For instance, it is found that viscosity increases when adding K to tendency with composition. Sometimes, an inverse optimization and improving the productive processes, one of the most important physical properties.

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 can be extrapolated. (ii) For aluminosilicate melts containing several basic oxides, the priority order is established when away from the range. (iii) The calculation results of these models can only give a decreasing tendency. (iv) The calculation results of these models can only give a decreasing tendency. (v) The calculation results of these models can only give a decreasing tendency. (vi) The calculation results of these models can only give a decreasing tendency. (vii) The calculation results of these models can only give a decreasing tendency. (viii) The calculation results of these models can only give a decreasing tendency. (ix) The calculation results of these models can only give a decreasing tendency. (x) The calculation results of these models can only give a decreasing tendency. (xi) The calculation results of these models can only give a decreasing tendency. (xii) The calculation results of these models can only give a decreasing tendency. (xiii) The calculation results of these models can only give a decreasing tendency. (xiv) The calculation results of these models can only give a decreasing tendency. (xv) The calculation results of these models can only give a decreasing tendency. (xvi) The calculation results of these models can only give a decreasing tendency. (xvii) The calculation results of these models can only give a decreasing tendency. (xviii) The calculation results of these models can only give a decreasing tendency. (xix) The calculation results of these models can only give a decreasing tendency. (xx) The calculation results of these models can only give a decreasing tendency. (xxi) The calculation results of these models can only give a decreasing tendency. (xxii) The calculation results of these models can only give a decreasing tendency. (xxiii) The calculation results of these models can only give a decreasing tendency. (xxiv) The calculation results of these models can only give a decreasing tendency. (xxv) The calculation results of these models can only give a decreasing tendency. (xxvi) The calculation results of these models can only give a decreasing tendency. (xxvii) The calculation results of these models can only give a decreasing tendency. (xxviii) The calculation results of these models can only give a decreasing tendency. (xxix) The calculation results of these models can only give a decreasing tendency. (xxx) The calculation results of these models can only give a decreasing tendency. (xxxi) The calculation results of these models can only give a decreasing tendency. (xxxii) The calculation results of these models can only give a decreasing tendency. (xxxiii) The calculation results of these models can only give a decreasing tendency. (xxxiv) The calculation results of these models can only give a decreasing tendency. (xxxv) The calculation results of these models can only give a decreasing tendency. (xxxvi) The calculation results of these models can only give a decreasing tendency. (xxxvii) The calculation results of these models can only give a decreasing tendency. (xxxviii) The calculation results of these models can only give a decreasing tendency. (xxxix) The calculation results of these models can only give a decreasing tendency. (xlix) The calculation results of these models can only give a decreasing tendency. (lix) The calculation results of these models can only give a decreasing tendency. (x) The calculation results of these models can only give a decreasing tendency.
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 lnA 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) 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 AlO₄³⁻ 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,

\[ \ln \eta = \ln A + \frac{E}{RT} \]  

where \( \mu \) 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, \( \mu T^{0.5} \) in \( E=572516 \times 10^{17.47} \) for multicomponent system \( \sum M_i O_{1-x} S_i O_{x} \), the value of parameter \( k \) is assumed to be the linear addition of that of the binary systems \( M_i O_{1-x} S_i O_{x} \) with the normalized mole fractions of oxides \( M_i O_{1-x} \) as the weighting factors,

\[ k = \sum_{i=1}^{n} (x_i k_i) / \sum_{i=1}^{n} x_i \]

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

\[ E = 572516 \times 2 \left\{ n_0 A_0 + \sum \alpha_{x} n_{0x} + \sum \sum \alpha_{x} \alpha_{y} n_{0xy} + \sum \sum \sum \alpha_{x} \alpha_{y} \alpha_{z} n_{0xyz} \right\} \]

where \( n \) is the mole number and \( \alpha \) 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 \( O_{ix} \), bonded with Si⁴⁺ ion; oxygen \( O_{ia} \), bonded with Al³⁺ ion not charge compensated; bridging oxygen \( O_{ia} \), bonded with Al³⁺ ion charge compensated by cation \( i \); non-bridging oxygen, bonded with Si⁴⁺ ion and metal cation \( i \); non-bridging oxygen \( O_{ia} \), bonded with metal cation \( j \) and Al³⁺ ion charge compensated by cation \( i \); free oxygen \( O_{ia} \), 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 \( \sum (M_iO_j) - SiO_2 \), the numbers of different types of oxygen ions can be calculated by the random mixing rule: firstly, calculate \( \sum n_{i0}^k \), \( \sum n_{i0}^r \), \( \sum n_{i0}^z \) 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 \( M_iO \) charge compensating \( Al_{2}O_3 \) is infinite: in the case \( x_{nM}/x_{nO} < 1 \), all \( M_iO \) act as charge compensators, while in the case of \( x_{nM}/x_{nO} > 1 \) all \( Al_{2}O_3 \) form \( AlO_2^- \) tetrahedrons, and the extra \( M_iO \) acts as network modifiers.

