of two is made in order to secure an integrable function. In all honesty it should be stated that the factor of two is based more on the requirements of integration than statistics. In any event the function is not very sensitive to the assignment of this constant, especially in the region of high perchlorate concentration. Also much of the variation in K is attributed to the error probably introduced here. It is also not only quite possible but likely that Mo^4 is removed in part by other reactions such as reaction with Mo^6 or with any of the many oxidants forming in the solution. This probably accounts for the apparent tendency of K to decrease slightly with decreasing molybdenum concentration.

Mo^3, if formed, must be rapidly oxidized for it is known that reduction of molybdate with stannous ion yields only pentavalent molybdenum.

If Mo^5 is produced, and is inert catalytically, it must be reoxidized to Mo^6, else the reaction would cease. Evidence that this probably occurs stems from the fact (unpublished) that the reduction of molybdate in perchloric acid by a Jones reductor yields only partial reduction to the pentavalent form, whereas in sulfuric or hydrochloric acid reduction proceeds smoothly to the trivalent state.

The removal of oxidants by complex formation followed by very fast reduction by stannous ion is postulated on the basis that it fits the reaction kinetics. Two experimental facts substantiate this assumption. The assumption predicts that at low stannous ion concentration equilibrium would be established between Mo^4 and oxidants, with a resultant build up of oxidant concentration and a speed up of the reaction as shown by the last two points on Fig. 4. In addition the reduction of chlorate ion by stannous ion in strong sulfuric acid is rather slow, but in the presence of molybdate, the reduction of chlorate to chloride by stannous ion is virtually instantaneous. This would indicate that although stannous tin probably reacts with the oxidants alone, it reacts very much faster in the presence of molybdenum.

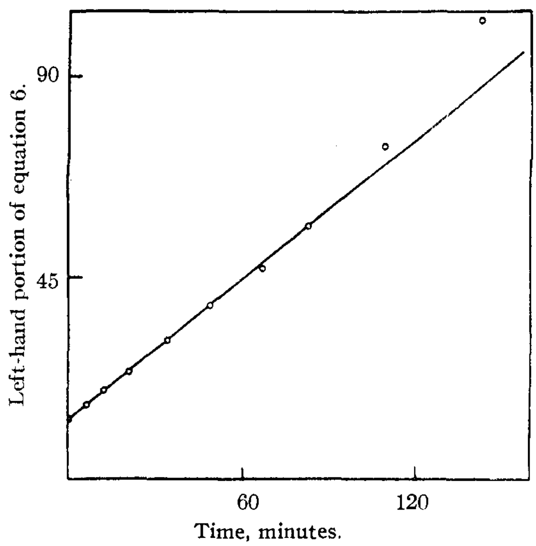

Fig. 4.—Run 9 showing deviation in favor of higher rate at very low (Sn^{++}); A = 1.265.

Besides elucidating the mechanism of a very complicated reaction, indicating a preference for one-step divalent reductions by stannous ion, and showing the catalytic activity of tetravalent molybdenum, this study indicates a promising new reducing agent may now be available. This Laboratory is now studying the reduction of nitrate, and nitro organic compounds with promising preliminary results. Its use for analysis of chlorates, perchlorates, nitrates and possible other oxy ions and compounds which may be irreversibly reduced is being investigated as well.

[CONTRIBUTION FROM THE GRASSELLI CHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Potassium Metaphosphate: Molecular Weight, Viscosity Behavior and Rate of Hydrolysis of Non-cross-linked Polymer

BY R. PFANSTIEL AND R. K. ILER

RECEIVED APRIL 18, 1952

New data are presented on the molecular weight, viscosity and rate of hydrolysis of a linear polymetaphosphate in an aqueous solution obtained by solubilizing crystalline KPO_3 by partial cation exchange with the sodium salt of an ion-exchange resin. The marked effect of minute variations in the original $K_2O:P_2O_5$ ratio on the viscosity indicates that when there is a deficiency of potassium in a KPO_3 melt, cross-linking occurs between the metaphosphate polymer chains in the resulting KPO_3 crystal. Excess potassium in a melt of KPO_3 does not reduce the molecular weight of KPO_3 by acting as a chain-stopper, but instead forms potassium tripolyphosphate as a separate phase. The accompanying KPO_3 is essentially non-cross-linked. The molecular weight of non-cross-linked KPO_3, determined in aqueous solution, may be as high as 120,000. The energy of activation of the hydrolysis of polymetaphosphate at pH 8.5 is about 25 kcal. per mole.

