

VISCOSITY MODEL FOR FULLY LIQUID SILICATE MELT

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(Received 22 Septembre 2011; accepted 26 October 2011)

Abstract

A model for estimating the viscosity of silicate melt as derived in our previous paper is extended to the system containing MgO, CaO, SrO, BaO, Li₂O, Na₂O, K₂O, which can express the nonlinear variation of activation energy of viscosity with the composition. It is found that the optimized parameters of model which characterize the deforming ability of bonds around non-bridging oxygen decrease with increasing the bond strength of M-O bond expressed by $I = \frac{2Q}{r}$ (where Q is the valence of cation M ; r is the radius). It is pointed out that viscosity is not only determined by the bond strength, but also by the radius of cation which is defined as the "hindrance effect". The radius of cation plays paradox roles in the two factors: smaller radius leads to a stronger bond, thus a higher viscosity; while cations with smaller radius are easier to diffuse when neglecting the interaction force, thus a lower viscosity will be.

Keyword: Viscosity; Non-bridging oxygen; Bridging oxygen; Free oxygen

1. Introduction

Viscosity is an important physical property of silicate melt for its significant role in the fields of pyrometallurgy, glass-making, pottery-making and geological

research *etc.* From the view point of the reaction kinetics, the rate of chemical reaction is always fast at high temperature, so most of the metallurgy reactions are diffusion controlling which is directly related to the viscosity of molten slag. Obtaining

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viscosity by model estimation will be a promising way for the high cost and low accuracy of high temperature measurement.

When using Arrhenius equation to correlate viscosity with temperature, the activation energy of viscosity for silicate melt is the nonlinear function of composition [1]: when the basic oxide content is low, activation energy decreases quickly with the addition of basic oxide; when the content is high, the activation energy decreases gently. Viscosity model should consider this nonlinear behavior. Among the different models proposed in the last two decades by Urbain [2], Riboud et al. [3], Zhang et al. [4], Iida et al. [5], NPL [6], KTH [7], Nakamoto et al. [8], Shu [9], Ghoshu et al. [10], different expressions are used to express the relation between the activation energy and composition, e.g. Urbain and Zhang et al. utilized a polynomial function with the highest order of 3; Shu applied a polynomial function with the highest order of 2; while Riboud et al. used a liner relation which obviously can not describe the nonlinear behavior, thus the application range is limited. In our previous paper [11], a new way of relating the activation energy and composition is proposed, which can express the nonlinear variation of activation energy with composition and has been successfully applied to the CaO-MgO-FeO-MnO-SiO₂ system. In the present study, the model is extended to the silicate system containing alkali oxides (Li₂O, Na₂O and K₂O) and alkali earth oxides (MgO, CaO, SrO and BaO), and the different influences of different components on viscosity are also distinguished.

2. Model

The temperature dependence of viscosity is expressed by the Arrhenius equation as follows,

$$\ln \eta = \ln A + E / RT \quad (1)$$

where η is viscosity, dPa·s; A is the pre-exponent factor, dPa·s; E is the activation energy, J/mol; R is the gas constant, J/(mol K); T is the absolute temperature, K. In Eq. (1), the temperature compensation effect is considered which shows that a linear relation exists between $\ln A$ and E . In order to incorporate the viscosity data of pure SiO₂ melt, the linear relation is expressed as follows,

$$\ln A = k(E - 572516) - 17.47 \quad (2)$$

where E of 572516 and $\ln A$ of 17.47 are the Arrhenius parameters for pure SiO₂; [11] k is a constant for a specific binary system M_xO_y-SiO₂. For multicomponent system $\sum_i (M_xO)_i$ -SiO₂, k can be calculated from the values of all the binary systems M_xO_y-SiO₂ according to the mole fraction of M_xO_y,

$$k = \sum_{i,i \neq \text{SiO}_2} (x_i k_i) / \sum_{i,i \neq \text{SiO}_2} x_i \quad (3)$$

The activation energy in Eqs. (1-2) is expressed as follows,

$$E = \frac{572516 \times 2}{n_{\text{O}_{\text{Si}}} + \sum \alpha_{\text{Si}}^i n_{\text{O}_{\text{Si}}}^i + \sum \alpha_i n_{\text{O}_i}} \quad (4)$$

where $n_{\text{O}_{\text{Si}}}$ is the number of bridging oxygen bonded with Si⁴⁺ ion; $n_{\text{O}_{\text{Si}}}^i$ is the number of non-bridging oxygen bonded with Si⁴⁺ ion and metal cation i ; n_{O_i} is the number of free oxygen bonded with metal cation i ; α is the parameter describing the deforming ability of bond around the non-bridging oxygen or free oxygen relative to bridging oxygen.

