776 BULLETIN OF THE CHEIMCAL SOCIETY OF JAPAN, VOL. 45, 776—780(1972) [Vol. 45, No. 3

The Electric Conductivity of the H_2O-B_2O_3 Melt

Hiroshi KODAMA, Toshio YOKOKAWA,* and Kichizo NIWA*
National Institute for Research in Inorganic Materials, 29-3, 2-chome, Honkomagome, Bunkyo-ku, Tokyo
**Faculty of Science, Hokkaido University, Sapporo*

(Received September 20, 1971)

Electric conductivity was measured over the whole composition range of H_2O–B_2O_3 in the liquid state. A peculiar conductivity-temperature relation was observed in a low B_2O_3-to-intermediate composition. The equivalent conductance of H_3BO_3 increases with its content in this range. Both the concentration of proton and its mobility through the proton-jump mechanism seem to change with the composition. The comparison of the results in the B_2O_3-rich range with those of alkali borates indicates a low extent of the dissociation of the –B–O–H group.

Various physico-chemical properties of binary metal borate melts have been investigated by many workers,[1] and it has been made clear that the addition of such metal oxides as Li_2O, Na_2O, K_2O, and PbO to B_2O_3 causes a variation in the coordination state from BO_3 to BO_4, that those binary borates completely dissociate into ionic liquids, and that the metal ion is the sole charge carrier in an electric field. Recently, Ag_2O has been shown to behave similarly, as determined from both the solubility of Ag_2O in Na_2O-B_2O_3 melt[2] and the electric conductivity.[3] H_2O-B_2O_3 provides another interesting system if its behavior is compared with that of the other borates. Considering such experimental evidence as the B–OH absorption band and the dependence of the solubility of water on its partial pressure,[4] the dissolution can be expressed by the following equation:

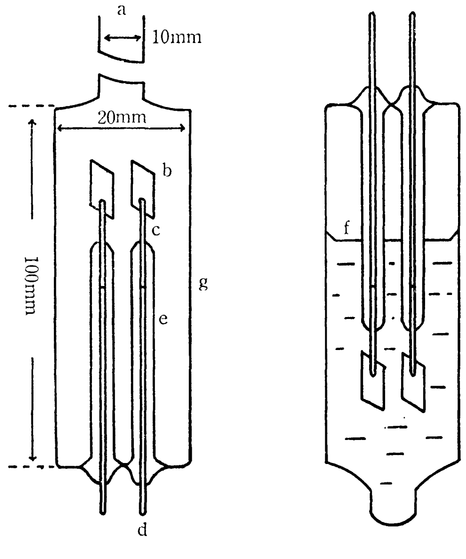
$$\rangle\text{B-O-B}\langle + \text{H}_2\text{O} = 2\rangle\text{B-O-H} \qquad (1)$$

Thus, the water molecule modifies the network as do the alkali metal oxides. The solubility of water in the alkali borate melt decreases with the alkali content. Water can be regarded as a basic oxide of the R_2O type, the basicity being quite weak. A recent study related to the density of H_2O-B_2O_3 suggests a change in the coordination number of oxygen around the boron atom in the composition range between $3B_2O_3\cdot H_2O$ and $B_2O_3\cdot H_2O$.[5]

The purpose of the present study is to make clear the conduction mechanism and to get structural information about this system through the whole composition range.

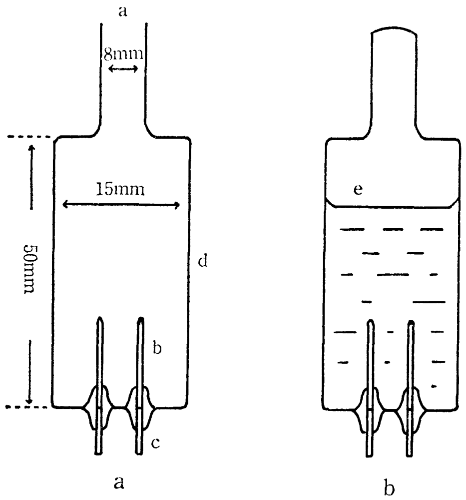
Experimental

The procedures used to prepare sample melts with desired compositions and to determine the melts' composition were similar to those used in the density measurements for this system.[5] Four types of cells, shown in Figs. 1, 2, 3, and 4, were used, depending on the compositions of the melts. The type of cell shown in Fig. 1 (cell A) was used in the composition range from 0.5 to 2.5 mol% B_2O_3. The B and C cells in Fig. 3 were used in the range from 5.0 to 25.4 and from 33.3 to 80.5 mol% respectively. Each type of cell was sealed and set up as is shown in the b sections of Figs. 1, 2, and 3.



