Modelling Viscosity of Silicate Melts

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ABSTRACT

A structurally related viscosity model for silicate melts has been proposed based on the available experimental data of viscosity for binary melts and theories of transport properties of liquids which describe the temperature dependence of viscosity. The viscosity model has been applied to a number of binary systems of $MO-SiO_2$ (M=Ca, Mg, Mn, Fe and Pb). Good agreement was obtained between the calculated values and the experimental data. The model parameters for higher order systems were assumed to be linear functions of those of the binary silicates. Such an assumption has been tested for some ternary and quaternary silicate systems which consist of the above-mentioned binary systems. It was found that the model provides satisfactory representation of experimental data for most systems studied within 25%, which is within the experimental uncertainty for most viscosity measurements. Furthermore the model can be used to represent the effect of different metal oxides on viscosity.

1. INTRODUCTION

The transport properties of slags play an important role in the metallurgical performance of smelting and refining processes. While the viscosity of slags is strongly composition and temperature dependent, the inherent problems and difficulties in high temperature measurements have limited the scope of experimental studies, and consequently the current knowledge on viscosity of slags does not satisfy the process metallurgist's needs. Experimentally measured viscosity data are available for binary and ternary systems which consist of most oxide components for metallurgical interests, such as CaO, MgO, MnO, PbO, FeO, Fe_2O_3, and Al_2O_3. As the order of the systems gets higher, less data in limited ranges are available [1]. Furthermore most measurements on multicomponent systems are for types of slags related to particular processes. The experimental findings on the general behaviour of BOS type of slags have been reviewed by Mills and Keene [2]. The review also discussed the applicability of the existing models. Recently, Utigard and Warczok [3] reviewed viscosity data on copper/nickel smelting and converting slags, including viscosity of the Fe_xO-SiO_2 binary and industrial slags. A correlation equation for calculation of viscosity for these slags was proposed based on the regression analysis of existing experimental data.

Our understanding on the general behaviour of viscosity in silicate melts has been developed gradually since a series of experiments carried out by Bockris and coworkers in the 1940's and 50's [4-9]. In these experimental studies the viscosity and other physical properties of a number of binary silicate melts were measured. This led to some basic understanding of the correlation between the structure of the silicate melts and other properties. The structural units which were described as discrete anions were postulated based on the analysis of the activation energy of transport properties. Since then the behaviour of viscosity has been discussed in close relation to the structural changes of the silicate melts. It is understood in general that the viscosity of silicate melts increases as the silica content increases. This can be considered a result of the gradual development of a network structure in the silicate melts, i.e., the degree of polymerization increases with silica content. However, the effect of other oxide components on viscosity should not be overlooked either. For example, when we consider melts at a fixed silica content, the effect of substitution of one oxide by another or addition of more metal oxides on viscosity becomes important. An improved knowledge on this subject would be beneficial to practical operations.

An objective of the on-going work at the G K Williams Cooperative Research Centre for Extractive Metallurgy is to develop suitable structurally related viscosity models of silicate melts, capable of representing the existing experimental data as well as predicting properties of melts for which experimental data are not available. Based on the analysis of a collection of viscosity data, a structurally related model for the viscosity of binary silicate melts was proposed by the present authors [10, 11]. The present work is essentially an extension of the previous study in which a systematic approach was taken by modelling individual binary systems to obtain an accurate description of the general behaviour of viscosity of these systems. The model parameters obtained for the binary systems were then used for extending the capability of the model to higher order systems. In this paper, firstly, a brief description of the model and modelling procedures will be given. Then the results obtained for the binary systems CaO-SiO_2, MgO-SiO_2, FeO-SiO_2, MnO-SiO_2 and PbO-SiO_2 will be presented. The results for ternary and higher order systems will be discussed mainly on the effect of substitution of one oxide by another or the addition of a particular kind of metal oxide on viscosity.

2. THE MODEL

It has been established from experimental studies that in general viscosity of silicate melts decreases as temperature increases for a given system, and increases as silica content increases at a given temperature. The present model was designed to provide a reasonable accurate description of the temperature and composition dependence of the viscosity of silicate melts.