3. The calculation of the number of oxygen ions

It has been pointed out [11] that thermodynamic models proposed by Toop *et al.* [12], Ottonello *et al.* [13], Yokokawa *et al.* [14], Masson *et al.* [15] can not be applied to the system containing Al_2O_3 ; furthermore the extension to multicomponent system is very complex, although they can give good results in $\text{M}_x\text{O}-\text{SiO}_2$ binary system. The cell model by Gaye *et al.* [16] can treat the system containing Al_2O_3 , but it is not applicable to slag containing alkali oxides. A simple method based on the assumption that the equilibrium constant for the reaction of free oxygen from basic oxide with bridging oxygen from silica to generate non-bridging oxygen is infinite (Assumption I). Therefore,

$$2x_{\text{SiO}_2} > x_{\text{M}_x\text{O}} : \\ n_{\text{O}_i} = 0; n_{\text{O}_{\text{Si}}}^i = 2x_{\text{M}_x\text{O}}; n_{\text{O}_{\text{Si}}} = 2x_{\text{SiO}_2} - x_{\text{M}_x\text{O}} \quad (5)$$

$$2x_{\text{SiO}_2} > x_{\text{M}_x\text{O}} : \\ n_{\text{O}_i} = x_{\text{M}_x\text{O}} - 2x_{\text{SiO}_2}; n_{\text{O}_{\text{Si}}}^i = 4x_{\text{SiO}_2}; n_{\text{O}_{\text{Si}}} = 0 \quad (6)$$

For the multicomponent system with several basic oxides, the numbers of different types of oxygen ions can be calculated by the random mixing rule (Assumption II): firstly, add the mole fraction of all the basic oxides and calculate the numbers of O_{Si} , $\sum \text{O}_{\text{Si}}^i$ and $\sum \text{O}_i$ by considering the system to be a pseudo-binary system; then multiply each term by the re-normalized mole fractions of basic oxides,

$$n_{\text{O}_{\text{Si}}}^i = \sum n_{\text{O}_{\text{Si}}}^i \cdot (x_{(\text{M}_x\text{O})_i} / \sum x_{(\text{M}_x\text{O})_i}) \quad (7)$$

$$n_{\text{O}_i} = \sum n_{\text{O}_i} \cdot (x_{(\text{M}_x\text{O})_i} / \sum x_{(\text{M}_x\text{O})_i}) \quad (8)$$

After obtaining the numbers of oxygen ions, two parameters α_{Si}^i and k_i are regressed

to represent the viscosity data of $(\text{M}_x\text{O})_i-\text{SiO}_2$ system; when applied to the multicomponent system, no new parameters is needed to regressed. It should be pointed out that parameter α_i is calculated as $\alpha_i = (\frac{T_{m,\text{FeO}}}{T_{m,i}})^{1.2} \alpha_{\text{Fe}}$ [11] (where T_m is the melting point of pure oxide) based on the assumption that the activation energy of viscosity is proportional to $T_m^{1.2}$ [17], for the reason that there is no viscosity data in literature at the composition range of $x_{\text{SiO}_2} < 1/3$ in binary system except FeO-SiO₂ system. Therefore, the numbers of free oxygen ions are zero for all the composition points whose viscosity are known, which makes it can not optimize parameter α_i . The optimized parameters for MgO-SiO₂, CaO-SiO₂, SrO-SiO₂, BaO-SiO₂, Li₂O-SiO₂, Na₂O-SiO₂ and K₂O-SiO₂ binary systems are given in Table 1.

