentation diagram for a 2 per cent solution of Graham's salt ($\bar{n}$ = approximately 250) in 0.4 *M* sodium thiocyanate (40). The peak results from a sharply defined sedimenting boundary. The heavy shaded area on the left indicates a substantial pile-up of heavy material. Philpot schlieren system; 835 R.P.S.

tance supported the view of the presence of polyphosphate molecules as *unbranched chains.* More recently a study of the viscosity behavior of the same Graham's salt in pure water (41) 12 hr. after dissolution showed that the intrinsic viscosity was proportional to the 1.87th power of the molecular weight, indicating a rod-like structure of the molecule-ions at infinite dilution. The absence of chain branching in such solutions was also confirmed by comparing the end-to-end distances of the molecule-ions at infinite dilution, as estimated

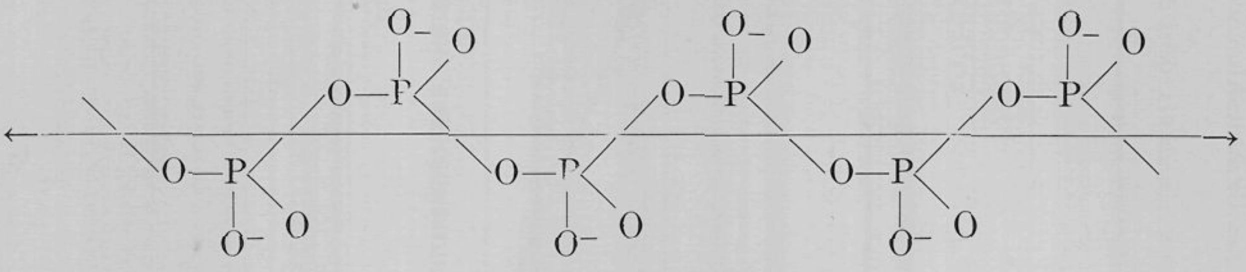

FIG. 4a

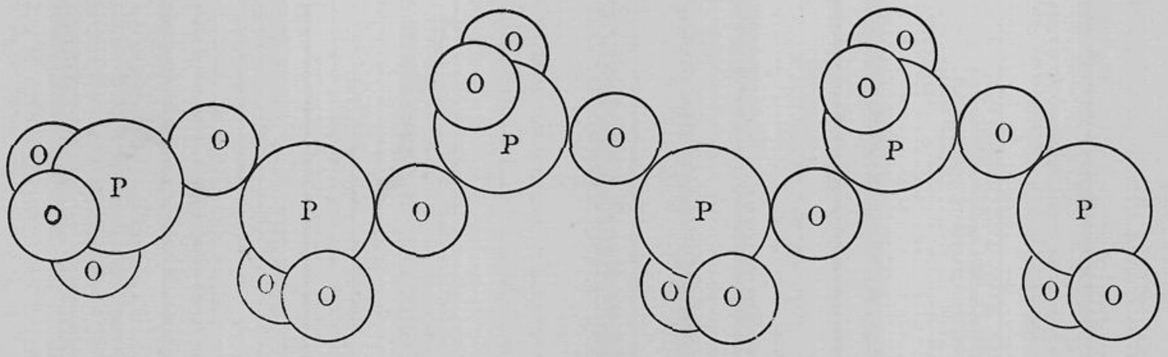

FIG. 4b

FIG. 4. Representations of a stretched-out polyphosphate chain: (a) rod model (Van Wazer, Goldstein, and Farber: J. Am. Chem. Soc. **75,** 1566 (1953)); (b) covalent radii model (*Encyclopedia of Chemical Technology*, Vol. X, p. 471, Interscience Publishers, Inc., New York (1953)). This chain is considerably shorter than an average chain in Graham's salt, being only a hexapolyphosphate.

from the intrinsic viscosity values, with their contour lengths calculated from a molecular weight based upon light-scattering data.

A similar conclusion concerning unstable branching was reached by Stern and Van Wazer (40) in sedimentation studies using the ultracentrifuge. In a typical sedimentation diagram of a freshly prepared solution (figure 3) a sharply defined sedimenting boundary was obtained, but in addition a very substantial pile-up of heavy material at the bottom of the cell was recorded. This pile-up is attributed to the presence of material of extra high molecular weight, presumably the same material which Strauss observed viscometrically.

