# Modeling the viscosities of alumino-silicate melts

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**Abstract:** The structurally based viscosity model for aluminosilicate melts has developed, in which the influence of melt structure on viscosity has expressed by the definitions of different types of oxygen ions: (i) bridging oxygen $\mathrm{O_{Si}}$, bonded to $\mathrm{Si^{4+}}$ ions (ii) non-bridging oxygen $\mathrm{O_{Si}^{\mathit{i}}}$, bonded to $\mathrm{Si^{4+}}$ ion and cation *i* from basic oxide, (iii) free oxygen $\mathrm{O}_i$, bonded to *i* ions, (iv) bridging oxygen $\mathrm{O}_{\mathrm{Al},\,i}$, bonded to an $\mathrm{Al^{3+}}$ ion charge compensated by cation *i*; (v) non-bridging oxygen $\mathrm{O}_{\mathrm{Al},\,i}^{j}$, bonded to the metal cation *j* and $\mathrm{Al^{3+}}$ ion charge compensated by cation *i*; (vi) oxygen $\mathrm{O_{Al}}$, bonded to an $\mathrm{Al^{3+}}$ ion which is not charge compensated. A systematic method is proposed to calculate numbers of these oxygen ions. According to the calculation results of the viscosity model, it has been found that the abilities of basic oxides decreasing viscosity follow the order: FeO>MnO>CaO>MgO, when $\mathrm{Al_2O_3}$ is absence. The viscosities of quinary, quarternary, ternary, binary and unary systems involving MgO, CaO, FeO, MnO, $\mathrm{Al_2O_3}$ and $\mathrm{SiO_2}$ components have been calculated by the present model with all the mean deviations not great than 30%. Furthermore, it indicates the better precision of the present model than that of other models for the same systems.

**Keywords:** Viscosity, model, alumino-silicate melt, structure base

## 1. Introduction

Viscosity is an important physical property for alumino-silicate melts because of their dramatic effect on pyrometallurgical processes and sensitivity to the slag structure. For instance, reliable viscosities are required (i) to guarantee smooth operation of the blast furnace (ii) for the successful separation of metal and slag during the basic oxygen steelmaking process (iii) for foaming processing and (iv) in the continuous casting process where the slag acts as a lubricant, etc.. From the viewpoint of reaction kinetics, most pyrometallurgical reactions are controlled by viscosity determined diffusion process in molten slags. Therefore, accurate viscosity values are essential for the optimization and improvement of metallurgical processes. However, obtaining data only by experimental measurements are both time-consuming and sometimes inaccurate because of the difficulties associated with high temperature operations. Consequently, the method of model estimation becomes very important.

Many viscosity models are proposed to estimate viscosity of aluminosilicate melts[1-10]. 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[4]. (iii) These models can not be extended to the viscosity estimation of oxide systems without $SiO_2$. Therefore, much work still should be done on the viscosity model.

## 2. Requirements to viscosity model

At constant pressure, viscosity is determined by temperature and chemical composition of molten slags. Modelling viscosity is finding a reasonable expression to describe the relationship between viscosity and temperature as well as composition. Generally, viscosity model must fulfill the following four requirements:

(i) Viscosity is sensitive to the structure of aluminosilicate melts, and different components (acidic oxide, e.g. $SiO_2$; basic oxide, e.g. CaO and MgO; amphoteric oxide, e.g. $Al_2O_3$) 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[1], Urbain[6], Kondratiev[7], NPL[2], Ray[5], etc., didn’t consider the influence of melt structure on the viscosity.

(ii) Generally, the temperature dependence of viscosity can be described by the Arrhenius equation[11] $\eta = A\exp(\frac{E}{RT})$ or Weymann equation[12] $\eta = AT\exp(\frac{E}{RT})$, in which 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[13]. Therefore, the compensation effect should also be taken into consideration in the viscosity model, while it is not considered in viscosity models of Riboud[1], NPL[2], KTH[3], Nakamoto[4], Iida[10], etc..

(iii) It has been pointed out that the activation energy of viscosity is a non-linear function of composition for binary silicate melts and shows an abrupt increase near pure silica[14]. Consequently, viscosity model should reflect the nonlinear variation behavior of activation energy with composition. Among the different viscosity models, the polynomial functions with the highest order of “$n$” were utilized by different authors to describe the relation between activation energy and composition: $n$=1 in model of Riboud [1]; $n$=2 in model of Shu [9]; $n$=3 in models of Urbain[6], Kondratiev[7] and Zhang[8].