Table 1 Values of model parameters for different MO-SiO₂ systems

Systems	α_i	α_{Si}^i	k_i
MgO-SiO ₂	15.54	6.908	-2.106×10 ⁻⁵
CaO-SiO ₂	17.34	7.422	-2.088×10 ⁻⁵
SrO-SiO ₂	18.5	9.502	-2.45×10 ⁻⁵
BaO-SiO ₂	23.74	10.3	-2.49×10 ⁻⁵
Li ₂ O-SiO ₂		11.06	-2.412×10 ⁻⁵
Na ₂ O-SiO ₂	40.56	13.35	-2.767×10 ⁻⁵
K ₂ O-SiO ₂		16.59	-3.2×10 ⁻⁵

4. Results

In order to evaluate the present model, the mean deviation is used which is calculated as follows:

$$\Delta = \frac{1}{N} \times \sum_{i=1}^N \frac{|\eta_{i,\text{mea}} - \eta_{i,\text{cal}}|}{\eta_{i,\text{mea}}} \times 100\% \quad (9)$$

where $\eta_{i,\text{cal}}$ and $\eta_{i,\text{mea}}$ are the estimated and

measured viscosity, respectively, and N represents the number of the samples.

4.1. Binary systems

In our previous paper [11], the viscosity data of MgO-SiO₂ and CaO-SiO₂ system are well represented by the present model. The viscosity data of SrO-SiO₂ system are from Bockris *et al.* [18], Urbain *et al.* [19] and Mizoguchi *et al.* [20], with the mole fraction of SiO₂ from 0.5 to 0.8. The comparisons between estimated values and these by experiments are shown in Figure 1, with the mean deviation 14.4%. In order to get a clear view on the composition dependence of viscosity, the variation of viscosity with the mole fraction of SiO₂ at 1873K and 1973K are shown in Figure 2, in which the experiment data of Bockris *et al.* are also given for comparison. It should be pointed out that in Figure 2 the hypothetical viscosities for compositions outside the liquid region are also plotted, and the same way is also adopted in the following text for the clear description of variation tendency of viscosity with composition.

The viscosity data of BaO-SiO₂ system are from Bockris *et al.* [18], Urbain *et al.* [19] and

Hofmaier *et al.* [21], with the mole fraction of SiO₂ from 0.5 to 0.75; while the viscosity data of Li₂O-SiO₂ system are from Bockris *et al.* [18], Mizoguchi *et al.* [20] and Shartsis *et al.* [22], with the mole fraction of SiO₂ from 0.5 to 0.8. The comparisons of estimated values with the measured values, and the variation of viscosity with composition are shown in Figure 3 and Figure 4 for BaO-SiO₂ system, with the deviation 13.1%; these for Li₂O-SiO₂ system are shown in Figure 5 and Figure 6, with the mean deviation 15.3%. Parameter α can not be obtained for the uncertainty of the melting point of Li₂O. However, in practical slag, mole fraction of Li₂O is always low, so the content of

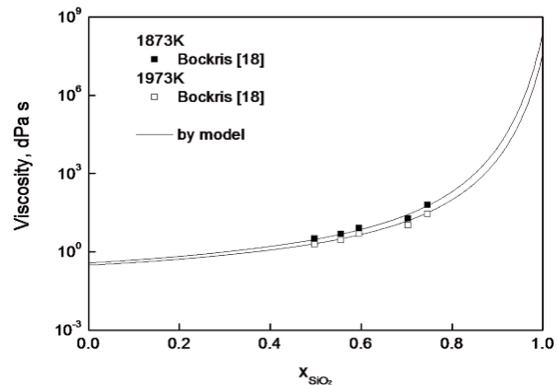


Fig. 2 Composition dependences of viscosity for SrO-SiO₂ system at 1873K and 1973K.

