The Chemical Compositions of Crystals and Glasses of the $NaPO_3$–Na_2SiO_3 and $NaPO_3$–SiO_2 Systems

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Several attempts to prepare condensed phosphates containing other oxoacid anions have been made. Thilo and his coworkers[1-7] have, for instance, succeeded in making condensed arsenate-phosphates,** which are composed of P–O–P, As–O–P, and As–O–As linkages. Some investigations have been carried out of the chemical compositions of condensed sulfate-phosphates[8] and condensed vanadate-phosphates,[9] which contain S–O–P and V–O–P linkages respectively.

Silicic acid has a tendency toward polymerization, which in turn leads to the formation of various condensed silicates. From the structural analogy between condensed phosphates and condensed silicates, it is to be expected that condensed phosphate-silicates containing P–O–Si linkages will be formed. Investigations[10-12] of the reaction of silicic acid with orthophosphoric acid have revealed the existence of silicon diphosphate, SiP_2O_7. An investigation of the CaO–P_2O_5–SiO_2 system by du Plessis[13] has disclosed that when a glass of calcium phosphate-silicate is dissolved in water, it gives a mixture of polyphosphates the average chain length of which decreases with the increase in the silicon dioxide content of the glass. Some physical and chemical properties of glasses of the Na_2O–P_2O_5–SiO_2, Na_2O–P_2O_5–B_2O_3, and Na_2O–P_2O_5–Al_2O_3 systems have recently been reported by Takahashi.[14] Although the $NaPO_3$–SiO_2 and KPO_3–SiO_2 systems have also been studied by du Plessis,[13] there have not been sufficient data available on the chemical compositions of the substances belonging to these systems.

The present investigation was undertaken to determine the chemical compositions of crystals and glasses of $NaPO_3$–Na_2SiO_3 and $NaPO_3$–SiO_2 systems. It was found by this work that glassy substances of these systems contain P–O–Si linkages, but not crystalline substances.

Experimental

Glassy Substances. — In a platinum crucible a certain amount (4∼12 g.) of monosodium dihydrogen orthophosphate dihydrate was dehydrated and melted by heating and then converted into a glass of sodium metaphosphate (Graham's salt) by cooling the melt in the platinum crucible. In the case of the $NaPO_3$-Na_2SiO_3 system, after the weight of the glass had been measured, calculated amounts of silicon dioxide and of sodium carbonate were placed on the glass in the crucible. As for the $NaPO_3$-SiO_2 system, a mixture of only sodium metaphosphate and silicon dioxide was used. Then, the mixture of these two or three materials was melted at 1400°C for 1.5 hr. The melt was quenched by pouring it onto a copper plate and by pressing it with another copper plate. By this procedure, glasses of the $NaPO_3$-Na_2SiO_3 system with P/Si ratios of 6, 10, 15, 20, 30, 50, 75, 100 and 200, and glasses of the $NaPO_3$-SiO_2 system with P/Si ratios of 10, 20 and 50 were prepared. All the glasses thus obtained were colorless.

Crystalline Substances. — A mixture of sodium metaphosphate, silicon dioxide, and sodium carbonate or a mixture of sodium metaphosphate and silicon dioxide was heated at 1500°C for 1.5 hr. The melt was crystallized by cooling it slowly down to 200°C at the rate of 100°C/hr. By this treatment, crystals of the $NaPO_3$-Na_2SiO_3 system with P/Si ratios of 0.5, 0.7, 0.85, 1, 1.15, 1.3, 1.5, 2, 3 and 4, and crystals of the $NaPO_3$-SiO_2 system with P/Si ratios of 0.5, 1, 2, 3 and 4

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** These compounds are tentatively named by the present authors according to Rule 6.3 for double salts, triple salts, etc. in "Nomenclature of Inorganic Chemistry" reported by the commission of International Union of Pure and Applied Chemistry in 1957.

1) E. Thilo and I. Plaetschke, *Z. anorg. u. allgem. Chem.*, **260**, 297 (1949).

2) E. Thilo and G. Schulz, ibid., **266**, 34 (1951).