**Assumption IV:** In the case of \( x_{nM}/x_{nO} > 1 \), when the extra \( M_iO \) breaks the bridging oxygen, it is assumed that the bridging oxygen in \( AlO_2^- \) and \( SiO_4^- \) andtetrahedron are equivalent, and the numbers of formed non-bridging oxygen bonded to \( Al_{2}O_3 \) ions and \( SiO_4^- \) ions are proportional to the numbers of bridging oxygen in \( AlO_2^- \) and \( SiO_4^- \) and tetrahedrons.

**Assumption V:** \( Ca^{2+} \) cation has higher priority of charge-compensating \( Al_{2}O_3 \) ion than \( Mg^{2+} \) ion. Only after all the \( Ca^{2+} \) ions have been exhausted, \( Mg^{2+} \) ions will participate into the charge compensation.

Among them, Assumption V endows \( Ca^{2+} \) ion an absolute priority over \( Mg^{2+} \) ion when charge compensating \( Al_{2}O_3 \) ion, with which the viscosity variation of \( CaO-MgO-\text{Al}_2\text{O}_3-\text{SiO}_2 \) system can be well represented. However, the previous work can only deal with the case of aluminosilicate system contain two basic oxides: \( CaO \) and \( MgO \). This is because when the basic oxides are not \( CaO \) and \( MgO \) or 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. Assumption V will be revised into a more general form as follows.

**Assumption IV:** Different metal cations have different abilities of charge-compensating \( Al_{2}O_3 \) 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 \( Al_{2}O_3 \) ions, cations with the lower priority can participate the charge compensation. The order for different cations can be determined as follows.

Theoretically, the cation \( M^{n+} \) that has strong bond strength with \( O^- \) ion should possess weaker ability of compensating \( Al^{3+} \) ion, for the reason that itself can form complex anion with oxygen ion, and strong repulsive force exists between cation \( M^{n+} \) and \( Al^{3+} \) 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,

\[
I = \frac{2Q}{(r_{M_{n+}} + r_{O^-})}
\]

where \( Q \) is the valence of \( M^{n+} \) ion \( r_{M_{n+}} \) and \( r_{O^-} \) are the radii of \( M^{n+} \) and oxygen ions, respectively. The ion radiuses (taken from the data compiled by Shannon [22]) of \( Mg^{2+} \), \( Ca^{2+} \), \( Na^+ \), \( K^+ \), \( Fe^{2+} \), \( Mn^{2+} \) and \( O^{2-} \) 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: \( K^+ < Na^+ - Ca^{2+} - Mn^{2+} < Fe^{2+} < Mg^{2+} \). The priority order of charge compensating \( Al_{2}O_3 \) ion is: \( K^+ < Na^+ - Ca^{2+} - Mn^{2+} < Fe^{2+} < Mg^{2+} \). The order of \( K^+ > Na^+ > Ca^{2+} > Mg^{2+} \) 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 \( Fe^{2+} \) and \( Mn^{2+} \) is 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 \( \sum (M_iO_j) - SiO_2 \) and \( M_iO-Al_{2}O_3-SiO_2 \) systems are given before, and the calculating formulae for \( (M_iO_j) - (M_iO_j) - Al_{2}O_3-SiO_2 \) system can be obtained following the formulae of \( CaO-MgO-Al_{2}O_3-SiO_2 \) system [21]. In the following sections, model will be applied to aluminosilicate systems containing \( FeO, MnsO, MgO, CaO, NaO \) and \( K.O \). 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 \( k, \alpha_i^a \) and \( \alpha_i^a \), are optimized according to the data of \( M_iO-SiO_2 \) binary system (have been accomplished in our previous work [17, 20]); parameters \( \alpha_i^a \) and \( \alpha_i^a \) are optimized according to the data of \( M_iO-\text{Al}_2\text{O}_3-SiO_2 \) system; while for the system \( (M_iO_j) - (M_iO_j) - Al_{2}O_3-SiO_2 \) with two basic oxides, one more parameter \( \alpha_i^a \) is needed. Theoretically, no more parameter is needed for even higher order system.