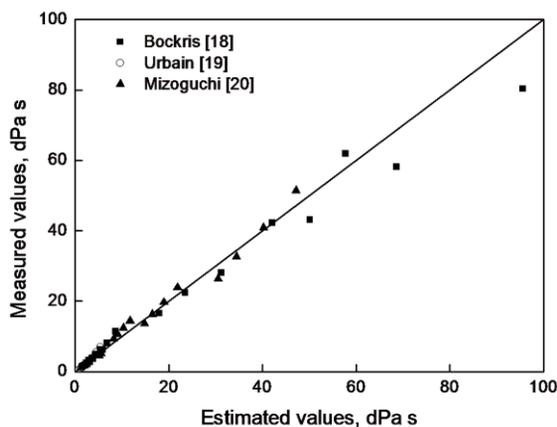


Fig. 1 Comparisons between estimated and measured viscosity values for SrO-SiO₂ system.

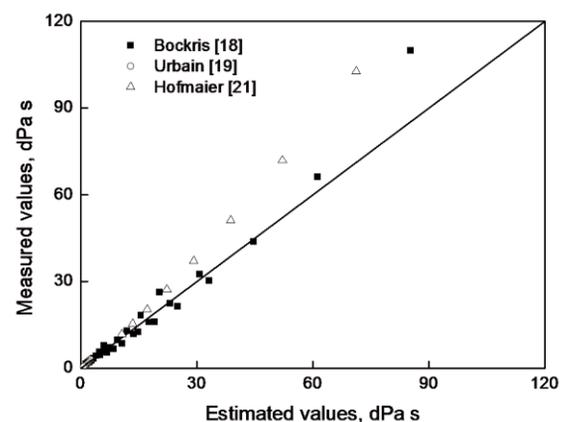


Fig. 3 Comparisons between estimated and measured viscosity values for BaO-SiO₂ system.

free oxygen bonded with Li^+ ion can be neglected. Parameters $\alpha_{\text{Si}}^{\text{Li}}$ and k_{Li} are enough to describe the viscosity variation of slag containing Li_2O .

Viscosity data of $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ systems are from Bockris *et al.* [18] and Eipeltaufer *et al.* [23], with the mole fractions of SiO_2 from 0.55 to 0.75 for $\text{Na}_2\text{O}-\text{SiO}_2$ system, and from 0.62 to 0.80 for $\text{K}_2\text{O}-\text{SiO}_2$ system. The comparisons of estimated values with the measured values, and the variation of viscosity with x_{SiO_2} are shown in Figure 7 and Figure 8 for $\text{Na}_2\text{O}-\text{SiO}_2$, with the mean deviation 24.5%; these for $\text{K}_2\text{O}-\text{SiO}_2$ system are shown

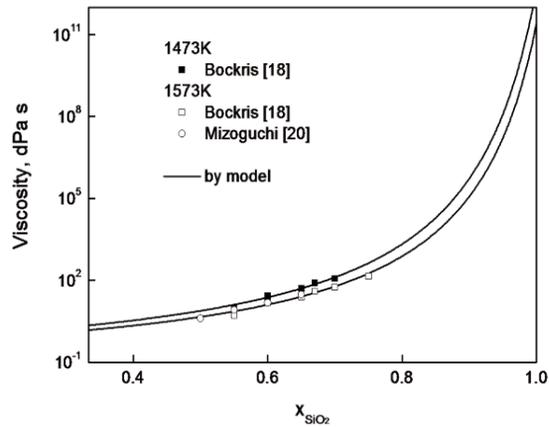


Fig. 6 Composition dependences of viscosity for $\text{Li}_2\text{O}-\text{SiO}_2$ system at 1473K and 1573K.

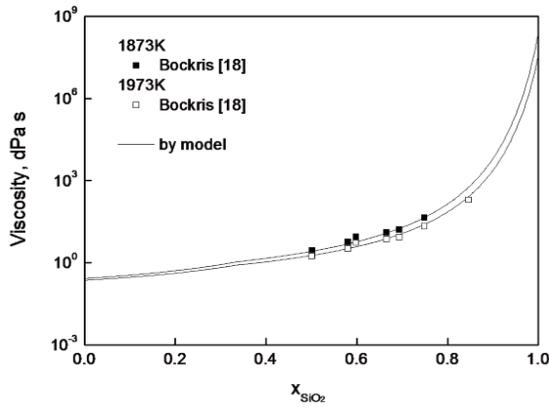


Fig. 4 Composition dependences of viscosity for $\text{BaO}-\text{SiO}_2$ system at 1873K and 1973K.