3) E. Thilo, G. Schulz and E.-M. Wichmann, ibid., **272**, 182 (1953).

4) E. Thilo and L. Kolditz, ibid., **278**, 122 (1955).

5) E. Thilo and K. Dostál, ibid., **298**, 100 (1959).

6) I. Grunze, K. Dostál and E. Thilo, ibid., **302**, 221 (1959).

7) F. Wodtcke and E. Thilo, *Monatsberichte der Deutschen Akademie der Wissenschaften zu Berlin*, **1**, 508 (1959).

8) K. J. Shaver and J. G. Stites, Jr., "The Heteropolymeric System Na_2O-P_2O_5-SO_3," a report presented at the 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957.

9) S. Ohashi and T. Matsumura, This Bulletin, **35**, 501 (1962).

10) A. Boulle and R. Jary, *Compt. rend.*, **237**, 161, 328 (1953).

11) R. Jary, *Ann. Chim.* (*Paris*), [13], **2**, 58 (1957).

12) V. N. Sveshnikova and E. P. Danilva, *Zhur. Neorg. Khim.*, **2**, 928 (1957).

13) D. J. du Plessis, *Angew. Chem.*, **71**, 697 (1959).

14) K. Takahashi, "Binary Phosphate, Silicophosphate, Borophosphate and Aluminophosphate Glasses, their Properties and Structure," a report presented at the 6th International Congress on Glass, Washington, July, 1962.

were prepared. All the crystals thus obtained were white.

X-Ray Diffractometry. — The samples were ground with an agate mortar until they could pass through a 150 mesh screen. Their diffraction patterns were taken with a Rigaku Denki Geigerflex diffractometer with nickel-filtered CuK_α radiation.

Paper Chromatography. — Solvents A and B as reported by Bernhart and Chess[15] were used. Solvent A was made by mixing 25 ml. of a 20% trichloroacetic acid solution, 10 ml. of water, and 65 ml. of acetone. Solvent B was made by mixing 25 ml. of a 20% trichloroacetic acid solution, 17 ml. of water, and 58 ml. of acetone.

Solvent A was used for the separation of ortho-, di-, tri-, trimeta-, and long-chain- phosphates. A sample solution was placed at the center of a circular paper, 18 cm. in diameter, of Toyo No. 51A and developed for 2 hr. at 10~12°C.

Solvent B was used for the separation of individual chain phosphates from ortho- through tridecaphosphate and long-chain phosphates. Filter paper of Toyo No. 51A was cut into a sheet of 60 by 8 cm., with one end tapered to leave a central 5 by 0.8 cm. strip. The sample solution was placed at the upper end of the central strip of the paper sheet and developed for 5 days at 5°C.

After it had dried, the paper was sprayed with a perchloric acid-molybdate solution so as to convert the phosphates into molybdophosphate. After it had again dried, the paper was exposed to ultraviolet radiation in order to reduce the molybdophosphate a blue complex. Each phosphate species on the paper chromatogram was identified by the similar treatment of a reference solution of a known mixture of phosphates.

The demarcation between the bands was made close to the rear edge of each band in order to minimize the effects of hydrolysis, and the elution of each band was carried out by Smith's[16] method. The paper was cut at the demarcation line, and each band was placed in a 25 ml. Erlenmeyer flask, to which 10 ml. of 0.1 N ammonia was added. The resulting solution was transferred into a 25 ml. volumetric flask, and 10 ml. of water and 2 ml. of Lucena-Conde and Prat's reagent[17] were added. All the bands from each paper must be treated in the same way. Therefore, all the flasks containing solutions from one paper were placed in a boiling water bath at one time, removed at the same time after they had been heated for 1 hr., cooled, and diluted to the mark with water. The absorbance of the solution was measured with a Hirama electrophotometer at 800 mμ.

