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Structure model and properties of alkali borate melts

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Experimental and thermodynamic modelling studies on the structure of alkali borate melts and properties are discussed. A thermodynamic structure model for alkali borate melts is developed to describe the distribution of structural groups in the alkali borate melts as a function of composition. A qualitative interpretation for the boron anomaly in viscosity has been proposed, which regards the boron anomaly as a manifestation of the various antithetical effects caused by the introduction of alkali oxide into boric oxide. It has been found that the viscosity of alkali borate melts increases or decreases according to the changes in rigidity and spatial connectivity of the glass network structure, which is the function of temperature and composition. These concepts with some key examples are discussed in relation to their usefulness and practicality in industrial slags.

Keywords: alkali borate melts; structural model; activities; structural groups; viscosity;

Introduction

The classic structural work on borate glasses dates back to Zachariasen[1] and Warren *et al.*[2, 3]. The existence of the 'boron anomaly' in the thermal expansion coefficient vs. glass composition curves for the sodium borate glasses served as the basis in the early models for the structure of the alkali borate glasses. Biscoe and Warren[3] suggested that the decrease in the thermal expansion coefficient between 0 and 16 mol% Na_2O was the result of the progressive change of boron from a three- to four-fold coordination as sodium oxide replaced boric oxide in the glass composition. The minimum of the thermal expansion coefficient at 16 mol% Na_2O was believed to be the result of an increase in the concentration of non-bridging oxygen atoms and a decrease in the concentration of tetrahedrally coordinated boron.

The NMR observations of Bray and coworkers[4,5], which indicated that the concentration of fourfold boron continued to increase up to at least 30 mol% Na_2O, raised considerable doubt about the validity of this interpretation of the earlier measurements. Bray *et al.* developed an elaborate model for the alkali borate glasses, which considers the principal types of structural sites.

From the melting-point depressions[6] and infrared spectroscopy[7], Krogh-Moe developed an idealized model for the structure of alkali borate glasses and concluded that alkali borate melts consist of four structural groups, depending on their compositions: boroxol ($B_3O_{9/2}$), pentaborate $(B_5O_8)^-$, triborate $(B_3O_5)^-$ and diborate $(B_4O_7)^{2-}$. The proportions of the threefold coordinated boron atoms to the fourfold coordinated boron atoms in these structural units are shown in Table I. Araujo proposed a statistical thermodynamic model to calculate the fraction of boron atoms that are in tetrahedral coordination in alkali borate glasses as a function of composition and temperature[8,9].

In the present study, based on reactions between intermediate compounds, which are confirmed by the spectroscopic studies in the literature, a thermodynamic model is developed to describe the structure of alkali borate glasses and simulate the distributions of structural species in the sodium borate melt. In this model, complete types of structural species, including $(O^-BO_{2/2})^-$ and $(O_4^-B_2O_{1/2})^{4-}$ as basic units in alkali borate melts, containing 50% and 80% nonbridging oxygen (NBO) respectively, and free oxygen O^{2-} containing 100% NBO (the '/2' subscript is used to identify the connection to two cations) are taken into consideration in the entire composition range.

Structure model of binary borate melts

X-ray diffraction studies[3,10] on vitreous boric oxide (pure) have shown that the basic building units are $(BO_{3/2})$ triangles, which are linked with neighbouring ones by three

Table I
The structural units in the alkali borate melts

Structural units in alkali borate melts	Ratio of threefold boron atoms to fourfold boron atoms
boroxol ($B_3O_{4.5}$)	3:0
pentaborate $(B_5O_8)^-$	4:1
tetraborate $(B_8O_{13})^{2-}$	6:2
triborate $(B_3O_5)^-$	2:1
diborate $(B_4O_7)^{2-}$	2:2
$(O^-BO_{2/2})^-$	1:0

bridging oxygen atoms, thereby forming an almost planar structure of continuous B-O-B bonds. The B-O bond distance is 0.137 nm. The bonding distance between the layer is ~0.43 nm**[11]**, which is a much greater distance; thus the bonds are weaker. The strong B-O bonds within the planar structure retain a two-dimensional configuration, while the weaker inter-sheet bonds permit relatively easy sliding.

The Raman spectrum of B_2O_3 glass is perhaps the strongest support for the concept of boroxol rings**[12, 13]**. The peak at 808 cm^{-1} is ascribed to the symmetrical stretching of the boroxol rings. As temperature increases, the inter-sheet distance increases, resulting in a decrease in viscosity. Some research has shown that the equilibrium between boroxol ↔ $BO_{3/2}$ triangle shifts to the right with increasing temperature**[13]**. Whatever the nature of the ring configuration, the triangular connections in the B_2O_3 glass do not make a very rigid structure.

Generally, sodium borate glass is treated as a binary system. B_2O_3 is considered as a single component. The activity data of boric oxide and sodium oxide for the binary system are available in literature. In the case of structural study, the binary system B_2O_3-Na_2O can also be considered as a multicomponent system composed of $(B_3O_{9/2})$, $(BO_{3/2})$, $(B_5O_8)^-$, $(B_8O_{13})^{2-}$, $(B_3O_5)^-$, $(B_4O_7)^{2-}$, $(O^-BO_{2/2})^-$, $(O^-_4B_2O_{1/2})^{4-}$, and O^{2-}. To calculate activities of these structural species, relationships between these activities and the activities of boric oxide and sodium oxide have to be established.