Introduction

Potassium metaphosphate, empirical formula KPO_3, crystallizes readily at 807° from a very fluid melt of the same composition. It gives no indication from this behavior that it is a linear inorganic polymer. Nevertheless, it has been known for many years that when this salt is brought into aqueous solution a highly viscous dispersion is obtained which is characteristic of a linear polymer of high molecular weight. It is the purpose of this paper to present new data on the molecular weight and on the viscosity and stability of aqueous solutions of KPO_3, and to demonstrate the marked effect of minute variations in the $K_2O:P_2O_5$ ratio on the viscosity of this salt in aqueous solution. The results suggest that cross-linking of the metaphosphate chains occurs as the ratio of $K_2O:P_2O_5$ in the KPO_3 crystal falls below unity.

Malmgren and Lamm[1] investigated the molecular weight of KPO_3 dissolved in 0.1 molar solution of sodium trimetaphosphate, and found indications that the molecular weight was of the order of millions, and that the polymer units were highly elongated. Earlier work on the metaphosphates, which has been summarized by Karbe and Jander,[2] has shown that the viscosity of the solution is strongly dependent upon ionic strength; there seems to be little doubt that this inorganic salt exhibits many characteristics of a polyelectrolyte.

Viscosity studies have heretofore been complicated by the fact that crystalline KPO_3 is practically insoluble in pure water; the solubility is reported by Madorsky and Clark[3] to be less than 0.004%. However, it can be dissolved in an aqueous solution of a sodium salt, and this procedure has commonly been employed to prepare solutions for viscosity studies. Based on the data of Volkerding and Bradfield,[4] it appears that at least one equivalent of a sodium salt is required to solubilize about 2 equivalents of KPO_3. We have avoided the complications arising from the presence of the additional electrolyte by dissolving the KPO_3 in an aqueous suspension of the sodium salt of a cation-exchange resin, thus obtaining a solution of mixed sodium–potassium polymetaphosphate free from foreign anions.[5]

While it has been found that crystalline KPO_3 is really a high molecular weight linear polyphosphate which does not correspond exactly to the metaphosphate composition, the term "metaphosphate" has been retained in view of its common usage and especially since most of the materials involved are very close to the metaphosphate composition.

Experimental

KH_2PO_4—Adjustment of K/P Ratio.—The *p*H of a solution of KH_2PO_4 as measured under standardized conditions, is a direct function of the K/P ratio. A 0.1 molar solution of Baker C.P. KH_2PO_4 (Lot 9947) was prepared in CO_2-free distilled water. The *p*H curve, which could be checked within ±0.01 *p*H unit, was obtained by titrating 200 ml. of this solution with *N*/100 solutions of phosphoric acid and KOH, respectively, in an enclosed vessel swept with CO_2-free air. The *p*H was followed with a laboratory model Beckman *p*H meter, standardized with *p*H 4.00 buffer, maintaining the temperature compensator within 0.5° of the temperature of the solution at all times. From the quantities of KOH and H_3PO_4 required to reach various *p*H values on either side of the inflection point 4.51 ± 0.01, the corresponding K/P ratios were calculated. This relationship between *p*H and K/P ratio is shown in Fig. 1. The K/P ratio of unknown samples of KH_2PO_4 can thus be determined by preparing a 0.1 molar solution in CO_2-free water and observing the *p*H. By this method it was found that most lots of C.P. KH_2PO_4 were slightly acidic. It is possible that C.P. KH_2PO_4 does not correspond exactly to the theoretical ratio because H^+ ions may be adsorbed on or within the crystal lattice. The K/P ratio of the KH_2PO_4 used in this work was 0.9996 ± 0.0002. This is low enough to cause appreciable cross-linking in the resulting KPO_3.

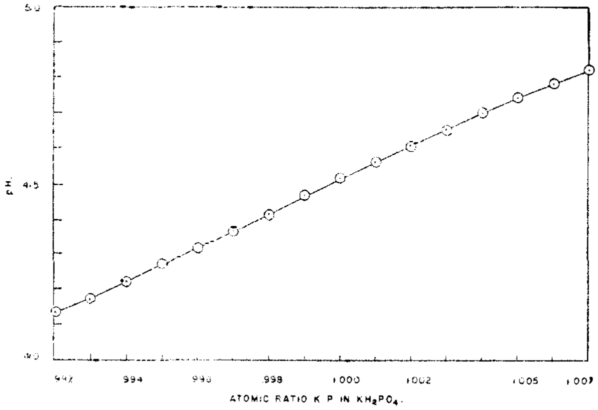

Fig. 1.

KH_2PO_4 having slightly different K/P ratios were prepared by adding calculated quantities of H_3PO_4 or KOH solutions to weighed samples of KH_2PO_4, and the mixtures dried with continued stirring so as to distribute the added component over the surface of the crystals.

