

VISCOSITY MODEL FOR ALUMINOSILICATE MELT

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Abstract

The structurally based viscosity model proposed in our previous study is extended to include more components, e.g. SiO_2 , Al_2O_3 , FeO , MnO , MgO , CaO , Na_2O and K_2O . A simple method is proposed to calculate the numbers of different types of oxygen ions classified by the different cations they bonded with, which is used to characterize the influence of composition on viscosity. When dealing with the aluminosilicate melts containing several basic oxides, the priority order is established for different cations for charge compensating Al^{3+} ions, according to the coulombic force between cation and oxygen anion. It is indicated that basic oxides have two paradox influences on viscosity: basic oxide with a higher basicity decreases viscosity more greatly by forming weaker non-bridging oxygen bond; while it increases viscosity more greatly by forming stronger bridging oxygen bond in AlO_4^{5-} tetrahedron after charge compensating Al^{3+} ion. The present model can extrapolate its application range to the system without SiO_2 . Furthermore, it could also give a satisfy interpretation to the abnormal phenomenon that viscosity increases when adding K_2O to $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt within a certain composition range.

Keywords: Viscosity; Model; Aluminosilicate melts; Non-bridging oxygen; Bridging oxygen

1. Introduction

Aluminosilicate melt plays significant roles in the fields of glass-making, pottery-making, geological research and pyrometallurgy *etc.*, with viscosity as one of the most important physical properties. Therefore, accurate viscosity values for aluminosilicate melts are necessary not only for optimizing and improving the productive processes, but for studying the structure of aluminosilicate melts. Estimating viscosity by model may be a useful method considering experimental measurements are both time consuming and sometimes inaccurate for the difficulty of high temperature operation.

Many viscosity models are proposed to estimate viscosity of aluminosilicate melts [1-11]. Though these models are successful to some extent, many shortcomings still exist: (i) The application ranges of these models are very narrow. They can only obtain good estimation results in or near the composition (or temperature) range, in which the model parameters are optimized, while the results will be inaccurate when away from the range. (ii) For aluminosilicate melts containing several basic oxides, these viscosity models can not well represent the viscosity variation tendency with composition. Sometimes, an inverse tendency with the experimental finding may be given. For instance, it is found that viscosity increases when adding K_2O to $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt [12], while all

the viscosity models can only give a decreasing tendency. (iii) The calculation results of these models for oxide systems without SiO_2 are very bad (e.g. Al_2O_3 , $\text{CaO-Al}_2\text{O}_3$ and $\text{CaO-FeO-Al}_2\text{O}_3$ systems, *etc.*), in other words, they can only be applied to the system containing SiO_2 . In view of these points, much work still should be done on the viscosity model.

2. Points must be considered in viscosity model

At constant pressure, viscosity is determined by temperature and chemical composition of molten slags. The main object of modeling viscosity of aluminosilicate melt is finding a proper relation to correlate viscosity with composition and temperature. Generally, the temperature dependence of viscosity expressed by Weymann equation [13] $A\text{Texp}(E/RT)$, or Arrhenius equation [14] $A\text{exp}(E/RT)$ which is same as Eyring equation [15]. The Weymann equation is used by Riboud *et al.* [1], Urbain [6], Kondratiev *et al.* [7], Zhang *et al.* [8], Ray *et al.* [5] and Shu [9] *etc.*; while the Arrhenius equation (or Eyring equation) is used by Iida *et al.* [10], Nakamoto *et al.* [4], KTH [3], NPL [2], and Shankar *et al.* [16]. It was pointed out by Shankar *et al.* [16] that both the two types can well describe the variation of viscosity with temperature. Then, the problem of incorporating the influence of composition on viscosity is the central issue. Generally, viscosity model must fulfill

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the following four requirements:

(i) Viscosity is sensitive to the structure of aluminosilicate melts, and different components (acidic oxide, *e.g.* SiO₂; basic oxide, *e.g.* CaO and MgO; amphoteric oxide, *e.g.* Al₂O₃) have different influences on the structure. Thereby, viscosity model should be built based on a reasonable description to the structure of aluminosilicate melts. However, the empirical models by Riboud *et al.* [1], Urbain [6], Kondratiev *et al.* [7], NPL [2], Ray *et al.* [5], Shankar *et al.* [16], *etc.*, didn't consider the influence of melt structure on the viscosity.

(ii) Generally, in the Arrhenius or Weymann equation, there is a linear relation between the logarithm of pre-exponent factor $\ln A$ and activation energy E which is called the *temperature compensation effect* and is a common rule in the fields of viscosity, kinetics, electrical conductivity and diffusion coefficient [17]. Therefore, the compensation effect should also be taken into consideration in the viscosity model, while it is not considered in viscosity models of Riboud *et al.* [1], NPL [2], KTH [3], Nakamoto *et al.* [4], Iida *et al.* [10], *etc.*

(iii) After considering the Arrhenius or Weymann equation as well as the *temperature compensation effect* between $\ln A$ and E , the remaining task of modelling viscosity is to find a proper expression to relate the activation energy E and composition. It has been pointed out that the activation energy of viscosity is a non-linear function of composition [18]. A reasonable viscosity model should consider this nonlinear behavior. Among the different viscosity models, the polynomial functions with the highest order of " n " were utilized by different authors to describe this behavior: $n=1$ in Riboud *et al.* model [1]; $n=2$ in Shu model [9]; $n=3$ in Urbain model [6], Kondratiev *et al.* model [7] and Zhang *et al.* model [8].

(iv) When Al₂O₃ exists in the melts, Al³⁺ can form AlO₄⁵⁻ tetrahedron, and replace the position of Si⁴⁺ ion when there are enough metal cations (*e.g.* Ca²⁺, and Na⁺) participating into the charge compensation of Al³⁺ ions. It is found that different cations have different abilities of compensating Al³⁺ ions [19], so viscosity model should distinguish the different priorities. However, no model has done this except NPL model [2] which achieves this goal according to the different optical basicity values of different basic oxides. But this way has defect for the reason that in NPL model many basic oxides have the same optical basicity values, for instance optical basicity of Li₂O, CaO, FeO and MnO using the same value of 1.0, but actually the compensating abilities of these cations are different.

New viscosity model considering all the four requirements should be developed. This work has

been done in our previous paper [17, 20, 21]. New model is structural based, and the model parameters for silicate melts (absence of Al₂O₃) are closely related to the bond strength [17, 20]. In the presence of Al₂O₃, viscosity of CaO-MgO-Al₂O₃-SiO₂ system is also well modeled [21]. However, the more complex or involving other basic oxides systems (containing Al₂O₃) are not considered, meanwhile, the abnormal phenomenon of viscosity increasing as adding K₂O to CaO-Al₂O₃-SiO₂ melt [12] is still unresolved. In this work, the model will be extended to resolve these problems.