(iv) $Al_2O_3$ is an amphoteric oxide, which exhibits as a basic oxide under the condition of low basicity, and as an acidic oxide under the condition of high basicity. Furthermore, $Al^{3+}$ can form $AlO_4^{5-}$ tetrahedron, and replace the position of Si when the basicity is higher in a proper range. As the covalence of aluminum ion is +3, which is less than that of silicon ion when it is in the position of Si, therefore an extra cation is needed to compensate the charge balance. The cation of basic oxide can act as the charge-compensator, e.g. $Ca^{2+}$ and $Na^+$, etc.. However, it is found that different cations have different abilities of compensating $Al^{3+}$ ions[15], so viscosity model should consider the different orders of different cations when compensating $Al^{3+}$ ions. However, no model can distinguish this ability of charge compensation except NPL model[2] which achieves this goal according to the different optical basicity values of different basic oxides. However, this way has defect for the reason that in NPL model many basic oxides has the same optical basicity values but the compensating abilities of the metal cations are different actually, e.g. optical basicity of $Li_2O$, CaO, FeO and MnO using the same value of 1.

## 3. Description of structure of aluminosilicate melts

Before modelling the viscosity, influences of different components on structure of aluminosilicate melts should be expressed quantitatively by a relatively simple method. In our previous papers[13, 16], the structure of melts was described in the sight of the different types of oxygen ions. Firstly, the possible existence of oxygen ions should be defined. In silica melts without $Al_2O_3$, three types of oxygen ions exist, namely, (i) bridging oxygen $\mathrm{O}_{\mathrm{Si}}$, bonded with $Si^{4+}$ ion (ii) non-bridging oxygen $\mathrm{O}_{\mathrm{Si}}^{i}$, bonded with $Si^{4+}$ ion and metal cation, *i*, and (iii) free oxygen $\mathrm{O}_{i}$, bonded with metal cation *i*. In aluminosilicate melts, except for the referred three types, other three types of oxygen ions appear, namely, (iv) bridging oxygen $\mathrm{O}_{\mathrm{Al},\,i}$, bonded with an $Al^{3+}$ ion charge compensated by cation *i*; (v) non-bridging oxygen $\mathrm{O}_{\mathrm{Al},\,i}^{j}$, bonded with metal cation *j* and $Al^{3+}$ ion compensated by cation *i*; (vi) oxygen $\mathrm{O}_{\mathrm{Al}}$, bonded to an $Al^{3+}$ ion which is not charge compensated. It should be pointed out that free oxygen bonded with metal cations *i* and *j*, and bridging oxygen bonded with $Si^{4+}$ ion and compensated $Al^{3+}$ ion, are not taken into consideration in the above classifications.

Several thermodynamic models have been proposed to calculate the numbers of different types of oxygen ions, such as thermodynamic models by Toop and Samis[17], Ottonello[18], Yokokawa and Niwa[19], Masson[20], Lin and Pelton[21], etc., while those models can only be applied to MO-$SiO_2$ binary system, and the extrapolations to the high order systems or systems containing $Al_2O_3$ are very hard (or impossible). Gaye[22] developed a cell thermodynamic model which could be used to $SiO_2$-$Al_2O_3$-$Fe_2O_3$-CaO-FeO-MgO-MnO system. Although the cell model provides better results, it can not be applied to the systems containing alkali oxides. The Susa method[23] can only calculate the numbers of three types of oxygen ions: non-bridging oxygen $\mathrm{O}_{\mathrm{Si}}^{i}$, bridging oxygen $\mathrm{O}_{\mathrm{Si}}$, bridging oxygen $\mathrm{O}_{\mathrm{Al},\,i}$. In view of these facts, a new method will be given based on the following five assumptions.

**Assumption I:** When adding basic oxide $M_xO$ to a pure silica, the free oxygen $\mathrm{O}_{i}$ from $M_xO$ reacts with the bridging oxygen $\mathrm{O}_{\mathrm{Si}}$ from $SiO_2$ to produce a non-bridging oxygen $\mathrm{O}_{\mathrm{Si}}^{i}$. It is assumed that the equilibrium constant of this reaction is infinite.

$2x_{\mathrm{SiO_2}} \ge x_{\mathrm{M}_x\mathrm{O}}$:

$$n_{\mathrm{O}_i} = 0;\quad n_{\mathrm{O}_{\mathrm{Si}}^{i}} = 2x_{\mathrm{M}_x\mathrm{O}};\quad n_{\mathrm{O}_{\mathrm{Si}}} = 2x_{\mathrm{SiO_2}} - x_{\mathrm{M}_x\mathrm{O}} \tag{1}$$

$2x_{\mathrm{SiO_2}} < x_{\mathrm{M}_x\mathrm{O}}$:

$$n_{O_i} = x_{M_xO} - 2x_{SiO_2}\;;\; n_{O_{Si}^i} = 4x_{SiO_2}\;;\; n_{O_{Si}} = 0 \tag{2}$$