Thus, it is generally believed that in solutions of Graham's salt that have stood for several hours, only linear polyelectrolyte molecule-ions are present, as shown in figure 4. Flow birefringence studies (55) offer independent evidence in support

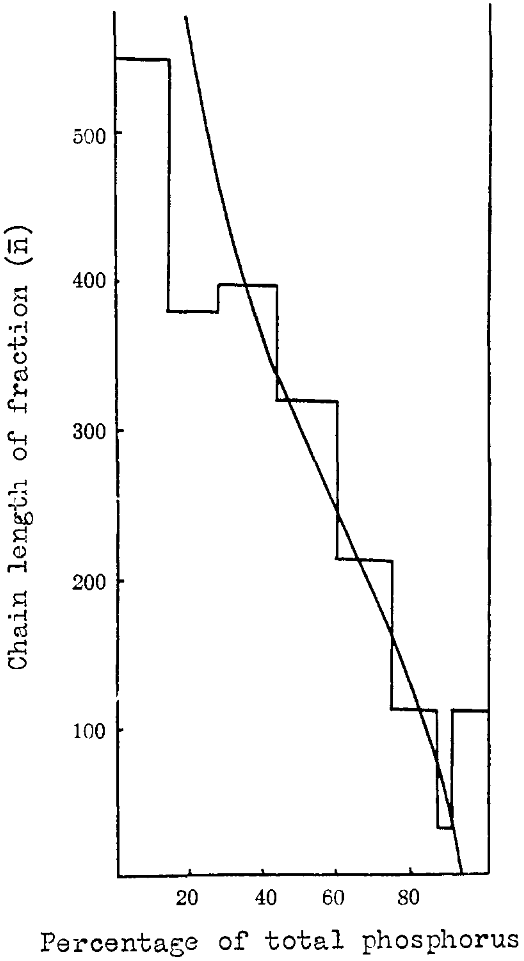

FIG. 5. A comparison of the distribution corresponding to random reorganization with the data from a fractionation experiment for a sample of Graham's salt having a number-average chain length of 193 (corrected for meta rings) (50).

of this belief, since the results show a reasonable agreement between the experimental points and the theoretical relationship for fully stretched molecule-ions.

Solubility fractionation studies (50) have shown that solutions of Graham's salt contain mixtures of phosphate molecule-ions. Data from an acetone fractionation experiment are reproduced in figure 5. The various fractions separated on successive additions of acetone were analyzed by pH titration. Values for the average chain length of from 500 to ca. 100 were obtained, using a glass with an original average chain length of 193. The experimental results agree with the theoretical random distribution function (49) which was calculated by a variation of the Boltzman H-theorem. This function is presented below:

$$f_x = \frac{x}{\bar{n}(\bar{n}-2)}\left(\frac{\bar{n}-2}{\bar{n}-1}\right)^{x-1} \quad \text{for} \quad x \geqslant 2; \bar{n} \geqslant 2 \qquad (7)$$

where f_x is the fraction of the total number of phosphorus atoms present in x-mers.

The most interesting conclusions to be drawn from these studies of the constitution of Graham's salt are the following: (*a*) solutions of the high-molecular-weight Na_2O–P_2O_5 glasses contain a mixture of linear molecule-ions and some ring phosphates. When computed on an $(NaPO_3)_x$ basis, the number-average molecular weight of the linear molecule-ions may run as high as 40,000—with the weight-average molecular weight being about twice as great—depending on the time and temperature of heating. (*b*) Graham's salt is no different except in degree from the other sodium phosphate glasses for which the Na_2O/P_2O_5 mole ratio is much greater than unity. (*c*) It is erroneous to formulate this material as a "hexametaphosphate," as has been done in the past (e.g., 16) and is still being done in the less precise literature.

C. Other glassy phosphates

The glasses in the water–phosphorus pentoxide system have been investigated by wet-chemical methods (4, 13) but not by the techniques of polymer physics. The most interesting data on these glasses show that orthophosphate ion is present to an appreciable extent in the condensed acids—those glasses for which $1 \leqslant H_2O/P_2O_5 \leqslant 2$—as shown in table 1.