3. Model

Details of the model have been given elsewhere [17, 20, 21]. Only a brief description of the model will be given here. The temperature dependence of viscosity is calculated by Arrhenius equation,

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

where μ is the viscosity, Poise; A is the pre-exponent factor, Poise; E is the activation energy, J/mol; R is the gas constant, 8.314 J/(molK); T is the absolute temperature, K. The *temperature compensation effect* is considered,

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

For multicomponent system $\sum M_x O_y$ -SiO₂, the value of parameter k is assumed to be the linear addition of that of the binary systems $M_x O_y$ -SiO₂ with the re-normalized mole fractions of oxides $M_x O_y$ as the weighting factors,

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

The activation energy of viscosity in equation (2) is expressed as follows,

$$E = 572516 \times 2 / \left(\frac{n_{\text{O}_{\text{Si}}} + \alpha_{\text{Al}} n_{\text{O}_{\text{Al}}} + \sum \alpha_{\text{Al},i} n_{\text{O}_{\text{Al},i}} + \sum \alpha_{\text{Si}}^i n_{\text{O}_{\text{Si}}^i} + \sum \alpha_{\text{Al},i}^j n_{\text{O}_{\text{Al},i}^j} + \sum \alpha_i n_{\text{O}_i}}{n} \right) \quad (4)$$

where n is the mole number and α describes the deforming ability of bond around the corresponding oxygen ion. The first, second, third, fourth, fifth, sixth terms in the denominator are the contributions of bridging oxygen O_{Si}, bonded with Si⁴⁺ ion; oxygen O_{Al}, bonded with Al³⁺ ion not charge compensated; bridging oxygen O_{Al,i}, bonded with Al³⁺ ion charge compensated by cation i ; non-bridging oxygen, bonded with Si⁴⁺ ion and metal cation i ; non-bridging oxygen O_{Si} ^{i} , bonded with metal cation j and Al³⁺ ion charge compensated by cation i ; free oxygen O_{Al,i} ^{j} , bonded with metal cation i , respectively.

4. Method of calculating the number of oxygen ion

Before using equations (1)~(4) to calculate viscosity, the numbers of different types of oxygen

ions must be known. In our previous paper [21], five assumptions are suggested to calculate the numbers for CaO-MgO-Al₂O₃-SiO₂ melt.

Assumption I: The equilibrium constant for the reaction of free oxygen from basic oxide with bridging oxygen to generate non-bridging oxygen is infinite

Assumption II: For system containing several basic oxides $\sum (M_xO)_i$ -SiO₂, the numbers of different types of oxygen ions can be calculated by the random mixing rule: firstly, calculate $\sum n_{O_{Si}}$, $\sum n_{O_{Si}}$ and $\sum n_{O_i}$ following **Assumption (I)** considering the system to be a pseudo-binary system; then multiply each term by the re-normalized mole fractions of basic oxides.

Assumption III: The equilibrium constant for the reaction of M_xO charge compensating Al₂O₃ is infinite: in the case $x_{M_xO} / x_{Al_2O_3} < 1$, all M_xO act as charge compensators, while in the case of $x_{M_xO} / x_{Al_2O_3} > 1$ all Al³⁺ ions form AlO₄⁵⁻ tetrahedrons, and the extra M_xO acts as network modifiers.

Assumption IV: In the case of $x_{M_xO} / x_{Al_2O_3} > 1$, when the extra M_xO breaks the bridging oxygen, it is assumed that the bridging oxygen in AlO₄⁵⁻ and SiO₄⁴⁻ and tetrahedron are equivalent, and the numbers of formed non-bridging oxygen bonded to Al³⁺ ions and Si⁴⁺ ions are proportional to the numbers of bridging oxygen in AlO₄⁵⁻ and SiO₄⁴⁻ and tetrahedrons.

Assumption V: Ca²⁺ cation has higher priority of charge-compensating Al³⁺ ion than Mg²⁺ ion. Only after all the Ca²⁺ ions have been exhausted, Mg²⁺ ions will participate into the charge compensation.

Among them, **Assumption V** endows Ca²⁺ ion an absolute priority over Mg²⁺ ion when charge compensating Al³⁺ ion, with which the viscosity variation of CaO-MgO-Al₂O₃-SiO₂ system can be well represented. However, the previous work can only deal with the case of aluminosilicate system contain two basic oxides: CaO and MgO, whereas, when the basic oxides are not CaO and MgO or when there are three or more basic oxides exist in more complex aluminosilicate system, how to establish the different priorities of different metal cations. This is one of the main tasks of the present study. **Assumptions V** will be revised into a more general form as follows.

Assumption V: Different metal cations have different abilities of charge-compensating Al³⁺ ions. When there are several basic oxides in aluminosilicate melts, a strict priority order exists for different metal cations. In other words, only after all the cations with the higher priority have been exhausted to compensate Al³⁺ ions, cations with the lower priority can participate the charge compensation. The order for different cations can be determined as follows.

Theoretically, the cation M^{z+} that has strong bond strength with O²⁻ ion should possess weaker ability of compensating Al³⁺ ion, for the reason that itself can

form complex anion with oxygen ion, and strong repulsive force exists between cation M^{z+} and Al³⁺ ion. So, in this study, parameter *I* expressed by the coulombic force between the cation and oxygen anion will be introduced to characterize the abilities of different cations,

$$I = \frac{2Q}{(r_{M^{z+}} + r_{O^{2-}})^2} \quad (5)$$

where *Q* is the valence of M^{z+} ion, $\frac{r_{M^{z+}}}{r_{O^{2-}}}$ are the radiuses of M^{z+} and oxygen ions, respectively. The ion radiuses (taken from the data compiled by Shannon [22]) of Mg²⁺, Ca²⁺, Na⁺, K⁺, Fe²⁺, Mn²⁺ and O²⁻ are 0.66 Å, 0.99 Å, 0.97 Å, 1.33 Å, 0.74 Å, 0.8 Å and 1.44 Å, respectively. So the order of *I* for different cations is: K⁺ < Na⁺ < Ca²⁺ < Mn²⁺ < Fe²⁺ < Mg²⁺. Therefore, the priority order of charge compensating Al³⁺ ion is: K⁺ > Na⁺ > Ca²⁺ > Mn²⁺ > Fe²⁺ > Mg²⁺. The order of K⁺ > Na⁺ > Ca²⁺ > Mg²⁺ has been proved by the evidences from thermochemical [23] and spectroscopic data [24, 25]. However, it was pointed out that [17] for chemical bond with a high percentage of covalent bond, e.g. Fe-O (52.3%), Mn-O (41.0%) (close to the value of Si-O bond which is 55.3%), the bond strength can not be characterized simply by *I*. So the position of Fe²⁺ and Mn²⁺ in the order is only an approximation. The same approximation in the order was also suggested by Mysen [19].