2.1. Temperature Dependence of Viscosity

Viscosity can be considered as a rate process similar to chemical reaction and diffusivity [12]. The temperature dependence of viscosity therefore can be described by a generalized form of the Andrade-Arrhenius equation,

$$\eta = A \cdot T^{\alpha} \cdot \exp(E_\eta/RT), \qquad (1)$$

where η is viscosity, A is a pre-exponential constant, T is temperature in K, α is a constant ($\alpha \geq 0$), E_η is the activation energy, and R is the gas constant. When $\alpha=0$, Eq.(1) becomes the Andrade-Arrhenius equation. Other theoretical equations for the calculation of viscosity of simple liquids were derived based on the 'hole' theory of liquid structure. Different theories result in different values of α (0.5, 1.0 and 1.5) in Eq.(1) [12-15].

In the present study the Weymann equation [14] or Frenkel equation [15] was used. The Weymann equation has been successfully applied by a number of workers [16, 17] for representing experimental data and calculation of the viscosity of metallurgical slags over a limited composition and temperature range. Furthermore, in the report on standard reference material (SRM) for high temperature viscosity measurements by Mills et al. [18], the Weymann equation was found to provide the best fit of the temperature dependence of viscosity for most glasses and slags.

Originally the Weymann equation was derived based on the 'hole' model of liquid structure for calculation of viscosity of simple one component liquids. However the description of the dynamic processes in simple liquids is not directly transferable to silicate melts, as the 'holes' and the jumping units are not well defined. For convenience the Weymann equation has been written in a simplified form

$$\eta = A^W T \exp(E_\eta^W/RT), \qquad (2)$$

where A^W and E_η^W are the pre-exponential term and the activation energy, respectively. The values of A^W and E_η^W can be calculated by fitting experimental data for a given system.

2.2. Composition Dependence of Viscosity

The composition dependence of the viscosity of silicate melts can be mainly considered as a result of structural changes. As the melts become rich in silica, the degree of polymerization of silicate melts increases. This causes an increase in the activation energy E_η^W. In the present study the fractions of three types of oxygen, i.e., N_{O^0}, N_{O^-} and $N_{O^{2-}}$ were used as structural parameters to describe the degree of the polymerization. Here O^0 is a bridging (or doubly bonded) oxygen bonded to two silicon atoms, O^- is an oxygen bonded only to one silicon atom, and O^{2-} is a free oxygen. These parameters can be determined by experimental techniques [19]. They can also be calculated from thermodynamic models, for example, by using Kapoor and Frohberg's Cell Model [20, 21].

Analysis of available data for the composition and temperature dependences of viscosity and of the fractions of the three types of oxygen in silicate melts has shown that the composition dependence of E_η^W can be expressed as functions of fractions of bridging and free oxygen (N_{O^0} and $N_{O^{2-}}$), i.e.,

$$E_\eta^W = a + b(N_{O^0})^3 + c(N_{O^0})^2 + d(N_{O^{2-}}), \quad (3)$$

where a, b, c and d are fitting parameters obtained from experimental results. The fractions of free and bridging oxygen were calculated from the Cell Model. The analysis also shown that there exists a strong correlation between the activation energy E_η^W and the pre-exponential term A^W. Such correlation may be explained by the compensation law[22]. Compensation phenomenon has been observed for many kinetic processes, as well as viscosity. It is associated with the Arrhenius temperature dependence of a rate related property. Most compensated experimental data exhibit a dependence that can be written as

$$\ln(A^W) = a' + b'E_\eta^W, \quad (4)$$

where coefficients a' and b' are unique for a particular system and mechanism. The usefulness of the compensation law is that when a particular system is compensated, an additional constraint is introduced in describing the system. In this case $\ln(A^W)$ can be calculated as a linear function of the activation energy E_η^W. Similar behaviour has been found for diffusion in silicate systems[22]. The modelling work by Urbain [17], which was also based on the Weymann equation, assumed the same values of a' and b' for all silicate melts. It was found that the accuracy of the calculated values was not satisfactory under such assumption. In the present model different sets of a' and b' were obtained for each binary systems.

It should be mentioned that the equation for calculation of the pre-exponential term A^W (Eq.(4)) is different from the one used in the previous version of the present model [10].