NMR spectra reported by Youngman and Zwanziger**[14]** and Hassan *et al.***[13]** indicate a structure for vitreous B_2O_3 with a 1:1 ratio of boroxol rings to boron trioxide unites. Thus, the chemical component B_2O_3 is best represented by the boroxol group and the boron trioxide group in terms of structural species. Based on mass balance, the relationship between B_2O_3 and $(B_3O_{9/2})$ as well as $(BO_{3/2})$ is given by

$$2n_{B_2O_3} = n_{(B_3O_{9/2})} + n_{(BO_{3/2})} \qquad [1a]$$

An equal amount of the same substance is represented on each side of the above expression using two different composition coordinate systems. The total Gibbs energy of the system will not change with various composition coordinate systems. From this, Equations [1b] and [1c] can be obtained.

$$\begin{aligned}\Delta G(left) &= \Sigma\mu(left) = 2\left(\mu^o_{B_2O_3} + RT\ln a_{B_2O_3}\right) \Leftrightarrow \\ \Delta G(right) &= \Sigma\mu(right) = \left(\mu^O_{B_3O_{9/2}} + RT\ln a_{B_3O_{9/2}}\right) \\ &\quad + \left(\mu^O_{BO_{3/2}} + RT\ln a_{BO_{3/2}}\right)\end{aligned} \qquad [1b]$$

$$a^2_{B_2O_3} = a_{B_3O_{9/2}} \cdot a_{BO_{3/2}} \qquad [1c]$$

Since each $(B_3O_{9/2})$ unit is in equilibrium with three $(BO_{3/2})$ units at any given temperature, and the equilibrium may shift with changing temperature, hence, it follows that

$$(B_3O_{9/2}) = 3(BO_{3/2}) \qquad [2a]$$

and

$$a_{BO_{3/2}} = K_o^{\frac{1}{3}} a^{\frac{1}{3}}_{B_3O_{9/2}} \qquad [2b]$$

K_O is the equilibrium constant for reaction [2a]. Substituting equation [2b] into [1c], Equation [3] can be obtained.

$$a_{B_3O_{9/2}} = K_o^{-\frac{1}{4}} a^{\frac{3}{2}}_{B_2O_3} \qquad [3]$$

By the progressive introduction of alkali oxide into the borate melts, boron atoms are partially converted from a threefold coordination state (B_3) to a fourfold coordination state (B_4). The distribution and concentration of complex structural groups in the melt change gradually such that the proportion of B_4 in the melt increases progressively to a maximum and then decreases due to the increase of non-bridging oxygen (NBO) in the melt. Initial addition of O^{2-} to the boroxol rings mainly leads to the formation of the pentaborate group $(B_5O_8)^-$ by partially converting B_3 to B_4. Every O^{2-} converts two boron atoms from B_3 to B_4. The formation reaction of the structural units can be expressed as reaction [4a]:

$$\frac{10}{3}\left(B_3O_{9/2}\right) + O^{2-} = 2\left(B_5O_8\right)^- \qquad [4a]$$

and

$$a_{B_5O_8} = K_1^{*\frac{1}{2}} a^{\frac{5}{3}}_{B_3O_{9/2}} a^{\frac{1}{2}}_O = K_1^{\frac{1}{2}} a^{\frac{5}{2}}_{B_2O_3} a^{\frac{1}{2}}_O \qquad [4b]$$

where K_1^* is the equilibrium constant for reaction [4a], and $K_1(=K_1^*K_o^{-5/6})$ is a combined equilibrium constant. K_1 will be equal to K_1^* when K_0 is equal to one. For simplicity, the charge numbers are not included in writing the activity Equation [4b] and other equations given below.

With further addition of O^{2-} to the borate glass melt, the tetraborate group content increases at the expense of the pentaborate group. Every O^{2-} converts two boron atoms from B_3 to B_4, and the B_3 to B_4 ratio in the melt changes from 4:1 to 3:1:

$$8\left(B_5O_8\right)^- + O^{2-} = 5\left(B_8O_{13}\right)^{2-} \qquad [5a]$$

and

$$a_{B_8O_{13}} = K_2^{\frac{1}{5}} a^{\frac{8}{5}}_{B_5O_8} a^{\frac{1}{5}}_O = K_2^{\frac{1}{5}} K_1^{\frac{4}{5}} a^4_{B_2O_3} a_O \qquad [5b]$$

With the further addition of O^{2-} to the borate glass melt, the triborate group content increases at the expense of the tetraborate group. Every O^{2-} converts two boron atoms from B_3 to B_4. The B_3 to B_4 ratio in the melt changes from 3:1 to 2:1:

$$3\left(B_8O_{13}\right)^{2-} + O^{2-} = 8\left(B_3O_5\right)^- \qquad [6a]$$

and

$$a_{B_3O_5} = K_3^{\frac{1}{8}} a^{\frac{3}{8}}_{B_8O_{13}} a^{\frac{1}{8}}_O = K_3^{\frac{1}{8}} \left(k_2^{\frac{1}{5}} K_1^{\frac{4}{5}}\right)^{\frac{3}{8}} a^{\frac{3}{2}}_{B_2O_3} a^{\frac{1}{2}}_O \qquad [6b]$$

As more O^{2-} is added to the borate glass melt, the diborate group content increases at the expense of the triborate group. Every O^{2-} converts two boron atoms from B_3 to B_4. The B_3 to B_4 ratio in the melt changes from 2:1 to 1:1:

$$4\left(B_3O_5\right)^- + O^{2-} = 3\left(B_4O_7\right)^{2-} \qquad [7a]$$

and

$$a_{B_4O_7} = K_4^{\frac{1}{3}} a^{\frac{4}{3}}_{B_3O_5} a^{\frac{1}{3}}_O = K_4^{\frac{1}{3}} \left(K_3^{\frac{1}{3}} K_2^{\frac{1}{5}} K_1^{\frac{4}{5}}\right)^{\frac{1}{2}} a^2_{B_2O_3} a_O \qquad [7b]$$

The diborate group is the structural group that can accommodate the maximum number of B_4. All the possible positions for an oxygen atom to go into tetrahedral coordination are filled. The borate glass melt cannot accommodate more O^{2-} by the B_3 to B_4 conversion. Further addition of O^{2-} leads to the formation of the non-bridging ionic species $(O^-BO_{2/2})^-$, designated as $(BO^2)^-$ for convenience, and the breakdown of the borate glass network, which lowers the viscosity. Every O^{2-} converts two boron atoms from B_4 back to B_3. Chain structures are formed when a triangle unit is connected with its neighbours only by two bridging oxygen atoms:

$$\left(B_4O_7\right)^{2-} + O^{2-} = 4\left(BO_2\right)^- \qquad [8a]$$

and

$$a_{BO_2} = K_5^{\frac{1}{4}} a_{B_4O_7}^{\frac{1}{4}} a_O^{\frac{1}{4}} = K_5^{\frac{1}{4}} K_4^{\frac{1}{12}} \left(K_3^{\frac{1}{3}} K_2^{\frac{1}{5}} K_1^{\frac{4}{5}}\right)^{\frac{1}{8}} a_{B_2O_3}^{\frac{1}{2}} a_O^{\frac{1}{2}} \qquad [8b]$$