**Assumption II:** For a system containing several basic oxides $\sum (M_xO)_i\text{-}SiO_2$, the numbers of different types of oxygen ions can be calculated by the random mixing rule: first, calculate $n_{O_{Si}}$, $n_{O_{Si}^i}$ and $n_{O_i}$ using Eqs. (1-2) and by assuming the system is a pseudo-binary system. Then each term is multiplied by the re-normalized mole fractions of basic oxides (Eqs. 3 and 4) to calculate the different types of oxygen ions.

$$n_{O_{Si}^i} = \sum n_{O_{Si}^i} \cdot (x_{(M_xO)_i} / \sum_i x_{(M_xO)_i}) \tag{3}$$

$$n_{O_i} = \sum n_{O_i} \cdot (x_{(M_xO)_i} / \sum_i x_{(M_xO)_i}) \tag{4}$$

**Assumption III:** In $M_xO$-$Al_2O_3$-$SiO_2$ system, the addition of basic oxide $M_xO$ can lead to more $Al^{3+}$ ion being incorporated into the $SiO_2$ network. It is assumed that the equilibrium constant for the reaction of $M^{z+}$ ion compensating $Al^{3+}$ ion is infinite. In the case of $x_{M_xO} / x_{Al_2O_3}$ <1, all $M_xO$ act as charge balancers, whereas in the case of $x_{M_xO} / x_{Al_2O_3}$ >1, all $Al^{3+}$ ions form the $AlO_4^{5-}$ tetrahedrons, the extra $M_xO$ act 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 $AlO_4^{5-}$ and $SiO_4^{4-}$ tetrahedron are equivalent, and the non-bridging oxygen ions formed (bonded to $Al^{3+}$ and $Si^{4+}$ ions) are proportional to the numbers of bridging oxygen in $AlO_4^{5-}$ and $SiO_4^{4-}$ tetrahedrons. The following cases may be present,

(I) $x_{M_xO} / x_{Al_2O_3}$ <1

In this case, the content of $M_xO$ is not enough to compensate all the $Al^{3+}$ ions. The numbers of oxygen ions can be calculated as follows:

$$n_{O_{Si}} = 2x_{SiO_2} \tag{5}$$

$$n_{O_{Al}} = 3(x_{Al_2O_3} - x_{M_xO}) \tag{6}$$

$$n_{O_{Al,\,i}} = 4x_{M_xO} \tag{7}$$

(II) $x_{M_xO} / x_{Al_2O_3}$ >1 and $(x_{M_xO} - x_{Al_2O_3}) < 2(x_{SiO_2} + 2x_{Al_2O_3})$

In this case, all the $Al^{3+}$ ions form $AlO_4^{5-}$ tetrahedra after the charge compensation by $M_xO$; extra $M_xO$ ($= x_{M_xO} - x_{Al_2O_3}$) can not break all the bridging oxygen bonded to $Al^{3+}$ and $Si^{4+}$ ions. The numbers of other types of oxygen ions are calculated as follows:

$$n_{\mathrm{O}_{\mathrm{Si}}^{i}} = 2(x_{\mathrm{M}_x\mathrm{O}} - x_{\mathrm{Al}_2\mathrm{O}_3}) \frac{x_{\mathrm{SiO}_2}}{x_{\mathrm{SiO}_2} + 2x_{\mathrm{Al}_2\mathrm{O}_3}} \tag{8}$$

$$n_{\mathrm{O}_{\mathrm{Al},\,i}^{i}} = 2(x_{\mathrm{M}_x\mathrm{O}} - x_{\mathrm{Al}_2\mathrm{O}_3}) \frac{2x_{\mathrm{Al}_2\mathrm{O}_3}}{x_{\mathrm{SiO}_2} + 2x_{\mathrm{Al}_2\mathrm{O}_3}} \tag{9}$$

$$n_{\mathrm{O}_{\mathrm{Si}}} = 2x_{\mathrm{SiO}_2} - \frac{n_{\mathrm{O}_{\mathrm{Si}}^{i}}}{2} \tag{10}$$

$$n_{\mathrm{O}_{\mathrm{Al},\,i}} = 4x_{\mathrm{Al}_2\mathrm{O}_3} - \frac{n_{\mathrm{O}_{\mathrm{Al},\,i}^{i}}}{2} \tag{11}$$

(III) $x_{\mathrm{M}_x\mathrm{O}} / x_{\mathrm{Al}_2\mathrm{O}_3} > 1$ and $(x_{\mathrm{M}_x\mathrm{O}} - x_{\mathrm{Al}_2\mathrm{O}_3}) > 2(x_{\mathrm{SiO}_2} + 2x_{\mathrm{Al}_2\mathrm{O}_3})$