Based on **Assumption I ~ Assumption IV** and **Assumption V**, the numbers of different types of oxygen ions can be calculated easily. The detailed calculating formulae for $\sum (M_xO)_i$ -SiO₂ and M_xO-Al₂O₃-SiO₂ systems are given before, and the calculating formulae for (M_xO)_i-(M_xO)_j-Al₂O₃-SiO₂ system can be obtained following the formulae of CaO-MgO-Al₂O₃-SiO₂ system [21]. In the following sections, model will be applied to aluminosilicate system containing FeO, MnO, MgO, CaO, Na₂O and K₂O. The literature data source utilized for the model parameters optimization and comparisons are shown in Table 1. The regressed parameters are shown in Tables 2 and 3, in which the parameters optimized in previous papers [17, 20, 21] are also included. Parameters for the present model are obtained as follows: parameters k_i , α_{Si}^i and α_i , are optimized according to the data of M_xO-SiO₂ binary system (have been accomplished in our previous work [17, 20]); parameters $\alpha_{Al,i}$ and $\alpha_{Al,i}^i$ and are optimized according to the data of M_xO-Al₂O₃-SiO₂ system; while for the system (M_xO)_i-(M_xO)_j-Al₂O₃-SiO₂ with two basic oxides, one more parameter $\alpha_{Al,i}^j$ is needed. Theoretically, no more parameter is needed for even higher order system.

5. Results

5.1. M_xO-Al₂O₃-SiO₂ ternary system

The viscosity data of FeO-Al₂O₃-SiO₂ and MnO-

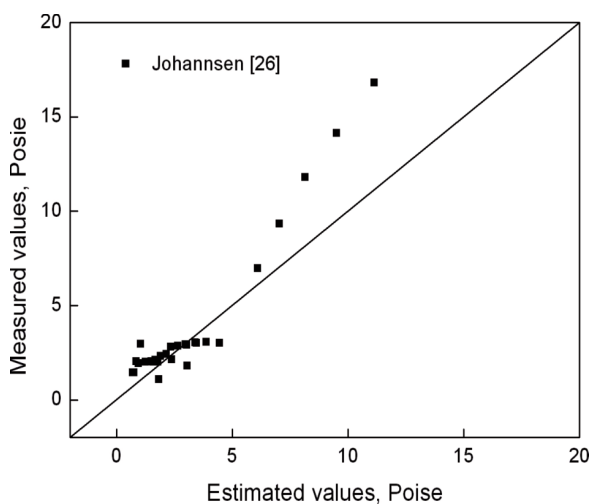
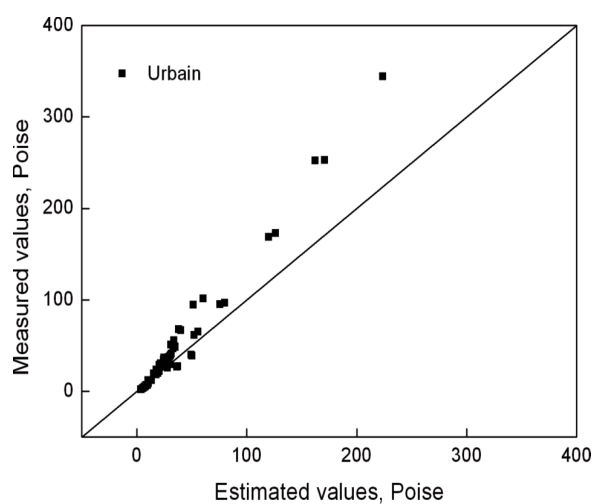
Table 1. Summary of the literature data source utilized in the present study

System	Source	Composition range (mole fraction)
FeO-Al ₂ O ₃ -SiO ₂	Johannsen <i>et al.</i> [26]	FeO: 0.44~0.73; SiO ₂ : 0.22~0.44
MnO-Al ₂ O ₃ -SiO ₂	Urbain <i>et al.</i> [27]	MnO: 0.15~0.54; SiO ₂ : 0.33~0.74
Na ₂ O-Al ₂ O ₃ -SiO ₂	Kou <i>et al.</i> [28]	Na ₂ O: 0.20~0.50; SiO ₂ : 0.4~0.65
	Toplis <i>et al.</i> [29]	Na ₂ O: 0.08~0.28; SiO ₂ : 0.5~0.82
	Toplis <i>et al.</i> [30]	Na ₂ O: 0.09~0.26; SiO ₂ : 0.5~0.82
K ₂ O-Al ₂ O ₃ -SiO ₂	Urbain <i>et al.</i> [27]	K ₂ O: 0.12; SiO ₂ : 0.75
	Mizoguchi <i>et al.</i> [31]	K ₂ O: 0.32~0.50; SiO ₂ : 0.40~0.60
CaO-FeO-Al ₂ O ₃ -SiO ₂	Higgins <i>et al.</i> [32]	Al ₂ O ₃ : 0.05~0.23; SiO ₂ : 0.33~0.47
	Kolesov <i>et al.</i> [33]	Al ₂ O ₃ : 0.02~0.05; SiO ₂ : 0.24~0.51
CaO-Na ₂ O-Al ₂ O ₃ -SiO ₂	Sukenaga <i>et al.</i> [12]	Al ₂ O ₃ : 0.10~0.12; SiO ₂ : 0.34~0.48
CaO-K ₂ O-Al ₂ O ₃ -SiO ₂	Sukenaga <i>et al.</i> [12]	Al ₂ O ₃ : 0.11~0.12; SiO ₂ : 0.34~0.49
CaO-FeO-Al ₂ O ₃	Vidacac <i>et al.</i> [34]	Al ₂ O ₃ : 0.26~0.39; FeO: 0.12~0.34
CaO-MgO-Na ₂ O-Al ₂ O ₃ -SiO ₂	Sykes <i>et al.</i> [35]	Al ₂ O ₃ : 0.02~0.23; SiO ₂ : 0.50~0.51
	Kim <i>et al.</i> [36]	Al ₂ O ₃ : 0.12~0.12; SiO ₂ : 0.28~0.38
CaO-MgO-FeO-Al ₂ O ₃ -SiO ₂	Higgins <i>et al.</i> [32]	Al ₂ O ₃ : 0.05~0.06; SiO ₂ : 0.34~0.42
	Kim <i>et al.</i> [37]	Al ₂ O ₃ : 0.06~0.11; SiO ₂ : 0.29~0.34

Table 2. Values of model parameters for different M_xO -SiO₂ and M_xO -Al₂O₃-SiO₂ systems

i	$k_i \times 10^5$	α_{Si}^i	α^i	$\alpha_{Al,i}$	$\alpha_{Al,i}^i$
Fe	-2.195	10.76	33.62	8.702	6.828
Mn	-2.147	8.452	27.83	5.857	4.204
Mg	-2.106	6.908	15.54	5.606	3.975
Ca	-2.088	7.422	17.34	4.996	7.115
Na	-2.767	13.35	40.56	4.308	10.46
K	-3.2	16.59		4.156	17.34
Al	-2.594		5.671		

Al₂O₃-SiO₂ systems are taken from the works of Johannsen *et al.* [26] and Urbain *et al.* [27], respectively. Based on the parameters k_i , α_i and α_{Si}^i optimized in binary systems, two parameters $\alpha_{Al,Fe}$ and $\alpha_{Al,Mn}^{Fe}$ ($\alpha_{Al,Mn}$ and $\alpha_{Al,Mn}^{Mn}$) are optimized in FeO-Al₂O₃-SiO₂ system (MnO-Al₂O₃-SiO₂ system). The comparisons of calculated values with those by experiments for these two systems are shown in Figure 1 and Figure 2, with the mean deviations 29.8% and 28.8%, respectively. The large deviations for these two systems may result from the reasons that both Fe and Mn are polyvalent metallic elements, and possible existences of Fe³⁺ or Mn³⁺ ions lead to the viscosity behavior departing from melts with pure FeO or MnO.