Preparation of KPO_3.—Samples of KH_2PO_4 with K/P ratios from 0.98 to 1.02 were prepared as described above, the ratios checked by *p*H measurement and then the samples were converted to KPO_3 by slow dehydration to 400°, heating for 40 minutes at 675° in a platinum dish, followed by immediate cooling.

The following procedure gives KPO_3 with minimum cross-linking, consistent with minimum triphosphate impurity, the K/P ratio being 1.001. In a typical preparation, Mallinckrodt C.P. KH_2PO_4 (Lot 7100) having a K/P ratio of 0.9996, was employed. To this material, Mallinckrodt C.P. "KOH + Aq." (85% KOH, 3% K_2CO_3) was added as follows: To 1500 g. of KH_2PO_4 was added just enough 95% ethyl alcohol (600 ml.) to cover the crystals in a four-liter stainless steel beaker. Then 1.41 g. of C.P. KOH, dissolved in 5 ml. of water diluted to 75 ml. with ethyl alcohol, was slowly added with continuous stirring. The alcohol was then evaporated with continuous stirring. A 3″ diameter platinum dish containing 100 g. of the adjusted KH_2PO_4 was placed in a furnace at 850°. After conversion to molten KPO_3 (30 minutes), it was allowed to cool to a few degrees below the melting point (about 800°), and the temperature was then gradually lowered over a four-hour period to 775° and held at this temperature for 40 minutes. The sample was then removed from the furnace and chilled by holding the lower part of the dish in water. The transparent crystalline product was then pulverized by means of a laboratory model Raymond Swing Hammer Mill to a fluffy mass of short microscopic fibers. An alternative method of heating, which gave about the same degree of polymerization, is to dehydrate the adjusted KH_2PO_4 at 775°, holding the dehydrated material at this temperature for 40 minutes and then cooling rapidly.

In preparations having a K/P ratio greater than 1.0 it was found that the potassium in excess of a K/P ratio of 1.0, formed tripolyphosphate, $K_5P_3O_{10}$, which could be washed out of the KPO_3 with ice-water (see Table IV). Thus, samples of KPO_3 prepared from KH_2PO_4 having K/P ratios of 1.001, 1.01 and 1.05, respectively, were pulverized to fine powders and then further ground in ice-water for 20 minutes. The suspension in each case was then filtered rapidly, washed with alcohol and ether, and dried.

Dissolving KPO_3 by Ion Exchange.—A typical method of preparing a solution for viscosity measurements is as follows: A 0.2–1.0% slurry of finely ground KPO_3 in boiled distilled water is prepared in a covered vessel fitted with a stirrer and *p*H electrodes. The suspension is vigorously stirred and brought to *p*H 8 with 0.1 *N* NaOH. Freshly washed sodium salt of "Nalcite HCR" ion-exchange resin is then added, in the ratio of 6 g. of air-dried resin per gram of KPO_3. The KPO_3 begins to swell immediately. The *p*H tends to drop slightly, but is maintained between 7.5 and 8.5 by the addition of more alkali in order to minimize degradation of the polymer.[6] Vigorous stirring is continued for 40 minutes to disperse any lumps, and the temperature is kept at 25–30°. The resulting solution at *p*H 8.0–8.5 is

---

(1) H. Malmgren and Ole Lamm, *Z. anorg. Chem.*, **B252**, 256 (1944).

(2) K. Karbe and G. Jander, *Kolloid-Beihefte*, **B54**, 1 (1943).

(3) S. L. Madorsky and K. G. Clark, *Ind. Eng. Chem.*, **32**, 247 (1940).

(4) C. C. Volkerding and R. Bradfield, *Soil Sci. Soc. Am. Proc.*, **8**, 159 (1943).

(5) U. S. Patent 2,557,109 (1951), R. K. Iler (du Pont).

(6) B. Ingelman and H. Malmgren, *Acta Chem. Scand.*, **1**, 422 (1947).

then filtered through a mat of glass wool under slight suction to remove the resin.

Viscosity Measurement.—Viscosity determinations were made with an Ostwald pipet, calibrated against water and standard oils, at 25 ± 0.2°. The viscosities of the KPO_3 solution were recorded in centipoises, since the densities of the solutions were close to 1.000.

