4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

VISCOSITY OF Na_2O-B_2O_3 MELTS

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Synopsis

A structure based model has been developed for the prediction of viscosities of Na_2O-B_2O_3 melts. These melts exhibit an anomalous behavior of viscosity with continuous variation in B_2O_3 content. The structural changes taking place in these melts on varying the sodium oxide content have been reviewed and are incorporated in developing this model. The predicted values are in excellent agreement with the experimental values over the entire temperature and composition range.

Key Words : Viscosity, Na_2O-B_2O_3 Melts, Structural Model, Ionic Units Distribution

1. Introduction

Sodium borate glasses are of particular interest because they exhibit a different trend of physical properties with continuous variation in B_2O_3 content [1]. Viscosity of glasses is a structure related property. To study viscosity behavior of glasses, the understanding of ionic distribution in glass melt is of considerable importance. X-ray diffraction studies [2,3] on glassy boric oxide (pure) have shown that the basic building units are BO_3 triangles, which share corners with one another. The coordination number of binary borate glasses depends on the temperature and the content as well as the type of metal oxide.

In this paper, we present a structure based model for the prediction of viscosity of sodium oxide-borate binary system. The predicted viscosity values are in excellent agreement with the experimental data. A brief review of the structural changes which take place in borate melts with change in composition and temperature is also presented.

2. Theoretical Considerations

For the ionic liquids containing holes, Bockris and Reddy [4] presented the following expression for the viscosity:

$$\eta = (2/3)N_h R_h (6.28\ mKT)^{1/2} \exp(E/RT) \qquad (1)$$

where E is the energy required to produce a hole (or to break the B_2O_3 bond to produce BO_3^{3-} ionic unit) and the structural unit to move into the hole, N_h is the number of holes per unit volume of the glass, R_h is the average radius of the hole, K is the Boltzman constant, m is the mass of the ionic unit, R is the gas constant.

Equation (1) is a general expression and its application to borate melts requires calculation of N_h, R_h, m and E. A brief description of the calculation method for these quantities is given below.
The term $(6.28\ mKT)^{1/2}$ was rewritten as follows:

$$(6.28\ \mathrm{mKT})^{1/2} = (6.28\ \mathrm{W/RT})^{1/2}.\mathrm{KT} \qquad (2)$$

where K is the Boltzman constant (1.3 X 10^{-23} J/K), R is the gas constant (8.3144 J/mole.K) and W is the molecular weight of an ionic unit (0.059 Kg/mole). Substituting R,W,Av and K into eq.(2), we obtain eq.(3).

$$(6.28\ \mathrm{mKT})^{1/2} = 2.74 \mathrm{X} 10^{-24}\ T^{1/2} \qquad (3)$$

Furth [5] has shown that the size of a typical hole in a liquid is roughly the same as the ionic unit and the hole can accommodate an ionic unit. In the case of sodium oxide-borate melts, the basic building units are BO_3 triangles. For BO_3 triangles, each boron atom is surrounded by three oxygen atoms with a coordination number of three. The ionic radius of oxygen is 1.39 Å, the radius of boron is 0.16 Å, and the radius of BO_3 can be calculated as 2.94 Å.

The number of holes N_h per unit volume was expressed in terms of NO^0, where NO^0 is the mole fraction of bridging oxygen connected to two Boron atoms. This calculation involves the assumption that the number of holes are equal to the number of BO_3 units present in the per mole of glass melt and that all the holes are occupied by the ionic species.

$$N_h = NO^0 \mathrm{X} Av = 6.023 \mathrm{X} 10^{23} \mathrm{X} NO^0 \qquad (4)$$

where Av is the Avogadro number (6.023 X 10^{23}/g mol). Substituting eq.(3), (4) and the R_h value in eq.(1), the following expression can be obtained.

$$\eta = 3.4 \mathrm{X} 10^{-9}\ NO^0\ T^{1/2} \exp(E/RT) \text{ poise} \qquad (5)$$

Calculation of NO^0

If N moles of B_2O_3 are mixed with M moles of alkali oxide, the charge and mass balance can be expressed, respectively, as

$$nO^0 = 3\ N - 1/2\ nO^- \qquad (6)$$

$$nO^{2-} = M - 1/2\ nO^- \qquad (7)$$

The total number of anions

$$nO^0 + nO^{2-} + nO^- = 3N + M \qquad (8)$$

where no^0 is the number of bridging oxygen, nO^- is the number of non bridging oxygen bonded to only one boron atom, and nO^{2-} is the number of free oxygen ion.

