BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 110—115 (1967)

Chemical Structures of Glasses of the $NaBO_2$-$NaPO_3$ System

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(Received June 9, 1966)

Glasses of the $NaBO_2$-$NaPO_3$ system with P/B ratios in the range from 1.0 to 98.9 have been prepared from sodium metaphosphate and sodium metaborate by quenching melts of their mixtures. By the paper chromatographic analysis and the pH titration of the solutions of the glasses, it has been found that the glasses have the chain and branched structures consisting of P-O-P, P-O-B and B-O-B linkages. On the assumption that the glasses are composed of polypohsphate and polyborate chain blocks and branched BO_3 units, the theoretical treatment has been made on the compositions of these blocks and units and compared with the experimental data. It has been concluded that (1) the glass with a P/B ratio of unity, *i. e.*, a mole fraction of sodium metaphosphate m is 0.5, may be composed of chains of the P–O–P, P–O–B and B–O–B linkages, (2) with the increase of P/B ratios, the amount of the B–O–B linkages decreases, while the amount of the branched BO_3 units increases and (3) in the glasses with P/B ratios larger than 4.0 ($m>0.8$), all boron atoms are present as the branched BO_3 units.

Many investigations on multicomponent oxide systems have been reported by chemists, glass and ceramic technologists, and mineralogists, and have covered such points as chemical structures and properties, phase equilibria and glass formation regions. It has been reported that in structures of condensed phosphates containing oxo acid anions of an element X other than phosphorus, there are P–O–X linkages.[1] The condensed compounds of this type so far investigated are phosphate - silicates,[2] sulfate - phosphates,[3] vanadate-phosphates,[4] and arsenate-phosphates.[5] It is well known that condensed phosphates are composed of interconnected PO_4 tetrahedra. All of the element X mentioned above have also XO_4 tetrahedra in their anions. The present paper will deal with condensed borate-phosphates, in which boron atoms may be present as BO_3 trigonal planes.

For the ternary mixed oxide system, Na_2O-B_2O_3-P_2O_5, some physical and chemical properties have been reported by Takahashi.[6] The present investigation was confined to the $NaBO_2$-$NaPO_3$ system, which is a particular case of the Na_2O-B_2O_3-P_2O_5 system with an Na/(B+P) ratio of unity, and undertaken to obtain some informations on glasses in this system by use of the pH titration and the paper chromatography. The results revealed that the glasses have high polymeric chain structures of condensed sodium polyborate-phosphates.

Experimental

Starting Materials. Monosodium dihydrogen orthophosphate dihydrate was converted into sodium metaphosphate by the thermal dehydration in a platinum crucible. The metaphosphate was kept in a molten state at 1000°C for 3 hr and then quenched by pressing the melt between two copper blocks. The glass thus obtained had an average chain length of more than 100. It was difficult to prepare pure sodium metaborate by the fusion of a mixture of boric acid and sodium carbonate with a mole ratio of 2 : 1 because of the escape of a part of the boric acid on heating. Therefore, boron trioxide was previously made by the dehydration of boric acid in a platinum crucible and then an equimolar mixture of boron trioxide and sodium carbonate was fused in a platinum crucible at 1000°C for 3 hr. The sodium metaborate prepared by this method had a B/Na ratio of unity.

Preparation of Glassy Substances. In a platinum crucible a mixture of sodium metaphosphate and sodium metaborate was melted at 1000°C for 3 hr and quenched in the same manner as in the preparation of sodium metaphosphate. Thus the glasses with P/B ratios in the range from 1.00 to 98.9 were prepared. The weights of the glasses produced by this method were approximately equal to those of the original mixtures of sodium metaphosphate and sodium metaborate,

1) S. Ohashi, "Condensed Phosphates Containing Other Oxo Acid Anions," ed. by M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry," Vol 1, Interscience, New York (1964), p. 189.

2) S. Ohashi and F. Oshima, This Bulletin, **36**, 1485 (1963).

3) 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.

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

5) K-H. Jost, H. Worzala and E. Thilo, *Z. Anorg. Allgem. Chem.*, **325**, 98 (1963).

6) 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.

the weight losses being less than 1%.

Paper Chromatography. The phosphate species in the solution of the glasses were separated by paper chromatography and then determined colorimetrically. The procedure was modified from the method of Smith.[2,7]

Filter Paper. Filter paper of Toyo No. 51A was cut into a sheet of 21 by 18 cm or 29 by 18 cm, and one side with the length of 18 cm was cut into six tongue shaped ends.