Lucena-Conde and Prat's Reagent.[17] — Ammonium molybdate tetrahydrate (8.15 g.) was dissolved in 60 ml. of water. To 30 ml. of this solution, 50 ml. of 12 N hydrochloric acid and 56 ml. of 36 N sulfuric acid were slowly added. After the mixture had cooled, 12 N hydrochloric acid was added to bring the volume back to 136 ml. To 25 ml. of the initial molybdate solution, 12.5 ml. of 12 N hydrochloric acid, 12.5 ml. of water, and finally, 10 ml. of mercury were added in turn. The mixture was shaken for 5 min. and filtered to obtain 40 ml. of a ruby-red solution of molybdenum (V). This ruby-red solution was stirred into the acid solution of molybdenum (VI) mentioned above and diluted to 200 ml. to give an emerald green solution.

The Measurement of the Average Chain Length of Polyphosphates. — In a 250 ml. Erlenmeyer flask, 0.1~1 g. of a glass was dissolved in about 150 ml. of water. After most of the silicate ions in the sample solution had been deposited, the deposit was filtered off. According to the pH titration method proposed by Van Wazer, Griffith, and McCullough,[18,19] the average chain length (polymerization degree) of the polyphosphates produced by the hydrolysis of a given sample was measured as follows.

An appropriate amount of the filtrate was acidified with dilute hydrochloric acid and then titrated with 0.1 N sodium hydroxide. The volume of the 0.1 N sodium hydroxide consumed between two inflection points located at approximately pH 4.5 and 9.5 was measured. Another suitable amount of the filtrate was mixed with 0.2 g. of potassium chloride and boiled with hydrochloric acid in order to hydrolyze completely all the condensed phosphates. The residue was treated with water and then titrated with the 0.1 N sodium hydroxide. If the titer for the first titration per unit weight of the sample is A and if the titer for the second one is A_h, the average chain length, $\bar{n}$, is given by the equation, $\bar{n}=2A_h/A$, on the assumption that ortho- and ring phosphates are not present.

Results and Discussion

The samples of both $NaPO_3$–Na_2SiO_3 and $NaPO_3$-SiO_2 systems with P/Si ratios smaller than 4 were obtained as crystalline substances containing amorphous substances. The chemical compositions of these crystalline substances can be estimated from the data obtained by the X-ray diffractometry and the paper chromatography. When the samples are treated with water, all the phosphates are dissolved in it. As for silicon, crystalline silicon dioxide is not dissolved in water, while a greater part of the soluble silicates deposits, only a smaller part of it remaining in the solution. Although the paper chromatographic behavior of silicate ions in the sample solution has not been confirmed, silicate ions do not interfere at all with the separation of condensed phosphates.

The data for the $NaPO_3$–Na_2SiO_3 system with P/Si ratios of 0.5~4.0 are given in Table I. In the X-ray diffraction patterns of the samples with P/Si ratios of 0.85~1.50,

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[15] D. N. Bernhart and W. B. Chess, *Anal. Chem.*, **31**, 1026 (1959).

[16] M. J. Smith, ibid., **31**, 1023 (1959).

[17] F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

[18] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954).

[19] E. J. Griffith, ibid., **28**, 525 (1956).

TABLE I. CHEMICAL COMPOSITIONS OF SUBSTANCES OF THE $NaPO_3$-Na_2SiO_3 SYSTEM WITH P/Si RATIOS OF 0.500∼4.00

	X-Ray diffractometry					Paper chromatography			
P/Si	Phosphate				α-Cristobalite	Phosphate, P%			
	Ortho	Unknown (ortho)	Di	Tri*		Ortho	Di	Tri	Higher
0.500	⧻	±	±	−	±	100	0	0	0
0.700	⧻	±	±	−	±	100	0	0	0
0.850	−	⧻	±	−	±	100	0	0	0
1.00	−	⧻	±	−	⧻	100	0	0	0
1.15	−	⧻	+	−	⧻	85.8	14.2	0	0
1.30	−	⧻	⧺	−	⧻	65.1	34.9	0	0
1.50	−	⧻	⧻	−	⧻	51.7	48.3	0	0
2.00	−	+	⧻	−	⧻	16.4	83.6	0	0
3.00	−	−	⧻	⧻	⧺	0	43.7	53.1	3.2
4.00	−	−	⧺	⧻	+	0	26.7	64.5	8.8

* High temperature form

there are unknown peaks of a strong intensity at spacings of 2.63 and 4.29 Å and of a medium intensity at spacings of 2.79 Å. According to an unpublished paper by Ohashi and Ikeda, these unknown peaks, which have been observed for certain samples of the $NaPO_3$-Na_2SO_4 system, are assumed to be due to one of the modifications of trisodium orthophosphate. The discussions below are based on this assumption.