Initially, an attempt was made to plot the data on viscosity *vs.* concentration in accordance with formulas proposed for polyelectrolytes, but it became apparent that this would require a much more complete study of the viscosity behavior of this polymer. Accordingly, a plot of log specific viscosity *vs.* log concentration was employed to correlate the viscosity data and find an empirical relationship between viscosity and molecular weight as determined by end-group titration. Time did not permit an investigation of intrinsic viscosity, measured in a solution of tetramethylammonium bromide in accordance with the method of Van Wazer.[7]

Titration of End-groups.—According to Quimby,[8] when any phosphoric acid is titrated to *p*H 4.3, one titratable hydrogen has been neutralized per atom of phosphorus; Britton[9] states that neutralization of metaphosphoric acid is complete at *p*H 5.0. For titration of the second hydrogen of end-groups, Samuelson[10] recommends *p*H 9.0. Accordingly, titration of metaphosphate solution between *p*H 5.0 and 9.0 was taken as equivalent to the end-groups. Titrations were carried out with 200 cc. of KPO_3 (or equivalent $NaPO_3$) solution at about 1% concentration in CO_2-free distilled water, using 0.01 *N* HCl and NaOH in a CO_2-free atmosphere. The titration value from *p*H 7 to 9, representing half of the end-groups, was first separately determined, since in this *p*H range it is certain that no degradation occurs, then the value from *p*H 5 to 9 was determined. Since the latter was not significantly greater than twice the titration from *p*H 7 to 9, it was concluded no appreciable degradation occurred at the lower end of the *p*H range during the titration.

Degradation of Metaphosphate in Solution.—In making viscosity measurements, the rate of degradation at 30° in the *p*H range 7 to 9 could be neglected providing the viscosities were measured within a period of two hours after preparation of the solution. However, degradation was noticeable in one hour at *p*H 5.2. The viscosity of a solution of free polymetaphosphoric acid dropped rapidly at 30°; measurable degradation occurred in one hour even at 0°. The rate of degradation at a fixed *p*H and temperature was not appreciably affected by the concentration of the polymer.

A slow hydrolysis of polymetaphosphate was carried out in order to obtain a series of samples by which the specific viscosity could be correlated with molecular weight as determined by end-group titration; *p*H 6.0 was selected as giving a rate of degradation at 35° which could be readily followed. The *p*H was lowered to 6.0 by treatment with a small quantity of resin in hydrogen form, which was then removed by filtration. The solution was held at 35° and samples removed at suitable intervals for characterization.

A more rapid experiment was also conducted with the free acid.

Two ion-exchange methods were used in the preparation of the free acid. In the first case the KPO_3 was solubilized by stirring with an aqueous suspension of sodium ion-exchange resin and the resulting sodium–potassium metaphosphate solution was then cooled to 0–5° and passed through a column of the ion-exchange resin in hydrogen form. Subsequently it was found that the KPO_3 could be solubilized directly at 0° by stirring with the hydrogen resin, after which the acidic KPO_3 solution was further converted to free acid by passage through a column of the hydrogen resin.[11]

In a typical preparation of the polymetaphosphoric acid, a 1% solution of KPO_3, solubilized by ion exchange with the sodium form of ion-exchange resin, was passed through a column of the hydrogen resin about 1.5 inches in diameter and 22 inches long which had been previously cooled with ice-water. Because of the high viscosity of the solution, 2.5 hours was required for the passage of the solution even though vacuum was applied to the receiver. As soon as the acid had been collected from the column, a portion was taken for titration with NaOH in order to determine the concentration of free acid, and to provide a sample of solution for viscosity measurement. At the same time, a portion of this neutralized sample was titrated to *p*H 5 with 0.1 *N* HCl, followed by titration to *p*H 9 with 0.01 normal NaOH, in order to determine the end-groups. Further samples of the acid stored at 0–5° were taken over the next 24 hours, for similar determination of viscosity and molecular weight.

Measurement of Rate of Hydrolysis of Metaphosphate at *p*H 8–9.—The temperature coefficient of hydrolysis was determined by following the viscosity of metaphosphate in solution at different temperatures, using a sample of KPO_3 made from KH_2PO_4 containing excess potassium to ensure absence of cross-linking and washing out the tripolyphosphate before use. The *p*H was maintained at as close to 8.5 as possible, but some variations occurred so that the range was actually from 8.2 to 9.0. Very small amounts of 1.0 normal NaOH solution were added as soon as the *p*H was noted below 8.5. In this *p*H range, the rate of degradation appears to change much less with *p*H than it does below *p*H 6.0. From the degree of polymerization estimated from viscosity, the corresponding normality of acidic end-groups was calculated, and the velocity constant calculated.

Let b = concentration of (PO_3) units in terms of g. mols of monomeric KPO_3 per liter and x = normality of end-groups at time, t. Then concentration of unhydrolyzed (PO_3) units = $b - (x/2)$.