a b

Fig. 1. Cell A used in the composition range of 0.5—2.5 mol % B_2O_3.
a: inlet of sample, b: Pt plate, c: Pt wire, d: W wire, e: thin Pyrex glass tube, f: liquid level of sample, g: Pyrex glass tube.



a b

Fig. 2. Cell B used in the composition range of 5.0—25.4 mol% B_2O_3.
a: inlet of sample, b: Pt wire, c: W wire, d: Pyrex glass tube, e: liquid level of sample.

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[1] J. D. Mackenzie, "Modern Aspect of the Vitreous State," **1**, **2**, **3**, Butterworths, London (1964).

[2] T. Maekawa, T. Yokokawa, and K. Niwa, This Bulletin, **42**, 677 (1969).

[3] H. Kodama, Y. Kimura, T. Yokokawa, and K. Niwa, *ibid.*, **42**, 681 (1969).

[4] H. Franz, *J. Amer. Ceram. Soc.*, **49**, 473 (1966).

[5] H. Kodama, T. Yokokawa, and K. Niwa, This Bulletin, **43**, 1036 (1970).

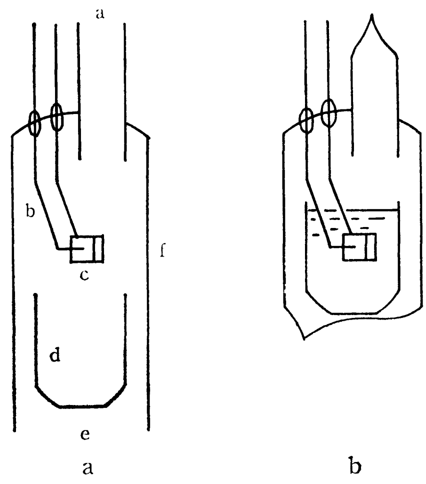

Fig. 3. Cell C used in the compositon range of 33.3—80.5 mol% B_2O_3.
a: inlet of sample, b: Pt wire, c: Pt plate, d: Pt crucible, e: inlet of Pt crucible.

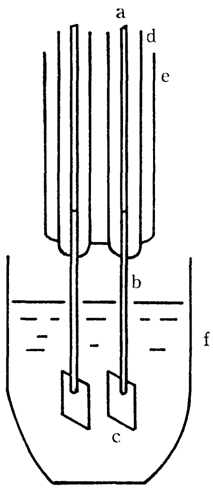

Fig. 4. Cell D used at the concentration of about 99.6 mol % B_2O_3.
a: W wire, b: Pt wire, c: Pt plate, d,e: quartz tube, f: Pt crucible.

For the glass-to-lead wire seal, we used tungsten wire. The last type of cell, the open cell (cell D), was used only in the range of a dilute water content (about 0.1 wt% H_2O). The platinum plate electrodes were platinized by the standard procedure.

Above the liquidus temperature, the vapor pressures of H_2O and HBO_2 become high in the intermediate composition range. The sealed cells, B or C, were so set in a autoclave that the stress due to pressure difference could be moderated. A diagramatic sketch of the apparatus is given in Fig. 5. Nitrogen gas was introduced into the autoclave to compensate the internal pressure of the cell. The data reported by Von Stackelberg⁶⁾ and F. Kracek *et al.*⁷⁾ were used for doing so.

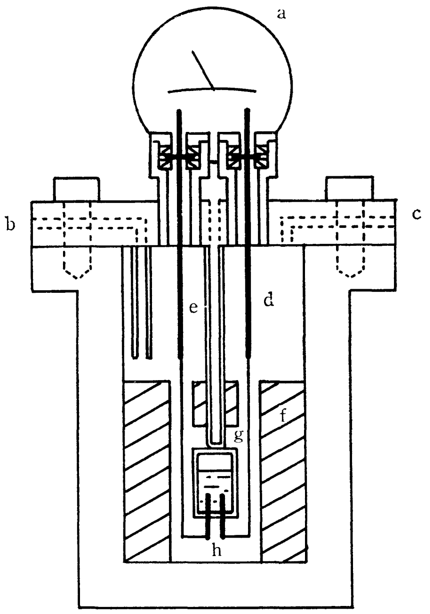

Fig. 5. Autoclave with cell B.
a: pressure gauge, b: gas inlet, c: gas outlet, d: lead wire(Cu), e: thermocouple seath, f: Cu-cylinder, g: cell, h: Pt electrodes.