The glasses in the sodium oxide–phosphorus pentoxide system contain no detectable amounts of orthophosphate. In the derivation of the theoretical dis-

TABLE 1

Orthophosphate content of strong phosphoric acid

Composition of Glass	Equivalent Acid Notation	Approximate Percentage of Total as Orthophosphoric Acid	Approximate Softening Point of Glass
			°C.
$2H_2O \cdot P_2O_5$	$H_4P_2O_7$ (pyro)	20	−15
$5H_2O \cdot 3P_2O_5$	$H_5P_3O_{10}$ (tripoly)	8	−13
$H_2O \cdot P_2O_5$	$(HPO_3)_x$ (meta)	2	0

tribution function for these glasses, no orthophosphate appeared because a single PO_4 group with three negative charges would represent a high charge concentration which would violate the law of detailed distribution of charge. The presence of orthophosphate in the equilibrium mixtures of strong phosphoric acids shows that some of the hydrogen atoms are covalently bound to PO_4 groups, so that the monohydrogen orthophosphate ion can be considered as being unionized in these concentrated acids. Naturally, this conclusion is in agreement with the very small ionization constant of the HPO_4^{--} ion in dilute aqueous solution.

Potassium and ammonium phosphate glasses have been prepared (54) and approximately typified. The potassium oxide–phosphorus pentoxide glasses appear to be similar in constitution to the glasses in the sodium oxide–phosphorus pentoxide system, as would be expected. It is interesting to note that potassium metaphosphate ($K_2O \cdot P_2O_5$) glasses are very difficult to prepare because of the ease with which potassium Kurrol salt crystallizes.

The technological literature contains numerous references (e.g., 6) to calcium phosphate glasses. Unfortunately, as might be expected from the presence of doubly charged, polarizable calcium ion, these glasses are extremely difficult to dissolve; hence their structures have not been extensively investigated.

D. Kurrol salts

Potassium Kurrol salts are crystalline compositions, the crystals of which exhibit fibrous cleavage. These salts are prepared from potassium dihydrogen phosphate, and different samples have different molecular weights, depending on the conditions of preparation, although the x-ray diffraction powder pattern

TABLE 2

Physical data on solutions of Kurrol salts prepared by heating KH_2PO_4 *for various periods at various temperatures (34, 35)*

Temperature of Preparation	Time at Temperature	Viscosity* in Salt Solution	Sedimentation Constant, S_0†	Diffusion Constant, D†	Degree of Polymerization, $\bar{n}$, from Equation 4 [Zeta Average (26)]
°C.	*hours*	*centipoises*	*Svedberg units*	10^7 *c.g.s. units*	
260	215–280	1.53	10	1.7	2,300
290	120–280	1.93	14	1.4	3,900
305	140–190	3.47	26	1.5	6,700
382		3.47	27	1.0	9,300
445	0.5	2.51			
445	2.0	3.09			
445	4.0	3.36			
445	20	4.36			
445	115–240	4.60	25	0.6	11,700
495		2.60	34	1.2	11,000
665	30–200	4.22	30	0.6	19,500

* Measurements made on solutions prepared by dissolving 2.36 g. of potassium Kurrol salt per liter of solution containing 10.2 g. of sodium trimetaphosphate.

† Sedimentation and diffusion were studied in a 0.4 *M* sodium thiocyanate solution.

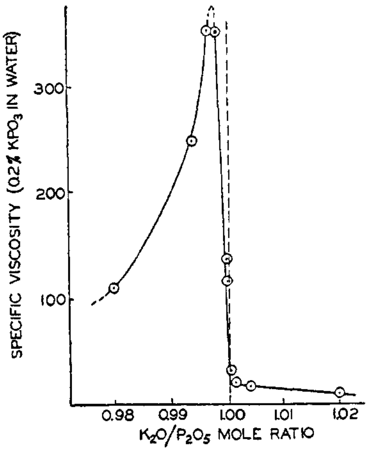

FIG. 6. Specific viscosity of Kurrol salts made by melting dipotassium hydrogen orthophosphate at 850°C. for 30 min., cooling to crystallization, and tempering for 4.7 hr. at 800–775°C. (37).