Thus, by the progressive introduction of the alkali oxide into the borate melt, the formation of the non-bridging ionic species $(O_4^-B_2O_{1/2})^{4-}$, designated as $(B_2O_5)^{4-}$ for convenience, occurs, the ionization of the boron triangle increases, and the number of bridging bonds per triangle decreases:

$$2\left(BO_2\right)^- + O^{2-} = \left(B_2O_5\right)^{4-} \qquad [9a]$$

and

$$a_{B_2O_5} = K_6 a_{BO_2}^2 a_O = K_6 K_5^{\frac{1}{2}} K_4^{\frac{1}{6}} \left(K_3^{\frac{1}{3}} K_2^{\frac{1}{5}} K_1^{\frac{4}{5}}\right)^{\frac{1}{4}} a_{B_2O_3} a_O^2 \qquad [9b]$$

By knowing K_i in Equations [4b] to [9b], a_{B2O3}, and a_O, the activities of all the structural groups can be calculated from Equations [4b] to [9b] respectively.

By E.M.F. measurements of binary alkali borate melts, Itoh *et al.*[15, 16] evaluated the partial molar Gibbs energies for Na_2O-B_2O_3, Li_2O-B_2O_3, and K_2O-B_2O_3 melts in the composition ranges of B_2O_3 to $M_2O{\bullet}2B_2O_3$ with high accuracy, compared to all available data[17]. Therefore, a_{M2O}, the activities of alkali oxides in the binary borate melts, referred to the pure solid M_2O, can be calculated from the values of $\Delta\overline{G}_{M2O}$. The relative molar Gibbs energies and the activities of B_2O_3 in the binary borate melts, referred to pure B_2O_3, are derived with the help of the Gibbs-Duhem relation:

$$X_{M_2O} d\overline{G}_{M_2O} + X_{B_2O_3} d\overline{G}_{B_2O_3} = 0 \qquad [10]$$

The activities of B_2O_3 in alkali borate melts are given in Figure 1. The activity of B_2O_3 in sodium borate melt at 1123 K can be expressed by a three-parameter Sigmoidal equation[11], with $R^2 = 0.9995$:

$$a_{B_2O_3} = \frac{1.0161}{1+\exp\left(\frac{-\left(X_{B_2O_3}-0.8399\right)}{0.0410}\right)} \left(0 \le X_{B_2O_3} \le 1\right) \qquad [11]$$

Figure 1 shows that when the mole fraction of B_2O_3 in the sodium borate melt at 1123 K reduces from 1.0 to 0.667, the activity of B_2O_3 decreases from 1 to 0.023. From 0.667 to 0.0 of X_{B2O3}, the activity of B_2O_3 will tend to zero. Although the experimental data[15,16] are available only in the composition ranges 0 to 0.333 of X_{Na2O}, the regressed equation[11] extended the activity values of B_2O_3 to the entire composition range. Again, with the help of the Gibbs-Duhem relation, a smoothed curve of a_{Na2O} vs X_{Na2O} was obtained, which made it possible to do further model calculations and evaluate the distribution of structural groups in the melt for the entire composition range. Figure 2 shows the activities of Na_2O and B_2O_3 in the binary sodium borate melt at 1123 K as a function of in the entire composition range.

Likewise, the activity of B_2O_3 in a lithium borate melt at 1198 K can be expressed as Equation [12], with $R^2 = 0.9999$:

$$a_{B_2O_3} = 1.044\times10^{-2} + \frac{0.9867}{1+\exp\left(\frac{-\left(X_{B_2O_3}-0.8459\right)}{0.0669}\right)} \left(0.667 \le X_{B_2O_3} \le 1\right) \qquad [12]$$

and the activity of B_2O_3 in a potassium borate melt at 1175 K can be expressed as equation [13], with $R^2 = 0.9995$:

$$a_{B_2O_3} = \frac{1.0758}{1+\exp\left(\frac{-\left(X_{B_2O_3}-0.8791\right)}{0.0469}\right)} \left(0 \le X_{B_2O_3} \le 1\right) \qquad [13]$$

Determination of equilibrium constants

To calculate the activities and the distribution of structural groups in the sodium borate melt, the equilibrium constants K_i for the above formation reactions given by Equations [4a] to [9a] have to be determined. No proper K_i values can

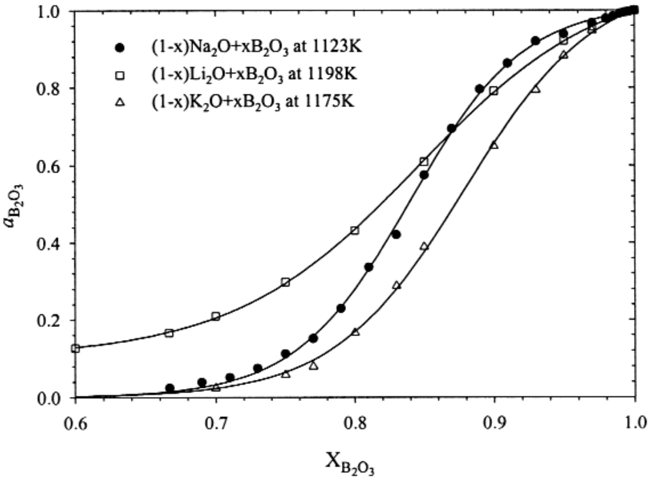

Figure 1. Activities of B_2O_3 in alkali borate melts (data after Itoh *et al.*[15, 16])