The cell constant of each cell was calibrated with a 0.1 or 0.01 F KCl aqueous solution prior to the measurement. The cell constant of the A cell was independent of the depth if the Pt plate electrodes were more than 3 cm below the liquid level. The cell constant of the B cell was also independent of the depth provided that the tips of the electrodes were 5 mm from the liquid level. The corresponding values of the C and D cells depended on the liquid level and had to be calibrated according to its function. The resistance was measured by means of the AC method. A Kohlrausch bridge (Y.H.P. type 4255A) was employed. A variable capacitor was coupled when effective. Since the resistance was shown to be independent of the frequency between 1 Hz and 10 kHz, except in the range of intermediate composition, an AC current of 1 kHz was used throughout the experiments.

Since the measured resistance was several hundred Ω and over, any error due to the solution-electrode interfacial capacitance seems to have been small.⁸⁾ The measurement with the A cell of a dilute aqueous solution of H_3BO_3 was carried out in an oil bath, its temperature being kept constant within ±0.05°C. Electric-resistance furnaces were used for the rest of the measurements. The temperature was controlled within ±0.2°C. The use of the autoclave made the region of homogeneous temperature shorter and the temperature reading somewhat ambiguous. However, the final uncertainty of the conductivity is estimated to be less than 5%, except when the C cell was employed in which case the uncertainty was estimated to be 10%.

Results

The results obtained in the present investigation are shown in Figs. 6, 7, and 8, in which the logarithm of the specific conductivity is plotted against the reciprocals of the absolute temperature.⁹⁾ One may note that the Arrhenius linear relation does not hold for most of the compositions. In a solution with an extremely

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6) Von Stackelberg, F. Quatram, and J. Dressel, *Z. Elektrochem.*, **43**, 14 (1937).

7) F. C. Kracek, G. W. Morey, and H. E. Merwin, *Amer. J. Sci.*, **35A**, 143 (1938).

8) G. D. Robbins, *J. Electrochem. Soc.*, **116**, 813 (1969).

9) For the numerical data, see the doctors thesis of Hiroshi Kodama, Hokkaido University (1970).

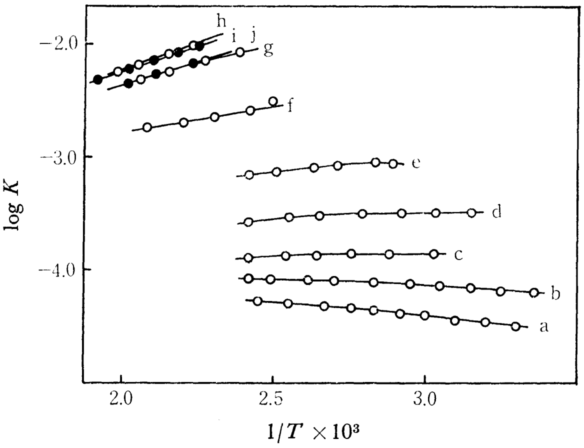

Fig. 6. Relation between specific conductivity and temperature.
a: 0.5, b: 0.7, c: 1.0, d: 1.5, e 2.5, f: 5.0, g(open circle): 10.0, h(open circle): 15.0, i(closed circle): 20.0, j(closed circle): 25.4 (mol% B_2O_3)’

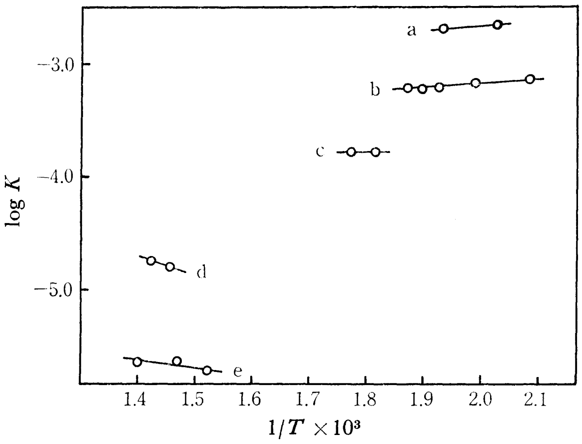

Fig. 7. Relation between specific conductivity and temperature.
a: 33.3, b: 42.2, c: 50.1, d: 74.3, e: 80.5 (mol% B_2O_3).