remains unchanged.[3] Data published by Malmgren and Lamm (30, 32, 34, 35) show that the viscosity, the diffusion constant, and the ultracentrifuge sedimentation constant vary with the temperature (and time) of preparation. This information is presented in table 2. In addition, Pfanstiel and Iler (37) have shown that the degree of polymerization, as indicated by the specific viscosity (53), depends very strongly on the exact K_2O/P_2O_5 ratio of the Kurrol salt, as illustrated in figure 6. The great increase in specific viscosity for K_2O/P_2O_5 mole ratios slightly less than 1 (with the viscosity maximum at $K_2O/P_2O_5 = 0.998$) is attributable to cross-linking. This conclusion is supported by hydrolysis data which show that there is an initial rapid change in specific viscosity with time after dissolution of the material for which the K_2O/P_2O_5 ratio is less than 1 (0.9996), as compared to an initial slow change in viscosity for a material with a K_2O/P_2O_5 ratio slightly greater than 1 (1.0001).

The Kurrol salts have been very extensively studied by several Swedish authors, who have used viscometry, ultracentrifugation, diffusion, and electrophoresis with a number of different swamping electrolytes (12, 20, 21, 22, 23, 24, 25, 32, 33, 34, 35.) Typical viscosity measurements are reproduced in figure 7 for a solution prepared by dissolving the potassium phosphate polymer in a solution of a sodium salt. Table 3 summarizes physical data for two preparations of Kurrol salts and illustrates the variation in these measurements with both the concentration and the nature of the swamping electrolyte. It should be noted that the molecular symmetry factor is 1 for a spherical non-solvated particle. The large values of table 3 indicate asymmetry and/or hydration of the molecule-ions. For a given Kurrol salt, the degree of polymerization (and hence molecular weight) as calculated from the ultracentrifugation data varies as much

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[3] It should be noted, however, that two crystalline modifications of sodium Kurrol salt have been prepared (45).

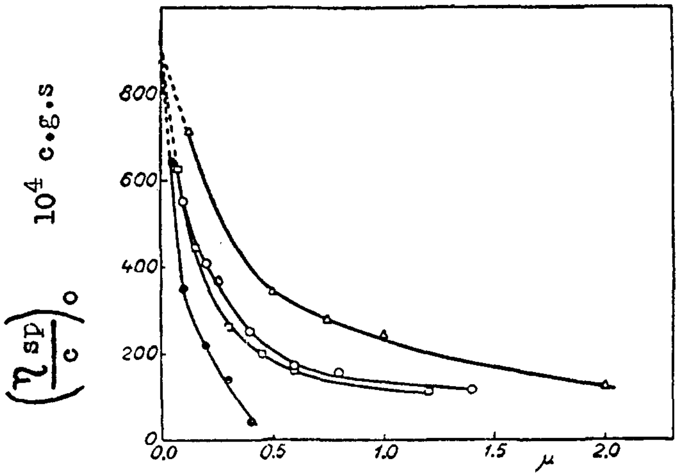

FIG. 7. Intrinsic viscosity of solutions of potassium Kurrol salts as a function of the ionic strength (32). △, $Na_4P_2O_7$; ○, $(NaPO_3)_3$; ●, NaSCN; □, Na_2SO_4. This particular salt was prepared by heating potassium dihydrogen orthophosphate at 495°C. for 250 hr. (H. Malmgren: Acta Chem. Scand. **2**, 149 (1948))

TABLE 3

Variation in properties of two given potassium Kurrol salts with the medium (32, 34)

Kurrol Salt Preparation	Medium Used	Sedimentation Constant at Infinite Dilution S_0	Diffusion Constant at Infinite Dilution D_0	Calculated Degree of Polymerization [Zeta Average]	Molecular Symmetry Factor (f/f_0)
K-14*.......	1.1 *N* NaCl	12	0.87	5,400	
	0.4 *N* NaCl	34	1.20	11,000	
	0.2 *N* $Na_4P_2O_7$	12	0.86	5,500	
	0.8 *N* $Na_4P_2O_7$	17	0.98	6,800	
K-15†.......	0.1 *N* NaCl	14	1.05	4,100	5.2
	0.4 *N* NaCl	32	1.08	9,300	3.8
	0.1 *N* NaCl in 5% ethanol	20	1.25	4,800	4.1
	0.1 *N* NaCl in 8% ethanol	25	1.36	5,500	3.6

* KH_2PO_4 heated several hours at 495°C.

