The Stability of Calcium Complexes of Purely-separated Polyphosphate

By Masaji MIURA and Yoshiki MORIGUCHI

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The complex formation of linear-chain polyphosphates with various metals has been studied by several authors.[1-5] Their studies, however, have dealt with polyphosphates with molecular weight distributions. The investigation of complexes of purely-separated polyphosphates, except pyrophosphate and triphosphate, has not yet been undertaken. This is probably in part due to the difficulty of separating individual polyphosphates from their mixture in sufficient quantities and in part to their low stability for a hydrolytic degradation.[6] As their stability decreases with decrease in the pH of the solution, the measurements of the stability constants of polyphosphate complexes must be carried out at as high a pH as possible, and so it is difficult to apply such an usual method as pH titration.

The purpose of this study is twofold, namely, 1) to investigate the effect of the thain length of purely-separated polyphosphates on the stability of their calcium complexes, and to compare the present results with those given by Irani et al. and others[1,2] and 2) to investigate the effect of the ionic strength on the structure of calcium complexes of polyphosphates with various chain lengths from the point of view that polyphosphate is a kind of polyelectrolyte.

Experimental

The Synthesis and Separation of Polyphosphates.[6,7] — A polyphosphate glass was prepared by the pyrolysis of a mixture of sodium dihydrogen phosphate and disodium hydrogen phosphate containing ^{32}P at 800°C for 5 hr. Each linear-chain polyphosphate with a chain length of 4—8 phosphorus atoms was separated from the mixture of polyphosphates by anion-exchange chromatography using the H-form of Dowex 1X4 (100~200 mesh).

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[1] R. R. Irani and C. F. Callis, *J. Phys. Chem.*, **64**, 1398 (1960).

[2] J. I. Watters and S. M. Lambert, *J. Am. Chem. Soc.*, **81**, 3201 (1959).

[3] J. R. Van Wazer and D. A. Campanella, ibid., **72**, 655 (1950).

[4] U. P. Strauss and P. D. Ross, ibid., **81**, 5295 (1959).

[5] W. Wieker, A. Grossmann and E. Thilo, *Z. anorg. u. allgem. Chem.*, **307**, 42 (1960).

[6] S. Otani, M. Miura and T. Doi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 593 (1963).

[7] W. Wieker, *Z. Elektrochem.*, **64**, 1047 (1960).

An aqueous solution of sodium chloride was used as an eluent. Each polyphosphate was precipitated from the effluent by adding benzidin, and the precipitate was repeatedly washed with distilled water until the filtrate was free from chloride ions.

The benzidin polyphosphates thus obtained were transformed into tetramethylammonium polyphosphates by adding an aqueous solution of tetramethylammonium hydroxide. The isolated benzidin was separated from the polyphosphate solution by extraction with chloroform.

The pH of tetramethylammonium polyphosphate solutions was kept over 10 by adding tetramethylammonium hydroxide, and the solutions were stocked in a refrigerator to avoid hydrolytic degradation.

The G. R.-grade pyrophosphate and triphosphate were repeatedly crystallized from water and an ethanol-water mixture respectively.8) Both of them were transformed into free acids by the use of cation-exchange resin.1)

The concentration of each polyphosphate was determined by a radio tracer technique, while those of pyrophosphate and triphosphate were determined by means of pH titration.

Reagents.—The tetramethylammonium hydroxide and bromide were both G. R.-grade reagents and were used without further purification. The calcium solutions used as titrants were $5.01_2\times10^{-2}$, $1.02_9\times10^{-1}$ and $2.05_8\times10^{-1}$ M calcium nitrate standardized with disodium ethylenediaminetetraacetate at a pH of 13 in the presence of a calcon indicator.9)

Apparatus and Procedure.—The nephelometer used in the present work was an A. K. A. spectrophotometer, which was reconstructed so we could keep the temperature in a cell-room constant and could stir a sample solution in a cell by means of a micromotor.

The solutions of polyphosphate and of oxalic acid as a precipitating agent were pipetted into a cell. The total ionic strength of the solution was adjusted to either 0.1 or 1.0 by adding a 3 M solution or crystals of tetramethylammonium bromide. Distilled water was added to the solution until its volume was 30∼33 ml., and then the pH of the solution was kept at 10∼12 by adding an aqueous solution of tetramethylammonium hydroxide.