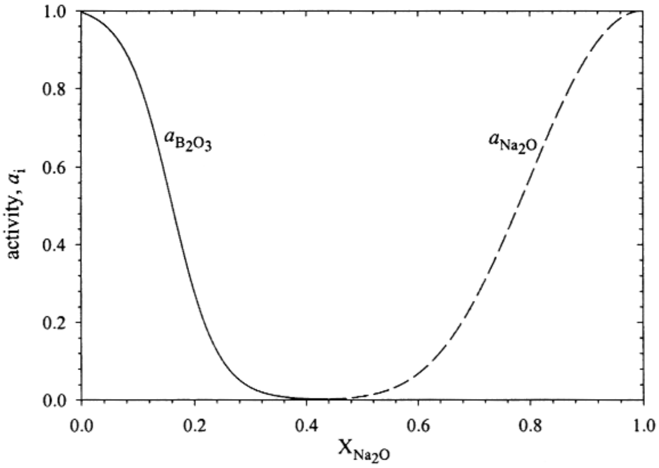

Figure 2. Activities of sodium oxide and boric oxide as a function of X_{Na_2O} at 1123 K

Table II
The determined equilibrium constants for the sodium borate melt at 1123 K

Equilibrium constant	Value	Equation
K_1	5.9173×10^{10}	[4b]
K_2	4.1675×10^{8}	[5b]
K_3	2.2146×10^{7}	[6b]
K_4	3.1310×10^{5}	[7b]
K_5	1.1031×10^{3}	[8b]
K_6	1.7639×10^{1}	[9b]

be obtained, however, from the literature or thermodynamic databases because the thermodynamic data required are either not available or are incomplete. Several authors have attempted to calculate the distribution of structural groups in alkali borate melts with a method similar to that of the present study by considering the equilibrium between the structural units**15,18**. They, however, have failed to present correct formation reactions and to determine the proper K_i values. Therefore, the activities of all the structural units in the melts for the entire composition range have not been presented correctly. As a result, these authors have assumed that the alkali borate melts are ideal solutions. From the activities of B_2O_3 in the binary melts, shown in Figures 1 and 2, it can be found easily, however, that the alkali borate melts are far from ideal solutions.

In Equation [4b], $a_{B_5O_8}$ and K_1 are unknown. To solve the two unknowns, an additional condition is needed. Fortunately, there is a special condition available for solving this problem. When we say that alkali borate melts consist of boroxol ($B_3O_{9/2}$), pentaborate $(B_5O_8)^-$, tetraborate $(B_8O_{13})^2$, triborate $(B_3O_5)^-$, and diborate $[B_4O_7]^{2-}$ groups, we have recognized that the alkali borate melts include all these stoichiometric compounds. That is, the sodium borate melt is a solution mixture of liquid boroxol, liquid pentaborate, liquid tetraborate, liquid triborate, and liquid diborate.

According to the definition of activity, the activity of a pure condensed phase, which is a liquid or solid phase, is unity at one bar. For pure liquid pentaborate, the glass formula $Na_2O•5B_2O_3$ corresponds to the stoichiometric composition of 16.67 mol% Na_2O and 83.33 mol% B_2O_3. This means that at this composition, the activity of the pentaborate group referred to its pure liquid pentaborate is unity and has a maximum value. Therefore, by substituting $a_{B_2O_3}$ and a_O at 0.1667 X_{Na_2O} and 1123 K into Equation [4b], K_1 can be calculated. K_1^* can also be determined if the relation of K_0 as a function of temperature is known.

For pure liquid tetraborate, the glass formula $Na_2O•4B_2O_3$ corresponds to the stoichiometric composition of 20 mol% Na_2O and 80 mol% B_2O_3. This means that at this composition the activity of the tetraborate group referred to its pure liquid tetraborate is unity and has a maximum value. By substituting the determined K_1, $a_{B_2O_3}$, and a_O at 0.20 X_{Na_2O} and 1123 K into Equation [5b], K_2 can be determined.

Consequently, at the stoichiometric compositions that correspond to the glass formulae $Na_2O•3B_2O_3$, $Na_2O•2B_2O_3$, $Na_2O•B_2O_3$ and $2Na_2O•B_2O_3$, the rest equilibrium constants—K_3, K_4, K_5, and K_6—in Equations [6b] to [9b] respectively can also be determined. Therefore, all the equilibrium constants are determined without any further assumption or adjustable parameters. Each equilibrium constant has a fixed value determined only by corresponding temperature, pressure, $a_{B_2O_3}$, and a_O. All the determined equilibrium constants at 1123 K are tabulated in Table II.

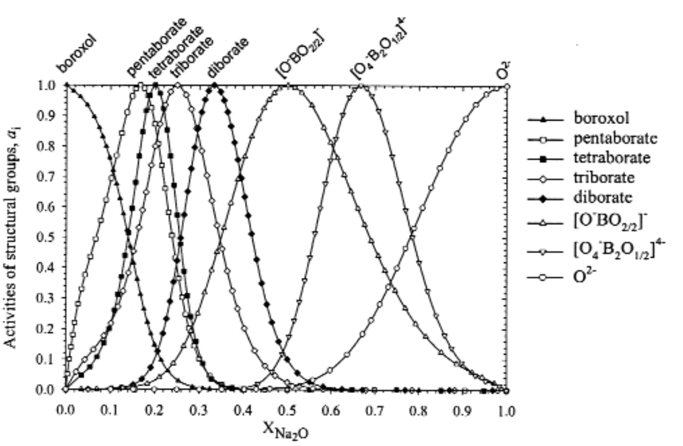

Figure 3. Activities of structural groups in the sodium borate melt as a function of composition at 1123 K

Results and discussion

Using the above K_i, $a_{B_2O_3}$, a_O and values at 1123 K and a given composition, the activities of the structural groups in the sodium borate melt referring to their pure liquid states can be calculated respectively. Figure 3 shows the activities of all the structural groups in the sodium borate melt as a function of the mole fraction of Na_2O at 1123 K in the entire composition range. All of the compositions, at which the activities of the structural groups reach a maximum, exactly match the stoichiometric compositions of the corresponding glass formula.

The activities decrease when the compositions are away from the stoichiometric compositions of the corresponding glass formula. This means that Equation [3] represents a correct relationship between the two different composition coordinate systems. Otherwise, the peak positions of the activities would shift to the right or left of the stoichiometric compositions.