**Figure 1.** Comparisons between estimated and measured viscosity values for FeO-Al₂O₃-SiO₂ system.**Figure 2.** Comparisons between estimated and measured viscosity values for MnO-Al₂O₃-SiO₂ system.

The data of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system are taken from Kou *et al.* [28] and Toplis *et al.* [29, 30], with viscosity values varying from 10 to 4×10^5 poise. Parameters $\alpha_{\text{Al,Na}}$ and $\alpha_{\text{Al,Na}}^{\text{Na}}$ are optimized in this system. The comparisons of calculated values with the measured values are shown in Figure 3, with the mean deviation 27.9%. For $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, Urbain *et al.* [27] only measured one composition point with high content of SiO_2 and high viscosity; Mizoguchi *et al.* [31] measured composition points with high content of K_2O and low viscosity. With the optimized parameters of $\alpha_{\text{Al,K}}$ and $\alpha_{\text{Al,K}}^{\text{K}}$, viscosity of this system can be calculated. The comparisons between the estimated values and those by experiments are shown in Figure 4, with the mean deviation 31.8%. The large deviations for these two systems may result from large measure errors at high viscosity and evaporations of Na_2O and K_2O at high temperature.

5.2. $(\text{M}_x\text{O})_i-(\text{M}_x\text{O})_j-\text{Al}_2\text{O}_3-\text{SiO}_2$ quarternary system

For $(\text{M}_x\text{O})_i-(\text{M}_x\text{O})_j-\text{Al}_2\text{O}_3-\text{SiO}_2$ quarternary system, one more parameter is needed. Parameter $\alpha_{\text{Al,Ca}}^{\text{Mg}}$ has been optimized in $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system [21]. In this work, according to the priority order of different cations when charge compensating Al^{3+} ion: $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{2+}$, oxygen ions $\text{O}_{\text{Al,Na}}^{\text{Ca}}$, $\text{O}_{\text{Al,K}}^{\text{Ca}}$ and $\text{O}_{\text{Al,Ca}}^{\text{Fe}}$, exist in $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{CaO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems, respectively, while oxygen ions $\text{O}_{\text{Al,Ca}}^{\text{Na}}$, $\text{O}_{\text{Al,Ca}}^{\text{K}}$ and $\text{O}_{\text{Al,Ca}}^{\text{Fe}}$ are absent. So, coresponding $\alpha_{\text{Al,Na}}^{\text{Ca}}$, $\alpha_{\text{Al,K}}^{\text{Ca}}$ and $\alpha_{\text{Al,Ca}}^{\text{Fe}}$ parameters will be optimized in $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{CaO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems, respectively.

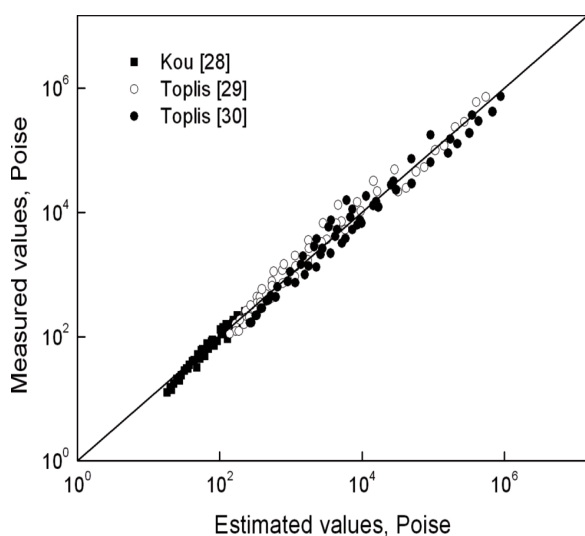


Figure 3. Comparisons between estimated and measured viscosity values for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.

Viscosity data of $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ are from Higgins *et al.* [32] and Kolesov *et al.* [33], while these for $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{CaO}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems are from Sukenaga *et al.* [12]. The comparisons of calculated values with those by experiments are shown in Figures 5-7, with the mean deviations 28.1%, 24.7% and 23.0%, respectively.

5.3. $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3$ ternary system

The viscosity of $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3$ system are from Vidacac *et al.* [34]. When calculating viscosity of this system, no parameter needs to be optimized.

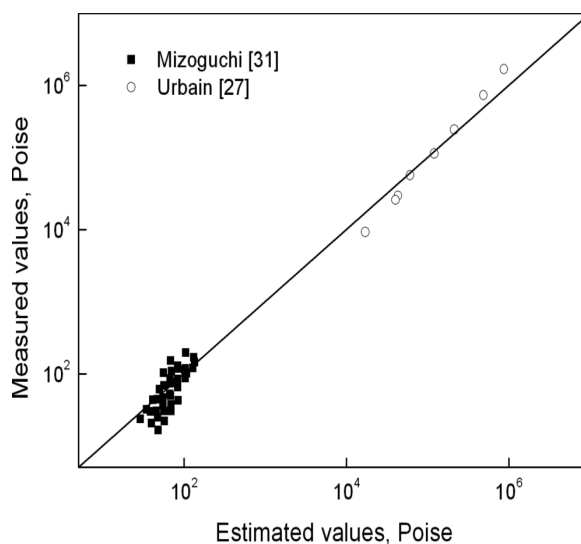


Figure 4. Comparisons between estimated and measured viscosity values for $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.

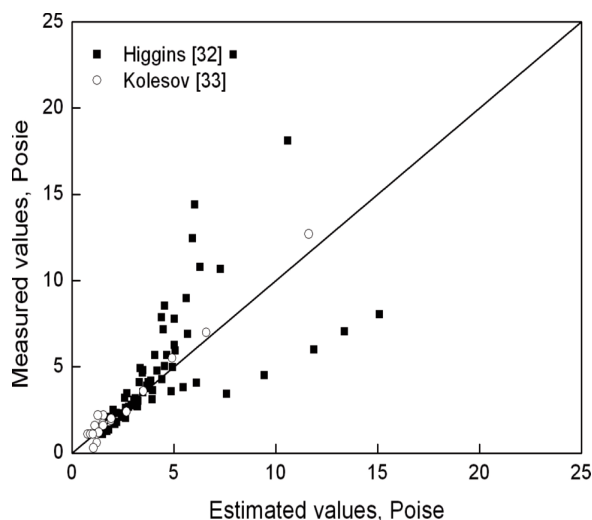


Figure 5. Comparisons between estimated and measured viscosity values for $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.