In this case, all the $\mathrm{Al}^{3+}$ ions form $\mathrm{AlO}_4^{5-}$ tetrahedra; the basic oxide $\mathrm{M}_x\mathrm{O}$ content is sufficient to break all the bridging oxygen, and all the oxygen ions bonded to $\mathrm{Al}^{3+}$ and $\mathrm{Si}^{4+}$ ions are non-bridging oxygen.

$$n_{\mathrm{O}_{\mathrm{Si}}^{i}} = 4x_{\mathrm{SiO}_2} \tag{12}$$

$$n_{\mathrm{O}_{\mathrm{Al},\,i}^{i}} = 8x_{\mathrm{Al}_2\mathrm{O}_3} \tag{13}$$

$$n_{\mathrm{O}_i} = x_{\mathrm{M}_x\mathrm{O}} - 2x_{\mathrm{SiO}_2} - 5x_{\mathrm{Al}_2\mathrm{O}_3} \tag{14}$$

**Assumption V:** Different metal cations have different abilities of charge-compensating $\mathrm{Al}^{3+}$ ion. The priority order can be defined by Parameter *I* (expressed by the coulombic force between the cation and oxygen anion) is introduced to characterize the abilities of different cations,

$$I = \frac{2Q}{(r_{\mathrm{M}^{z+}} + r_{\mathrm{O}^{2-}})^2} \tag{15}$$

where *Q* is the covalence of $\mathrm{M}^{z+}$ ion; $r_{\mathrm{M}^{z+}}$ and $r_{\mathrm{O}^{2-}}$ are the radiuses of M and oxygen ions, respectively. When there is several basic oxides in aluminosilicate melt, for instance, as adding basic oxide $(\mathrm{M}_x\mathrm{O})_i$ to $(\mathrm{M}_x\mathrm{O})_j$-$\mathrm{Al}_2\mathrm{O}_3$-$\mathrm{SiO}_2$ melt, the cation *i* with the higher priority will substitute the position of *j*. It is assumed the equilibrium constant of substitution reaction of *i* ion for *j* ion is infinite. The following cases may be present,

(IV) $x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_j} < x_{\mathrm{Al}_2\mathrm{O}_3}$

This is similar to case (I), the calculation is carried out as follows：

$$n_{\mathrm{O}_{\mathrm{Si}}} = 2x_{\mathrm{SiO}_2} \tag{16}$$

$$n_{\mathrm{O_{Al}}} = 3(x_{\mathrm{Al_2O_3}} - x_{(\mathrm{M}_x\mathrm{O})_i} - x_{(\mathrm{M}_x\mathrm{O})_j}) \tag{17}$$

$$n_{\mathrm{O_{Al,}}_{\,i}} = 4x_{(\mathrm{M}_x\mathrm{O})_i} \tag{18}$$

$$n_{\mathrm{O_{Al,}}_{\,j}} = 4x_{(\mathrm{M}_x\mathrm{O})_j} \tag{19}$$

(V) $x_{(\mathrm{M}_x\mathrm{O})_i} < x_{\mathrm{Al_2O_3}}$ , $x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_j} > x_{\mathrm{Al_2O_3}}$ and $x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} < 2(x_{\mathrm{SiO_2}} + 2x_{\mathrm{Al_2O_3}})$

In this case, *i* ions first compensate the $\mathrm{Al}^{3+}$ ions; any $\mathrm{Al}^{3+}$ ions not charge-compensated by *i* ions will be charge-balanced by *j* ions. Any excess *j* ions will be used for network breaking but are insufficient to break all the bridging oxygen ions.

$$n_{\mathrm{O}^j_{\mathrm{Si}}} = 2(x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_j} - x_{\mathrm{Al_2O_3}}) \frac{x_{\mathrm{SiO_2}}}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{20}$$

$$n_{\mathrm{O}^j_{\mathrm{Al},\,i}} = 2(x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_j} - x_{\mathrm{Al_2O_3}}) \frac{2x_{(\mathrm{M}_x\mathrm{O})_i}}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{21}$$

$$n_{\mathrm{O}^j_{\mathrm{Al},\,j}} = 2(x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_j} - x_{\mathrm{Al_2O_3}}) \frac{2(x_{\mathrm{Al_2O_3}} - x_{(\mathrm{M}_x\mathrm{O})_i})}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{22}$$

$$n_{\mathrm{O_{Si}}} = 2x_{\mathrm{SiO_2}} - \frac{n_{\mathrm{O}^j_{\mathrm{Si}}}}{2} \tag{23}$$

$$n_{\mathrm{O}_{\mathrm{Al},\,i}} = 4x_{(\mathrm{M}_x\mathrm{O})_i} - \frac{n_{\mathrm{O}^j_{\mathrm{Al},\,i}}}{2} \tag{24}$$

$$n_{\mathrm{O}_{\mathrm{Al},\,j}} = 4(x_{\mathrm{Al_2O_3}} - x_{(\mathrm{M}_x\mathrm{O})_i}) - \frac{n_{\mathrm{O}^j_{\mathrm{Al},\,j}}}{2} \tag{25}$$