Based on these relations and in accordance with Yokokawa's model [6], NO^0 can be derived as follows:

$$NO^0 = no^0/(3N+M)$$

If expressed N and M in term of X_{B2O3} and X_{Na2O} respectively, then

$$NO^0 = (6-6X_{MO}-nO^-)/(2(3-2X_{MO})) \qquad (9)$$

where no^- further can be calculated by eq.(10)

$$(1-\exp(\Delta G^0/RT))(nO^-)^2 + (4X_{MO}-6)(nO^-) + 12X_{MO}(1-X_{MO}) = 0 \qquad (10)$$

where ΔG^0 is the standard free energy change associated with the following reaction:

$$B_2O_{3(l)} + Na_2O_{(l)} = Na_2B_2O_{4(l)} \qquad \Delta G^0 = -288484.3 - 5.778T \text{ J/mole} \tag{11}$$

Calculation of E

In the case of borate melts the energy term is considered to be composed of the energy required to break the borate bonds into BO_3^{3-} triangles units and move the specie unit into the adjacent hole.
The value of E was calculated based on the available experimental viscosities and using eq.(5). A wide range of data has been used to give more accurate predictions. Experimental viscosity data of all the alkali oxide-borate systems were used in deducing the polynomial expression that is given by eq.(12):

$$E = \alpha + \beta NO^0 + \gamma(NO^0)^2 + \delta(NO^0)^3 + \epsilon(NO^0)^4 \tag{12}$$

where α, β, γ, δ, and ϵ are constants. This equation gives a correlation of E values as a function of calculated NO^0 values. These constants were further a linear function of temperature and can be expressed by the following general equation:

$$\zeta = A + BT \tag{13}$$

where ζ represents $\alpha,\beta,\ldots$, and values of A and B for various constants are given in table 1. The constants $\alpha,\beta,\gamma,\delta$, and ϵ are calculated using the eq.(13) and table 1. They were inserted in the polynomial expression (12) and E values were calculated. These calculated E and NO^0 values were inserted into the eq.(5) to obtain the viscosity.

TABLE 1: VALUES OF CONSTANTS A AND B FOR THE CURVEFIT $\zeta = A + BT$

Constant	A	B
α	9.017212×10^7	-4.7426×10^5
β	-4.30468×10^8	-2.2487×10^5
γ	7.656456×10^8	-3.95655×10^5
δ	-6.00023×10^8	3.05930×10^5
ϵ	1.7475×10^8	-8.7611×10^4

3. Results and Discussion

The viscosities of Na_2O-B_2O_3 melts were calculated over a wide temperature range by substituting the calculated values of E and NO^0 into eq.(5). The predicted values were compared with the experimental viscosities. The average percentage deviation i.e. ($\log \eta_{cal.} - \log \eta_{expt.}$) is calculated and the probable reasons for the deviations are discussed.

Na_2O-B_2O_3 SYSTEM:

The experimental data [7-9] is available in the range of 0 to 0.333 mole fraction of sodium oxide and in the temperature range of 973K to 1273K. The viscosity isotherms for this system at 1073K and 1173K have been plotted in Fig.1 and 2. The viscosity isotherm at 973K shows a minimum at $X_{Na2O}=0.06$ and a maxima at $X_{Na2O}=0.2$. At 1073K, a minimum and a maximum are observed at $X_{Na2O}= 0.08$ and 0.19, respectively. The corresponding values for 1173K are $X_{Na2O}=0.10$, and 0.18, respectively. Thus, with an increase in temperature, the minimum shifts towards its right and the maximum shifts towards its left, and also the maximum tends to become less prominent. The maximum and the minimum almost disappear above 1173K and a rather smooth curve is obtained at higher temperatures. Addition of sodium oxide causes a lowering

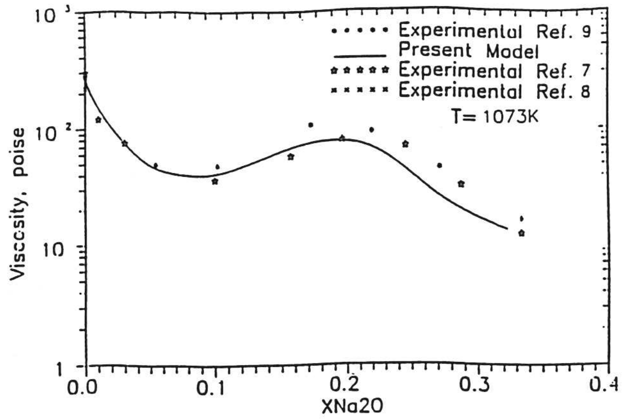

Figure 1. Viscosity of Na_2O-B_2O_3 at 1073K.