Assuming a first-order reaction

$$\frac{dx}{dt} = K\left(b - \frac{x}{2}\right)$$

where K = rate constant under fixed conditions. Whence

$$\ln \frac{(2b - x_0)}{(2b - x)} = \frac{Kt}{2}$$

where $x = x_0$ at $t = 0$. Since x and x_0 are much smaller than $2b$ in the following experiments, the above equation may be reduced to

$$\frac{x - x_0}{b} = Kt$$

In Table I, there is also included a sample of KPO_3 made from KH_2PO_4 having a K/P ratio of 1.000, degraded in a 10% solution. The rate of degradation is similar to that of the sample made with excess potassium present and degraded in 1% solution.

TABLE I

Degradation of a 1% solution of $(KPO_3)_x$ made from KH_2PO_4 having a K/P ratio of 1.01

	Heating period	Specific viscosity	Degree of polymerization	Calcd. end-group normality $\times 10^{-4}$
(A)	0	33.46	1150	1.47
Temp. 90°	24 min.	15.26	715	2.36
	48 min.	9.70	530	3.19
	95 min.	5.49	375	4.51
(B)	0	33.79	1170	1.45
Temp. 59°	2.00 hr.	28.57	1040	1.62
	4.75 hr.	24.61	950	1.78
	76.75 hr.	4.25	320	5.29
(C)	0	33.37	1160	1.46
Temp. 26.7°	48 hr.	31.02	1100	..
	132 hr.	27.07	1000	..
	216 hr.	24.28	950	1.78
Sample $(KPO_3)_x$ made from KH_2PO_4 with K/P = 1.000				
(D)	0	102.2	2400	0.70
Temp. 90°	24 min.	27.43	960	1.76
(10% solution)	48 min.	14.73	690	2.47
	95 min.	6.84	430	3.94

---

[7] J. R. Van Wazer, THIS JOURNAL, **72**, 906 (1950).

[8] O. T. Quimby, *Chem. Revs.*, **40**, 141 (1947).

[9] H. T. S. Britton, "Hydrogen Ions," Vol. 1, 3rd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 180.

[10] O. Samuelson, *Svensk Kem. Tid.*, **56**, 343 (1944).

[11] U. S. Patent 2,557,132 (1951), W. E. Mochel (du Pont).

Table II

	Temp., °C.	b	x_0 (10^4)	t, hr.	$K \times 10^4$
A	90	0.0847	1.47	0.4	26.6
				0.8	25.4
				1.58	22.8
				Av.	24.9
B	59	.0847	1.45	2.0	1.06
				4.75	0.85
				76.75	0.60
				Av.	0.83
C	26.7	.0847	1.46	216	0.0175
D	90	.0847	0.71	0.40	31.1
				0.80	26.0
				1.58	24.2
				Av.	27.1

Results and Conclusions

KPO_3 Deficient in K_2O: Cross-linked.—Van Wazer[12] has shown that in the case of $NaPO_3$ glasses, the rate of solution in water is much less when the molar ratio of Na_2O to P_2O_5 is less than unity. By analogy with linear organic polymers, it might be expected that a slight deficiency of potassium in a KPO_3 would likewise give a cross-linked product. As shown in Fig. 2, a very slight deficiency of K_2O in KPO_3 results in a marked increase in the viscosity of the aqueous solution, which has a ropy character suggestive of a slightly cross-linked highly swollen polymer. Although Fig. 2 indicates only that the break in the curve occurs at a K/P ratio of about 1.00 detailed experiments show that the break occurs at 1.000. For example, the viscosities of 0.2% solutions of KPO_3 having K/P ratios of 1.0002 and 0.9996 were 30 and 120 c.p.s., respectively. With a large deficiency of K_2O, the KPO_3 crystals fail to pass into solution when stirred with a suspension of the sodium salt of an ion-exchange resin, but merely swell, giving a viscous mass in a concentrated suspension which, upon dilution, gives only a low viscosity. Many of the variations in the viscosity behavior and molecular weight, which were reported in the past, may therefore have arisen from slight variations in composition.

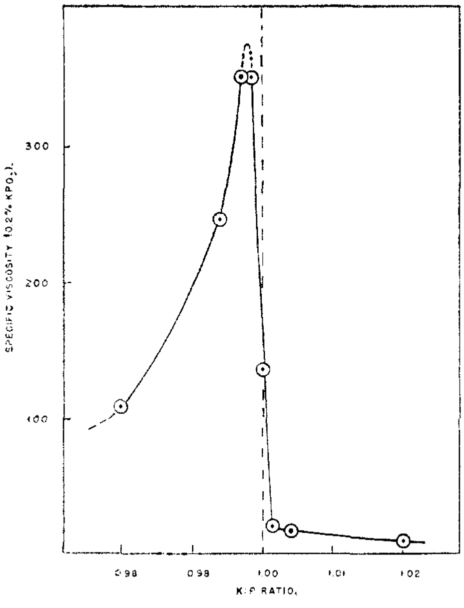

Fig. 2.