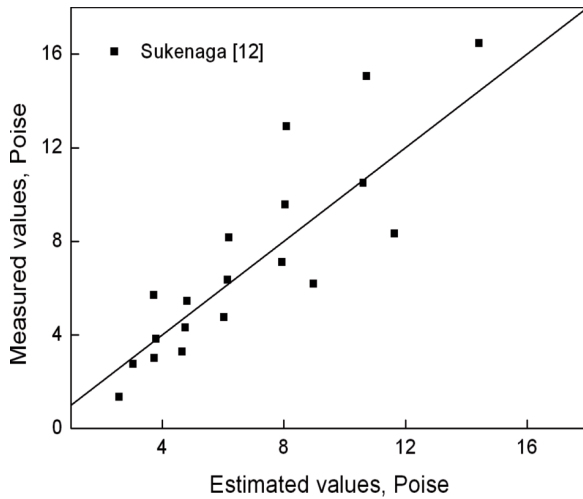


Figure 6. Comparisons between estimated and measured viscosity values for $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system

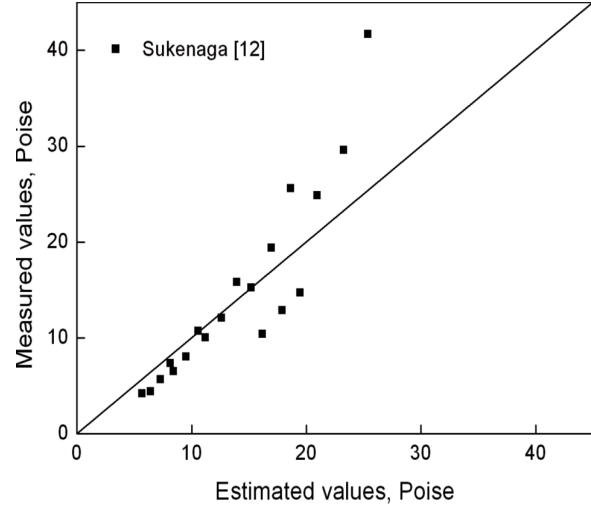


Figure 7. Comparisons between estimated and measured viscosity values for $\text{CaO-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system.

Extrapolating the viscosity calculation of $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$ system to the limiting case of content of SiO_2 equal to 0, with parameters optimized in other systems, the viscosity for this system can be obtained. The comparisons of calculated values with measured values are shown in Figure 8, with the mean deviation 24.4%. In the following section, it can be seen that the existing viscosity models can not well represent the viscosity variation behavior of this system which is absence of SiO_2 .

5.4. Complex systems

$\text{CaO-MgO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system

The parameter $\alpha_{\text{Al,Na}}^{\text{Mg}}$ is optimized in $\text{CaO-MgO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system for the lack of viscosity data

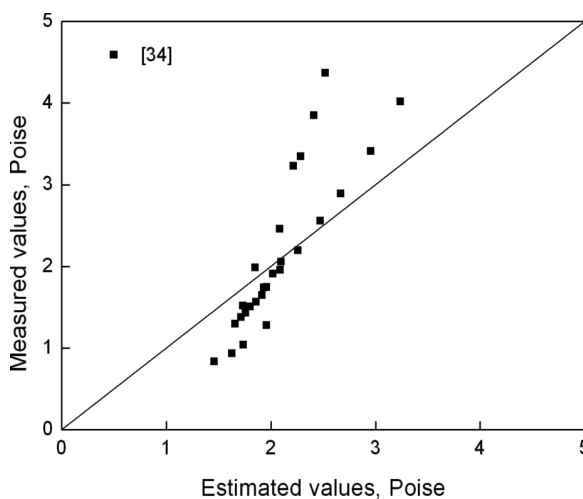


Figure 8. Comparisons between estimated and measured viscosity values for $\text{CaO-FeO-Al}_2\text{O}_3$ system.

in $\text{MgO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system. In this system, there are three types of cations: Na^+ , Ca^{2+} and Mg^{2+} ions, could compensate Al^{3+} ion, and the priority order is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, thereby, oxygen ions $\text{O}_{\text{Al,Na}}^{\text{Mg}}$, $\text{O}_{\text{Al,Na}}^{\text{Ca}}$ and $\text{O}_{\text{Al,Ca}}^{\text{Mg}}$ exist. Considering the corresponding parameters $\alpha_{\text{Al,Na}}^{\text{Ca}}$ and $\alpha_{\text{Al,Ca}}^{\text{Mg}}$ have been optimized in $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ systems, only parameters $\alpha_{\text{Al,Na}}^{\text{Mg}}$ is optimized in this system.

Parts of the composition points of Sykes *et al.* [35] fulfill the condition: $x_{\text{Na}_2\text{O}} > x_{\text{Al}_2\text{O}_3}$ and, $x_{\text{CaO}} + x_{\text{MgO}} + x_{\text{Na}_2\text{O}} - x_{\text{Al}_2\text{O}_3} < 2(x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2})$ in which case all the Al^{3+} ions are compensated Na^+ ions; the remaining Na^+ , Ca^{2+} and Mg^{2+} ions participate in forming non-bridging oxygen, but are not enough to break all the bridging oxygen. According to the five assumptions, numbers of different types of oxygen ions can be calculated as follows:

Non-bridging oxygen bonded to Al^{3+} ion:

$$n_{\text{O}_{\text{Al,Na}}^{\text{Na}}} = 2(x_{\text{Na}_2\text{O}} - x_{\text{Al}_2\text{O}_3}) \frac{2x_{\text{Al}_2\text{O}_3}}{2x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2}} \quad (6)$$

$$n_{\text{O}_{\text{Al,Na}}^{\text{Ca}}} = 2x_{\text{CaO}} \frac{2x_{\text{Al}_2\text{O}_3}}{2x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2}} \quad (7)$$

$$n_{\text{O}_{\text{Al,Na}}^{\text{Mg}}} = 2x_{\text{MgO}} \frac{2x_{\text{Al}_2\text{O}_3}}{2x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2}} \quad (8)$$

Non-bridging oxygen bonded to Si^{4+} ion:

$$n_{\text{O}_{\text{Si}}^{\text{Na}}} = 2(x_{\text{Na}_2\text{O}} - x_{\text{Al}_2\text{O}_3}) \frac{x_{\text{SiO}_2}}{2x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2}} \quad (9)$$

$$n_{\text{O}_{\text{Si}}^{\text{Ca}}} = 2x_{\text{CaO}} \frac{x_{\text{SiO}_2}}{2x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2}} \quad (10)$$

$$n_{\text{O}_{\text{Si}}^{\text{Mg}}} = 2x_{\text{MgO}} \frac{x_{\text{SiO}_2}}{2x_{\text{Al}_2\text{O}_3} + x_{\text{SiO}_2}} \quad (11)$$

Bridging oxygen:

$$n_{O_{Al,Na}} = 4x_{Al_2O_3} - \frac{n_{O_{Al,Na}}}{2} - \frac{n_{O_{Ca,Na}}}{2} - \frac{n_{O_{Mg,Na}}}{2} \quad (12)$$

$$n_{O_{Si}} = 2x_{SiO_2} - \frac{n_{O_{Si}}}{2} - \frac{n_{O_{Ca}}}{2} - \frac{n_{O_{Mg}}}{2} \quad (13)$$