Solvent. Solvent A was prepared by mixing 150 m*l* of a 20% trichloroacetic acid solution, 60 m*l* of water and 390 m*l* of acetone and used for the separation of ortho-, di-, tri-, tetra- and highly polymeric chain phosphates.[8] Solvent B was prepared by mixing 400 m*l* of isopropyl alcohol, 200 m*l* of isobutyl alcohol, 390 m*l* of water and 10 m*l* of concentrated ammonia and used for the separation of trimeta- and tetrametaphosphate from ortho- and chain phosphates.[9]

Sample Solution. About 0.1 g of a glass was dissolved in 5 m*l* of water and stored at 5°C to prevent the hydrolysis of phosphate species.

Procedure of Development. The development with solvent A was carried out on a filter paper of 29 by 18 cm at 5°C for 10 hr and that with solvent B on a filter paper of 21 by 18 cm at room temperature for 24 hr. In both cases, rectangular glass battery jars sealed with glass plates were used as chromatographic chambers and the ascending method was employed.

Chromatographic Spray. A perchloric acid - molybdate solution[10] was used as the chromatographic spray solution for phosphates and a 0.02% curcumin solution[11] in a mixture of ethyl alcohol and water with a volume ratio of 1 : 1 as that for borate. Borate ions gave a red to pink colored spot by spraying the curcumin solution to filter paper. After the spot of borate was marked with a pencil, the filter paper was sprayed with the perchloric acid - molybdate solution and dried. By this second spray, the yellow colored background of the filter paper changed to red on the whole area, and gray colored spots of phosphates appeared. In quantitative analysis, the filter paper was sprayed only with the perchloric acid - molybdate solution, and after dried, it was exposed to ultraviolet rays until the blue spots of phosphates appeared.

Colorimetric Determination of Phosphorus. The determination of the separated phosphates on the paper chromatograms was carried out as follows. A part of the filter paper containing each separated phosphate species was cut into small pieces, and then immersed to 25 to 50 m*l* of 0.1 N aqueous solution of ammonia in a 50 m*l* Erlenmeyer flask. A portion of the resulting solution was transferred to a 25 m*l* volumetric flask. After the addition of 2 m*l* of the molybdenum(V)-molybdenum(VI) reagent,[2,12] the solution was diluted with water, heated in boiling water for 1 hr, cooled and diluted to the mark with water. An absorbance of the solution was measured with Hitachi photoelectric photometer FPW-4 at 815 mμ. The distribution of phosphate species was calculated from the absorbance data. In this method, the coexistence of borate did not influence on the determination of phosphorus. This was confirmed by the fact that the same calibration curves were obtained for the standard phosphate solutions containing boric acid with B/P ratios in the range from 0 to 50.

The Measurement of the Average Chain Length of Polyphosphates. In the pH titration of an acid solution of the mixture of ortho- and polyphosphates,[13,14] the total amount of orthophosphate and end hydroxyl groups of polyphosphates was calculated from the volume of 0.1 N sodium hydroxide consumed between two inflection points located approximately at pH 4.5 and 9.5. When borate ions exist in the solution of phosphates, the inflection point at pH 9.5 did not appear in the titration curve. This difficulty was able to be eliminated by the addition of D-mannitol to the phosphate solution containing borate, but in this case the volume of the titrant consumed between the two inflection points gave the sum of borate, orthophosphate and end hydroxyl groups of polyphosphates. The accuracy of this method was examined as follows. Mixed solution of potassium dihydrogen orthophosphate

TABLE 1. THE INFLUENCE OF BORIC ACID ON THE DETERMINATION OF AVERAGE CHAIN LENGTH BY pH TITRATION

Sodium polyphosphate ($\bar{n}=10$)

v_1	v_2	v_3	v_4	E
12.34	3.46	15.80	15.90	0.63
12.52	3.46	15.98	16.05	0.44
11.97	3.46	15.43	15.52	0.58
12.26	6.93	19.19	19.42	1.20
12.72	6.93	19.65	19.84	0.97
14.58	6.93	21.51	21.58	0.33