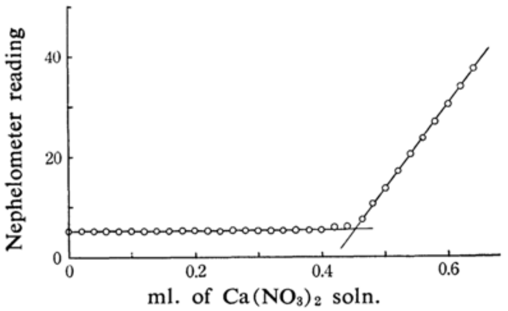

Fig. 1. An example of nephelometric titrations for the calcium-oxalate-polyphosphate system.

The nephelometric titration was carried out at 25±0.5°C under a nitrogen atmosphere by adding a standard solution of calcium nitrate through a calibrated microburet. The solution was vigorously stirred during the titration. At five-minute intervals titrant shots were taken. This procedure was proved by a preliminary test to avoid supersaturation and to give equilibrium values. An example of the results of the titration is shown in Fig. 1.

It was verified by ion-exchange chromatography and paper chromatography that the degradation of polyphosphate did not occur during the titration.6,10)

The Treatment of Date

The evaluation of the stability constants of the calcium polyphosphate complexes was performed by a method similar to that reported by Irani et al.1) Assuming that a polyphosphate chain consists of some sites, $L(\theta)$, which can bind a calcium ion to θ phosphorus atoms,* that these sites are mutually independent, and that the concentration of free calcium ions is negligibly small at the end-point compared with that of the calcium complex, the stability of the calcium complex at pH over 10 can be evaluated by means of the following equation:

$$\beta=\left(\frac{L_tA}{\theta yz}-1\right)\frac{K_{sp}}{[\mathrm{C_2O_4}]_t} \tag{1}$$

where β is the dissociation constant of the complex given by Eq. 2; L_t, the total concentration of the polyphosphate expressed by moles of phosphorus per liter; A, the total volume of the sample solution at the end-point; y, the number or ml. of z M calcium solution added until the end-point; $[\mathrm{C_2O_4}]_t$, the concentration of oxalic acid, and K_{sp}, the solubility product of calcium oxalate expressed by Eq. 3. The literature values of K_{sp} are 1.32×10^{-8} and 7.80×10^{-8} at the ionic strengths of 0.1 and 1.0 respectively.1)

$$\beta=\frac{[\mathrm{Ca}]\,[L(\theta)]}{[\mathrm{Ca}L(\theta)]} \tag{2}$$

$$K_{sp}=[\mathrm{Ca}]\,[\mathrm{C_2O_4}] \tag{3}$$

Thus, β can be calculated from Eq. 1 if θ is known. θ can be evaluated by the measurements at two different concentrations of oxalic acid, if the temperature, ionic strength and pH are kept constant. Namely, if y_1 and y_2 are obtained at two different concentrations of oxalic acid, $[\mathrm{C_2O_4}]_{t_1}$ and $[\mathrm{C_2O_4}]_{t_2}$, the elimination of β from Eq. 1 gives Eq. 4:

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8) R. N. Bell, *Anal. Chem.*, **24**, 1997 (1952).

9) C. A. Goetz and R. C. Smith, *Iowa State J. Sci.*, **34**, No. 1, 81 (1959).

10) H. Grunze and E. Thilo, *Sitz. ber. deut. Akad. Wiss. Berlin Kl. Math. u. allgem. Naturw.*, **1953**, No. 5.

* The θ does not always indicate a so-called "co-ordination number," since it has not yet been clarified whether or not the bond between polyphosphate and calcium ions is a definite co-ordination one.

$$\theta = \frac{(L_{t_1}A_1/y_1z_1)\,[\mathrm{C_2O_4}]_t - (L_t\,A_2/y_2z_2)\,[\mathrm{C_2O_4}]_{t_1}}{[\mathrm{C_2O_4}]_t - [\mathrm{C_2O_4}]_{t_1}} \tag{4}$$

Charges on the ions in Eqs. 1—4 were omitted for purposes of simplification.

Results and Discussion

The nephelometric titration data are summarized in Table I. The θ values are plotted against the chain lengths of polyphosphate in Fig. 2. From this figure, the values of θ at an ionic strength of 0.1 are found to be about 2 regardless of the chain length, while the corresponding values at an ionic strength of 1.0 vary between 2 and 4 with the number of phosphorus atoms per chain. This may be due to an effect on the configuration of the polyphosphate chain of the supporting electrolyte added in order to adjust the ionic strength. As the polyphosphate is a kind of polyelectrolyte, the presence of the supporting electrolyte may cause the polyphosphate chain to coil up as a result of the decrease in electrostatic repulsion on the chain.[11] The coiled chain with an appropriate configuration may easily assume a value of θ higher than two.