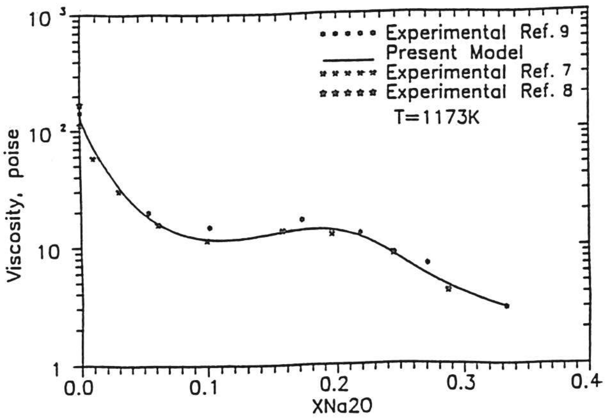

Figure 2. Viscosity of Na_2O-B_2O_3 at 1173K.

of viscosity. Further addition of sodium oxide causes an increase in viscosity up to a certain mole percent beyond which viscosity starts decreasing, again.

The shape of viscosity isotherms for borate glasses is quite different from that for silicate glasses. For the latter, a structure based model [10,11,12] gave a good prediction of viscosities. The so called "boron anomaly" can be explained by calculation of ionic distribution in borate melts [13] which described as follows.

According to Krogh-Moe's studies [14,15], alkali borate glass consists of several structural units, BO_3, B_3O_6, B_3O_7, B_4O_9, B_5O_{10} and B_8O_{10}. For a given temperature, the calculated amounts of complex ionic species, such as B_3O_7, B_5O_{10} and B_8O_{10} are small [13]. These structural units consist of different proportion of three coordinated borons and four coordinated borons, i.e. BO_3 has one triangle, B_3O_6 has two triangles and B_4O_9 has two triangles and two tetrahedra. The ionic distribution at 1123K is shown in Fig.3. Fig.4 shows the relation between viscosity and structural change in sodium oxide-borate melts. The ratio of $X_{tetrahedra}/X_{triangle}$, which represents the change of structural units was calculated as total amount of tetrahedra structural units divided by total amount of triangular structural units. The initial addition of sodium oxide results in glass network breakdown and formation of triangular structure. Viscosities of alkali borate melts significantly decrease in the range of X_{Na2O} 0 to 0.09. For $X_{Na2O} > 0.09$, the ratio of $X_{tetrahedra}/X_{triangle}$ start to increase significantly. Therefore, the viscosity isotherm showed a minima where the viscosity start to increase. At $X_{Na2O}=0.2$, ratio of $X_{tetrahedra}/X_{triangle}$ showed a maximum value which is also the maxima of viscosity isotherm. Above $X_{Na2O}=0.2$, the tetrahedra structure start to decrease, thus viscosities also start to decrease. The glass network were almost completely breakdown into BO_3 structure units with addition of alkali oxide. This agree with the theoretical considerations, the complete depolymerization of glass network of B_2O_3 and occupance of non-bridging oxygens (oxygen bonded to one boron atom) in borate melts at $X_{Na2O}= 0.33$. The predicted viscosity values are in excellent agreement with the experimental data [7]. The average percentage deviation for this system from the experimental data of Kauira et al is -7.37% which is very small considering the large amount of variation in the reported data itself.The deviation may be due to the presence of water in their samples. It is difficult to demoisturize B_2O_3 completely because of its hygroscopic nature. It is known that the presence of water in the borate melts decreases their viscosity. Viscosity values reported by Shartsis et.al. were found to be less than-those reported in more recent study [9].

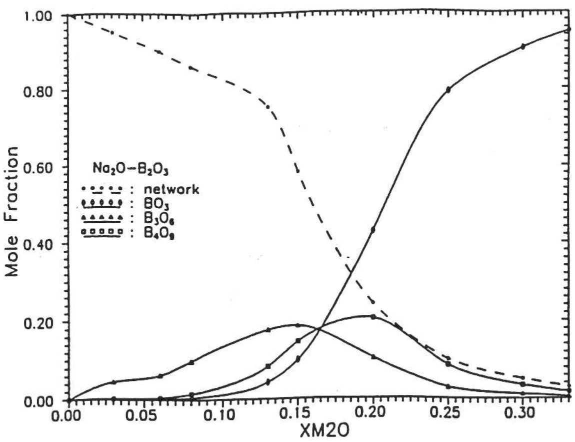

Figure 3. Distribution of polymeric species and glass network in Na_2O-B_2O_3 at 1123K.

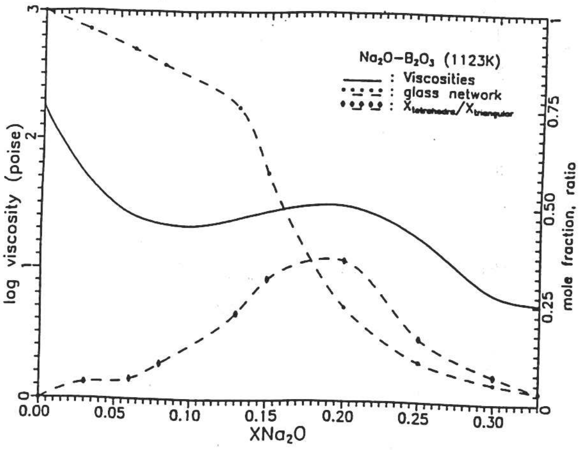

Figure 4. Viscosity isotherm versus glass network breakdown formation of tetrahedra structure in Na_2O-B_2O_3 at 1123K.

Effect of Temperature:

The effect of temperature on the viscosity of sodium oxide-borate melts is shown in Fig.5. Temperature has a significant effect on the viscosities of borate melts. The equilibrium between 3-coordinated borons and 4-coordinated boron units is a function of the temperature of the melt and as discussed above, the fraction of 4-coordinated borons present in the melt governs its viscosity. Viscosity increases with a decrease in temperature for all mole fraction of sodium oxide. As mentioned before, the energy "E" comprises of two terms. The first term, i.e. the energy required for breaking the network to create the hole does not change appreciably with temperature. On the other hand, the second term, i.e. the energy required to move the boron unit into the hole changes significantly with temperature.

4. Conclusions

Our model considers the structural aspects of sodium oxide-borate melts and the calculated viscosity values are in excellent agreement with the experimental values over the entire composition and temperature range. The average percentage deviation of the predicted values is well within the experimental deviation. Both the temperature and the composition have significant effect on the viscosities of borate melts. For a given composition of melt, viscosity decreases with an increase in temperature. The viscosity isotherms of sodium borate melts exhibit the so called "boron anomaly" where a minimum and a maximum is observed in the viscosity with a continuous variation in B_2O_3 content. On increasing the temperature, the minimum and the maximum disappear. This anomaly is attributed to the structural changes which takes place in these borate melts due to the change in the composition and temperature. This behavior is in accordance with the calculated results [13]. Further work on the determination of distribution of polymeric species in borate melts and the prediction of viscosities of other binary and ternary borate systems is in progress.

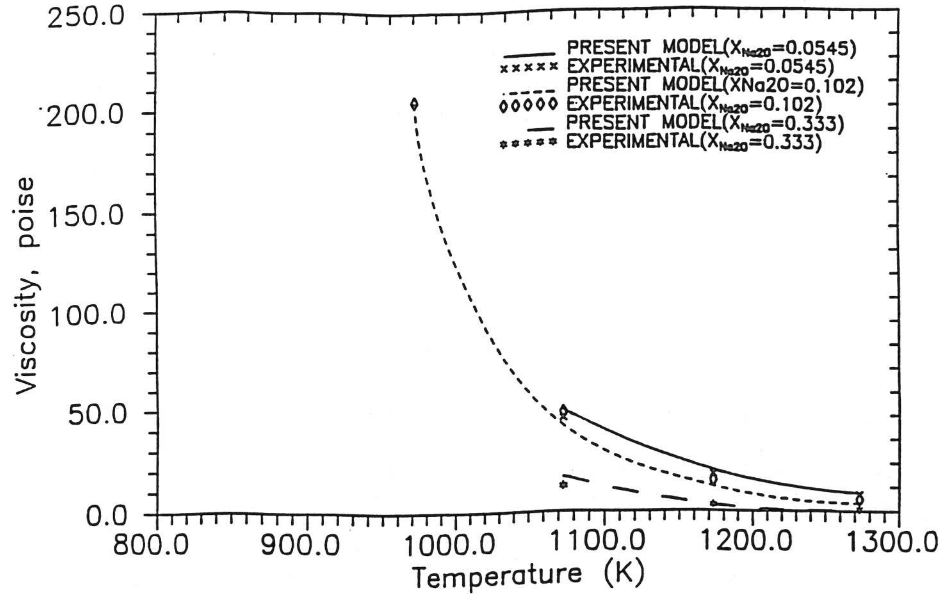

Figure 5. Variation of viscosity of Na_2O-B_2O_3 system with temperature.

5. Acknowledgements

This work was supported by the ALCOA Foundation, Grant# 20585, Pittsburgh, PA.

6. References

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