† KH_2PO_4 heated several hours at 500°C.

as twofold with change in the swamping electrolyte. Although this effect might be attributable to changing degree of aggregation between molecule-ions, it is believed that the effect is probably an artifact, introduced by ignoring or imperfectly treating (29, 30, 46) charge interactions in the mathematical interpretation of such data. Present-day studies are unearthing many similar anomalies in the field of polyelectrolytes, in studies of ionized organic macromolecules which definitely do not change their degree of polymerization and are not believed to form aggregates. At present only relative sizes are known with certainty, and today's measurements are but guesses as to absolute sizes of the molecule-ions of polyelectrolytes.

Based on the $(KPO_3)_x$ formula, the molecular weights of the Kurrol salts are 118 times the degree of polymerization. It should be noted that an ultracentrifuge measures a zeta-average molecular weight, which is larger than either a number-average or a weight-average molecular weight (26).

E. Maddrell salt

Chemical studies by Thilo (45) have been interpreted to mean that the crystalline sodium metaphosphate called Maddrell salt or $NaPO_3$-II is a long-chain phosphate. Maddrell salt is considerably more difficult to dissolve than are Kurrol salts. No physicochemical measurements have been reported on this salt.

IV. COMPARISON OF DATA OBTAINED BY THE VARIOUS METHODS

Few data are available for careful evaluation of the consistency of the various results reported on the degree of polymerization of the phosphates. Samuelson (38) has compared the end-group titrations on Graham's salt with the dialysis values of Karbe and Jander (27) and with the ultracentrifugation values reported by Lamm (30). This comparison is reproduced in figure 8. The agreement is believed to be purely fortuitous, since no allowance was made for the large differences between the various types of averages which the different methods should measure for a random reorganization polymer. Since the amount of water removed from a $Na_2O \cdot P_2O_5$ melt will vary with both time and temperature (1), a plot such as that given by Samuelson would appear to be a logical way of attempting a correlation if the time of heating were constant.

Sibert (39) has compared molecular weights determined by the end-group titration method with molecular weights from the cryoscopic method, the latter based on the transition point of sodium sulfate decahydrate. The values which he obtained for several sodium phosphate glasses are graphically presented in figure 9. The differences in the values from the two methods are greatest for the higher molecular weights, and it is in this range that the accuracy of both methods decreases. However, the two methods give values of the same order of magnitude even for the largest molecule-ions measured, and the results are always within reasonable agreement. Both methods of measurement lead to number averages.

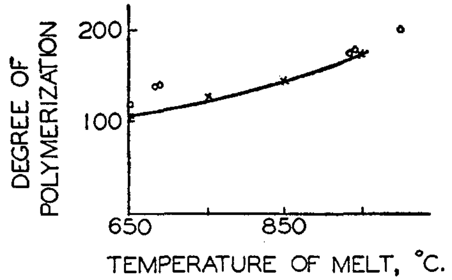

FIG. 8. Molecular weight of Graham's salt (38). ×, titration curve studies by Samuelson (38); ○, diffusion studies by Karbe and Jander (27); □, ultracentrifugation experiments by Lamm (30). Molecular weight = 102 × degree of polymerization.

In figure 10 the light-scattering results reported by Strauss (42) are compared with the end-group titration determinations of Van Wazer (51) by way of viscosity measurements on the solutions. In this comparison, corrections are made for the kind of average molecular weight measured. The number-average molecular weights, as determined by end-group titrations, are about one-half the

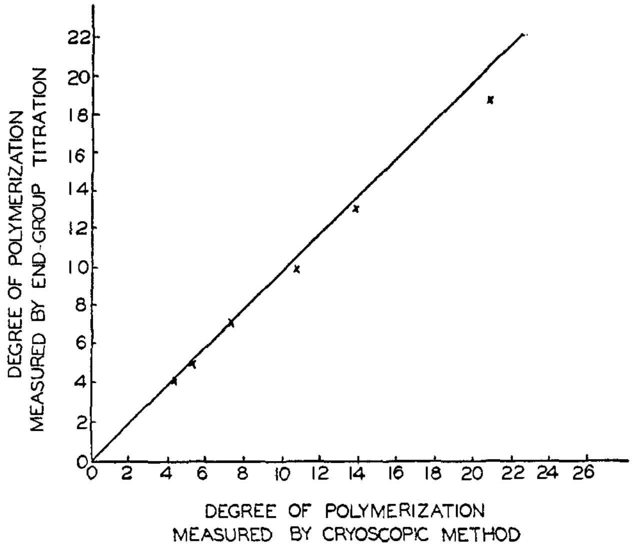

FIG. 9. Comparison of transition point and titration molecular weights for sodium polyphosphate glasses (39).