The crystalline substance of the sample with the P/Si ratio of 1.00 is composed of trisodium orthophosphate and α-cristobalite. Therefore, it is quite evident that when a mixture of sodium metaphosphate and sodium metasilicate with a mole ratio of 1 : 1 is melted, the following reaction occurs:

$$NaPO_3 + Na_2SiO_3 \rightarrow Na_3PO_4 + SiO_2 \qquad (1)$$

The crystalline substances of the samples with P/Si ratios smaller than 1.00 contain trisodium orthophosphate but not α-cristobalite. For these samples, the silicon dioxide produced by Eq. 1 reacts further with an excess of sodium metasilicate to form a glassy sodium silicate. The crystalline substances of the samples with P/Si ratios larger than 1.00 contain α-cristobalite and two of the following three phosphate species; trisodium orthophosphate, tetrasodium diphosphate, and pentasodium triphosphate (high-temperature form). The α-cristobalite content in these samples, of course, decreases with the increase in the P/Si ratio. The orthophosphate content decreases and that of diphosphate increases when the P/Si ratio increases from 1.00 to 2.00. With the further increase in the P/Si ratio, the diphosphate content decreases and that of triphosphate increases. These facts indicate that the trisodium orthophosphate produced by Eq. 1 reacts further with an excess of sodium metaphosphate to form di- and triphosphate.

Small amounts of chain phosphates longer than triphosphate were found in the aqueous solutions of the samples with P/Si ratios of 3.00 and 4.00. Since anhydrous crystals of such chain phosphates as hexasodium tetraphosphate and heptasodium pentaphosphate have not been obtained as yet, it is reasonable to consider that the chain phosphates longer than triphosphate in the samples mentioned above compose an amorphous phase, in which di- and triphosphate are probably incorporated to some extent.

The data for the $NaPO_3$-SiO_2 system with P/Si ratios of 0.5∼4.0 are given in Table II. The crystalline phases of all the samples are composed of α-cristobalite and trisodium trimetaphosphate. Some of them also contain small amounts of α-tridymite. Ortho-, di-, and triphosphates were found by paper chromatography in the aqueous solutions of the samples. These ortho- and chain phosphates may be derived from amorphous substances, because the X-ray diffraction patterns of these samples do not exhibit any peaks due to phosphates other than trisodium trimetaphosphate. However, the structure of these amorphous substances can not be determined from only the data presented here. It was disclosed that the crystalline substances of neither system contains P–O–Si linkages.

When the samples of the glassy substances with P/Si ratios larger than 6 are treated with water, almost all of the silicate ions deposit as silicic acid. All phosphate species and a trace amount of silicate ions come into the solution. The compositions of the phosphate species in the sample solutions were determined

TABLE II. CHEMICAL COMPOSITIONS OF SUBSTANCES OF THE $NaPO_3$-SiO_2 SYSTEM WITH P/Si RATIOS OF 0.500~4.00

P/Si	X-Ray diffractometry			Paper chromatography phosphate, P%		
	Trimeta-phosphate	α-Cristo-balite	α-Tridy-mite	Ortho	Di+Tri	Trimeta
0.500	+	⧻	−	4.8	20.5	74.7
1.00	⧺	⧻	+	0.9	20.7	78.4
2.00	⧻	⧻	+	1.0	21.3	77.4
3.00	⧻	⧺	+	1.6	21.9	76.5
4.00	⧻	⧺	±	1.8	21.8	76.4

TABLE III. CHEMICAL COMPOSITIONS OF POLYPHOSPHATES PRODUCED BY THE HYDROLYSIS OF GLASSY SUBSTANCES OF THE $NaPO_3$-Na_2SiO_3 AND $NaPO_3$-SiO_2 SYSTEMS