The other parts of composition points measured by Sykes *et al.* [35] and those measured by Kim *et al.* [36] fulfill the conditions: $x_{Na_2O} < x_{Al_2O_3}$, $x_{Na_2O} + x_{CaO} > x_{Al_2O_3}$ and $x_{CaO} + x_{MgO} + x_{Na_2O} - x_{Al_2O_3} < 2(x_{Al_2O_3} + x_{SiO_2})$. In this case, all the Na^+ ions compensate Al^{3+} ion; while Al^{3+} ions not compensated by Na^+ ions are completed by Ca^{2+} ions; the remaining Ca^{2+} ions and Mg^{2+} ions participate in forming the non-bridging oxygen, but are not enough to break all the bridging oxygen. The numbers of different types of oxygen ions can be calculated as follows:

Non-bridging oxygen bonded to Ca^{2+} ion:

$$n_{O_{Al,Na}^{Ca}} = 2(x_{CaO} + x_{Na_2O} - x_{Al_2O_3}) \frac{2x_{Na_2O}}{2x_{Al_2O_3} + x_{SiO_2}} \quad (14)$$

$$n_{O_{Al,Ca}^{Ca}} = 2(x_{CaO} + x_{Na_2O} - x_{Al_2O_3}) \frac{2(x_{Al_2O_3} - x_{Na_2O})}{2x_{Al_2O_3} + x_{SiO_2}} \quad (15)$$

$$n_{O_{Si}^{Ca}} = 2(x_{CaO} + x_{Na_2O} - x_{Al_2O_3}) \frac{x_{SiO_2}}{2x_{Al_2O_3} + x_{SiO_2}} \quad (16)$$

Non-bridging oxygen bonded to Mg^{2+} ion:

$$n_{O_{Al,Na}^{Mg}} = 2x_{MgO} \frac{2x_{Na_2O}}{2x_{Al_2O_3} + x_{SiO_2}} \quad (17)$$

$$n_{O_{Al,Ca}^{Mg}} = 2x_{MgO} \frac{2(x_{Al_2O_3} - x_{Na_2O})}{2x_{Al_2O_3} + x_{SiO_2}} \quad (18)$$

$$n_{O_{Si}^{Mg}} = 2x_{MgO} \frac{x_{SiO_2}}{2x_{Al_2O_3} + x_{SiO_2}} \quad (19)$$

Bridging oxygen:

$$n_{O_{Al,Na}} = 4x_{Na_2O} - \frac{n_{O_{Al,Na}^{Ca}}}{2} - \frac{n_{O_{Al,Na}^{Mg}}}{2} \quad (20)$$

$$n_{O_{Al,Ca}} = 4(x_{Al_2O_3} - x_{Na_2O}) - \frac{n_{O_{Al,Ca}^{Ca}}}{2} - \frac{n_{O_{Al,Ca}^{Mg}}}{2} \quad (21)$$

$$n_{O_{Si}} = 2x_{SiO_2} - \frac{n_{O_{Si}^{Ca}}}{2} - \frac{n_{O_{Si}^{Mg}}}{2} \quad (22)$$

According to the above equations, parameter $\alpha_{Al,Na}^{Mg}$ can be optimized which are shown in Table 3. The comparisons of calculated viscosities with those measured by experiments are shown in Figure 9, with the mean deviation 25.7%.

CaO-MgO-FeO- Al_2O_3 - SiO_2 system

The viscosity data of this system are taken from

Table 3. Value of model parameter $\alpha_{Al,i}^j$

Parameters	$\alpha_{Al,Ca}^{Mg}$	$\alpha_{Al,Ca}^{Fe}$	$\alpha_{Al,Na}^{Ca}$	$\alpha_{Al,K}^{Ca}$	$\alpha_{Al,Na}^{Mg}$
	8.334	8.694	9.787	7.593	8.015

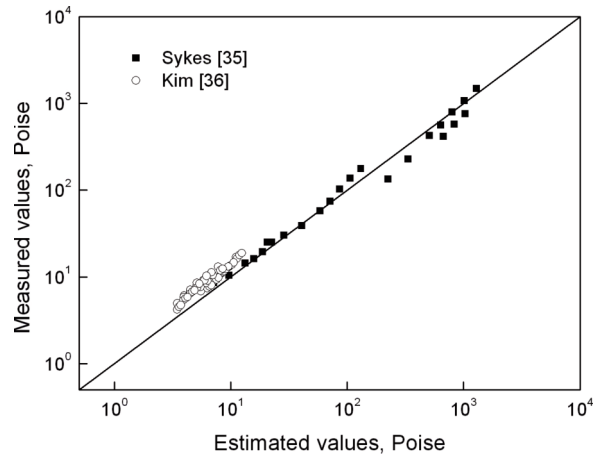


Figure 9. Comparisons between estimated and measured viscosity values for $CaO-MgO-Na_2O-Al_2O_3-SiO_2$ system

the work of Higgins *et al.* [32] and Kim *et al.* [37]. All the composition points fulfill the condition: $x_{CaO} > x_{Al_2O_3}$ and $x_{CaO} + x_{MgO} + x_{FeO} - x_{Al_2O_3} < 2(x_{Al_2O_3} + x_{SiO_2})$. In this case, all the Al^{3+} ions are compensated by Ca^{2+} ions; the remaining Ca^{2+} , Mg^{2+} and Fe^{2+} ions participate in forming non-bridging oxygen, but can not break all the bridging oxygen. The numbers of different types of oxygen ions can be calculated following equations (6-13). Calculate viscosity of this system with the optimized parameter in other systems, comparisons between the estimated values and those by experiments are shown in Figure 10, with the mean deviation 13.5%. Thereby, to some extent, the present model has strong extrapolation ability.

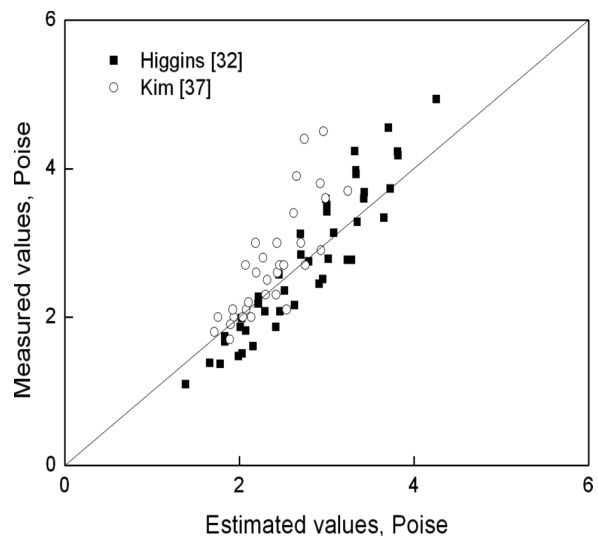


Figure 10. Comparisons between estimated and measured viscosity values for $CaO-MgO-FeO-Al_2O_3-SiO_2$ system.