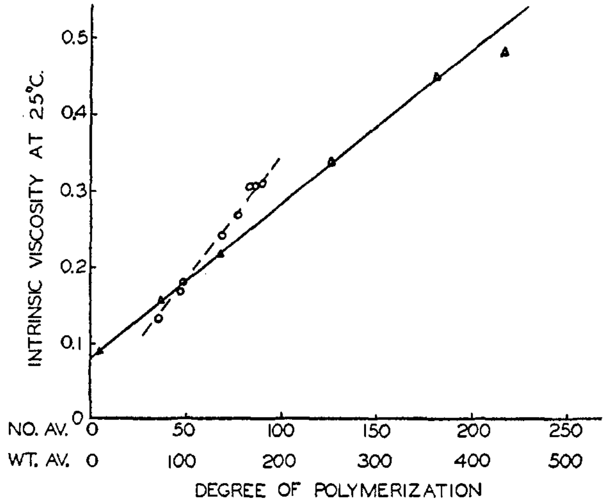

FIG. 10. Comparison of light-scattering molecular weights with titration molecular weights using intrinsic viscosity. Solutions of sodium polyphosphate glasses: ○, light-scattering data, viscosity in 0.35 *M* sodium bromide (42); △, end-group titration data, viscosity in 0.65 *M* tetramethylammonium bromide (51).

weight-average molecular weights (3) in the region of number-averages greater than about 8, for the logarithmic distribution corresponding to random reorganization. Unfortunately, the measurements were not made in the same medium (variations with the medium have been mentioned). Viscosity measurements offer a means of interrelating the various methods and perhaps for studying the effect of solvents.

V. ELECTROLYTIC PROPERTIES OF THE PHOSPHATES

The early literature abounds in references concerning the electrolytic and colligative properties of solutions of the high-molecular-weight phosphates. For example, one of Hittorf's (17) original papers on transference number mentions Graham's salt. Unfortunately, there has not been a modern interpretation of such colligative measurements as the lowering of freezing point or the osmotic pressure of dilute aqueous solutions of the condensed phosphates. However, there are two up-to-date articles on the electrolytic properties of the high-molecular-weight material.

Davies and Monk (8) measured the conductivity of an unspecified preparation of Graham's salt and came to the conclusion that the anion has an extremely high molecular weight. Dilute-solution conductivity curves of the Graham's salt and of the acid prepared from it are compared with the curve for the colloidal electrolyte octadecylamine hydrochloride in figure 11, in order to show that the high

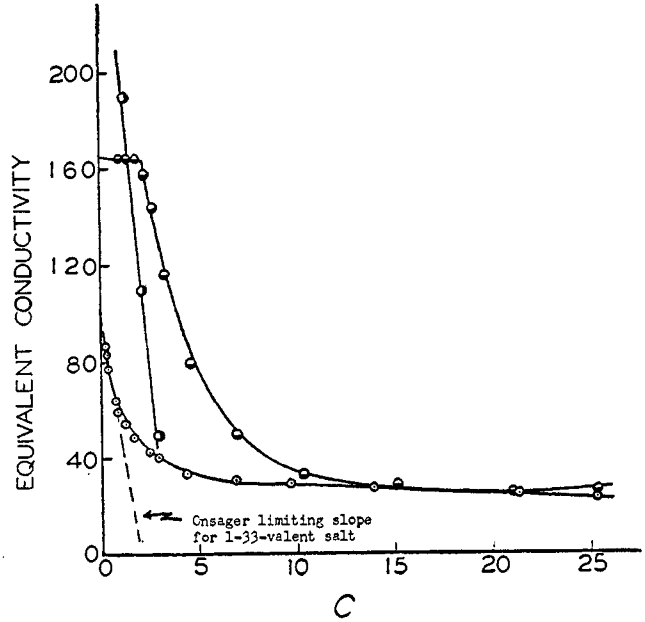

FIG. 11. Equivalent conductivities of solutions of Graham's salt and the acid prepared from Graham's salt at various concentrations (8). C is the equivalent concentration. ○, unspecified preparation of Graham's salt; ◑, acid prepared from Graham's salt; ⊖, octadecylamine hydrochloride.