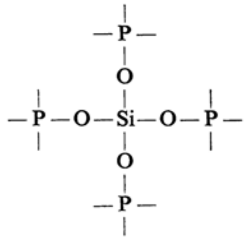
P/Si	Phosphate, P%													
	Ortho	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Ennea	Deca	Hen-deca	Do-deca	Tri-deca	High poly
The $NaPO_3$-Na_2SiO_3 system														
6.00	3.1	12.8	14.4	16.8	14.7	10.8	7.6	5.2	4.3	3.2	2.4	4.7		0
10.0	2.7	11.1	11.3	11.5	12.3	9.8	8.4	7.2	5.7	4.6	3.3	3.0	2.8	6.3
15.0	2.3	8.8	9.3	9.4	10.7	8.7	8.3	7.6	5.3	4.8	3.7	3.3	2.9	14.9
20.0	1.9	5.6	6.1	7.8	9.1	7.6	7.8	7.1	6.3	5.3	3.8	3.7	3.4	24.5
30.0	1.3	3.5	4.5	4.7	7.4	5.3	6.2	5.9	4.9	4.9	3.5	3.3	3.1	41.5
50.0	0.6	2.2	3.6	3.0	5.0	4.5	5.2	4.0	4.5	4.0	3.0	2.8	2.6	55.0
75.0	0.4	1.3	2.0	2.2	4.3	3.2	4.3	3.5	3.5	3.6	2.3	1.9	1.8	65.7
100	0.3	1.2	1.3	1.9	2.8	2.1	3.2	3.3	2.8	2.4	2.1	1.8	1.7	73.1
200	0.3	0.6	0.7	1.1	2.9	1.4	2.2	1.8	2.1	1.8	1.7	1.4	1.3	80.7
The $NaPO_3$-SiO_2 system														
10.0	2.3	7.1	7.2	7.4	8.0	7.4	6.8	5.8	5.6	4.6	4.3	3.9	2.9	26.7
20.0	1.5	4.5	4.8	5.7	7.5	5.7	5.9	5.8	5.0	4.6	3.8	3.1	3.1	39.0
50.0	0.7	2.1	3.1	3.5	5.8	3.7	5.2	3.4	4.1	3.7	3.3	2.8	2.5	56.1
R_f	0.72	0.58	0.52	0.47	0.42	0.37	0.32	0.27	0.23	0.19	0.16	0.13	0.11	

by paper chromatography. The results for the samples of the $NaPO_3$–Na_2SiO_3 and $NaPO_3$–SiO_2 systems are given in Table III. By the technique employed in the present investigation, it was possible to separate each member of the chain phosphates from orthophosphate through tridecaphosphate. The contents of the chain phosphats longer than tridecaphosphate were determined as a whole and are given as high polyphosphates in Table III.

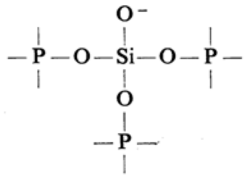
Paper chromatograms developed with Solvent B for the reference solutions of trimeta- and tetrametaphosphate reveal that trimeta- and tetrametaphosphate have the same R_f values as penta- and heptaphosphate respectively. The paper chromatographic analysis by the use of Solvent A disclosed that the sample solutions contain small quantities of trimeta-, tetrametaphosphate, and, probably, ring phosphates larger than tetrametaphosphate. For instance, in the solutions of the samples of the $NaPO_3$–Na_2SiO_3 system with P/Si ratios of 10 and 20, 2.1 and 2.0 percent of the phosphorus are present as trimetaphosphate, and 1.1 and 1.5 per cent of the phosphorus, as tetrametaphosphate respectively. Therefore, the true penta- and heptaphosphate contents are considered to be a little smaller than the values given in Table III. Although it is not sure where the ring phosphates larger than tetrametaphosphate are located on the paper chromatograms developed with Solvent B, their quantities are probably small enough to be disregarded. When the P/Si ratio increases, the contents of the chain phosphates from ortho- to hexaphosphate decrease, while those of the high polyphosphates increase. With the increase in the P/Si ratio, the contents of the chain phosphates from hepta- to tridecaphosphate first increase and then decrease. If all the distributions of the phosphate species are considered, it is evident that the average chain length of the polyphosphates increases with the increase in the P/Si ratio. Conversely speaking, when the quantity of sodium metasilicate added to a sodium metaphosphate glass increases, the contents of the shorter chain phosphates in the sample solutions increase.