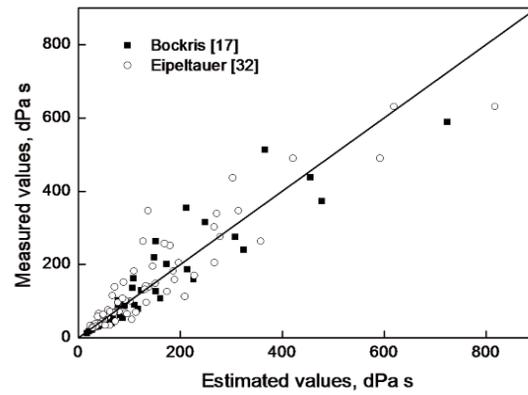


Fig. 7 Comparisons between estimated and measured viscosity values for $\text{Na}_2\text{O}-\text{SiO}_2$ system.

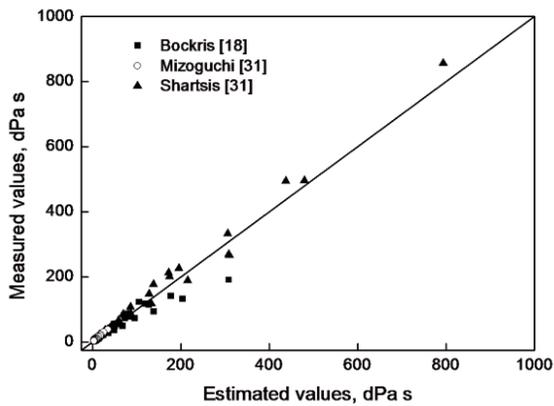


Fig. 5 Comparisons between estimated and measured viscosity values for $\text{Li}_2\text{O}-\text{SiO}_2$ system.

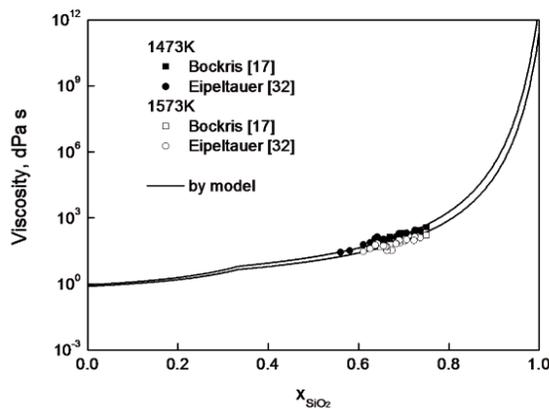


Fig. 8 Composition dependences of viscosity for $\text{Na}_2\text{O}-\text{SiO}_2$ system at 1473K and 1573K.

in Figure 9 and Figure 10, with the mean deviation 29.9%. The large deviations for these systems may result from the volatilization of Na_2O and K_2O at high temperature, especially in the case of high content of Na_2O or K_2O . Similar to Li_2O , parameter α_k can not be calculated for the unknown melting point of K_2O which decomposes at 623K.

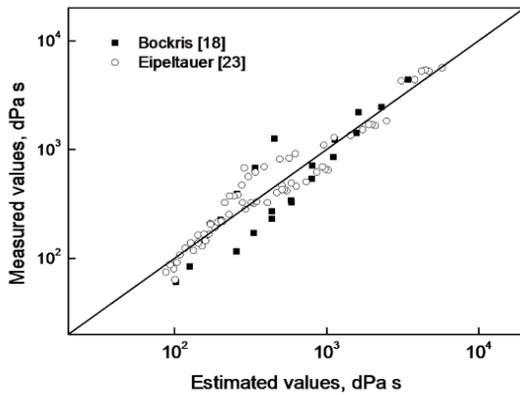


Fig. 9 Comparisons between estimated and measured viscosity values for $\text{K}_2\text{O-SiO}_2$ system.