(VI) $x_{(\mathrm{M}_x\mathrm{O})_i} > x_{\mathrm{Al_2O_3}}$ and $x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} < 2(x_{\mathrm{SiO_2}} + 2x_{\mathrm{Al_2O_3}})$

In this case, all $\mathrm{Al}^{3+}$ ions are charge-compensated by *i* ions; *j* and any excess *i* tend to form non-bridging oxygen ions but are insufficient concentrations to break all the bridging oxygen ions.

$$n_{\mathrm{O}^i_{\mathrm{Si}}} = 2(x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}}) \frac{x_{\mathrm{SiO_2}}}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{26}$$

$$n_{\mathrm{O}^j_{\mathrm{Si}}} = 2x_{(\mathrm{M}_x\mathrm{O})_j}\frac{x_{\mathrm{SiO_2}}}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{27}$$

$$n_{\mathrm{O}^i_{\mathrm{Al},\,i}} = 2(x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}})\frac{2x_{\mathrm{Al_2O_3}}}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{28}$$

$$n_{\mathrm{O}^j_{\mathrm{Al},\,i}} = 2x_{(\mathrm{M}_x\mathrm{O})_j}\frac{2x_{\mathrm{Al_2O_3}}}{2x_{\mathrm{Al_2O_3}} + x_{\mathrm{SiO_2}}} \tag{29}$$

$$n_{\mathrm{O}_{\mathrm{Si}}} = 2x_{\mathrm{SiO_2}} - \frac{n_{\mathrm{O}^i_{\mathrm{Si}}}}{2} - \frac{n_{\mathrm{O}^j_{\mathrm{Si}}}}{2} \tag{30}$$

$$n_{\mathrm{O}_{\mathrm{Al},\,i}} = 4x_{\mathrm{Al_2O_3}} - \frac{n_{\mathrm{O}^i_{\mathrm{Al},\,i}}}{2} - \frac{n_{\mathrm{O}^j_{\mathrm{Al},\,i}}}{2} \tag{31}$$

(VII) $x_{(\mathrm{M}_x\mathrm{O})_i} > x_{\mathrm{Al_2O_3}}$ and $x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} > 2(x_{\mathrm{SiO_2}} + 2x_{\mathrm{Al_2O_3}})$

In this case, all the $\mathrm{Al}^{3+}$ ions are compensated by *i* ions; the *j* and any excess *i* can break all the bridging oxygen bonded to $\mathrm{Al}^{3+}$ and $\mathrm{Si}^{4+}$ ions to form the non-bridging oxygen ions.

$$n_{\mathrm{O}^i_{\mathrm{Al},\,i}} = 8x_{\mathrm{Al_2O_3}}\frac{x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}}}{x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} + x_{(\mathrm{M}_x\mathrm{O})_j}} \tag{32}$$

$$n_{\mathrm{O}^j_{\mathrm{Al},\,i}} = 8x_{\mathrm{Al_2O_3}}\frac{x_{(\mathrm{M}_x\mathrm{O})_j}}{x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} + x_{(\mathrm{M}_x\mathrm{O})_j}} \tag{33}$$

$$n_{\mathrm{O}^i_{\mathrm{Si}}} = 4x_{\mathrm{SiO_2}}\frac{x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}}}{x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} + x_{(\mathrm{M}_x\mathrm{O})_j}} \tag{34}$$

$$n_{\mathrm{O}^j_{\mathrm{Si}}} = 4x_{\mathrm{SiO_2}}\frac{x_{(\mathrm{M}_x\mathrm{O})_j}}{x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} + x_{(\mathrm{M}_x\mathrm{O})_j}} \tag{35}$$

$$n_{\mathrm{O}_i} = x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} - \frac{n_{\mathrm{O}^i_{\mathrm{Al},\,i}}}{2} - \frac{n_{\mathrm{O}^i_{\mathrm{Si}}}}{2} \tag{36}$$

$$n_{\mathrm{O}_j} = x_{(\mathrm{M}_x\mathrm{O})_j} - \frac{n_{\mathrm{O}^j_{\mathrm{Al},\,i}}}{2} - \frac{n_{\mathrm{O}^j_{\mathrm{Si}}}}{2} \tag{37}$$

(VIII) $x_{(\mathrm{M}_x\mathrm{O})_i} < x_{\mathrm{Al_2O_3}}$ and $x_{(\mathrm{M}_x\mathrm{O})_i} + x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} > 2(x_{\mathrm{SiO_2}} + 2x_{\mathrm{Al_2O_3}})$