The marked difference between cross-linked KPO_3 and relatively non-cross-linked material is shown in Table III. The rapid drop in the initial viscosity of the solution of cross-linked material, with attendant greater drop in pH of the solution, indicates the instability of what we believe to be the phosphorus–oxygen–phosphorus cross-links.

Table III

Relative Viscosity of 1% KPO_3 Solutions at 25° (Solubilized by Na Resin)

K/P ratio in KPO_4	0.9996		1.0001	
Age of solution at 35°, days	pH	Relative viscosity	pH	Relative viscosity
0	7.90	1525	8.00	260
1	7.33	132	7.73	114
5	6.47	22.3	6.85	19

It is also significant that when the cross-linked polymers, which initially show a high viscosity, are degraded by hydrolysis, the viscosity–concentration relationship then approaches that of the purely linear metaphosphate polymers (see Fig. 3). This indicates that the cross-linkages are much more rapidly hydrolyzed than the linkages along the metaphosphate chains.

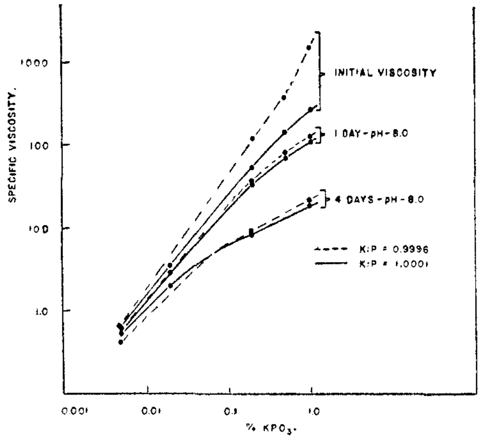

Fig. 3.

It may be that cross-links are formed by the omission of two potassium atoms and one oxygen atom from a point in the KPO_3 crystal lattice. This may permit an oxygen bridge to be formed directly between adjacent metaphosphate chains; although this must bring about some local irregularity in the crystal lattice, attempts to detect such irregularities by means of X-ray diffraction have been unsuccessful.

Maximum viscosity might be expected when there are only a few cross-links between the long potassium metaphosphate chains. This would permit the chains to separate to a considerable extent, although still linked together, resulting in an extremely large molecule composed of many chains

---

(12) J. R. Van Wazer, This Journal, 72, 651 (1950).

held together in a flexible, extended form. If a larger excess of H_3PO_4 is used so that a more highly cross-linked polymer is obtained, the polymer cannot be as completely dispersed in dilute solution so that maximum viscosity cannot be developed.

KPO_3 Containing Excess K_2O. Non-cross-linked.—By analogy with linear organic polymers, it might also be expected that an excess of potassium oxide might reduce the length of the metaphosphate chain by acting as a "chain-stopper." This is not the case. Apparently the structure of the KPO_3 crystal is such that excess potassium in the melt cannot enter the crystal, but remains in the liquid phase and later crystallizes out as $K_5P_3O_{10}$; this has also been observed by Osterheld and Audrieth.[13]

As shown in Table IV, the viscosity of a solution of the crude KPO_3 formed from a potassium-rich melt decreases with increasing potassium content, but this is due to the electrolyte effect of the tripolyphosphate in the aqueous solution. When the latter soluble salt is removed by washing the crushed KPO_3 with distilled water, it is found that the viscosity of the KPO_3, when then dissolved by ion exchange, is relatively independent of the amount of excess K_2O in the original melt. In the case of the sample with ratio 1.05, the viscosity is doubled by removing the soluble salts. In the sample with a K/P ratio of 1.000, there is probably a slight amount of cross-linking; the ratio might have fallen very slightly below 1.000. This suggests that in order to eliminate cross-linking from a practical standpoint, a slight excess of potassium should be present in the melt.

TABLE IV

KPO_3 CONTAINING EXCESS POTASSIUM: VISCOSITY AT 25° OF $(KPO_3)_x$ SOLUBILIZED WITH SODIUM ION-EXCHANGE RESIN

K/P ratio	As $(KPO_3)x$, %	Specific visc. Before water extraction	Specific visc. After water extraction	Extracted solids %	Extracted solids Ratio[a] K/P	Degree of polym. of washed samples
1.05	1.0	16.7	35.6	12.0	1.65	1200
1.05	0.2	6.1	14.0	...	..	..
1.01	1.0	28.3	34.7	4.1	1.69	1180
1.000	0.2	55.7	59.0	1.9	..	..
1.000	1.0	269.0	..	..	..	4200

[a] Ratio of K/P in $K_5P_3O_{10}$ 1.66.