At any composition between pure B_2O_3 and pure Na_2O, the sodium borate melt consists of more than one structural group. For example, as it can be seen from Figure 3, at 0.333 of X_{Na_2O}, the melt is mainly composed of diborate, triborate, and $[O^-BO_{2/2}]^-$. Each structural group is only a fraction of the sodium borate melt. At a given composition,

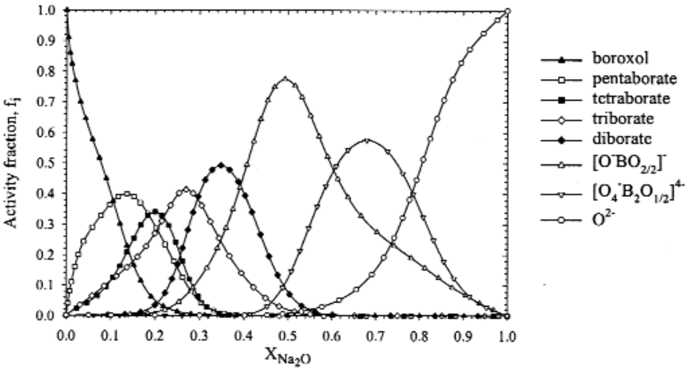

Figure 4. Effective concentrations of structural groups in the sodium borate melt as a function of composition at 1123 K

the higher the activity of a structural group relative to the total activities of the structural groups, the higher the effective concentration of the structural group in the sodium borate melt. Therefore, the effective concentration of each structural group in the sodium borate melt can be represented by the activity fraction of the structural group. The activity fraction of the structural group i, at a given composition, can be expressed as the following equation:

$$f_i = \frac{a_i}{\sum_{i=1}^{i=n} a_i} \qquad [14]$$

where f_i is the activity fraction of component i. The effective concentrations of all the structural groups in the sodium borate melt as a function of the composition are shown in Figure 4. Various structural groups are distributed in different composition ranges. Between the compositions of pure Na_2O and pure B_2O_3, all of the activity fractions of the structural groups are less than one. In the case of equal activity coefficients for all components, the activity fraction becomes the mole fraction. That is, the ideal solution is only one special case of the non-ideal solution.

The initial introduction of the sodium oxide into the boric oxide glass results in a significant decrease in the effective concentration of the boroxol group. Simultaneously, the effective concentrations of pentaborate, tetraborate, and triborate groups start to increase at different rates. The threefold coordinated boron atoms are partially converted to the fourfold coordinated boron atoms. At about 0.2 X_{Na_2O}, the effective concentration of the boroxol group is close to a minimum. At 0.14, 0.20, and 0.27 of X_{Na_2O}, the effective concentrations of pentaborate, tetraborate, and triborate groups reach their maxima, 0.40, 0.34, and 0.41 respectively.

The activity fraction of the diborate group starts to increase significantly from 0.20 X_{Na_2O}, reaches a maximum value of 0.49 at 0.35 X_{Na_2O}, and then gradually decreases to zero at about 0.60 X_{Na_2O} due to the B_4 to B_3 conversion by NBO. The effective concentration of the $[O^-BO_{2/2}]^-$ group that contains 50% NBO starts to increase at 0.20 X_{Na_2O} and reaches a maximum value of 0.76 at 0.49 X_{Na_2O}. The activity fraction of the $[O_4^-B_2O_{1/2}]^{4-}$ group that contains 80% NBO first appears at about 0.40 X_{Na_2O} and reaches a maximum value of 0.58 at 0.68 X_{Na_2O}. At over 0.5 X_{Na_2O}, due to the excess of sodium oxide content, free oxygen O^{2-} appears, and the effective concentrations of other intermediate compounds in the melt gradually decrease to zero with the increase in X_{Na_2O}.

By summarizing the fractions of B_3, B_4, and NBO in each type of the structural units, the total fractions of B_3, B_4, and NBO in the sodium borate melt can be calculated by the following expressions:

$$f_{B_3} = \frac{\Sigma f_i \times (\%B_3)}{100} \qquad [15]$$

$$f_{B_4} = \frac{\Sigma f_i \times (\%B_4)}{100} \qquad [16]$$

and

$$f_{NBO} = \frac{\Sigma f_i \times (\%NBO)}{100} \qquad [17]$$

where f_i is the activity fraction of the structural group .

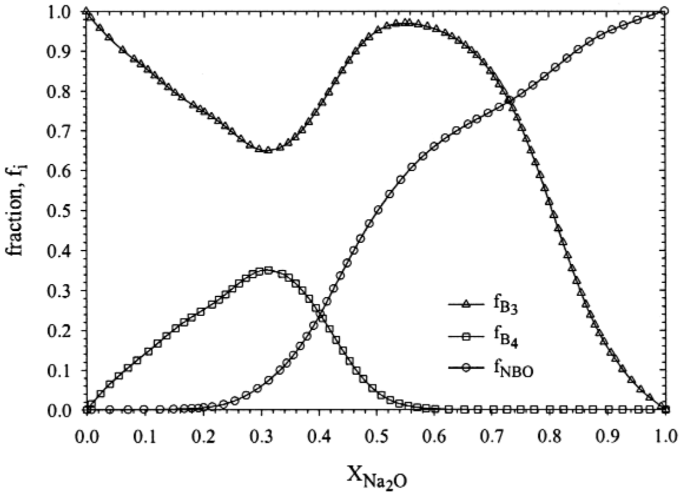

Figure 5: Fractions of B_3, B_4, and NBO in the sodium borate melt as a function of composition at 1123K

Figure 5 shows fractions of B_3, B_4, and NBO in the sodium borate melt as a function of the mole fraction X_{Na_2O}. The fraction of boron atoms that are in tetrahedral coordination in total boron atoms can be calculated as the following:

$$N_{B_4} = \frac{f_{B_4}}{f_{B_3} + f_{B_4}} \qquad [18]$$

Compared with NMR results reported by Bray and O'Keefe[4] and Svanson *et al.*[19], Araujo[9] calculated and plotted the fraction of boron atoms in tetrahedral coordination as a function of the composition of alkali borate glasses. Their results compared with the calculated values from the present model are replotted in Figure 6. The present modelling result is in good agreement with their results in simulating the increase of the fourfold coordinated boron atoms as a function of the composition. Figure 6 also revealed some uncertainty of quantification between NMR measurements on the maximum and the decrease of the fourfold coordinated boron atoms as a function of the composition. The higher fractions of four-fold boron atoms resulted from previous studies are