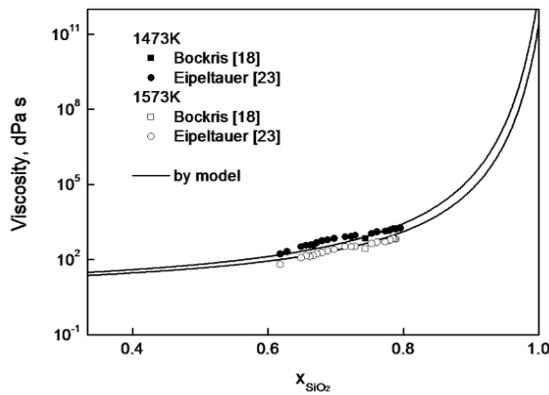


Fig. 10 Composition dependences of viscosity for $\text{K}_2\text{O-SiO}_2$ system at 1473K and 1573K.

4.2. Multicomponent systems

Only using the parameters regressed from binary systems, the viscosity of

multicomponent system at specific temperature and composition can be estimated. It has been shown that the model calculated viscosity agree well with the measured values for CaO-MgO-SiO_2 system [11]. The values of viscosity for $\text{CaO-Na}_2\text{O-SiO}_2$, $\text{CaO-K}_2\text{O-SiO}_2$ and CaO-BaO-SiO_2 systems have been measured by Yasukouchi *et al.* [24], and the comparisons with the estimated values are shown in Figures. 11-13, with the mean deviations 5.0%, 15.4% and 12.2%, respectively.

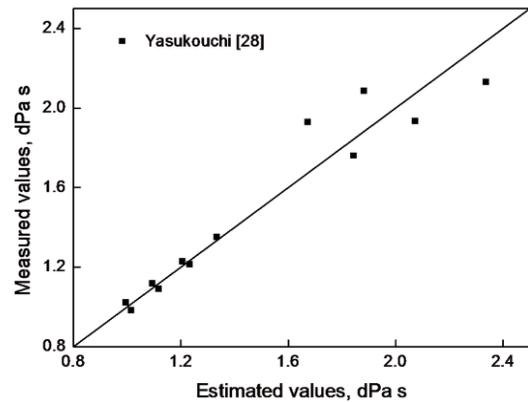


Fig. 11: Comparisons between estimated and measured viscosity values for $\text{CaO-Na}_2\text{O-SiO}_2$ system.

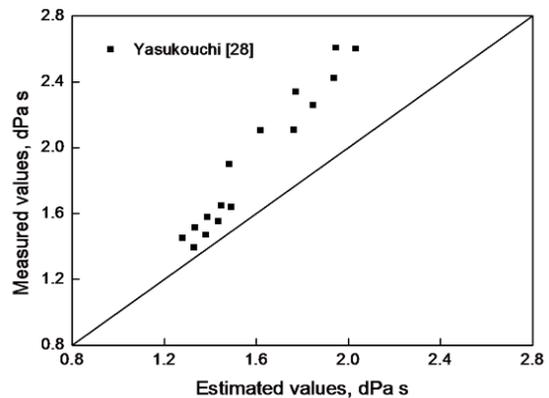


Fig. 12 Comparisons between estimated and measured viscosity values for $\text{CaO-K}_2\text{O-SiO}_2$ system.

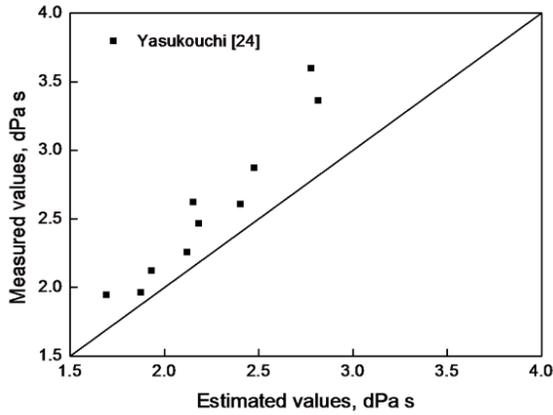


Fig. 13 Comparisons between estimated and measured viscosity values for CaO-BaO-SiO₂ system.