It is estimated that the degree of polymerization of non-cross-linked KPO_3, prepared at 775° may be as high as 1000, corresponding to a molecular weight of about 120,000 when it is first brought into solution. The distribution of molecular weight is not known, but Malmgren[14] has shown that in freshly prepared solutions, poly-dispersibility is low and that even in degraded solutions, very little orthophosphate is present.

Crystallinity of KPO_3 and Molecular Weight.—The fact that molten KPO_3, only a few degrees above the melting point, is about as fluid as water, strongly suggests that high molecular weight metaphosphate chains are not present in the melt. As shown in Table V, the semi-vitreous product obtained by sudden quenching of the melt gives an aqueous solution of very low viscosity, verifying the low molecular weight nature of the melt.

TABLE V

VARIATIONS IN TEMPERATURE OF PREPARATION OF NON-CROSS-LINKED KPO_3 (K/P = 1.000)

Method of preparation	Appearance	Specific viscosity (25°) 0.2% soln.	Specific viscosity (25°) 1.0% soln.
I, KH_2PO_4 slowly heated to 665°, held at 665° for 40 min.; crucible chilled in water (KPO_3 was never molten)	White, opaque micro-crystalline	31.1	102
II, Same, except to 775°	White, opaque micro-crystalline	51.5	170
III, Heated KH_2PO_4 slowly to 850°, cooled melt of KPO_3 to 775°; held at 775° for 40 min.; crucible chilled in water	Clear, massive crystalline	55.7	180
IV, KPO_3 from I melted at 850°, quenched between porcelain plates chilled with Dry Ice	White translucent semi-vitreous	..	2.8
V, Heated KH_2PO_4 suddenly to 850°, quickly cooled to 795°, cooled to 775° in 4 hr., held at 775° for 40 minutes	Transparent, massive crystalline	50	164

On the other hand, crystalline KPO_3 obtained either by heating KH_2PO_4 up to just below the melting point, or by crystallizing the KPO_3 melt and holding it for a short time just below the melting point, is a fibrous high molecular weight material. In the first case there is obtained a white, opaque, micro-crystalline powder, and in the second case, a clear solid crystalline mass, yet both products are fibrous when pulverized and give about the same viscosity when dissolved.

Two conclusions may be drawn. (a) The high molecular weight polymer is formed in the process of crystallization and, in fact, the process of crystallization undoubtedly involves stepwise addition of PO_3^- units to the crystal, and is equivalent to a polymerization. (b) The clear massive crystal obtained by slowly cooling the melt, and aging the crystal at 775°, undoubtedly is full of crystal imperfections, since the polymer chain length is not related to the size of the massive crystal, but is instead probably determined by the length of the fibrous micro-crystallites. Since a micro-crystalline KPO_3 powder produced at 775° without melting had the same molecular weight as the massively crystalline product produced at the same temperature, the size of the micro-crystalline units may be a function only of the temperature and composition. A product made at 665° had a somewhat lower molecular weight. This decrease in molecular weight of KPO_3 with decreasing temperature of preparation below the melting point, is in line with the observations of Malmgren.[14]

Viscosity, Concentration and Molecular Weight.—As shown in Fig. 4, the viscosity of non-cross-linked KPO_3, solubilized by ion exchange, varies with concentration in a manner characteristic of polyelectrolytes, the viscosity varying linearly with the (1.2) power of the concentration up to 0.02% by weight of KPO_3, and thereafter approximately with the square root of concentration. The vis-

---

(13) R. K. Osterheld and L. F. Audrieth, *J. Phys. Chem.*, **56**, 38 (1952).

(14) H. Malmgren, *Acta Chem. Scand.*, **2**, 147 (1948).