Sodium metaphosphate ($\bar{n}=136$)

v_1	v_2	v_3	v_4	E
4.50	6.93	11.43	11.43	0.00
4.42	6.93	11.35	11.37	0.18
4.47	6.93	11.40	11.50	0.88
4.58	3.46	8.04	8.12	1.00
4.66	3.46	8.12	8.15	0.37
6.48	3.46	9.94	9.87	−0.70
6.90	6.93	13.83	14.02	1.37

v_1=the calculated volume of 0.1 N NaOH solution to be consumed by the end hydroxyl groups of phosphates.

v_2=the calculated volume of 0.1 N NaOH solution to be consumed by boric acid in the presence of D-mannitol

v_3=the sum of v_1 and v_2

v_4=the volume of 0.1 N NaOH solution consumed between the two inflection points in the pH titration

E=the error defined by the following equation

$$E = (v_4 - v_3) \times 100 / v_3$$

7) M. J. Smith, *Anal. Chem.*, **31**, 1023 (1959).
8) D. N. Bernhart and W. B. Chess, *ibid.*, **31**, 1026 (1959).
9) E. K.-Kroupa, *ibid.*, **28**, 1091 (1956).
10) C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1949).
11) S. Muto, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 949 (1954).
12) F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).
13) J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954).
14) E. J. Griffith, *ibid.*, **28**, 525 (1956).

TABLE 2. DISTRIBUTION AND AVERAGE CHAIN LENGTH OF PHOSPHATE SPECIES IN THE HYDROLYTIC PRODUCTS OF GLASSES OF THE $NaBO_2$-$NaPO_3$ SYSTEM

x	m	Phosphate, P%							$\bar{n}$
		Ortho (1P)	Di (2P)	Tri (3P)	Tetra (4P)	Highly polymeric (HP)	Tri-meta (3M)	Tetra-meta (4M)	
1.00	0.500	76.3	22.0	1.63					1.14
1.20	0.545	75.4	22.9	1.71					1.14
1.40	0.583	71.6	26.3	2.22					1.17
1.59	0.614	68.1	29.3	2.53					1.20
1.80	0.643	58.2	36.6	4.70	0.55				1.28
1.99	0.666	52.7	40.6	5.94	0.85				1.33
2.25	0.692	44.1	46.3	8.17	1.49				1.42
2.48	0.713	37.6	49.7	10.4	2.29				1.50
2.99	0.749	25.3	54.7	14.2	4.16	1.70			1.70
3.99	0.800	12.0	53.0	18.5	8.87	3.99	0.54		2.05
4.89	0.830	9.53	44.5	16.3	8.90	20.0	0.69	0.10	2.36
7.39	0.881	3.54	23.7	9.47	6.62	54.0	1.84	0.87	2.93
10.0	0.909	2.91	21.9	8.91	6.20	57.1	1.87	1.10	4.55
14.9	0.937	0.91	8.76	3.40	2.77	79.7	2.90	1.60	6.57
19.4	0.951	1.03	8.15	3.31	2.63	84.1	3.23	1.91	9.11
24.9	0.961	0.73	9.44	4.03	3.38	77.7	3.06	1.61	11.6
29.7	0.967		5.02	1.93	1.70	85.7	3.29	2.32	12.0
39.9	0.976		3.18	1.27	1.03	88.4	3.41	2.75	15.3
49.8	0.980		2.60	0.94	0.83	89.5	3.28	2.89	21.7
73.7	0.987		0.97	0.53	0.22	91.3	3.68	3.29	30.8
98.9	0.990		0.89	0.34	0.26	91.6	3.67	3.25	33.3

and sodium polyphosphates, whose average chain lengths are 10 and 136, were titrated with 0.1 N sodium hydroxide in the presence or absence of boric acid. These titration data given in Table 1 indicate that the existence of boric acid causes no great errors. An appropriate amount of a glass was dissolved in about 100 m*l* of water and kept stand for more than 12 hr. After the addition of about 0.5 of D-mannitol, this solution was acidified with diluted hydrochloric acid and then titrated with 0.1 N sodium hydroxide using a Hirama automatic recording titrator.

Results

The glasses with the P/B ratios smaller than unity were composed of an opaque and a transparent portion. The amount of the opaque portion increased when the P/B ratio decreased from 0.8 to 0.2. However, the observation of powder of these glasses under a polarizing microscope indicated that only negligibly small amount of crystalline substances were present in these glasses. On the other hand, the glasses with the P/B ratio larger than unity were completely transparent and contained only negligibly small amount of crystalline substances. For the present investigation, only the glasses with the P/B ratios larger than unity were used, because they were homogeneous.