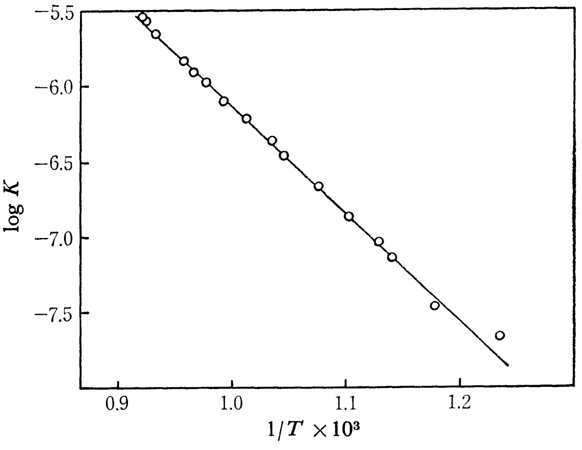

Fig. 8. Relation between specific conductivity and temperature at the concentration of 99.6 mol% B_2O_3.

small B_2O_3 content, the specific conductivity increases with the temperature. With the rise in B_2O_3 content, however, the temperature coefficients of the specific conductivity fall to negative values. The temperature coefficient, strangely enough, returns to positive values beyond a 50 mol % B_2O_3 melt.

Discussion

In ionic conductors, the specific conductivity is given by the following equation:

$$K_{sp} = n_i \times |z_i| \times eu_i \qquad (2)$$

where n_i, z_ie, and u_i are the number of ions per cubic centimeter, the charge, and the mobility of the ion respecitively. Any change in the conductivity can be attributed to a change in either the carrier's concentration or its mobility, or both. The present experimental results indicate that: (1) an Arrhenius-type linear relation does not hold in the H_2O-rich region and (2) the fact that the apparent activation energy is negative in the intermediate range must be interpreted in accordance with the above equation. It is convenient to divide the whole system into ranges from H_2O to H_3BO_3 (25 mol % B_2O_3) and from H_3BO_3 to B_2O_3. The former will be considered as a aqueous solution, and the latter, as a B_2O_3 melt containing H_2O.

H_2O-H_3BO_3 range. H_3BO_3 dissociates into four ionic species, H^+, $H_2BO_3^-$, HBO_3^{2-}, and BO_3^{3-}. Among these species, the numbers of the last two ions are negligible compared with the other two over all the composition ranges in the present measurements. The first dissociation constant (pK) of H_3BO_3 is 9.234 at 25°C. Although there are nearly equal numbers of H^+ and $H_2BO_3^-$ in the solution, the mobility of the hydrogen ion is considerably greater than that of the other. The electric current must be carried mostly by the hydrogen ion.

The mobility of the hydrogen ion in an aqueous solution does not increase steadily with an increase in the temperature. For example, the conductivity of the hydrochloric acid solution has been throughly studied by Owen and Sweeton[10] over a wide range of concentrations and temperatures. They measured the mobilities of the hydrogen and chloride ions separately and found that the absolute temperature coefficient, $(\partial\lambda_-/\partial T)_C$, of the anoin increases from 1.405 at 5°C to 1.753 at 45°C. This increase is about 20%. Under the same conditions, the $(\partial\lambda_+/\partial T)_C$ for H^+ decreases about 18%. This decrease at higher temperatures can be partly explained by the proton-jump mechanism[11,12], since the rate of the proton jump is closely related with the liquid structure, especially the ordering. However, the decreases in the specific conductivity in the present work can not be interpreted only in terms of the decrease in the mobility resulting from the increase in the disorder with the rise in the temperature, for the temperature at which disordering becomes effective may vary from system to system. Further, since the information of the dissociation constant is available at present only for extremely dilute solutions, no firm conclu-

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[10] B. Owen and F. Sweeton, *J. Amer. Chem. Soc.*, **63**, 2811 (1941).