5. Discussions

(1) From the composition dependences of viscosity at specific temperatures shown in Figure 2, Figure 4, Figure 6, Figure 8 and Figure 10, it can be seen that viscosity decreases quickly with the addition of basic oxide when its content is low, while the variation becomes gently when the content of basic oxide is high. The reason for this may be that when the basic oxide content is low, the network of silica is destroyed severely from the random network structure to a gradually broken down structure containing chains and rings with the addition of basic oxide. When the content of basic oxide is high, most of the complex anions are those with short length as SiO_4^{4-} , $\text{Si}_2\text{O}_8^{8-}$ etc, which are supported by the Masson's polymer theory [15]. Therefore, the further addition of basic oxide can not lead to a large variation of structure, thus a small change of viscosity will be.

(2) In the present model, parameter α_{Si}^i is related to the deforming ability of non-bridging oxygen bond, therefore it can

reflect the bond energy of M-O to some extent. For chemical bond with a high percentage of ionic bond, the bond strength of M-O can be described approximately by the parameter I expressed by the coulombic force between the cation and oxygen anion defined as follows,

$$I = \frac{2Q}{(r_{\text{M}^{z+}} + r_{\text{O}^{2-}})^2} \quad (10)$$

where Q is the covalence of M ion; $r_{\text{M}^{z+}}$ and $r_{\text{O}^{2-}}$ are the radiuses of M and oxygen ions, respectively. While for the chemical bond with a high percentage of covalent bond, e.g. Fe-O (52.3%), Mn-O (41.0%) and Si-O (55.3%), the bond strength can not be characterized simply by I [11]. The large polarizations of ions lead to the inaccurate description of bond strength by electric attraction I .

Calculate parameters I for each chemical bond M-O with the radiuses taken from the data compiled by Shannon [25], and then plot the parameter α_{Si}^i with parameter I (shown in Figure 14). It can be seen from Figure 14 that α_{Si}^i decreases with increasing I , the reason for this may be that parameter α_{Si}^i can describe the deforming ability of M-O bond, and the larger the value of α_{Si}^i , the higher the deforming ability is. While the larger value of I corresponds to a stronger bond of M-O, which means a weaker deforming ability. Therefore, a decreasing relation should exist between parameter α_{Si}^i and I . It can also be seen from Figure 14 that the data of FeO-SiO₂ and MnO-SiO₂ systems not fit the relation for their high percentage of covalent bond.

(3) If the viscosity is determined only by the bond strength of M-O, viscosity should

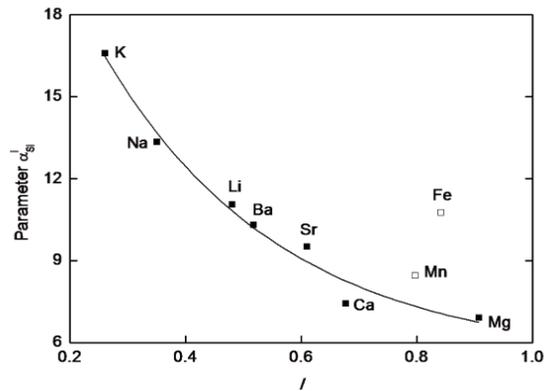


Fig. 14 The relation between parameters and I

decrease with increasing the radius of metal cation of alkali oxides or alkali earth oxides. However, the experimental results of Bockris *et al.* [18] showed that when the basic oxide content is low, the viscosity of M_2O-SiO_2 system follows the order: $K_2O-SiO_2 < Na_2O-SiO_2 < Li_2O-Na_2O$; when the content is high, the order is: $K_2O-SiO_2 > Na_2O-SiO_2 > Li_2O-Na_2O$, which is also supported by the present model shown in Figure 15. For $MO-SiO_2$ ($M=Mg, Ca, Sr, Ba$) system, there are also intersections among different curves of composition dependences of viscosity (shown in Figure 16), but the intersections occur at higher contents of basic oxides relative to alkali oxides. Therefore, there is at least one other factor that could affect the viscosity except the bond strength.