5. Results

5.1. \( M_iO-Al_{2}O_3-SiO_2 \) ternary system

The viscosity data of \( FeO-Al_{2}O_3-SiO_2 \) and \( MnO-\text{Al}_2\text{O}_3-SiO_2 \) systems were also included; parameters \( k, \alpha_i^a \) and \( \alpha_i^a \) were optimized according to the data of \( M_iO-SiO_2 \) binary system.
Table 1. Summary of the literature data source utilized in the present study

<table>
<thead>
<tr>
<th>System</th>
<th>Source</th>
<th>Composition range (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO-Al₂O₃-SiO₂</td>
<td>Johannsen et al. [26]</td>
<td>FeO: 0.44<del>0.73; SiO₂:0.22</del>0.44</td>
</tr>
<tr>
<td>MnO-Al₂O₃-SiO₂</td>
<td>Urbain et al. [27]</td>
<td>MnO: 0.15<del>0.54; SiO₂:0.33</del>0.74</td>
</tr>
<tr>
<td>Na₂O-Al₂O₃-SiO₂</td>
<td>Kout et al. [28]</td>
<td>Na₂O:0.20<del>0.50; SiO₂: 0.4</del>0.65</td>
</tr>
<tr>
<td></td>
<td>Tophis et al. [29]</td>
<td>Na₂O:0.08<del>0.28; SiO₂: 0.5</del>0.82</td>
</tr>
<tr>
<td></td>
<td>Tophis et al. [30]</td>
<td>Na₂O:0.09<del>0.26; SiO₂: 0.5</del>0.82</td>
</tr>
<tr>
<td>K₂O-Al₂O₃-SiO₂</td>
<td>Urbain et al. [27]</td>
<td>K₂O: 0.12; SiO₂: 0.75</td>
</tr>
<tr>
<td>CaO-FeO-Al₂O₃-SiO₂</td>
<td>Higgins et al. [32]</td>
<td>Al₂O₃:0.05<del>0.23; SiO₂: 0.33</del>0.47</td>
</tr>
<tr>
<td></td>
<td>Kolesov et al. [33]</td>
<td>Al₂O₃:0.02<del>0.05; SiO₂: 0.24</del>0.51</td>
</tr>
<tr>
<td>CaO-NaO-Al₂O₃-SiO₂</td>
<td>Sukenaga et al. [12]</td>
<td>Al₂O₃:0.10<del>0.12; SiO₂: 0.34</del>0.48</td>
</tr>
<tr>
<td>CaO-K₂O-Al₂O₃-SiO₂</td>
<td>Sukenaga et al. [12]</td>
<td>Al₂O₃:0.11<del>0.12; SiO₂: 0.34</del>0.49</td>
</tr>
<tr>
<td>CaO-FeO-Al₂O₃</td>
<td>Vidacak et al. [34]</td>
<td>Al₂O₃:0.26<del>0.39; FeO: 0.12</del>0.34</td>
</tr>
<tr>
<td>CaO-MgO-NaO-Al₂O₃-SiO₂</td>
<td>Sykes et al. [35]</td>
<td>Al₂O₃:0.02<del>0.23; SiO₂: 0.50</del>0.51</td>
</tr>
<tr>
<td></td>
<td>Kim et al. [36]</td>
<td>Al₂O₃:0.12<del>0.12; SiO₂: 0.28</del>0.38</td>
</tr>
<tr>
<td>CaO-MgO-FeO-Al₂O₃-SiO₂</td>
<td>Higgins et al. [32]</td>
<td>Al₂O₃:0.05<del>0.06; SiO₂: 0.34</del>0.42</td>
</tr>
<tr>
<td></td>
<td>Kim et al. [37]</td>
<td>Al₂O₃:0.06<del>0.11; SiO₂: 0.29</del>0.34</td>
</tr>
</tbody>
</table>

Table 2. Values of model parameters for different M₂O-SiO₂ and M₂O-Al₂O₃-SiO₂ systems