In this case, *i* ions first charge-compensate $Al^{3+}$ ions. Any $Al^{3+}$ ions not compensated by *i* ions will be charge-balanced by *j* ions. Any excess *j* can be used to break all the bridging oxygen to form the non-bridging oxygen ions.

$$n_{\mathrm{O}^{j}_{\mathrm{Al},\,i}} = 8x_{(\mathrm{M}_x\mathrm{O})_i} \tag{38}$$

$$n_{\mathrm{O}^{j}_{\mathrm{Al},\,j}} = 8(x_{\mathrm{Al_2O_3}} - x_{(\mathrm{M}_x\mathrm{O})_i}) \tag{39}$$

$$n_{\mathrm{O}^{j}_{\mathrm{Si}}} = 4x_{\mathrm{SiO_2}} \tag{40}$$

$$n_{\mathrm{O}_j} = x_{(\mathrm{M}_x\mathrm{O})_j} + x_{(\mathrm{M}_x\mathrm{O})_i} - x_{\mathrm{Al_2O_3}} - \frac{n_{\mathrm{O}^{j}_{\mathrm{Al},\,i}}}{2} - \frac{n_{\mathrm{O}^{j}_{\mathrm{Al},\,j}}}{2} - \frac{n_{\mathrm{O}^{j}_{\mathrm{Si}}}}{2} \tag{41}$$

In the even higher system, numbers of different types of oxygen ions can also be calculated following the above method. After obtaining the numbers of oxygen ions, the new viscosity model will given in next section.

## 4. Model

The temperature dependence of viscosity is described by the Arrhenius law,

$$\ln\eta = \ln A + E / RT \tag{42}$$

where $\eta$ is the viscosity, $\mathrm{dPa\cdot S}$; *A* is the pre-exponent factor, $\mathrm{dPa\cdot S}$; *E* is the activation energy, J/mol; *R* is the gas constant, $8.314\,\mathrm{J/(mol\cdot K)}$; *T* is the absolute temperature, K. The compensation effect between the logarithm of pre-exponent factor ln*A* and activation energy *E* is expressed as follows:

$$\ln A = k(E\text{-}572516)\text{-}17.47 \tag{43}$$

where constants of 572516 and 17.47 are used to describe the viscosity of pure $SiO_2$. For multicomponent systems, parameter *k* can be calculated as follows,

$$k = \sum_{i,i\neq\mathrm{SiO_2}} (x_i k_i) / \sum_{i,i\neq\mathrm{SiO_2}} x_i \tag{44}$$

The activation energy *E* in Eq. (43) is expressed using the equation

$$E = \frac{572516\times 2}{n_{\mathrm{O_{Si}}} + \sum \alpha' \cdot n_{\mathrm{O'}}} \tag{45}$$

where $n_{\mathrm{O_{Si}}}$ is the number of bridging oxygen bonded with $Si^{4+}$ ion; $n_{\mathrm{O'}}$ is the number of other type of oxygen ion; parameter $\alpha'$ describes the deforming ability of bond around the oxygen ion $\mathrm{O'}$ relative to $\mathrm{O_{Si}}$. Corresponding to the different types of oxygen ions, 5 types of parameters: $\alpha^{i}_{\mathrm{Si}}$, $\alpha_i$, $\alpha_{\mathrm{Al},\,i}$, $\alpha^{j}_{\mathrm{Al},\,i}$ and $\alpha_{\mathrm{Al}}$, are assigned to describe the deforming ability of bonds around $\mathrm{O}^{i}_{\mathrm{Si}}$, $\mathrm{O}_i$, $\mathrm{O}_{\mathrm{Al},\,i}$, $\mathrm{O}^{j}_{\mathrm{Al},\,i}$ and $\mathrm{O_{Al}}$ respectively.

## 5. The application of the new model

**Table 1** Values of model parameters

| $i$ | $k_i \times 10^5$ | $\alpha_{\mathrm{Si}}^{i}$ | $\alpha_i$ | $\alpha_{\mathrm{Al},\, i}$ | $\alpha_{\mathrm{Al},\, i}^{i}$ | $\alpha_{\mathrm{Al,\, Ca}}^{\mathrm{Mg}}$ | $\alpha_{\mathrm{Al,\, Ca}}^{\mathrm{Fe}}$ |
|---|---|---|---|---|---|---|---|
| Mg | -2.106 | 6.908 | 15.54 | 5.606 | 3.975 | 8.334 | 8.694 |
| Ca | -2.088 | 7.422 | 17.34 | 4.996 | 7.115 | | |
| Fe | -2.195 | 10.76 | 33.62 | 8.702 | 6.828 | | |
| Mn | -2.147 | 8.452 | 27.83 | 5.857 | 4.204 | | |
| Al | -2.594 | | 5.671 | | | | |