[11] S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York and London (1941).

[12] R. Gurney, "Ionic Processes in Solution," Dover, New York (1962).

sion can be reached as to the reason for the negative temperature coefficient. However, the present authors feel on the basis of the following data that the variation in the dissociation constant with the temperature must lead to the variation in the hydrogen ion concentration.

In 1934, Harned and Embree,[13] surveying all the data on aqueous solutions, found a remarkable generality in the dissociation of acids. When a parabola of the form

$$\log K = \log K_m - P(T-\theta)^2 \tag{3}$$

was applied to a set of data for each system, a single value of P, namely $P=5\times10^{-5}$, was found to fit all the data very well. Here θ is the temperature at which the dissociation constant reaches its maximum value, K_m. This phenomenon is related to the temperature dependence of the dielectric constant of water, which plays a decisive role in an acid's dissociation. Only in the case of boric acid do the results appear to be anomalous; there, P is 8×10^{-5} [14]. Although alternative equation,[15] which are thermodynamically more reasonable, have since been proposed, the simpler Eq. (3) is serviceable for the present discussion. For a dilute boric acid solution, the value of θ lies at 77.0°C.[16] In Fig. 9, the logarithmic specific conductivity is plotted against the temperature. These curves may be regarded as parts of a parabola. These results suggest that the concentration of the charge carrier plays an important role in the change of the specific conductivity with the temperature of the present system. As a matter of fact, the relation of the specific conductivity to the concentration was found to be puzzling. In Fig. 10, log K is plotted as a function of log $C_{H_3BO_3}$ at 144°C, where C denotes the number of moles per cubic cm. An almost linear line is obtained up to 25 mol % H_3BO_3. The slope was found to be 1.76, while it should be 0.5 if H_3BO_3 dissociates only at the first step and if the activity coefficients of the species are constant. This extra increase in conductivity with the H_3BO_3 content may be attributable to the change in mobility. In accordance with this the equivalent conductance of H_3BO_3 shown in Fig. 11 reaches a maximum at 25 mol % H_3BO_3. The proton jump mechanism may still be operative in the solution incorporated with the boric acid molecule. One must also note the decrease in the equivalent conductivity with the concentration in an extremely dilute solution, which is not shown in Fig. 11.

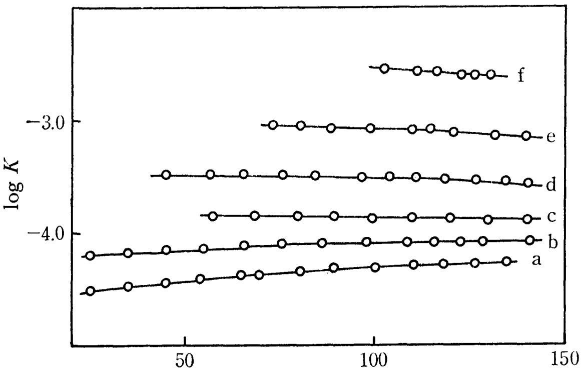

Fig. 9. Relation between specific conductivity and temperature (°C). see Fig. 6 for composition.

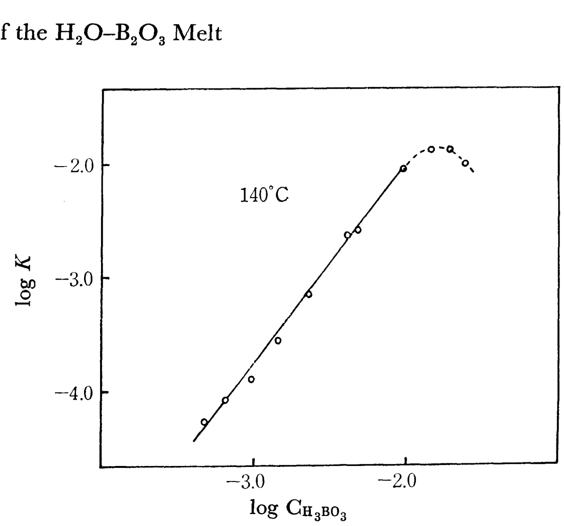

Fig. 10. Relation between the logarithmic specific conductivity and the logarithmic concentration of H_3BO_3 in mole per cm^3 at 144°C. Three points beyond −2.0 by $C_{H_3BO_3}$, extrapolated values below the solidus line.