6. Discussion

(1) According to the results of our previous paper [21], the model can be extrapolated to Al_2O_3 , $\text{CaO-Al}_2\text{O}_3$ systems without optimizing new parameters. In this work, the model can also well describe the composition and temperature dependences of viscosity for $\text{CaO-FeO-Al}_2\text{O}_3$ system. Therefore, the present model can be applied to system without SiO_2 .

(2) From the values of parameters shown in Table 2, it can be seen that the following orders exist:

$$\alpha_{\text{Si}}^{\text{Mg}} < \alpha_{\text{Si}}^{\text{Ca}} < \alpha_{\text{Si}}^{\text{Na}} < \alpha_{\text{Si}}^{\text{K}}, \alpha_{\text{Al,Mg}}^{\text{Mg}} < \alpha_{\text{Al,Ca}}^{\text{Ca}} < \alpha_{\text{Al,Na}}^{\text{Na}} < \alpha_{\text{Al,K}}^{\text{K}},$$

$\alpha_{\text{Al,Mg}}^{\text{Mg}} > \alpha_{\text{Al,Ca}}^{\text{Ca}} > \alpha_{\text{Al,Na}}^{\text{Na}} > \alpha_{\text{Al,K}}^{\text{K}}$. Therefore, the deforming ability of bonds around the non-bridging oxygen bonded with different cations increase following the order: $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Na}^+ < \text{K}^+$. While, the order is opposed for the bridging oxygen bonded with Al^{3+} ions compensated by different cations: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$. It is known that the basicity order for these four oxides is $\text{K}_2\text{O} > \text{Na}_2\text{O} > \text{CaO} > \text{MgO}$. Therefore, basic oxide with a higher basicity leads to the forming of a weaker non-bridging oxygen bond, which decreases viscosity; while forming a stronger bridging oxygen bond in a more stability AlO_4^{5-} tetrahedron structure by charge compensating Al^{3+} ion, which increases viscosity. So basic oxide plays a paradox role in influencing viscosity when Al_2O_3 exists.

(3) It is found by Sukenaga *et al.* [12] that the addition of K_2O to $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slag increases viscosity. However, all the theoretical models can not interpret this abnormal phenomenon, and only give a decreasing tendency. Nakamoto *et al.* [4] claimed that their model was a progressive for this problem relative to other models. However, it can only decrease the decreasing tendency, but still can not give an increasing tendency. Figure 11 shows the variations of viscosity for $\text{CaO-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$

quaternary system with content of K_2O , in which the theoretical lines estimated by Nakamoto *et al.* model and the present model are also given. It can be seen that the present model can well describe this phenomenon.

According to the description of aluminosilicate melt structure in our model, the reason for the increase of viscosity may be that when adding K_2O to $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, K^+ ion will substitute the position of Ca^{2+} ion to compensate Al^{3+} ion for its higher priority relative to Ca^{2+} ion. The displaced Ca^{2+} ions will form more non-bridging oxygen ions, and this factor decreases viscosity. But as the contents of basic oxides ($x_{\text{K}_2\text{O}} + x_{\text{CaO}}$) are not very high, and there are still enough bridging oxygen ions (including those bonded with Al^{3+} ion and Si^{4+} ion). In the case that content of K_2O is smaller than that of Al_2O_3 (the case of Sukenaga *et al.* [12]), all the added K^+ ion will substitute the position of Ca^{2+} to compensate Al^{3+} ion. Therefore, parts of the bridging oxygen bonded with Al^{3+} ion will transform from $\text{O}_{\text{Al,Ca}}$ to $\text{O}_{\text{Al,K}}$. According to parameters values shown in Table 2 ($\alpha_{\text{Al,K}}^{\text{K}} = 4.156 < \alpha_{\text{Al,Ca}}^{\text{Ca}} = 4.996$), the bond around $\text{O}_{\text{Al,K}}$ is stronger than that around $\text{O}_{\text{Al,Ca}}$, thus substitution of K^+ ion for Ca^{2+} ion leads to the forming of more stability bridging oxygen bond, and this factor increases viscosity. When the increasing tendency (resulting from the change of bridging oxygen type) exceeds the decreasing tendency (resulting from the increase of the non-bridging oxygen number), viscosity increases, which may be the cause of experiment finding by Sukenaga *et al.* [12].

It is conceivable that when the content of Al_2O_3 is very small relative to the content of K_2O addition, the decreasing tendency of viscosity will be dominated, since in this case most of the added K^+ ions do not form bridging oxygen $\text{O}_{\text{Al,K}}$ but non-bridging oxygen ($\text{O}_{\text{Al,K}}^{\text{K}}$ and $\text{O}_{\text{Si}}^{\text{K}}$), thereby, viscosity may decrease. In the limiting case of content of Al_2O_3 equal to 0, the addition of K_2O to CaO-SiO_2 melts will obviously decrease viscosity for the decrease of absolute content of SiO_2 and forming of more non-bridging oxygen. In another cases that the contents of basic oxides ($x_{\text{K}_2\text{O}} + x_{\text{CaO}}$) is very high to break all the bridging oxygen or only few bridging oxygen ions remaining, the viscosity may also decrease with the addition of K_2O , because it is the forming of bridging oxygen $\text{O}_{\text{Al,K}}$ increasing viscosity, while its number is very limited in this case.

(4) In order to see clearly the accuracy of the present model relative to other models, the mean deviations of our model and models of Riboud *et al.* [1], NPL [2], Nakamoto *et al.* [4], Ray *et al.* [5], Urbain [6], Kondratiev *et al.* [7] and Iida *et al.* [10] are given in Table 4, from which it can be seen that our model has strong ability for viscosity estimation, especially for complex aluminosilicate systems and systems absence of SiO_2 .

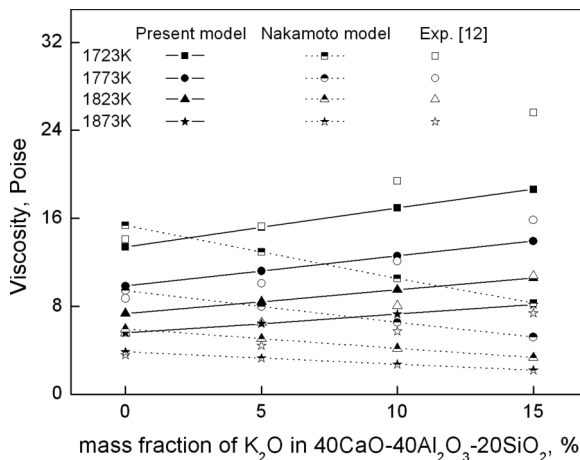


Figure 11. Variation of viscosity with the content of K_2O in $\text{CaO-K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system

Table 4. Mean deviations for different viscosity models (%)