The average chain lengths of the polyphosphates in the sample solutions were determined by the pH titration method. Since the quantities of orthophosphate and ring phosphates in the sample solutions are less than several per cent, the effect of their presence on the calculation of the average chain length of the polyphosphates is disregarded in the following discussion. The fact that the average chain length, $\bar{n}$, increases in the P/Si ratio is indicated by curves A and B in Fig. 1. It is well known that the average chain length, $\bar{n}$, of polyphosphates in a sodium phosphate glass is given by the equation, $Na/P=(\bar{n}+2)/\bar{n}$, where Na/P is the atomic ratio of both the elements. Assuming that there is no interaction between a sodium phosphate glass and silicon dioxide in a melted state, one can calculate the average chain length of polyphosphates in the sample solution. If the P/Si ratio of the $NaPO_3$-Na_2SiO_3 system is x, the Na/P ratio is equal to $(x+2)/x$ and, therefore, $\bar{n}$ is equal to x. Curve C in Fig. 1 indicates this relation, $\bar{n}=x$. The great discrepancy between curves A and C means that the above assumption is not correct. As for the $NaPO_3$-SiO_2 system, the average chain length of polyphosphates based on the same assumption should be the same as that of a sodium metaphosphate glass, approximately 80∼200. Curve B again indiate that the above assumption can not be employed.

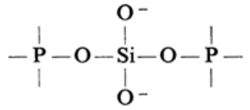
Therefore, a sodium phosphate glass seems to react with silicon dioxide at a high temperature to form P–O–Si linkages. There are four types of possible structures containing one or more P–O–Si linkages.



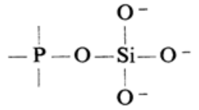
Structure A



Structure B



Structure C



Structure D

The average chain length, $\bar{n}$, of polyphosphates produced by the hydrolytic scission of P–O–Si linkages in condensed phosphate-silicate of the $NaPO_3$-Na_2SiO_3 system is given by Eq. 2:

$$(\bar{n}+2)/\bar{n}=(x+y+2-z)/x \tag{2}$$

where x, y, or z is the number of phosphorus atoms, P–O–Si linkages, or $Si-O^-$ linkages per atom of silicon respecctively. Similarly, $\bar{n}$ for the $NaPO_3$-SiO_2 system is given by Eq. 3:

$$(\bar{n}+2)/\bar{n}=(x+y-z)/x \tag{3}$$

For structure A, B, C, or D, y is 4, 3, 2, or 1 and z is 0, 1, 2, or 3 respectively. The average chain lengths of polyphosphates derived from the condensed phosphate-silicates with various P/Si ratios, x, were calculated by Eq. 2 or 3. As is shown in column I of Table IV, even the calculated values of the average chain length based on structure A are considerably larger than the experimental values when x is greater than 50.

Other factors that shorten the average chain length of the polyphosphates produced from the condensed phosphate-silicates are the existence of branching points in phosphate chains and the presence of composition water and of other impurities. If all these factors are represented by the factor b, Eqs. 2 and 3 are modified into Eqs. 4 and 5 respectively:

$$(\bar{n}+2)/\bar{n}=(x+y+2-z+bx)/x \tag{4}$$

$$(\bar{n}+2)/\bar{n}=(x+y-z+bx)/x \tag{5}$$

where b is given with respect to an atom of phosphorus. If b is arbitrarily set at 0.04, the average chain lengths shown in column II of Table IV are obtained by means of Eqs. 4 and 5. When b is zero, Eqs. 4 and 5 are reduced to Eqs. 2 and 3 respectively. Therefore, if $0<b<0.04$, the average chain length

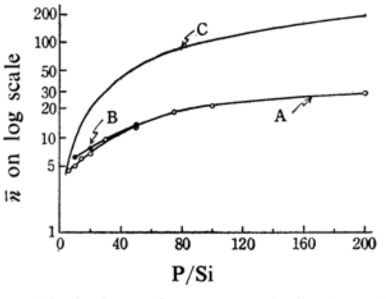


Fig. 1. Variation of average chain lengths of polyphosphates derived from the glasses with P/Si ratios.