In the paper chromatographic analysis of the glasses, borate ions appeared as a separated spot, which was located between those of ortho- and diphosphate, when they were developed with either solvent A or solvent B. Each phosphate species gave the same R_f values whether borate ions existed or not. These facts indicated that P–O–B and B–O–B linkages, if they are present in the glasses, are hydrolyzed to give isolated borate.

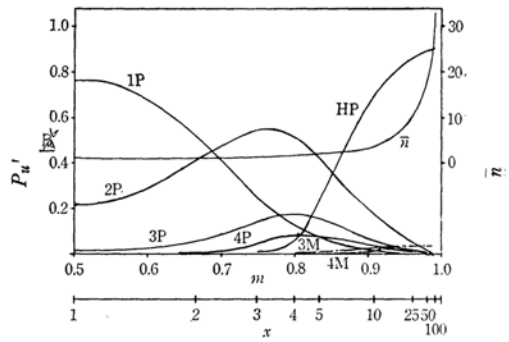
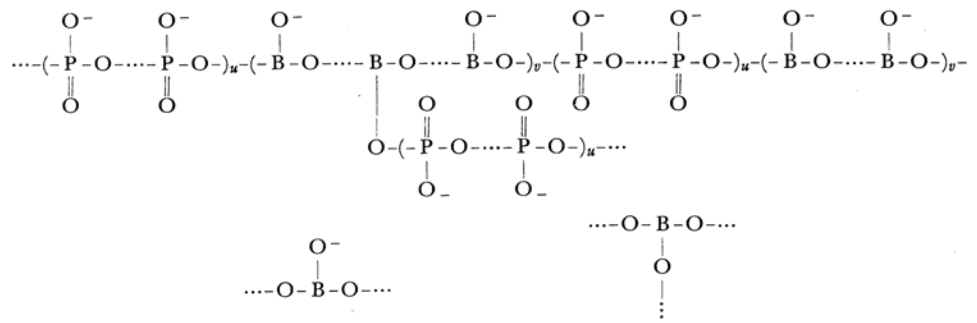


Fig. 1. Distribution and average chain length of phosphate species in the hydrolytic products of glasses of the $NaBO_2$-$NaPO_3$ system.
P_u' and $\bar{n}$ are defined by Eqs. (6) and (4), respectively.
1P: Orthophosphate, 2P: Diphosphate, 3P: Triphosphate, 4P: Tetraphosphate, HP: Highly polymeric chain phosphates, 3M: Trimetaphosphate, 4M: Tetrametaphosphate



middle BO_3 unit branched BO_3 unit

Fig. 2. The schematic chemical structure of the glasses of the $NaBO_2$-$NaPO_3$ system.

ions, when the glasses are dissolved in water, and that the borate ions thus produced do not interfere with the paper chromatographic separation of phosphates. Furthermore, previous investigations suggest that polyphosphate chain blocks in the glasses may be left unchanged, when the glasses are dissolved in water.[15] The distribution of phosphate species were determined by the paper chromatographic separation followed by the colorimetric analysis of phosphorus. The results are shown in Table 2 and Fig. 1. In the present definition of an average chain length $\bar{n}$, orthophosphate will be considered as one of the members of chain phosphates, but ring phosphates, trimeta- and tetrametaphosphate, are left out of consideration. From the data of the distribution of phosphates given in Table 2, the average chain length can be calculated for the glasses not containing more highly polymeric chain phosphate blocks than tetraphosphate blocks.

The pH titration method is available for the determination of the average chain length of the glasses containing highly polymeric chain phosphate blocks. Under the consideration of the existence of borate ions, the average chain length $\bar{n}$ of polyphosphates produced by the dissolution of a glass was calculated from Eq. (1)

$$\bar{n} = 2A/(B+C-D) \tag{1}$$

where A, B, C and D mean the following amounts per an unit weight of the glasses.

A = a sum of gram atoms of phosphorus present as ortho- and chain phosphates

B = moles of sodium hydroxide consumed between the two inflection points in the pH titration

C = moles of orthophosphate

D = moles of borate

The values of A, C and D can be caululated from the distribution of phosphate species given in (Table 2) and the composition of the glass. The values of the average chain length $\bar{n}$ thus obtained are also given in Table 2 and Fig. 1.

15) E. Thilo and G. Schulz, *Z. Anorg. Allgem. Chem.*, **266**, 34 (1951).