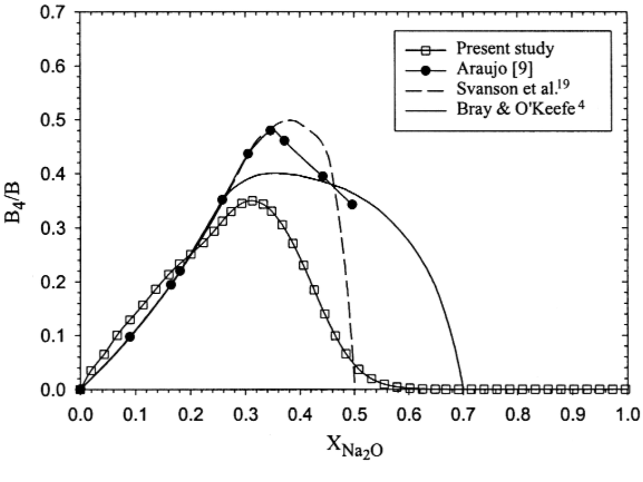

Figure 6. The fraction of boron atoms in tetrahedral coordination in alkali borate glasses as a function of composition

probably due to that low temperature was applied for the measurements and calculation.

The present thermodynamic structure model is also in agreement with Bray *et al.* and Krogh-Moe's models, which derived from NMR observations and from melting point depression measurements respectively[20,21]. The compositions, at which according to the present model the boroxol group disappears, the maximum effective concentrations of the tetraborate group and the diborate group appear, and NBO first occurs, are in close agreement with their results, although, it is impossible to compare the concentrations of structural groups calculated in this study with those from Bray's work. This thermodynamic structure model includes complete intermediate compounds for sodium borate melt, covers the entire composition range, and quantitatively explicates the equilibrium relations between all the intermediate compounds.

It should be noted that the present structural model does not assume the temperature independence of the structural species of the melt. Araujo[8,9] and Vedishcheva *et al.*[22] studied the temperature dependence of structural species in the borate melts. Some recent NMR studies[13] also documented the structure changes with temperature. In this study, the activities and distribution of the structural groups in the sodium borate melt as a function of composition are calculated using EMF experimental data at 1123 K. As we know, a_{M_2O} is a function of composition and temperature. It follows that the calculated distribution of the structural groups in the alkali borate melts may change when a_{M_2O} changes with temperature.

The method used in this study is very valuable. It may be used for other binary systems with intermediate compounds. The thermodynamic properties of these intermediate compounds can be quantitatively estimated from the corresponding properties of pure oxides. Therefore, by using this method, the thermodynamic databases can be enriched significantly with reliable experimental data.

Structural interpretation of the boron anomaly

Silicate melts exhibit a smooth variation in physical properties on changing the silica content at a constant temperature[23-26]. On the other hand, alkali borate melts exhibit a maximum and a minimum, or one of them, in physical properties, such as viscosity, thermal expansivity, molar volume, and other properties, with continuous variation in B_2O_3 content. This phenomenon has been discussed in detail[27-29]. Referring to the experimental data of Shartsis and coworkers[27], the isothermal viscosities of alkali borate melts are plotted as a function of alkali oxide content in Figure 7.

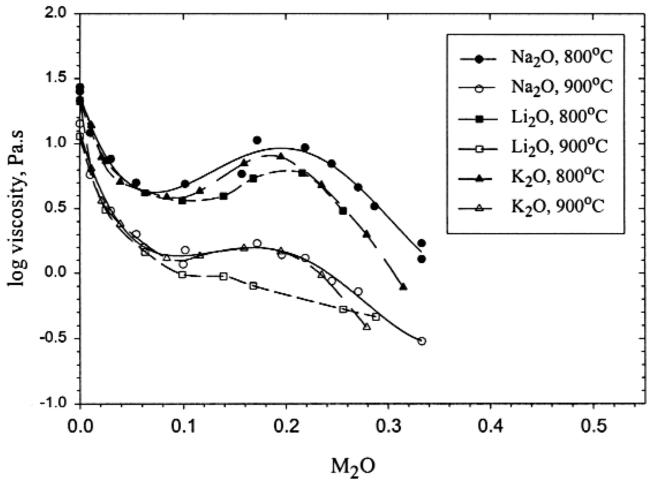

Figure 7. Isothermal viscosities of alkali borate melts (data after Shartsis *et al.* [27])

Between 800ºC and 900ºC, the viscosities of alkali borate melts show minima at 10 mol% M_2O and maxima at 20 mol% M_2O. Since it seems that the boron anomaly definitely does exist in the temperature range that the alkali borate glasses are of Newtonian type, it would be informative to study the relationship of the boron anomaly and the structure of borate glasses. As Shelby[20] has pointed out the disappearance of the boroxol group, a maximum in the concentration of the tetraborate group, the first appearance of the diborate group, and the first appearance of the $(O^-BO_{2/2})^-$ group all occur at 20 mol% Na_2O. Exactly at 20 mol% sodium oxide, the viscosity maximum of the sodium borate melts is found to occur. This strongly suggests that there is a direct structural connection between what happens at this composition and the presence of the boron anomaly.

Shartsis and coworkers[27] earlier postulated that at any given temperature, there were two opposing tendencies caused by the introduction of alkali oxide into boric oxide, namely (1) the weakening effect of forming singly bonded oxygen atoms and (2) the strengthening effect of forming fourfold coordinated boron groups. They suggested that the dominant action of the oxygen atoms introduced in the low alkali oxide range was to break the B-O-B bonds and form B-O bonds, which lowered the viscosity.

Some of the oxygen atoms introduced, however, might also have formed fourfold coordinated boron groups that would have had an opposing effect on viscosity. As more alkali oxide was added, the equilibrium was shifted in the direction of increasing the concentration of fourfold boron groups so that the downward trend of viscosity was first halted and then reversed. At high alkali oxide concentrations, where all of the possible positions for an oxygen atom to go into tetrahedral coordination are filled, only the formation of singly bonded oxygen is possible, and further introduction of alkali oxide can only reduce the viscosity.