For electrical conductivity, the small cation is easy to diffuse through the hole among other ions when neglecting the interaction force, which enhances the electrical conductivity [26]. Similarly, viscosity is also the response of melt to the external force. Therefore, it should be not only determined by the interaction force among different ions described by bond

strength, but also by the radius of cation called hindrance effect as in electrical conductivity. And there is competition between hindrance effect and interaction force effect. If the interaction forces can be neglected, instinctively, the smaller ions are easier to diffuse which leads to a lower viscous resistance, thus a lower viscosity. Therefore, on one hand, the smaller size of cation can lead to a stronger interaction force

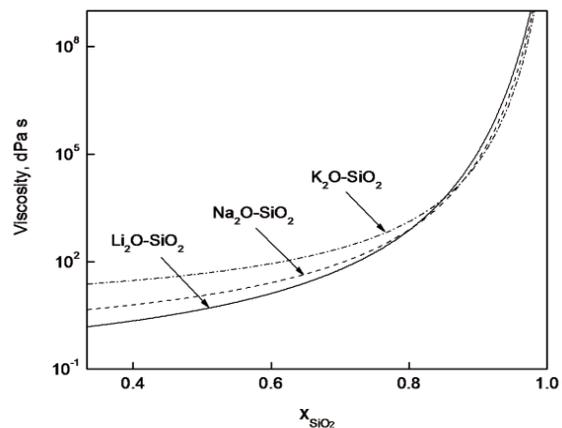


Fig. 15 The influences of different metal oxides on the viscosity of M_2O-SiO_2 ($M=Li, Na, K$) binary system at 1573K.

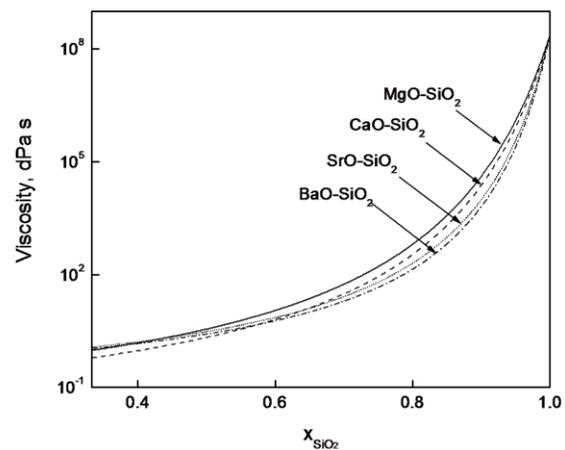


Fig. 16 The influences of different metal oxides on the viscosity of M_2O-SiO_2 ($M=Mg, Ca, Sr, Ba$) binary system at 1873K.

between cation and oxygen ion which increases the viscosity; on the other hand, it can also decrease viscosity according to the hindrance effect. Generally, the higher the valence of cation is, the more important the interaction force should be. The roles of hindrance effect and the interaction force effect for viscosity may change at different composition range, for instance, the variation of viscosity order for M_2O-SiO_2 ($M=Li, Na, K$) at different composition range may result from the reason that when the content of basic oxide is low, the interaction force may be dominated, so viscosity decreases with increasing the radius of alkali ion; while when there is a high content of basic oxide, the hindrance effect of cation may be dominated, so viscosity increases with increasing the radius of alkali ion. For alkali earth oxide, the case will be more complex for the larger valence of alkali earth cation, thus the change from interaction force dominated to hindrance effect dominated occurs at a higher content of basic oxide relative to M_2O-SiO_2 system. The coexistence of two factors in the fully composition range leads to the complex variation of viscosity with composition.

6. Conclusions

The proposed viscosity model is extended to the silicate melts containing $Li_2O, Na_2O, K_2O, MgO, CaO, SrO, BaO$ and SiO_2 , in which the different types of oxygen ions are used to characterize the structure of melt, with the numbers calculated based on the Assumptions I and II. There is a decreasing function relation between the model parameter α'_{si} and the parameter I . The

hindrance effect of cation and the interaction force effect between cation and oxygen ion can both affect the viscosity, and the roles of the two factors change at different composition range: in the case of low basic oxide content or valence of cation is high, the interaction force is dominates, and the viscosity decreases with increasing the radius of metal cation; when the content of basic oxide is high, the hindrance effect of cation is dominated, and the viscosity increases with increasing the radius of metal cation.

Acknowledgement

The authors wish to thank the Chinese Natural Science Foundation for their kind support under the contract 51174022.

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