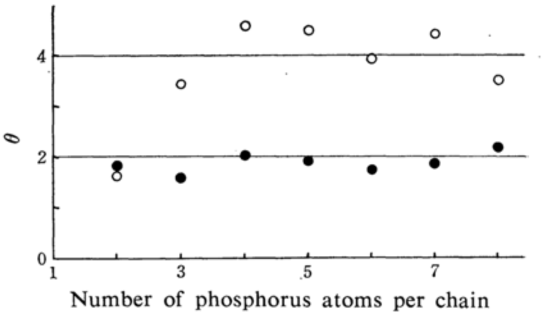

Fig. 2. Relation between the number of phosphorus atoms bound by a calcium ion and the chain length of the polyphosphate. Ionic strength; ●: 0.1, ○: 1.0.

The negative logarithms of the dissociation constants, β, of calcium polyphosphate complexes are summarized in Table II, along with the results of Irani et al., and they are plotted against the chain length in Fig. 3. As for the value of θ used to evaluate β from Eq. 1, an 2, 3 or 4 integer, near the value shown in Fig. 2, was used. The values of θ reported by Irani et al. are independent of the ionic strengths and take the same values at the ionic strengths of both 0.1 and 1.0 (θ; 2, 3 and 4 for the chain lengths of 2, 3 and 6 phosphorus atoms respectively), whereas in this paper, the values of θ at an ionic strength of 0.1 are different from those at 1.0, except for pyrophosphate. Therefore, the stability constants given by Irani et al. were recalculated using the same values of θ as those used in the present study; the results are shown in Table II.

As may be seen in Fig. 3, the stability of calcium polyphosphate complexes increases with the chain length at the ionic strengths

TABLE I. SUMMARY OF DATA FOR NEPHELOMETRIC TITRATION OF CALCIUM-OXALATE-POLYPHOSPHATE SYSTEM AT 25°C

Polyphosphate	Number of phosphorus atoms per chain	Ionic strength	Moles of phosphorus per liter		Concn. of Ca. soln. $z\times10^2$ mol./l.	ml. of Ca soln. (y) added to end-point for the following ml. of 0.2 M $\mathrm{H_2C_2O_4}$ soln.		Total vol. at end-point ml.	
			$L_{t_1}\times10^3$	$L_{t_2}\times10^3$		1.0 (y_1)	2.0 (y_2)	A_1	A_2
Pyro-phosphate	2	0.1	21.5_0	21.5_0	20.5_8	0.557	0.334	30.557	30.668
		1.0	64.8_7	64.8_7	10.2_9	0.304	0.172	33.447	33.378
Tri-	3	0.1	10.8_9	18.1_5	20.5_8	0.498	0.548	30.498	30.548
		1.0	9.85_7	9.77_9	10.2_9	0.684	0.534	33.826	33.941
Tetra-	4	0.1	3.02_2	3.25_8	5.01_2	0.582	0.453	30.582	30.453
		1.0	2.94_9	2.94_4	10.2_9	0.199	0.193	33.341	33.401
Penta-	5	0.1	2.88_1	2.88_1	5.01_2	0.518	0.356	30.518	30.356
		1.0	2.60_8	2.60_3	10.2_9	0.175	0.165	33.317	33.373
Hexa-	6	0.1	2.72_6	2.90_0	5.01_2	0.569	0.419	30.569	30.419
		1.0	2.62_5	2.62_0	10.2_9	0.189	0.168	33.330	33.376
Hepta-	7	0.1	2.70_3	2.70_3	5.01_2	0.559	0.401	30.559	30.401
		1.0	2.40_2	2.44_2	10.2_9	0.179	0.176	33.942	33.384
Octa-	8	0.1	2.24_6	2.24_6	10.2_9	0.218	0.169	30.218	30.169
		1.0	2.11_7	2.11_4	10.2_9	0.163	0.163	33.306	33.345

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[11] R. M. Fuoss, *Discussions Faraday Soc.*, **11**, 125 (1951).