It can be seen from Figure 5 that, by the progressive introduction of Na_2O, boron atoms were gradually converted from a threefold coordination state (B_3) to a fourfold coordination state (B_4). The increased connectivity in the network structure caused the thermal expansion to decrease and flow-related properties to decrease, which meant the viscosity increased. The concentration of the fourfold boron continued to increase up to 0.31 X_{Na_2O} and then was converted back to threefold coordinated boron. The non-bridging oxygen in the melt only appeared at above 0.2 X_{Na_2O}. Therefore, the monotonic increase of f_{B_4} and no appearance of f_{NBO} in the composition range of 0 to 0.2 X_{Na_2O}, shown in the present structure model, do not support Shartsis and coworkers'[27] postulation. There must be some other reason that caused the viscosity minimum to occur. An alternative explanation is needed.

Glass-forming B_2O_3 is regarded as a relatively strong liquid. For oxide glasses in general, strong covalent bondings prevent the structure from any drastic changes when temperature is raised above glass transition temperature T_g. Above T_g the high degree of connectivity results in high viscosity. The initial introduction of the alkali oxide into the boric oxide melts, as Equations [4a] to [7a] have suggested, does not lead to the appearance of non-bridging oxygen in the borate melt.

However, it does result in the increase of bond ionization and the disorder of the random network of the glass melt. The bonds in the glass network are converted from strong covalent bonds to weaker ionic bonds. This decreases the bonding energy, in other words, the rigidity of the glass network and the viscosity of the melt. After the conversion of boron from a threefold coordination state to a fourfold coordination state, all the oxygen remains bridging; the extra negative charges on the fourfold boron groups are satisfied by alkali ions M^+ in the vicinity. The electron transfer from the ions M^+ occurs as a distributed charge density over a large effective diameter of the structural group, and is not localized between the M atom and any specific oxygen.

Based on the above discussion, a qualitative interpretation for the boron anomaly is proposed. Of course, the validity of these interpretations is a matter of opinion. The explanation is stated as follows:

The boron anomaly that appeared in the temperature range in which the alkali borate glasses are of Newtonian type, is a manifestation of the various antithetical effects in equilibrium. At any given temperature and composition, the structure of alkali borate glasses tends to change in two opposing directions caused by the introduction of alkali oxide into boric oxide and reaches an equilibrium between the two opposing tendencies.

The dominant effect on the structure by the initial introduction of alkali oxide into boric oxide is the ionization of the covalent bonded network. Associated with alkali ions in their vicinity, anionic structural groups, such as pentaborate, tetraborate, and triborate, are formed. Increase of the ionization of the covalent bonded network and the disorder of the random network of the glass melt reduces bond energy in the melt and causes the viscosity to decrease. In the meantime, the initial introduction of the alkali oxide leads to the conversion of the boron atom from a threefold coordination state to a fourfold coordination state. The increased rigidity and spatial connectivity in the network structure tends to cause the thermal expansion to decrease and the viscosity to increase. A lower temperature or a higher alkali content is in favour of the latter effect. As more alkali oxide is added, the structure-strengthening effect of converting B_3 to B_4 outweighs the structure-weakening effect of ionizing the bonds in the melt. Therefore, the equilibrium is shifted in the direction of strengthening the network structure so that the downward trend of viscosity is first halted at 0.1 X_{Na_2O}, and then reversed.

Although the concentration of the fourfold boron atoms continues to increase up to 0.31 X_{Na_2O}, the upward trend of the viscosity is halted immediately, once the non-bridging oxygen in the melt occurs at 0.2 X_{Na_2O}. The structure-weakening effect of the non-bridging oxygen outweighs the structure-strengthening effect of converting B_3 to B_4. Visser and Stevels[30] suggested that the effect of non-bridging oxygen on decreasing the viscosity was larger than that of converting B_3 to B_4 on increasing the viscosity. Therefore, there is no justification for assuming that the effect of f_{B4} and f_{NBO} on the viscosity of alkali borate glasses is numerically equal but opposite in sign. As more alkali oxide is added, the increased non-bridging oxygen breaks the connection and rigidity of the network; therefore, the viscosity of glass decreases.

Summary

Based on the thermodynamic considerations, a quantitative structure model for alkali borate melts is developed to describe the distribution of structural groups in the alkali borate melts as a function of the composition. The equilibrium relations between the activities of the structural groups are quantitatively explicated over the entire composition range. Fractions of threefold coordinated boron atoms and fourfold coordinated boron atoms in the sodium borate glass are calculated for the entire composition range and compared with results reported in the literature. A qualitative interpretation for the boron anomaly in viscosity has been proposed, which regards the boron anomaly as a manifestation of the various antithetical effects caused by the introduction of alkali oxide into boric oxide. At any given temperature and composition, the structure-weakening effects of bond ionization in the glass network and the bond break by non-bridging oxygen are in equilibrium with the structure-strengthening effect of converting boron atoms from the threefold coordination state to the fourfold coordination state. The viscosity increases or decreases according to the changes in the spatial connectivity of the glass network structure, governed by a dominant effect.

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References

1. ZACHARIASEN, W.H. The Atomic Arrangement in Glass. *J. Am. Chem. Soc.* , vol. 54, no.10. 1932. pp. 3841–3851.
2. WARREN, B.E., KRUTTER, H., and MORNINGSTAR, O., Fourier Analysis of X-ray Patterns of Vitreous SiO_2 and B_2O_3. *J. Am. Ceram. Soc.*, vol. 19, no. 7. 1936. pp. 202–206.
3. BISCOE, J. and WARREN, B.E., X-Ray Diffraction Study of Soda-Boric Oxide Glass. *J. Am. Ceram. Soc.*, vol. 21, no.8. 1938. pp. 287–293.
4. BRAY, P.J., and O'KEEFE, J.G., Nuclear Magnetic Resonance Investigations of the Structure of Alkali Borate Glasses, *Phys. Chem. Glasses*, vol. 4, no.2. 1963. pp.37–46.
5. BRAY, P.J., NMR Studies of Borates. *Borate Glasses: Structure and Properties, and Applications* (Materials Science Research, vol. 17), Pye, L.D., Frechette, V.D. and Kreidi, N.J. (eds.). Plenum, New York, 1978. pp. 321–51.
6. KROGH-MOE, J. Structural Interpretation of Melting Point Depression in the Sodium Borate System. *Phys. Chem. Glasses*, vol. 3, no. 4. 1962. pp. 101–10.
7. KROGH-MOE, J. Interpretation of the Infrared Spectra of Boron Oxide and Alkali Borate Glasses. *Phys. Chem. Glasses*, vol. 6, no.2. 1965. pp. 46–54.