TABLE VI

END-GROUP TITRATIONS AND VISCOSITY

K/Na metaphosphate solution aged at 35°, initial *p*H 6.5, 1.005% as KPO_3, titration with 0.0103 alkali and acid per 200-ml. sample

Age, day	(A) *p*H 7–9	(B)[a] Est. *p*H 5–9	(C) Found *p*H 5–9	(D) Average of B & C	(E) End-groups[b] per 1000 P.	Specific viscosity 1.0%	0.008%	0.004%	0.002%	0.001%
0	1.5	3.0	2.9	2.9	0.9	26	2.247	1.578	1.188	. .
1	2.7	5.4	5.1	5.2	2.3	28	2.389	1.625	1.268	. .
6	2.4	4.8	5.1	5.0	2.1	23	1.848	1.318	1.140	. .
9	3.1	6.2	5.8	6.0	2.7	19.65	1.793	1.273	1.132	1.05
14	4.2	8.4	7.3	7.8	3.8	11.68	1.540	1.237	1.112	. .
23	5.0	10.0	10.5	10.3	5.3	6.33	1.301	1.101	1.056	. .
37	8.0	16.0	15.1	15.5	8.5	3.78	1.255	. . .	. . .	. .
	H_2O blank	. .	1.4							

[a] Double the titer (A). [b] E calculated from D minus water blank.

cosity, extrapolated or interpolated if necessary, at 1% KPO_3 was used as a basis for comparison in following changes in molecular weight. Based on Fig. 5, the empirical relationship is

$$Y = 0.61x \times 2.12$$

where $x = \log_{10}$ (specific viscosity) and $y = \log_{10}$ (degree of polymerization), the degree of polymerization being calculated from end-group titrations as shown in Table VI.

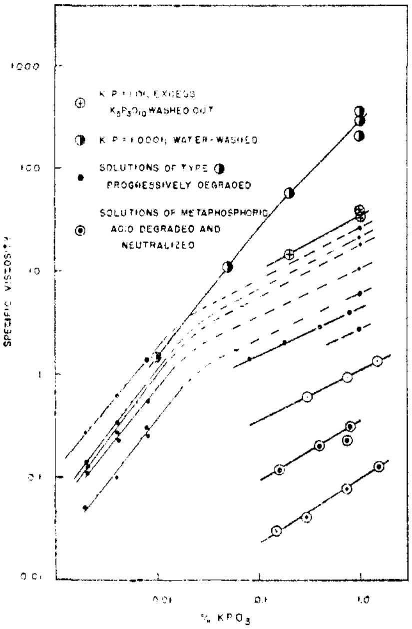

Fig. 4.

Effect of the Na/K Ratio on Viscosity.—The ratio of sodium to potassium in the polymetaphosphate solution has very little effect on the viscosity. For example, when 1 g. of KPO_3 was solubilized with from 5 to 30 g. of the sodium salt of an ion-exchange resin, the relative viscosity of the 0.2% solution (KPO_3 basis) varied only from 63 to 77. There is no evidence that the exchange of sodium ions for potassium in solution accelerates degradation. However, it is possible that some degradation of the original polymer chains in KPO_3 crystals may occur during the ion-exchange process of bringing the polymer into solution.

The addition of sodium and potassium salts of monovalent anions markedly reduces the viscosity of metaphosphate solutions. The anion appears to have little or no influence on viscosity, as shown by the identical effects of sodium chloride and sodium benzene sulfonate at equivalent concentrations. The potassium ion is roughly equivalent to sodium ion in repressing viscosity as indicated by viscosity measurements in solutions containing equivalent amounts of KCl and NaCl. These observations are consistent with the general behavior of anionic polyelectrolytes.[15]

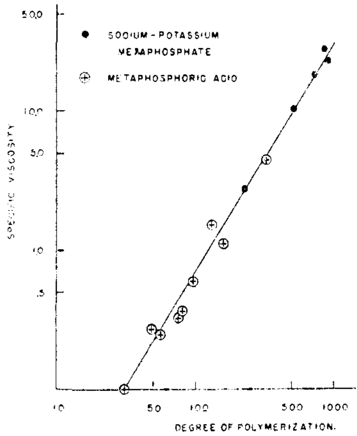

Fig. 5.

Hydrolysis of Non-cross-linked Polymetaphosphate.—Based on the rate of degradation of the polymer given in Table II, the energy of activation of the hydrolysis of the P-O-P linkage in 1% KPO_3 solution at *p*H 8.5 is estimated to be about 25 ± 2 kcal. per mole. Since Malmgren[14] has shown that very little orthophosphate is found even in solutions of degraded polyphosphates, it is probable that most chains break on the average near the middle. It might also be expected that the rate of hydrolysis will increase with increasing negative charge on the chain, since the mutual repulsion between the charges probably causes the chain to become extended in solution, thus imposing a maximum strain at the middle of the chain. It might be predicted that the energy of activation of hydrolysis will be higher in solutions of high ionic strength where the charge is reduced.

WILMINGTON 98, DELAWARE

---

(15) Fuoss and Strauss, *J. Polymer Sci.*, **3**, 246, 603 (1948).