A: Experimental values for the $NaPO_3$-Na_2SiO_3 system

B: Experimental values for the $NaPO_3$-SiO_2 system

C: Calculated values for the $NaPO_3$-Na_2SiO_3 system on the assumption that there is no interaction between a sodium metaphosphate glass and silicon dioxide in a melted state

TABLE IV. AVERAGE CHAIN LENGTHS OF POLYPHOSPHATES DERIVED FROM CONDENSED PHOSPHATE-SILICATES

	x P/Si	$\bar{n}$ Found	Column I $\bar{n}$ calcd. by Eq. 2 or 3 Structure				Column II $\bar{n}$ calcd. by Eq. 4 or 5 ($b=0.04$) Structure			
			A	B	C	D	A	B	C	D
$NaPO_3$-Na_2SiO_3 system	6	4.5	2.0	**3.0**	**6.0**	∞	1.9	**2.8**	**5.3**	50
	10	5.1	3.3	**5.0**	10	∞	3.1	**4.5**	8.3	50
	15	6.0	5.0	**7.5**	15	∞	**4.5**	**6.5**	12	50
	20	6.7	**6.7**	10	20	∞	**5.9**	**8.3**	14	50
	30	9.6	**10**	15	30	∞	**8.3**	**12**	19	50
	50	12.7	17	25	50	∞	**13**	17	25	50
	75	17.7	25	38	75	∞	**17**	21	30	50
	100	21.2	33	50	100	∞	**20**	25	33	50
	200	28.9	67	100	200	∞	**29**	33	40	50
$NaPO_3$-SiO_2 system	10	6.2	**5.0**	10	∞		**4.5**	**8.4**	50	
	20	7.7	10	20	∞		**8.3**	14	50	
	50	14.2	25	50	∞		**17**	25	50	

calculated by Eq. 4 or 5 for a sample with a certain P/Si ratio lies between the corresponding values of $\bar{n}$ given in columns I and II of Table IV. The average chain length of a pure sodium metaphosphate (Graham's salt) is usually in the range from 80 to 200, depending on the conditions of the preparation. Hence, the b factor for Graham's salt is calculated by the equation, $(\bar{n}+2)/\bar{n}=(1+b)/1$, to be 0.025~0.01. Therefore, the assumption that b is less than 0.04 in the present discussion is not unreasonable. As can be seen in Table IV, the calculated values for the average chain lengths printed in boldface type are close to the experimental values. Structure D appears unlikely to occur. In view of the above discussion, it seems reasonable to conclude that, with the increase in the P/Si ratio, the structural framework of the glasses of the condensed phosphate-silicates is transformed successively from structure C to structure B and then to structure A.

Summary

Crystals and glasses of the $NaPO_3$-Na_2SiO_3 and $NaPO_3$-SiO_2 systems with various P/Si ratios have been prepared from sodium metaphosphate, silicon dioxide, and sodium carbonate. The samples with P/Si ratios in the range from 0.05 to 4.00 have been obtained as crystalline substances containing amorphous substances, while those with P/Si ratios in the range from 6.00 to 200 have been obtained as glassy substances. By the X-ray diffractometry and the paper chromatography, it has been revealed that the crystals of neither system contains any P-O-Si linkages. By the paper chromatography and the pH-titration method, it has been disclosed that the glassy substances of either system with P/Si ratios higher than 6 are hydrolyzed to give mixtures of polyphosphates when dissolved in water. The lower the P/Si ratio, the more shorter chain polyphosphates are formed. The variation in the average chain length of the polyphosphates with the P/Si ratio indicates that these glassy substances are condensed phosphate-silicates containing P-O-Si linkages. Three structural types of P-O-Si linkages have been proposed for the condensed phosphate-silicates.

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