8. ARAUJO, R.J. Statistical Mechanics of Chemical Disorder: Application to Alkali Borate Glasses. *J. Non-Cryst. Solids*, vol. 58, 1983. pp. 201–208.

9. ARAUJO, R.J. Temperature Dependence of Boron Coordination in Alkali Borate Glasses as an Example of a Second Order Transition. *Phys. Chem. Glasses*, vol. 21, no.5. 1980. pp. 193–196.

10. GREEN, R.L. X-Ray Diffraction and Physical Properties of Potassium Borate Glasses. *J. Am. Ceram. Soc.*, vol. 25, no.3, 1942, pp. 83–89.

11. MIYAKA, M., SUZUKI, T., MORIKAWA, H., TAKAGI, Y., and MARUMO, F. Structural Analysis of Molten B_2O_3. *J. Chem. Soc.*, Faraday Trans., Part I, vol. 80, 1984, pp. 1925–31.

12. GASKELL, P.H., PARKER, J.M., and DAVIS, E.A. *The Structure of Non-crystalline Materials*. New York, Taylor & Francis, Inc., 1983. 343. pp.

13. HASSAN, A.K., TORELL, L.M., and BÖRJESSON, L. Structural Changes of B_2O_3 through the Liquid-glass Transition Range: A Raman-scattering Study. *Phys. Rev. B*, vol. 45, no. 22, 1992. pp. 12797–12805.

14. YOUNGMAN, R.E. and ZWANZIGER, J.W. Multiple Boron Sites in Borate Glass Detected with Dynamic Angle Spinning Nuclear Magnetic Resonance, *J. Non-Cryst. Solids*, vol. 168, 1994. pp. 293–297.

15. ITOH, H., SASAHIRA, A., MAEKAWA, T., and YOKOKAWA, T. Electromotive-force Measurements of Molten Oxide Mixtures. *J. Chem. Soc.*, Faraday Trans., vol. 80, no. 1, 1984. pp. 473–87.

16. ITOH, M., SATO, S., and YOKOKAWA, T. E.M.F. Measurements of Molten Mixtures of Lithium Oxide +, Sodium Oxide +, and Potassium Oxide + Boron Oxide. *J. Chem. Thermodynamics*, vol. 8, 1976. pp. 339–52.

17. SHAKHMATKIN, B.A. and VEDISHCHEVA, N.M. Thermodynamic Studies of Oxide Glass-forming Liquids by the Electromotive Force Method. *J. Non-Cryst Solids*, vol. 171, 1994. pp. 1–30.

18. REDDY, R. G., YEN, J. Y., and ZHANG, Z. Chemical Properties of Sodium Borate Coatings. *Elevated Temperature Coatings: Science and Technology II, Proceedings of a symposium held during the TMS Annual Meeting'96* (Anaheim, CA, February 4–8, 1996). Dahotre, N.B. and Hampikian, J.M. (eds.). TMS, 1996. pp. 31–46.

19. SVANSON, S.E., FORSLIND, E. and O'KEEFE, J.G. Nuclear Magnetic Resonance Study of B Coordination in Potassium Borate Glasses. *J. Phys. Chem.*, vol. 66, 1962. pp. 174–175.

20. SHELBY, J. E. Thermal Expension of Alkali Borate Glasses. *J. Am. Ceram. Soc.*, vol. 66, no. 3, 1983, pp. 225–27.

21. GRISCOM, D.L. Borate Glass Structure. *Borate Glasses: Structure, Properties, and Applications* (Materials Science Research, vol. 12). Pye, L.D., Frechette, V.D., and Kreidel, N.J. (eds.). New York, Plenum, 1978. pp. 11–149.

22. VEDISHCHEVA, N.M., SHAKHMATKIN, B.A., SHULTZ, M.M., and WRIGHT, A.C. Simulation of the Structure of Borate Glasses and Melts on the Basis of Thermodynamic. *Proc. Second Intl. Conf. On Borate Glasses, Crystals, and Melts*, Wright, A.C. (ed.). The Society of Glass Technology, Sheffield, 1997. pp. 215–222.

23. TURKDOGAN, E.T. Pheological and Transport Properties. *Physico-Chemical Properties of Molten Slags and Glasses*, London, The Metals Society, 1983. pp. 1–63.

24. ZHANG, Z. and REDDY, R. G. Viscosity of Lead Silicate Slags, *Minerals & Metallurgical Processin*g, vol. 19, no. 1, 2002, pp. 37–42.

25. REDDY, R. G., and HEBBAR, K., Viscosity of FeO-SiO_2 Slags, *Minerals & Metallurgical Processing*, vol. 18, no. 4, 2001, pp. 195–199.

26. ZHANG, Z., and REDDY, R. G., Distribution of Various Structural Species in Alakali Borate Melts, *EPD Congress*, P. R. Taylor, (ed.), TMS, Warrendale, USA, 2001, pp. 353–367.

27. SHARTSIS, L., CAPPS, W., and SPINNER, S. Viscosity and Electrical Resistivity of Molten Alkali Borates. *J. Am. Ceram. Soc.*, vol. 36, no. 10, 1953. pp. 319–26.

28. VARSHNEYA, A.K. The Boron Anomaly. *Fundamentals of Inorganic Glasses*, New York, Academic Press, Inc., 1994. pp. 106–111.

29. LI, P., GHOSE, A.C., and SU, G. Viscosity Determination of Boron Oxide and Binary Borates. *J. Am. Ceram.* Soc., vol. 45, no. 2. 1962. pp. 83–88.

30. VISSER, T.J.M. and STEVELS, J.M. Rheological Properties of Boric Oxide and Alkali Borate Glasses. *J. Non-Cryst. Solids*, vol. 7, 1972. pp. 376–394.