TABLE II. STABILITY OF CALCIUM POLYPHOSPHATES AT 25°C

Polyphosphate	Ionic strength	θ	Neg. log. of dissociation constant			
			$[C_2O_4]_{t_1}$	$[C_2O_4]_{t_2}$	Av.	Ref.
Ortho-phosphate	0.2					1.63[14]
Pyro-	0.1	2	5.43	5.42	5.42	5.39[1]
	1.0	2	4.49	4.48	4.49	4.89[1]
Tri-	0.1	2	5.90	5.83	5.87	5.90[1]
	1.0	3	5.12	5.17	5.15	5.36[1]
Tetra-	0.1	2	5.93	5.92	5.93	
	1.0	4	5.58	5.81	5.69	
Penta-	0.1	2	5.86	5.84	5.85	
	1.0	4	5.57	5.74	5.65	
Hexa-	0.1	2	6.03	5.96	6.00	5.92[1]
	1.0	4	5.79	5.76	5.77	5.78[1]
Hepta-	0.1	2	6.02	5.98	6.00	
	1.0	4	5.86	6.07	5.96	
Octa-	0.1	2	5.99	6.03	6.01	
	1.0	4	6.16	5.79	5.98	

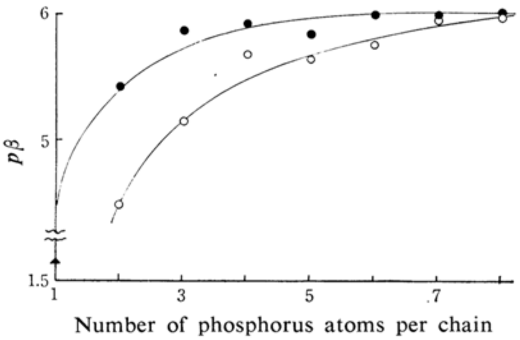

Fig. 3. Relation between stability constants of calcium polyphosphate complexes and chain lengths of the polyphosphates at 25°C. Ionic strength; ●: 0.1, ○: 1.0, ▲: 0.2.[14]

of both 0.1 and 1.0 and levels off at the chain length of 6—7 phosphorus atoms when the ionic strength is 0.1, though not yet when it is 1.0. The increase in the stability with the chain length was also reported by Irani et al. and by Van Wazer et al.[12] This phenomenon is probably in part due to an increase in the charge density on a polyphosphate chain and in part to an effect of the chain configuration on the complex formation.

A comparison of the present results with those of Irani et al. shows that the stability constant of unfractionated polyphosphate with an average chain length of 6 phosphorus atoms agrees with that of purely-separated hexaphosphate in this work within the range of experimental error. From this result, it seems reasonable to conclude that the stability constant of the calcium complex of any polyphosphate is equivalent to that of a mixture of polyphosphates with the same average chain length, if the mixture does not contain ortho- or pyrophosphate. It has been verified by means of ion-exchange chromatography that ortho- and pyrophosphate are not present in the polyphosphate mixture prepared by the method described above.

It raises some questions that Irani et al. carried out the nephelometric titration using the precipitating agent not only at the same concentrations as ours, but at higher concentrations up to about eight times that of polyphosphate. As the stability constant of the calcium oxalate complex is considerably large, i. e., 10^3,[13] the dissolution of the complex can not be disregarded when the concentration of oxalic acid is too high compared with that of polyphosphate. This is supported by the fact that the dissociation constant of the triphosphate complex tends to decrease with an increase in the concentration of oxalic acid (e. g., β; 3.84, 1.22 and 1.06×10^{-6} for the 1.33, 2.00 and 2.67×10^{-2} M concentrations of oxalic acid respectively, at the ionic strength of 0.1).

The assumptions for the site in the derivation of Eq. 1 still remain to be discussed in more detail with regard to the structure of such polyelectrolyte complexes as calcium polyphosphate; these questions will be clarified in due course.

Summary

The formation of calcium complexes of purely-separated linear chain polyphosphates

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[12] J. R. Van Wazer and C. F. Callis, *Chem. Revs.*, **58**, 1011 (1958).

[13] R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

[14] R. M. Smith and R. A. Alberty, *J. Am. Chem. Soc.*, **78**, 2376 (1956).

with chain lengths of 2~8 phosphorus atoms has been studied by means of nephelometric titration at 25°C, pH values of 10~12, and ionic strengths of 0.1 and 1.0. The following results have been obtained: 1) The number of phosphorus atoms bound to a calcium ion is about 2, regardless of the chain length at an ionic strength of 0.1, while it varies from 2 to 4 according to the chain length at an ionic strength of 1.0; 2) The stability of calcium polyphosphates increases with the chain length at both ionic strengths and levels off at a chain length of 6~7 when the ionic strength is 0.1, though not yet when it is 1.0; and 3) The stability constant of a calcium complex of any long-chain polyphosphate is almost equal to that of a mixture of polyphosphates with the same average chain length.

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Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima