Alkali distribution in borosilicate glasses

T. Nanba & Y. M iura

Department of Environmental Chemistry and Materials, Okayama University, 3-1-1 Tsushima-Naka, Okayama 700-8530, Japan

The alkali distribution in borosilicate glass has been discussed on the basis of the different quantities obtained by various experimental methods. The NBO fraction was chosen as a common quantity for evaluating the alkali distribution models. The NBO fractions in sodium borosilicate glasses were estimated from $^{11}$B and $^{29}$Si NMR as well as XPS. However, the best model was not found among the existing models. The amounts of sodium oxide consumed for the NBO formation in borate and silicate networks and for the formation of $\text{BO}_4$ units were separately estimated from the $^{11}$B and $^{29}$Si NMR data. A new trend was found in the alkali distribution suggesting the possibility for a new universal distribution model.

Borosilicate glass consists of borate and silicate networks formed by $\text{BO}_3$ and $\text{SiO}_4$ units, and the addition of network modifiers such as alkali and alkaline earth oxides to the glass leads to complicated structural changes. When alkali ions are associated with a silicate network, nonbridging oxygens (NBOs) are formed in the network. When associated with a borate network, fourfold coordinated borons ($\text{B}_4$) and NBOs are produced in the borate network. Hence, the amount of the structural species present in the glass is dependent on the amount of the alkali ions associated with silicate and borate networks. Several alkali distribution models have been proposed for alkali borosilicate glasses, in which the glass composition has been commonly represented as $R\text{B}_2\text{O}_3\text{SiO}_2$, where $R$ and $K$ denote the molar ratios, $R=\text{R}_2\text{O}/\text{B}_2\text{O}_3$, and $K=\text{SiO}_2/\text{B}_2\text{O}_3$. Dell et al. (1) described the fraction of borons having various coordination structures determined from $^{11}$B NMR, in which they assumed macroscopic structural units such as reedmergnerite and diborate groups in the glasses. Zhong et al. (2) also described the boron fractions given from $^{11}$B NMR and their assumption is, however, quite different from that of Dell et al. (1). It was assumed in the Zhong model (2) that alkali ions were distributed only within a borate network below the critical $R_0$ content, $R_0$, and for $R>R_0$. However, alkali ions were proportionally distributed within the borate $1/(1+K)$ and silicate $K/(1+K)$ networks. The optimum $R_0$ value was determined in every K-family of glasses. Martin et al. (3-5) performed $^{29}$Si MAS-NMR measurements, the chemical shift being described on the basis of the Zhong model. However, the optimum $R_0$ values derived from $^{29}$Si and $^{11}$B NMR were different from one another. (3) Recently Miura et al. (6) proposed a new alkali distribution model on the basis of XPS and an appropriate acid-base concept. They also introduced a critical $R_\alpha$ content, $R_\alpha$, assuming the alkali distribution that for $R<R_\alpha$, alkali oxides distributed within the borate network were consumed only in the formation of tetrahedral $\text{BO}_4$ units, and NBOs associated with borate network were produced only after exceeding $R_\alpha$. In the Miura model, furthermore, alkali ions are differently distributed between borate and silicate networks, where the alkali distribution coefficient, $\alpha$, is introduced to represent the $R_\alpha$O content associated with borate and silicate networks. The amount of $R_\alpha$O associated with silicate network, $R_{\alpha\text{Si}}$, is given by

$$R_{\alpha\text{Si}} = \begin{cases} \alpha R & \text{for } R \leq R_\alpha \\ (R-R_\alpha)(1+K)^{-1}+\alpha R & \text{for } R > R_\alpha \end{cases}$$

(1)

The coefficient $\alpha$ was optimised to reproduce the NBO fraction evaluated from XPS measurements. The $\alpha$ value so-determined seemed to be in good agreement with the relative amount of Si–O–Si bonds in a $\text{B}_2\text{O}_3\text{SiO}_2$ glass, suggesting that alkali oxides added to the glass were preferentially consumed in breaking Si–O–Si bonds. In the case $\alpha=0$, Equation (1) is identical to the Zhong model. The physical meaning of $R_\alpha$ is, however, quite different between the Zhong and Miura models, that is, $R_\alpha$ is the critical $R_\alpha$O content for the formation of NBO in silicate network in the Zhong model and for the NBO formation in borate network in the Miura model.

These alkali distribution models are evaluated on the basis of different experiments and physical quantities, that is, the Dell and Zhong models are commonly based on the fractions of borons with various coordination structures estimated from $^{11}$B NMR, the Martin model is derived from the chemical shift in $^{29}$Si MAS-NMR and the Miura model is derived for the NBO fraction determined with XPS. If a common quantity is chosen, it will be possible to compare the models without prejudice. In the present study, the amount of NBO was chosen as a common quantity to review the alkali distribution models.

1 Author to whom correspondence should be addressed. (email: tokuro_n@cc.okayama-u.ac.jp)
Evaluating NBO Fraction

In borosilicate glasses, alkali oxides are consumed to produce B4 and NBO. If we assume that B2O3 tetrahedra have no NBO, NBO should be included in either BO3 triangles or SiO4 tetrahedra. If such is the case, we can evaluate the amount of NBO from the fraction of fourfold-coordinated borons, N4, according to the following procedures.

1. 1 mole of R2O forms 2 moles of BO4 unit
   
   \[
   2\text{BO}_3+\text{R}_2\text{O}\rightarrow\text{BO}_4 
   \]

   Then, when R44 moles of R2O are consumed to form BO4 units, 2R44 moles of BO4 will be produced. A n R33, R2O3, KSiO3 glass contains 2 moles of B, and N4 will hence be given by
   
   \[
   \text{N}_4=2\text{R}_{44}/2=\text{R}_{44} \tag{2} 
   \]

2. 1 mole of R2O forms 2 moles of NBO.

   \[
   \text{(Si-O-Si)}+\text{R}_2\text{O}\rightarrow2\text{(Si-O-R)} 
   \]

   Then, when R44 and R43 moles of R2O are consumed to produce NBO in the silicate and borate networks, respectively, 2R44 and 2R43 moles of NBO will be produced.

3. Let us assume that R44 moles of R2O are associated with the borate network. R44 and R43 moles of R2O are consumed to produce BO4 and NBO, respectively. Here, R44=R43+R44 and N4=R44 from Equation (2) so that we can obtain R44=R43+R44. Consequently, 2R44 and 2R43=2(R43-N4) moles of NBO will be produced, and the total amount of NBO in the glass will be 2R44+2(R43-N4)=2R44-N4, where \( \text{N}_4=\text{R}_{44}+\text{R}_{43} \).

4. Thus, the total amount of NBO formed in the glass is independent of alkali distribution and it depends only on N4, that is, the fraction of fourfold borons. Finally, the NBO fraction in the glass, f(NBO), is given by

   \[
   f(\text{NBO})=(2R-2N)/2(R+3+2K) \tag{3} 
   \]

According to the equation, we can estimate the NBO fraction both from experiments and models.

In XPS analysis, the NBO fraction can be obtained directly from the separation of O1s signal into BO and NBO components, and the further separation such as NBO in borate and silicate networks, however, would not be useful.\(^{6} \)

We can experimentally obtain the N4 value from boron NMR, but the alkali distribution, R43, cannot be determined from boron NMR experiments. Assuming that R43/R44 is proportional to R43, Zhong et al\(^{\text{[2]} \}) evaluated R43 from \(^{11}\text{B} \) NMR, but the assumption is not valid. Silicon NMR is probably the only method that can experimentally determine the alkali distribution, R43. The amount of NBO in the silicate network can be estimated from the distribution obtained from silicon NMR, but no information is given from silicon NMR as for the NBO fraction in borate network. Full information on the alkali distribution will be provided with the combination of B and Si NMR experiments.

In the present paper, the experimental data for RNa2O.B2O3.KSiO2 glasses were collected from the literature, XPS reported by Miura et al\(^{\text{[6]} \}) \), 11B NMR by Dell et al\(^{\text{[6]} \}) \), and 29Si-MAS NMR by Bhasin et al\(^{\text{[6]} \}) \) evaluating the NBO fraction.

NBO fractions evaluated from experiments and models

The NBO fractions evaluated from the various methods are summarised in Figure 1 for the glasses, RNa2O.B2O3.KSiO2 (K=2.0, 4.0 and 6.0), in which the NBO fractions evaluated from the experimental data are indicated by the markers and those from the models are shown by the lines. As mentioned above, the amount of NBO estimated from XPS or boron NMR should be the total amount of NBO in a glass. In these experiments NBOs in BO4 and SiO4 units are indistinguishable. On the other hand, we can evaluate the amount of NBO only in SiO4 units from the Q4 distribution obtained by silicon NMR. As also described above, R moles of Na2O are divided into R44 and R43 moles, being distributed within the silicate and borate networks, respectively. Therefore, the fraction of NBO in SiO4 units must not exceed the total NBO fraction. In Figure 1 some points obtained from silicon NMR exceed the points from XPS and boron NMR. Apart from that, the difference in the NBO fraction between the experiments is quite small, since NBO in SiO4 units is the predominant species in these higher K-family glasses. If the Q4 distribution in the smaller K-family glasses such as K=0.5 were available, the difference from silicon NMR would be more obvious.

In the alkali distribution models proposed by Dell et al\(^{\text{[6]} \}) \), Zhong et al\(^{\text{[2]} \}) \), and Miura et al\(^{\text{[6]} \}) \) the amounts
The results shown in Figure 2 are in good agreement with the experimental data. Unfortunately, it is hard to judge the best model from Figure 1.

As shown in Figure 1, the difference in the experimental NBO fraction between XPS and boron NMR is small, while in the higher R regions, the NBO fraction from boron NMR is somewhat higher than that from XPS. According to Equation (3), the fraction of fourfold boron, N4, is inversely estimated from the total NBO fraction. The N4 values were calculated from the experimental NBO fraction obtained from XPS. The result is shown in Figure 2 together with the experimental N4 data reported elsewhere. As compared with the NBO fraction, the difference in N4 is quite obvious, particularly in the higher R regions. These evaluations are based on two assumptions: that the tetrahedral BO4 units include no NBO and the NBO component separated from O1s XPS signal contains all NBOs. These assumptions imply the consistency between the results of XPS and boron NMR. The inconsistency shown in Figure 2 suggests that one or both the assumptions are inapplicable in the present case. The basicity of a BO4 unit with one NBO is 0.71, which is much higher than the average basicity of the glass matrix, 0.44–0.65. Therefore, it is reasonable to assume that the BO4 units in the present glasses include no NBOs, and NBOs in borate network are preferentially bound to threefold borons.

It should also be noted in Figure 1 that the NBO fractions obtained from XPS are much closer to those from silicon NMR than from boron NMR, excepting the glasses in which silicon NMR shows the highest NBO fraction. It leads to another interpretation in the NBO component separated from O1s XPS signal: NBOs only in the SiO4 units contribute to the NBO component and NBOs in BO3 units are put into the BO component. Hsieh et al. separated the O1s XPS signal for sodium borosilicate glasses into three components, bridging oxygen, B–O–Na and Si–O–Na, concluding that the area fraction of these components follows the Dell model. As shown in Figure 1, however, the NBO fraction obtained from XPS shows the fraction of NBO in SiO4 units much higher than predicted from the Dell model. Chemical species in the borosilicate glasses are quite complicated; as for BO, B3–O–B3 (λ = 0.42), B3–O–Si (0.45), Si–O–Si (0.48), B3–O–B4 (0.49), B4–O–Si (0.52) and B4–O–B4 (0.57) are present, and as for NBO, B3–O–Na (0.79) and Si–O–Na (0.81) are present, where λ indicates the theoretical microscopic optical basicity of individual oxide ions. The difference in basicity of NBOs is too small to separate O1s XPS signal into B3–O–Na and Si–O–Na components. Furthermore, it is expected in the present glasses that electrons on oxide ions easily delocalize through vacant B2p orbital in planar BO3 triangles. The electron delocalization as well as the structural diversity probably brings about great difficulty in O1s peak separation.

Alkali distribution in sodium borosilicate glasses

As already mentioned, full information for the alkali distribution is expected from B and Si NMR experiments; the amount of alkali oxide consumed in producing the BO4 unit, Rb, is identical with the fraction of fourfold coordinated boron, N4. The amount of R2O distributed to silicate network, RSi, is given by \( \frac{1}{2} \times (\text{the amount of NBO in SiO}_4 \text{ units}) \), and the residual RSi, Rb = RSi is consumed to form NBO in BO3 units, where the assumption that BO3 units include no NBO is still valid. The amounts of Rb, RSi and RSi are estimated from the experiments of \( ^{11} \text{B NMR} \) and \( ^{29} \text{Si MAS-NMR} \) and the relative amounts to the total Na2O content, R, are plotted in Figure 3, where some Si NMR data giving higher NBO fraction than B NMR are excluded. The relative amount of Na2O consumed to form BO4 units, Rb, decreases continuously with increasing R. The relative amount of Na2O distributed within the silicate network, RSi is almost constant in higher R regions. The relative amount of Na2O consumed to form NBO in BO3 units, RSi has a critical threshold, and RSi increases monotonically above the threshold. Consequently, each K family glasses are divided into three R regions, being defined by two critical R values, Rc1 and Rc2. At R ≤ Rc1, Rb/R
decreases and $R_{3s}/R$ increases with increasing $R$, and no $Na_2O$ is consumed to produce NBO in BO$_4$ units ($R_{3s}/R = 0$) until $R$ reaches $R_{C1}$. At $R_{C1} < R < R_{C2}$, $R_{3s}/R$ is constant so that the relative amount of $Na_2O$ distributed to borate network, $R_N = R_{B3} + R_{B4}/R$ is also constant. In that region, $R_{B4}/R$ still decreases and $R_{B3}/R$ increases with increasing $R$. At $R_{C2} < R$, little structural information is available. It is expected in the glasses that there are no BO$_4$ units ($R_{B4}/R = 0$) and $R_{B3}/R$ still increases from the previous region and $R_{3s}/R$ turns into decreasing.

A mentioned, some Si NMR data are omitted from Figure 3 because $R_{Na} + R_{B4}$ exceeds the total $Na_2O$ amount $R$. The strange results are seen at small $R$ regions, which is probably due to the overestimation of NBO amount in the Si NMR analysis, i.e. part of BO in B-O-Si bonds might be assigned to NBO in Si NMR. As shown in the previous section, BO in the B4-O-Si bond ($\lambda = 0.52$) surely possesses higher basicity than BO in Si-O-Si (0-48), but the difference in basicity is much smaller than that from BO in Si-O-Na (0-81). Therefore, it is hard to explain the overestimation on the basis of the simple basicity concept. Nevertheless, it is supposed that in electronic population there is no great difference between BO in B4-O-Si and NBO in Si-O-Na. According to M. Iura et al., (6) NBOs in SiO$_4$ units donate lone pair electrons to the vacant B2p orbital in the neighbouring BO$_3$ units, and they turn into BOs forming B4-O-Si bonds in the end. The electronic delocalisation through B4-O bonds is much less than that through B3-O bonds due to the lower pi-bonding character of B4-O, and it is therefore expected that BOs in the B4-O-Si bonds formed in this way possess electrons similar to the NBOs in Si-O-Na units and they have been assigned to NBO in Si NMR. Probably, it is also the case in XPS. As shown in Figure 2, the discrepancy in the B4 fraction, $N_{4a}$, between B NMR and XPS is not negligible particularly in higher K-family glasses; at small $R$ regions, XPS gives smaller $N_{4a}$ values than B NMR, suggesting that XPS also overestimates the NBO amount in these regions. At high $R$ regions, however, XPS seems to underestimate the NBO amount. In these glasses, BO$_3$ units are abundant and it is therefore supposed that in XPS the amount of NBO in BO$_3$ units is underestimated due to the electronic delocalisation through B3-O bonds and the resultant decrease in electronic population of the NBO in the BO$_3$ units.

For interpreting the experimental inconsistencies correctly, theoretical approaches, such as computational modelling and molecular orbital calculation, might be indispensable. Furthermore, the whole set of measurements, including boron and silicon NMR and XPS, should be performed on the same specimens. After collecting the full information, it should be possible to propose a new universal model for the alkali distribution in borosilicate glasses.

**Conclusions**

Alkali distribution models were reexamined for the sodium borosilicate glasses (RNa$_2$O.B$_2$O$_3$.KSiO$_2$) by comparing the NBO fraction between experiments and the predictions. The NBO fractions were evaluated from O1s XPS signal and the fraction of fourfold boron, $N_{4a}$ determined from $^{11}$B NMR, and the amount of NBO in SiO$_4$ units was also estimated from the Q$_4$ distribution determined from $^{29}$Si MAS-NMR. The difference in the NBO fractions derived from the experiments was too small to choose the best model for alkali distribution.

The amounts of $Na_2O$ consumed for the formation of BO$_4$ units and NBOs in SiO$_4$ units, $R_{B4}$ and $R_{N}$, were evaluated from $^{11}$B NMR and $^{29}$Si MAS-NMR, respectively. The relative distribution $R_{3s}/R$ showed a monotonic decrease with increasing $R$. The alkali distribution to the silicate network $R_{3s}/R$, however, showed a complicated change against $R$; in the small $R$ region, the alkali distribution $R_{3s}/R$ increased continuously until $R$ reached the critical content $R_{C1}$, and at $R_{C1} < R < R_{C2}$, $R_{3s}/R$ was almost constant. In the higher $R$ region at $R_{C2} < R$, $R_{3s}/R$ turned into decreasing. The residual $Na_2O$ served the NBO formation in BO$_4$ units only in the region at $R_{C1} < R$.

The discrepancy was found in $N_{4a}$ obtained from $^{11}$B NMR and XPS; in XPS, the NBO amount seemed to be overestimated at small $R$ region and underestimated at high $R$ region. The overestimation of NBO amount in the small $R$ region was also recognised in $^{29}$Si MAS-NMR. It was supposed that part of the BOs in the B4-O-Si bonds had been originally NBOs in SiO$_4$ units and they possessed much higher electronic density than the other BOs. It was also supposed that NBOs in BO$_3$ units carried lower electronic densities than NBOs in SiO$_4$ units, resulting in the underestimation of the NBO amount in the high $R$ region. A universal alkali distribution model would be constructed by the correct interpretation of these experimental findings.
References