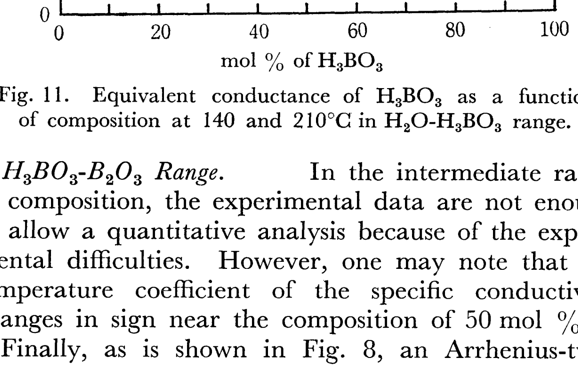

Fig. 11. Equivalent conductance of H_3BO_3 as a function of composition at 140 and 210°C in H_2O-H_3BO_3 range.

H_3BO_3-B_2O_3 Range. In the intermediate range of composition, the experimental data are not enough to allow a quantitative analysis because of the experimental difficulties. However, one may note that the temperature coefficient of the specific conductivity changes in sign near the composition of 50 mol %.

Finally, as is shown in Fig. 8, an Arrhenius-type equation is obtained in the melt of 0.1 wt % (0.4 mol %) water. The apparent activation energy is about 32 kcal/mol. Mackenzie[17] has measured the electric conductivity of B_2O_3 containing a small amount of water (0.1 to 0.2 wt %). He reported a value of about 25 kcal/mol for the activation energy in the region from 850 to 1300°C. The absolute value of the specific consuctivity is $1.9\cdot10^{-6}$ at 850°C, while the extra-

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[13] H. Harned and N. Embree, *J. Amer. Chem. Soc.*, **56**, 1050 (1934).

[14] B. Owen, *J. Amer. Chem. Soc.*, **57**, 1526 (1935).

[15] E. King, "Acid-Base Equilibria" "The International Encyclopedia of Physical Chemistry and Chemical Physics: Equilibrium Properties of Electrolyte Solutions," **4**, Pergamon Press, Oxford (1965).

[16] H. S. Harned and B. Owen, *Chem. Rev.*, **25**, 50 (1939).

[17] J. D. Mackenzie, *J. Phys. Chem.*, **63**, 1875 (1959).

polation of the present results gives $4.5\cdot10^{-6}$ at this temperature. Since the specific conductivity and its temperature coefficient are sensitive to the content of water and any impurities, the agreement seems to be satisfactory.

The activation energy for alkali borates, as measured by Shartsis *et al.*,[18] is about 20 kcal at 800°C, which is of an order of magnitude similar to that of the present system. The equivalent conductance of the alkali-metal ions is about unity at a high dilution and increases with the concentration (10 at 20 mol % alkali oxide) at 900°C, while the corresponding H value of the present system varies, being $1.5\cdot10^{-4}$ (0.4 mol % water, 560°C), $2.2\cdot10^{-4}$ (19.5 mol %, 407°C), and $1.3\cdot10^{-3}$ (25.7 mol %, 429°C). Considering the higher mobility of the proton compared with that of any other cation, we may consider that the extent of the dissociation of the –B–O–H group is quite small. The rather perculiar tendency for the equivalent conductance to increase with the concentration is common to both systems, it must be related to the disintegration of the network. No appreciable influence of the coordination change from BO_3 to BO_4 was observed. It is highly desirable to measure the mobility and the concentration of the proton separately.

Conclusion

Electric conductivity was measured over the whole composition range of H_2O–B_2O_3 in the liquid state. The previous data on the dilute aqueous solution of H_3BO_3 and on the B_2O_3 melt with a trace of water are in good agreement with the present results. A perculiar conductivity-temperature relation was observed in the intermediate composition range. As to the conduction mechanism, the proton-jump mechanism and the usual ionic migration seem to be operative in the H_2O-rich and B_2O_3-rich ranges respectively. In the B_2O_3 melt, water behaves in the same manner as do alkali metal oxides except for a partial dissociation of the –B–O–H group.

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18) L. Shartsis, W. Capps, and S. Spinner, *J. Amer. Ceram. Soc.*, **36**, 319 (1953).