Discussion

In previous investigations, it is known that glassy sodium metaphosphates and some glassy condensed phosphates containing other oxo acid anions have long chain structures. Sodium metaphosphate - sodium metaborate glasses also seem to have such a long chain structure as shown in Fig. 2. Here, the number of phosphorus atoms in this model as well as in the following discussion means the number of phosphorus atoms composing ortho- and polyphosphate chain blocks, the number of phosphorus atoms composing trimeta- and tetrametaphosphates being excluded.

In this model, there are P–O–P, P–O–B and B–O–B linkages and two types of BO_3 units, the middle BO_3 and branched BO_3 units. The number of polyphosphate chain blocks or polyborate chain blocks with a polymerization degree of u or v will be represented by P_u or B_v. The number of branched BO_3 units will be given by B_b. All of P_u, B_v and B_b will be counted with respect to an unit weight of the glasses. Then, Eq. (2) is introduced from the calculation of P–O–P, P–O–B and B–O–B linkages in the above model.

$$\sum_{u=1}(u-1)P_u + \sum_{v=1}(v-1)B_v + 2\sum_{v=1}B_v + B_b = \sum_{u=1}u\cdot P_u + \sum_{v=1}v\cdot B_v \tag{2}$$

$$u = 1, 2, 3, \cdots; \quad v = 1, 2, 3, \cdots$$

The ratio m of the number of phosphorus atoms to the total number of phosphorus and boron atoms is given by Eq. (3),

$$m = \sum_{u=1}u\cdot P_u / (\sum_{u=1}u\cdot P_u + \sum_{v=1}v\cdot B_v) \tag{3}$$

The average chain length of polyphosphate chain blocks $\bar{n}$ is given by Eq. (4).

$$\bar{n} = \sum_{u=1}u\cdot P_u / \sum_{u=1}P_u \tag{4}$$

Substituting Eqs.(3) and (4) to Eq.(2), one obtains Eq. (5).

$$B_b = (\bar{n}/m)\cdot\sum_{u=1}P_u - \sum_{u=1}(u-1)P_u - 2\sum_{v=1}B_v - \sum_{v=1}(v-1)B_v \tag{5}$$

For the convenience of calculations, P_u', B_v' and B_b' are introduced as follows,

$$P_u' = P_u/\sum_{u=1} u\cdot P_u, \quad B_v' = B_v/\sum_{v=1} v\cdot B_v, \quad B_b' = B_b/\sum_{v=1} v\cdot B_v \tag{6}$$

where P_u' or B_v' and B_b' are counted with respect to the total phosphorus or total boron atoms in an unit weight of glasses. Then, Eq. (7) can be obtained.

$$B_b' = (\sum_{u=1} u\cdot P_u/\sum_{v=1} v\cdot B_v)[(\bar{n}/m)\cdot \sum_{u=1} P_u' - \sum_{u=1}(u-1)P_u'] - \sum_{v=1}(v-1)B_v' - 2\sum_{v=1} B_v' \tag{7}$$

The value of $\sum_{u=1} u\cdot P_u/\sum_{v=1} v\cdot B_v$ in Eq. (7) is equal to the ratio of the total phosphorus atoms to the total boron atoms, which is the P/B ratio and expressed by x.

$$x = \sum_{u=1} u\cdot P_u/\sum_{v=1} v\cdot B_v \tag{8}$$

$$m = x/(x+1) \tag{9}$$

Eqs. (10), (11) and (12) are given because $\sum_{u=1} u\cdot P_u'$ or $\sum_{v=1} v\cdot B_v'$ is equal to unity.

$$\sum_{u=1}(u-1)P_u' = 1 - \sum_{u=1} P_u' \tag{10}$$

$$\sum_{v=1}(v-1)B_v' = 1 - \sum_{v=1} B_v' \tag{11}$$

$$\bar{n} = \sum_{u=1} u\cdot P_u/\sum_{u=1} P_u = \sum_{u=1} u\cdot P_u'/\sum_{u=1} P_u' = 1/\sum_{u=1} P_u' \tag{12}$$

Substituting Eqs. (8)—(12) to Eq. (7), then, Eq. (13) is finally obtained.

$$B_b' = (x/\bar{n}) - \sum_{v=1} B_v', \quad \text{or} \quad B_b' = [m/\bar{n}(1-m)] - \sum_{v=1} B_v' \tag{13}$$

If there is no B–O–B linkage in the structures of this model, $B_1'=1$ and $B_2'=B_3'=\cdots=0$. Therefore,

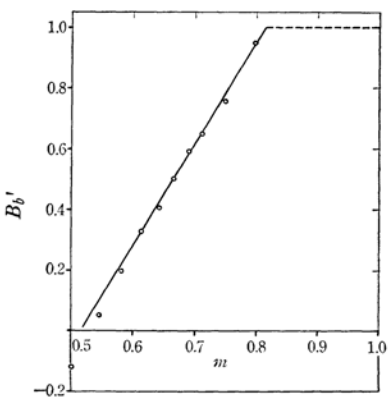


Fig. 3. Relation between m and B_b'.