**Table 2** Mean deviations for different viscosity models (%)

| Systems | Riboud | Urbain | Kondratiev | Iida | NPL | Ray | Nakamoto | Present model |
|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 75.0 | 65.7 | 14.5 | x | 82.8 | 184 | 69.4 | 4.8 |
| $MgO$-$SiO_2$ | 12.0 | 45.1 | | x | 74.2 | 582 | 33.2 | 8.6 |
| $CaO$-$SiO_2$ | 37.6 | 20.6 | 10.3 | 239 | 64.4 | 34.1 | 32.0 | 8.4 |
| $FeO$-$SiO_2$ | 314 | | 11.5 | 29.2 | 183 | 301 | 113 | 7.2 |
| $MgO$-$FeO$-$SiO_2$ | 236 | | | 84.1 | 207 | 311 | | 8.3 |
| $CaO$-$MgO$-$SiO_2$ | 12.4 | 27.4 | | 197 | 59.8 | 136 | 88.2 | 11.0 |
| $CaO$-$FeO$-$SiO_2$ | 220 | | 7.8 | 39.3 | 136 | 258 | 147 | 12.1 |
| $CaO$-$MnO$-$SiO_2$ | 41.1 | 18.2 | | 42.9 | 39.6 | 35.8 | | 17.1 |
| $CaO$-$FeO$-$MnO$-$SiO_2$ | 113 | | | 48.0 | 69.7 | 129 | | 13.8 |
| $CaO$-$MgO$-$MnO$-$SiO_2$ | 26.1 | | | 274 | 63.6 | 112 | | 23.3 |
| $Al_2O_3$-$SiO_2$ | 452 | 99.0 | 90.7 | x | 89.2 | 212 | 28.5 | 30.5 |
| $CaO$-$Al_2O_3$ | 82.2 | 83.2 | 76.1 | x | 51.8 | 50.3 | 62.5 | 25.7 |
| $MgO$-$Al_2O_3$-$SiO_2$ | 127 | 48.6 | | x | 33.0 | 107 | 32.0 | 21.0 |
| $CaO$-$Al_2O_3$-$SiO_2$ | 104 | 20.6 | 27.6 | x | 79.2 | 44.1 | 42.5 | 21.1 |
| $FeO$-$Al_2O_3$-$SiO_2$ | 622 | | 63.0 | 324 | 39.1 | 86.4 | 34.7 | 29.8 |
| $MnO$-$Al_2O_3$-$SiO_2$ | 441 | 45.0 | | x | 93.6 | 66.2 | | 28.8 |
| $CaO$-$FeO$-$Al_2O_3$ | 200 | | | x | 37.4 | 50.6 | 73.3 | 24.4 |
| $CaO$-$MgO$-$Al_2O_3$-$SiO_2$ | 106 | 25.6 | | x | 105 | 60.5 | 46.9 | 18.4 |
| $CaO$-$FeO$-$Al_2O_3$-$SiO_2$ | 395 | | 25.9 | 95.1 | 58.1 | 75.3 | 36.7 | 28.1 |
| $CaO$-$MgO$-$FeO$-$Al_2O_3$-$SiO_2$ | 103 | | | 57.5 | 46.9 | 63.4 | 24.7 | 13.5 |