Systems	Riboud	Urbain	Kondratiev	Iida	NPL	Ray	Nakamoto	Present model
FeO-Al ₂ O ₃ -SiO ₂	622		63	324	39.1	86.4	34.7	29.8
MnO-Al ₂ O ₃ -SiO ₂	441	45		x	93.6	66.2		28.8
Na ₂ O-Al ₂ O ₃ -SiO ₂	72.6			x	91.8	87.2	x	27.9
K ₂ O-Al ₂ O ₃ -SiO ₂	75.8			95.4	96.3	95.5	x	31.8
CaO-FeO-Al ₂ O ₃	200			x	37.4	50.6	73.3	24.4
CaO-FeO-Al ₂ O ₃ -SiO ₂	395		25.9	95.1	58.1	75.3	36.7	28.1
CaO-Na ₂ O-Al ₂ O ₃ -SiO ₂	32.4			48.2	76.1	53.6	35.2	24.7
CaO-K ₂ O-Al ₂ O ₃ -SiO ₂	42			66	87.1	73.5	44	23
CaO-MgO-FeO-Al ₂ O ₃ -SiO ₂	103			57.5	46.9	63.4	24.7	13.5
CaO-MgO-Na ₂ O-Al ₂ O ₃ -SiO ₂	89.3			160	95.4	179	152	25.7

* the blank indicates the system can not be calculated for the absence of parameters; 'x' represents the mean deviation is higher than 1000%.

7. Conclusions

A structurally based viscosity model is proposed for aluminosilicate melt containing MgO, CaO, FeO, MnO, Na₂O and K₂O, in which a simple method of calculating the numbers of different types of oxygen ions is proposed, to describe influence of structure on viscosity. When several basic oxides exist, the priority order for different cations when compensating Al³⁺ ions is suggested: K⁺>Na⁺>Ca²⁺>Mn²⁺>Fe²⁺>Mg²⁺, according to the coulombic force between the cation and oxygen anion. The values of the optimized parameters indicate that existence of Al₂O₃ can lead to two inverse influences of basic oxides on viscosity. The basic oxide with a higher basicity can decrease viscosity by forming weaker non-bridging oxygen bond; while it can also increase viscosity by forming stronger bridging oxygen bond by charge compensating Al³⁺ ion. The present viscosity model can extrapolate its application range to the system without SiO₂, and give well results for complex aluminosilicate system. Furthermore, a satisfy interpretation can be given by the present model to the abnormal phenomenon of viscosity increasing when adding K₂O to CaO-Al₂O₃-SiO₂ melt.

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References

- [1] P.V. Riboud, Y. Roux, L.D. Lucas and H. Gaye, Facber. Hüttenprax. Metallweiter Verarb., 19 (1981) 859.
- [2] K.C. Mills and S. Sridhar, Ironmaking & Steelmaking, 26 (1999) 262.
- [3] S.C. Du, J. Bygden and S. Seetharaman, Metall. Mater. Trans. B, 25B (1994) 519.
- [4] M. Nakamoto, Y. Miyabayashi, L. Holappa and T. Tanaka, ISIJ Int., 47, (2007), 1409.
- [5] H.S. Ray and S. Pal, Ironmaking & Steelmaking, 31 (2004) 125.
- [6] G. Urbain, Steel Res. Int., 58 (1987) 111.
- [7] A. Kondratiev and E. Jak, Fuel, 80 (2001) 1989.
- [8] L. Zhang and S. Jahanshahi, Metall. Mater. Trans. B, 29B (1998) 177.
- [9] Q.F. Shu, Steel Res. Int., 80 (2009) 107.
- [10] T. Iida, H. Sakai, Y. Ikita and K. Shigeno, ISIJ Int., 40 (2000) 110.
- [11] D. Ghosh, V.A. Krishnamurthy and S.R. Sankaranarayanan, J. Min. Metall. B, 46 B (2010) 41.
- [12] S. Sukenaga, N. Saito, K. Kawakami and K. Nakashima, ISIJ Int., 46 (2006) 352.
- [13] H.D. Weymann, Colloid Polym. Sci., 181 (1962) 131.
- [14] S. Arrhenius, Z. Phys. Chem., 1 (1887) 285.
- [15] S. Glasstone, K.J. Laidler and H. Eyring, The theory of rate processes, McGraw-Hill, New York, 1941.
- [16] A. Shankar, M. Gernerup, A.K. Lahiri and S. Seetharaman, Ironmaking & Steelmaking, 34 (2007) 477.
- [17] G.H. Zhang, K.C. Chou, Q.G. Xue and K.C. Mills, Metall. Mater. Trans. B, 43B (2012) 64.
- [18] J.D. Mackenzie, Chem. Rev., 56 (1956) 455.
- [19] B.O. Mysen, Structure and properties of silicate melts, Elsevier Science Publishers B.V., Amsterdam, 1988.
- [20] G.H. Zhang and K.C. Chou, J. Min. Metall. B, 48B (2012) 1.
- [21] G.H. Zhang, K.C. Chou and K.C. Mills, ISIJ Int., 52 (2012) 355.
- [22] R.D. Shannon, Acta Crystallogr., A32 (1976) 751.
- [23] A. Navrotsky, G. Peraudeau, P. Mcmillan and J.P. Coutures, Geochim. Cosmochim. Acta, 46 (1982) 2039.

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- [24] F. Domine and B. Piriou, *Am. Mineral.*, 71 (1986) 38.
- [25] B.O. Mysen and D. Virgo, *Geochim. Cosmochim. Acta*, 44 (1980) 1917.
- [26] F. Johansen and H. Brunion, *Z. Erz. Metall.*, 12 (1959) 211.
- [27] G. Urbain, Y. Bottinga and P. Richet, *Geochim. Cosmochim. Acta*, 46 (1982) 1061.
- [28] T. Kou, K. Mizoguchi and Y. Suginoara, *J. Jpn. Inst. Met.*, 42 (1978) 775.
- [29] M.J. Toplis, D.B. Dingwell, K.U. Hess and T. Lenci, *Am. Mineral.*, 82 (1997) 979.
- [30] M.J. Toplis, D.B. Dingwell and T. Lenci, *Geochim. Cosmochim. Acta*, 61 (1997) 2605.
- [31] K. Mizoguchi, K. Okamoto and Y. Suginoara, *J. Jpn. Inst. Met.*, 46 (1982) 1055.
- [32] R. Higgins and T.J.B. Jones, *Bull. Inst. Min. Metall.*, 682 (1963) 825.
- [33] V.D. Eisenhüttenleute, *Slag atlas*, Verlag Sthaleisen GmbH, Dusseldorf, 1995.
- [34] B. Vidacak, S.C. Du and S. Seetharaman, *Metall. Mater. Trans. B*, 32B (2001) 679.
- [35] D. Sykes, J. Dickinson, E. James, R.W. Luth and C.M. Scarfe, *Geochim. Cosmochim. Acta*, 57 (1993) 1291.
- [36] H. Kim, W.H. Kim, J.H. Park and D.J. Min, *Steel Res. Int.*, 81 (2010) 17.
- [37] J.R. Kim, Y.S. Lee, D.J. Min, S.M. Jung and S.H. Yi, *ISIJ Int.*, 44 (2004) 1291.