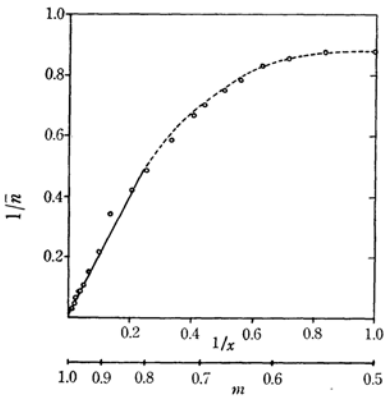


Fig. 4. Relation between $1/x$ and $1/\bar{n}$.

$$B_b' = (x/\bar{n}) - 1 \quad \text{or} \quad B_b' = [m/n(1-m)] - 1 \tag{14}$$

If there is no B–O–B linkage and moreover, if all boron atoms are present as branched BO_3 units, B_1' and B_b' must be equal to unity. Then,

$$1/\bar{n} = 2\cdot(1/x) \tag{15}$$

In order to examine the validity of these models, the values of B_b' were calculated from Eq. (14) and plotted against the values of m in Fig. 3. The values of $1/\bar{n}$ were plotted against the values of $1/x$ in Fig. 4. Figure 3 shows that the values of B_b' increase approximately linearly with the increase of the values of m between 0.6 and 0.8. The deviation of the values of B_b' from the straight line in the range of the values of m between 0.5 and 0.6 is interpreted by the reason that Eq. (14) must be applied only to the glasses not containing B–O–B linkages.

Unfortunately the values of B_v' can not be obtained experimentally. However, when the values of m decrease, *i. e.*, the relative amounts of BO_3 units increase, it is reasonable to suppose that B–O–B linkages will appear in the glasses. When the glasses contain the B–O–B linkages, the values of B_b' should be calculated by Eq. (13) and will be larger than those calculated by Eq. (14), because a sum of B_1', B_2', B_3', *etc.*, $\sum_{v=1} B_v'$, is smaller than unity as for the glasses with the values of v larger than unity. For example, under the assumption that the glass with the m value of 0.50 has the same distribution of B_v' as that of P_u', *i. e.*, $P_1'=B_1'=0.76$, $P_2'=B_2'=0.22$ and $P_3'=B_3'=0.016$, the value of B_b' becomes zero. If the above assumption is correct, it appears that the number of branched BO_3 units is zero when $m=0.5$ and increases with the increase of m, while the B–O–B linkages are present in the glass with the m value of 0.5 and decrease with the increase of m.

The values of B_b' calculated from Eq. (14) using the experimental data for the glasses with the values of m larger than 0.8 were slightly higher than unity, though the maximum value of B_b'

should be unity from the definition of it.

On the other hand, if these glasses contain no B–O–B linkage and if all boron atoms are present as the branched BO_3 units, the straight line with the slope of 2 should be obtained according to Eq. (15) when one plots the values of $1/\bar{n}$ against the values of $1/x$. As shown in Fig. 3, the slope of the straight line obtained by using experimental data of x and $\bar{n}$ is 2.01, which coincides well with the theoretical value 2. Therefore, all boron atoms in these glasses are present as the branched BO_3 units and do not form B–O–B linkages.

From the discussion mentioned above, it can be concluded that the structures of these glasses are composed of chain-type copolymers of borate and phosphate as shown in Fig. 2 and that (1) the glass with a P/B ratio of unity, *i. e.*, a mole fraction of sodium metaphosphate m is 0.5, may be composed of chains of the P–O–P, P–O–B and B–O–B linkages, (2) with the increase of P/B ratios, the amount of the B–O–B linkages decreases, while the amount of branched BO_3 units increases and (3) in the glasses with P/B ratios larger than 4.0 ($m>0.8$), all boron atoms are present as the branched BO_3 units.