molecular weight of the polyphosphate molecule-ion is not due to loose association of the numerous units of low molecular weight to form a micelle. It should be noted that there is a break in the conductivity curve for the octadecylamine hydrochloride at the concentration below which the micelles reversibly dissociate into their constituent ions. Such a critical concentration for micelles is not found for solutions of Graham's salt, even at concentrations as low as 5 × 10^{-4} g. per liter.

The dotted line shown in figure 11 has been added by the authors to show the limiting slope for a 1-33-valent salt. This slope was calculated from the Onsager equation, using 100 as the assumed chain length of the Graham's salt, 67 per cent for the amount of sodium bound to the phosphate molecule-ion (from extrapolation of the data given by Wall and Doremus (58)), 50 for the limiting ion conductance of the sodium, and 100 for the limiting equivalent conductance of the Graham's salt. As can be seen from figure 11, the limiting slope of the experimental data agrees very well with the calculated slope of the dotted line.

A recent article by Wall and Doremus (58) has shown that in ionic transference measurements Graham's salt exhibits the behavior of a typical polyelectrolyte. This is demonstrated by table 4, in which the conductance and transference properties of Graham's salt are compared with the lower-molecular-weight phosphates, the sodium tripoly-, pyro-, and orthophosphates. It should be noted from this table that the amount of sodium bound to the polyphosphate ions increases with molecular weight, so that for the Graham's salt having a chain

TABLE 4

Conductance and transference properties of polyphosphates (58)

Solution	Temperature	Polymer Concentration in Equivalents of P per Liter	Fraction of Cations Bound to Polymer	Equivalent Conductance of Polymer Molecule-Ions	Polymer Ion Transference Number	Degree of Polymerization × Polymer Ion Mobility (10^{-9})
	°C.			*cm.²/equiv.-ohm*		
Na_2HPO_4	25	0.0346	0.046	48	0.52	0.34
$Na_4P_2O_7$	25	0.010	0.149	67	0.58	0.51
		0.025	0.203	62	0.58	0.50
		0.040	0.210	54	0.55	0.44
		0.050	0.210	51	0.52	0.42
		0.100	0.315	50	0.54	0.48
$Na_5P_3O_{10}$	25	0.010	0.191	65	0.58	0.52
		0.025	0.277	61	0.57	0.54
		0.040	0.285	51	0.53	0.47
		0.050	0.289	51	0.54	0.46
		0.100	0.366	47	0.53	0.49
Graham's salt	0	0.041	0.708	20	0.44	0.41
	25	0.0425	0.701	37	0.44	0.82
		0.0925	0.707	37	0.46	0.82
$(Na[\frac{1}{2}Sr]PO_3)_n$	25	0.0554		36	0.44	0.82
Strontium			0.989			
Sodium			0.686			

length of about 150 phosphorus atoms, 70 per cent of the sodium ions are associated with the polyanions. When strontium ions are substituted for some of the sodium ions, nearly all of the strontium becomes bound to the polyphosphate anions, but the charge and mobility of the phosphate molecule-ions remain substantially unchanged. As is shown in the last column in table 4, the mobility decreases with increasing chain length because of the increase in ion size. The fact that the product of chain length times mobility increases less than threefold when going from the monomer to the chain consisting of 150 units means that the ionic mobility is roughly proportional to the degree of polymerization.

In this study of electrolytic transference, the rate of exchange between the completely dissociated sodium ion and that bound to the phosphorus molecule-ion was also measured, and an exchange rate constant of 4 min.$^{-1}$ was obtained. This means that half of the bound sodium ion will exchange with the completely ionized sodium in about 10 sec. Since the value of the rate constant for exchange between the bound and free sodium ions was found to remain constant with the time of electrolysis, the conclusion is drawn that the cation exchange rate is independent of the location of the bound cation on the polyphosphate chain. Similar experiments on organic polymers led to an exchange rate constant which varies with the length of time for which hydrolysis has proceeded.