<table>
<thead>
<tr>
<th>Element</th>
<th>( k \times 10^6 )</th>
<th>( \alpha_{\text{Fe}} )</th>
<th>( \alpha' )</th>
<th>( \alpha_{\text{Fe}} )</th>
<th>( \alpha'_{\text{Fe}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-2.195</td>
<td>10.76</td>
<td>33.62</td>
<td>8.702</td>
<td>6.828</td>
</tr>
<tr>
<td>Mn</td>
<td>-2.147</td>
<td>8.452</td>
<td>27.83</td>
<td>5.857</td>
<td>4.204</td>
</tr>
<tr>
<td>Mg</td>
<td>-2.106</td>
<td>6.908</td>
<td>15.54</td>
<td>5.606</td>
<td>3.975</td>
</tr>
<tr>
<td>Ca</td>
<td>-2.088</td>
<td>7.422</td>
<td>17.34</td>
<td>4.996</td>
<td>7.115</td>
</tr>
<tr>
<td>Na</td>
<td>-2.767</td>
<td>13.35</td>
<td>40.56</td>
<td>4.308</td>
<td>10.46</td>
</tr>
<tr>
<td>K</td>
<td>-3.2</td>
<td>16.59</td>
<td>4.156</td>
<td>17.34</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>-2.594</td>
<td>5.671</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Al₂O₃-SiO₂ systems are taken from the works of Johannsen et al. [26] and Urbain et al. [27], respectively. Based on the parameters \( k, \alpha, \) and \( \alpha' \) optimized in binary systems, two parameters \( \alpha_{\text{Fe}} \) and \( \alpha'_{\text{Fe}} \) (\( \alpha_{\text{Mn}} \) and \( \alpha'_{\text{Mn}} \)) 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 Mn²⁺ 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 Na$_2$O-Al$_2$O$_3$-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 $a_{\text{Na}}$ and $a_{\text{Al}}$ 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 K$_2$O-Al$_2$O$_3$-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$_2$O and low viscosity. With the optimized parameters of $a_{\text{Na}}$ and $a_{\text{Al}}$, viscosity of this system can be calculated. The comparisons between the calculated 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$_2$O and K$_2$O at high temperature.

5.2. (M$_x$O)$_y$-(M$_z$O)$_i$-Al$_2$O$_3$-SiO$_2$ quaternary system

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

5.3. CaO-FeO-Al$_2$O$_3$ ternary system

The viscosity of CaO-FeO-Al$_2$O$_3$ system are from Vidacak et al. [34]. When calculating viscosity of this system, no parameter needs to be optimized.
Extrapolating the viscosity calculation of CaO-FeO-Al\(_2\)O\(_3\)-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
CaO-MgO-Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\) system

The parameter \(\alpha_{\text{Na}}\) is optimized in CaO-MgO-Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\) system for the lack of viscosity data in MgO-Na\(_2\)O-Al\(_2\)O\(_3\)-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 Na\(^+\)\(\succ\)Ca\(^{2+}\)\(\succ\)Mg\(^{2+}\), thereby, oxygen ions O\(_{\text{Na}}\), O\(_{\text{Ca}}\), and O\(_{\text{Mg}}\) exist. Considering the corresponding parameters \(\alpha_{\text{Na}}\), \(\alpha_{\text{Ca}}\), and \(\alpha_{\text{Mg}}\), have been optimized in CaO-Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\) and CaO-MgO-Al\(_2\)O\(_3\)-SiO\(_2\) systems, only parameters \(\alpha_{\text{Na}}\) is optimized in this system.

Parts of the composition points of Sykes et al. [35] fulfill the condition: \(x_{\text{Na},0} > x_{\text{Al},0}\) and \(x_{\text{Na},0} + x_{\text{Ca},0} + x_{\text{Mg},0} - x_{\text{Si},0} < 2(2x_{\text{Al},0} + x_{\text{Na},0})\), 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:

\[
\begin{align*}
\eta_{\text{O}_4} &= 2(x_{\text{Na},0} - x_{\text{Al},0}) / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\eta_{\text{O}_6} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\eta_{\text{O}_8} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\end{align*}
\]  
(6)

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

\[
\begin{align*}
\eta_{\text{O}_4} &= 2(x_{\text{Na},0} - x_{\text{Al},0}) / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\eta_{\text{O}_6} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\eta_{\text{O}_8} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\end{align*}
\]  
(9)

Bridging oxygen:

\[
\begin{align*}
\eta_{\text{O}_4} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\eta_{\text{O}_6} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\eta_{\text{O}_8} &= 2x_{\text{Al},0} / 2x_{\text{Al},0} + x_{\text{Na},0} \\
\end{align*}
\]  
(11)
The other parts of composition points measured by Sykes et al. [35] and those measured by Kim et al. [36] fulfill the conditions: $x_{Na_2O} < x_{SiO_2}$, $x_{Na_2O} + x_{CaO} > x_{SiO_2}$ and $x_{CaO} + x_{Al_2O_3} - x_{SiO_2} < 2(2x_{Al_2O_3} + x_{SiO_2})$. 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:

$$n_{O_{Ca}} = 2x_{CaO} + x_{SiO_2} - x_{CaO} - x_{Al_2O_3}$$

(14)