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

The viscosities of aluminosilicate systems involving the components of MgO, CaO, FeO, MnO, $Al_2O_3$, $SiO_2$ have been simulated in our previous papers[13, 16, 24], with the optimized parameters shown in Table 1. Parameters $k_i$, $\alpha_i$ and $\alpha_{\mathrm{Si}}^{i}$ are optimized in $(\mathrm{MO})_i$-$\mathrm{SiO_2}$ system; $\alpha_{\mathrm{Al}}$ and $k_{\mathrm{Al}}$ are optimized in $\mathrm{Al_2O_3}$-$\mathrm{SiO_2}$ system; $\alpha_{\mathrm{Al},\,i}$ and $\alpha_{\mathrm{Al},\,i}^{j}$ are optimized in $(\mathrm{MO})_i$-$\mathrm{Al_2O_3}$-$\mathrm{SiO_2}$ ternary system; $\alpha_{\mathrm{Al},\,i}^{j}$ is optimized in $(\mathrm{MO})_i$-$(\mathrm{MO})_j$-$\mathrm{Al_2O_3}$-$\mathrm{SiO_2}$ system. It should be pointed out that parameter $\alpha_i$ ($i$=Mg, Ca, Mn) are calculated by $(\frac{T_{m,\mathrm{FeO}}}{T_{m,i}})^{1.2}\alpha_{\mathrm{Fe}}$ (where $T_m$ is the melting point of component $i$) for the absence of data in $(\mathrm{MO})_i$-$\mathrm{SiO_2}$ system with the silica content lower than 1/3 except FeO-$\mathrm{SiO_2}$ system[13]; $k_i$ and $\alpha_{\mathrm{Si}}^{i}$ are optimized in CaO-MnO-$\mathrm{SiO_2}$ system for the weak compatibility of viscosity data from different references in MnO-$\mathrm{SiO_2}$ system[8]. The systems of CaO-MgO-$\mathrm{SiO_2}$, CaO-FeO-$\mathrm{SiO_2}$, MgO-FeO-$\mathrm{SiO_2}$, CaO-MgO-MnO-$\mathrm{SiO_2}$, CaO-FeO-MnO-$\mathrm{SiO_2}$, $\mathrm{Al_2O_3}$, CaO-$\mathrm{Al_2O_3}$, CaO-FeO-$\mathrm{Al_2O_3}$ are not participated into the parameters optimization, and the viscosity estimation of these systems are done by the parameters optimized in other systems. The mean deviation $\Delta$ (defined as $\Delta = \frac{1}{N} \times \sum_{i=1}^{N} \frac{\left|\eta_{i,mea} - \eta_{i,cal}\right|}{\eta_{i,mea}} \times 100\%$, where $\eta_{i,cal}$ and $\eta_{i,mea}$ are the estimated and measured viscosities, respectively, and $N$ represents the number of the samples) is used to evaluate the calculating result of the present model. The mean deviations of our model and models of Riboud[1], Urbain[6], Kondratiev[7], Iida[10], NPL[2], Ray[5] and Nakamoto[4] are given in Table 2, from which it can be seen that our model has the strongest ability for viscosity estimation, even for the system without $\mathrm{SiO_2}$.

## 6. Discussions

(1) In order to see clearly the different influences of different basic oxides (FeO, MnO, MgO and CaO) on viscosity, the theoretical viscosity variations (estimated by the present model) of the MgO-$\mathrm{SiO_2}$, CaO-$\mathrm{SiO_2}$, MnO-$\mathrm{SiO_2}$, FeO-$\mathrm{SiO_2}$ four binary systems with the mole fraction of $\mathrm{SiO_2}$ at 1873K are given in Fig. 1, from which the viscosity of melts at the same temperature and composition follow the order: FeO-$\mathrm{SiO_2}$<MnO-$\mathrm{SiO_2}$<CaO-$\mathrm{SiO_2}$<MgO-$\mathrm{SiO_2}$, or the ability of basic oxides to decrease viscosity follows the order: FeO>MnO>CaO>MgO, when $\mathrm{Al_2O_3}$ is absence. The same order is also obtained by Zhang[8] and Shu[9].

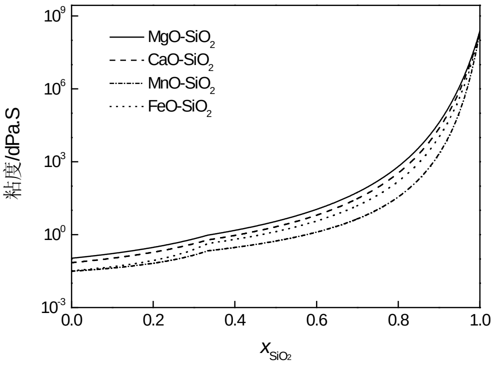

**Fig.1** The influences of different metal oxides on the viscosity of MO-$SiO_2$ binary system at 1873K

(2) The present model can fulfill all the four requirements: different types of oxygen ions are defined to describe the structure of aluminosilicate melts, and a systematic method is proposed to calculated the numbers of different types of oxygen ions; the compensation effect between the logarithm of pre-exponent ln$A$ and activation energy of viscosity $E$ is taken into consideration in the present model. Meanwhile, in order to incorporate the viscosity estimation of pure silica, only one parameter is needed in the compensation relationship; the reciprocal function is utilized to express the nonlinear behavior between activation energy of viscosity and composition; a priority order is set for different metal cations when charge compensating $Al^{3+}$ ion based on the coulombic force between the cation and oxygen anion. However, none of the other viscosity models consider all the four requirements. So, the present model has strong ability for viscosity estimation, which can be seen from Table 2.

## 7. Conclusions

New viscosity method is proposed based on defining different types of oxygen ions to describe the structure of aluminosilicate melts. And five assumptions are suggested to calculate the numbers of these oxygen ions. When several basic oxides exist in the $Al_2O_3$ containing melts, different priorities are determined for different metal cations when charge compensating $Al^{3+}$ ion, according to the coulombic force between cation and oxygen anion. According to the comparisons of different models in calculating the viscosities of aluminosilicate melts involving MgO, CaO, FeO, MnO, $Al_2O_3$, $SiO_2$ components, it is concluded that the present model has the strongest ability for viscosity estimation.

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