Binding of the cation by the highly charged phosphate molecule-ion also shows up in pH titration curves of the condensed phosphoric acids (57). As shown in figure 12, the strong acid portion of the titration curve of the polyphosphates approaches the neutralization point corresponding to the removal of one hydrogen ion for each phosphorus ion in a more gradual manner as the chain length increases. Unlike the titration curve of a true weak acid, in which the hydrogen is attached to the acid radical through a bond having appreciable covalent character, titration of the strong hydrogen of long-chain phosphates starts out like that of a strong acid and ends up like that of a weak acid. The greatest change in curvature of the titration curves occurs between chain lengths of 5 and 50.

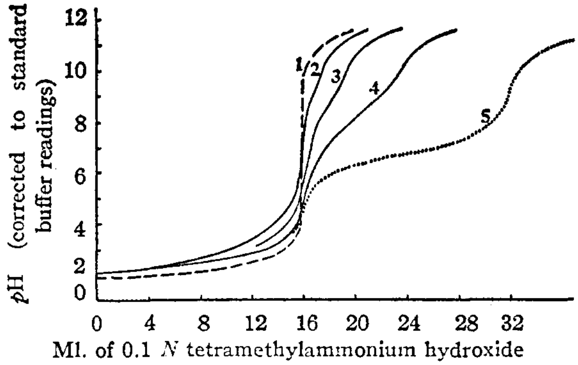

FIG. 12. pH titration curves of fresh solutions of various condensed phosphoric acids (57). These acids were made from the following salts: curve 1, sodium trimetaphosphate curves 2, 3, and 4, anhydrous sodium phosphate glasses for which $\bar{n}$ = 20, 8.7, and 4.0, respectively. Curve 5 corresponds to the orthophosphoric acid formed by complete hydrolysis of the condensed acids.

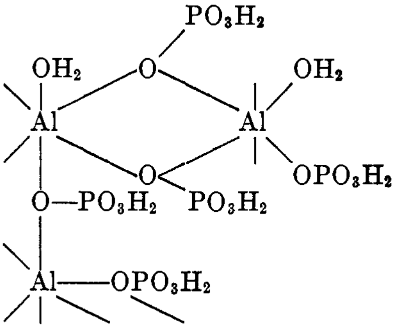

FIG. 13. Polymeric aluminum phosphates

VI. AGGREGATION POLYMERS

In addition to the series of condensation polymers just discussed, there is a second type of phosphate polymer, the *aggregation polymers*, mentioned earlier. The aggregation polymers exhibit a degree of polymerization that is extremely sensitive to the environment in which they are found. The best known examples in phosphate chemistry are the polymers formed with aluminum and orthophosphate ions (14). The stability and degree of polymerization are greatly dependent upon the pH of the medium, probably in much the same way as are those properties of such water-soluble polymers as the chromates and vanadates. The aluminum phosphate polymers are stable in a highly acid medium, but precipitation occurs on making the material alkaline.

The polymeric character of these aggregates in acid solution is evident from their high viscosity and their colloidal properties. A hypothetical structure for the polymers in which the PO_4 tetrahedra are held together by aluminum ions is suggested in figure 13.

In the early literature (36, 52), numerous descriptions are given of gels and oily or amorphous precipitates which are formed when condensed phosphates are precipitated by multiply charged metal ions (such as Ca^{++} or Al^{+++}) or high-molecular-weight cations (such as acidified proteins). This type of system has recently been described with emphasis on the practical utilization of such materials as film-forming plastics (19). Such systems can be considered as combinations of aggregation and covalently bound polymers. Naturally, these systems are very numerous in the field of phosphate chemistry.

VII. SUMMARY

There are a number of condensed phosphates which consist of long chains of alternate phosphorus and oxygen atoms held together by predominantly covalent bonding. Each phosphorus atom in these chains is surrounded by a tetrahedron of oxygen atoms. A description is given of the various methods which have been used to characterize these completely inorganic, strongly ionized polyelectrolytes. These methods include end-group titration, cryoscopy, light scattering, dialysis and diffusion, ultracentrifugation, flow birefringence, relative and intrinsic viscosities in salt solutions, solubility fractionation, and interpretation of dilute-solution viscosity in pure water. The methods agree in demonstrating degrees of polymerization ranging from 2 to 20,000, depending on the exact composition of the salt.

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