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

$$n_{O_{Mg}} = 2x_{MgO} - x_{SiO_2} - x_{MgO} - x_{Al_2O_3}$$

(15)

Bridging oxygen:

$$n_{O_{Al}} = 4x_{Al_2O_3} - x_{SiO_2} - x_{Al_2O_3}$$

(16)

According to the above equations, parameter $a^{Na}_{SiO_2}$ 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$_2$O$_3$-SiO$_2$ system**

The viscosity data of this system are taken from the work of Higgins et al. [32] and Kim et al. [37]. All the composition points fulfill the condition: $x_{CaO} > x_{FeO}$ and $x_{CaO} + x_{Al_2O_3} - x_{SiO_2} < 2(2x_{Al_2O_3} + x_{SiO_2})$. In this case, all the Al$^{3+}$ ions are compensated by Ca$^{2+}$ ions: the remaining Ca$^{2+}$, Mg$^{2+}$ and Fe$^{3+}$ 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.
6. Discussion

(1) According to the results of our previous paper [21], the model can be extrapolated to AlO3, CaO-AlO3 systems without optimizing new parameters. In this work, the model can also well describe the composition and temperature dependences of viscosity for CaO-FeO-AlO3 system. Therefore, the present model can be applied to system without SiO2.

(2) From the values of parameters shown in Table 2, it can be seen that the following orders exist:
\[ \alpha_{\text{Al}}^{\text{Na}} < \alpha_{\text{Al}}^{\text{Ca}} < \alpha_{\text{Al}}^{\text{Mg}} < \alpha_{\text{Al}}^{\text{K}}. \]
Moreover, the deforming ability of bonds around the non-bridging oxygen bond of different cations increases following the order: Mg2+<Ca2+<Na+<K+. While, the order is opposite for the bridging oxygen bond with Al3+ ions compensated by different cations: Mg2+<Ca2+<Na+<K+. It is known that the basicity order for these four oxides is K2O>Na2O>CaO>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 AlO4 tetrahedron structure by charge compensating Al3+ ion, which increases viscosity. So basic oxide plays a paradox role in influencing viscosity when Al2O3 exists.

(3) It is found by Sukenaga et al. [12] that the addition of K2O to CaO-Al2O3-SiO2 slag increases viscosity. However, all the theoretical models cannot 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 cannot give an increasing tendency. Figure 11 shows the variations of viscosity for CaO-K2O-Al2O3-SiO2 quaternary system with content of K2O, 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 K2O to CaO-Al2O3-SiO2 system, K+ ion will substitute the position of Ca2+ ion to compensate Al3+ ion for its higher priority relative to Ca2+ ion. The displaced Ca2+ ions will form more non-bridging oxygen ions, and this factor decreases viscosity. But as the contents of basic oxides (Na2O+K2O) are not very high, and there are still enough bridging oxygen ions (including those bonded with Al3+ ion and Si4+ ion). In the case that content of K2O is smaller than that of Al2O3 (the case of Sukenaga et al. [12]), all the added K+ ion will substitute the position of Ca2+ ion to compensate Al3+ ion. Therefore, parts of the bridging oxygen bonded with Al3+ ion will transform from O<sub>Si</sub>-O<sub>Ca</sub> to O<sub>Si</sub>-O<sub>K</sub> according to parameters values shown in Table 2 (\[ \alpha_{\text{Al}} = 4.156 < \alpha_{\text{K}} = 4.996 \]), the bond around O<sub>Si</sub>-O<sub>K</sub> is stronger than that around O<sub>Si</sub>-O<sub>Ca</sub>, thus substitution of K+ ion for Ca2+ 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 Al2O3 is very small relative to the content of K2O addition, the decreasing tendency of viscosity will be dominated, since in this case most of the added K+ ions do not form bridging oxygen O<sub>Si</sub>-O<sub>K</sub> but non-bridging oxygen (O<sub>Si</sub>-O<sub>Ca</sub> and O<sub>Si</sub>-O<sub>K</sub>), thereby, viscosity may decrease. In the limiting case of content of Al2O3 equal to 0, the addition of K2O to CaO-SiO2 melts will obviously decrease viscosity for the decrease of absolute content of SiO2, and forming of more non-bridging oxygen. In another cases that the contents of basic oxides (Na2O+K2O) 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 K2O, because it is the forming of bridging oxygen O<sub>Si</sub>-O<sub>K</sub> 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 SiO2.

![Figure 11. Variation of viscosity with the content of K2O in CaO-K2O-Al2O3-SiO2 system](image-url)
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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