2.3. Modelling Procedures

The model parameters in Eq.(3) and (4) were determined for the binary systems of CaO-SiO_2, MgO-SiO_2, FeO-SiO_2, MnO-SiO_2 and PbO-SiO_2 by fitting experimental data [6,23-34].

There is no viscosity data available for the Fe_2O_3-SiO_2 system. Two studies on the viscosity of Fe_2O_3-FeO-SiO_2 melts reported different findings. Kaiura et al. [35] have shown that at a given silica content, the ratio of Fe^{3+}/Fe^{2+} has no significant effect on viscosity apart from a slight decrease as the Fe^{3+}/Fe^{2+} ratio increases. The study by Bodnar et al. [36] reported the opposite effect, which showed a steady increase in viscosity as Fe^{3+}/Fe^{2+} ratio increases. In the present study the parameters for FeO-SiO_2 were used for the Fe_2O_3-SiO_2 system as a first approximation.

The model parameters for higher order systems are assumed to be linear functions of those of the binary silicate systems. If y is used to represent any of the fitting parameters a, b, c and d in Eq.(3), and a' and b' in Eq.(4) for a multicomponent system, y was obtained by

$$y = \sum_{i=1}^{m} X'_i \cdot y_i, \qquad (5)$$

where m is the number of non-silica components, i is the ith non-silica component, and X'_i is a normalized mole fraction of the ith non-silica component which is calculated from the mole fractions of the non-silica components in the silicate melts. For example, in the FeO-CaO-SiO_2 system, the normalized mole fraction for FeO is calculated as $X'_{FeO} = X_{FeO}/(X_{FeO} + X_{CaO})$.

The fractions of free and bridging oxygens in the expression of the activation energy in Eq.(3) were calculated by using the Cell Model. The Cell Model parameters assessed by Taylor and Dinsdale [37] were used for the CaO-SiO_2 system, while for other binary and higher order systems, the parameters determined by researchers from our group were used. A further assumption made is that the values of N_{O^0} and $N_{O^{2-}}$ are constant over the temperature ranges where viscosity was studied. They were calculated at an intermediate temperature for each binary system.

3. RESULTS AND DISCUSSIONS

3.1. Binary Silicate Melts

The calculated viscosity values from the present model are shown in Figures 1(a)-(e) and compared with the experimental data for the binary silicate melts of CaO-SiO_2 [6,23-25] , MgO-SiO_2 [6, 24, 25], FeO-SiO_2 [25-28], MnO-SiO_2 [25,29-31] and PbO-SiO_2 [32-34]. Results for only two temperatures are presented for clarity. Figures 1.(a)-(e) show that good agreement was obtained between the calculated viscosity values from the present model and the experimental data.

In the FeO-SiO_2 system the experimental studies have shown that at a given temperature viscosity reaches a maximum at the fayalite formation composition; this relative maximum decreases as temperature increases. This type of behaviour due to structural changes of particular systems can not be represented at present as the current model is developed to represent the general behaviour of viscosity in the wider composition range.

It is noted that the calculated viscosity from the models covers the entire composition range. However, over the temperature range in which viscosities of these binary systems were measured, at lower or high silica content regions, some of these binary systems are in two-phase regions. The calculated values in these regions are purely an extrapolation of liquid viscosity from the liquid region continuously to both sides. Although the viscosity values in the two-phase regions have no real significance in these binary systems, because the model is only valid for homogeneous liquids, the model parameters in these regions will influence viscosity values in some higher order systems where the liquid region extends to a wider composition range.

3.2. Ternary and Quaternary Systems

The analysis of the fit by the present model to most of the available experimental data of ternary and higher order systems which include combinations of the above-mentioned binary silicate systems have been shown that the overall discrepancy between the experimental data and the model prediction was less than 25% for most of the systems [11]. This is similar to the experimental uncertainties for viscosity measurements as pointed out by Mills and Keene [2].

As mentioned in the modelling procedures in the present approach the viscosities of ternary and higher order melts were calculated by using the linear combination of the binary silicates. The contribution of each cation species is proportional to its normalized mole fraction.

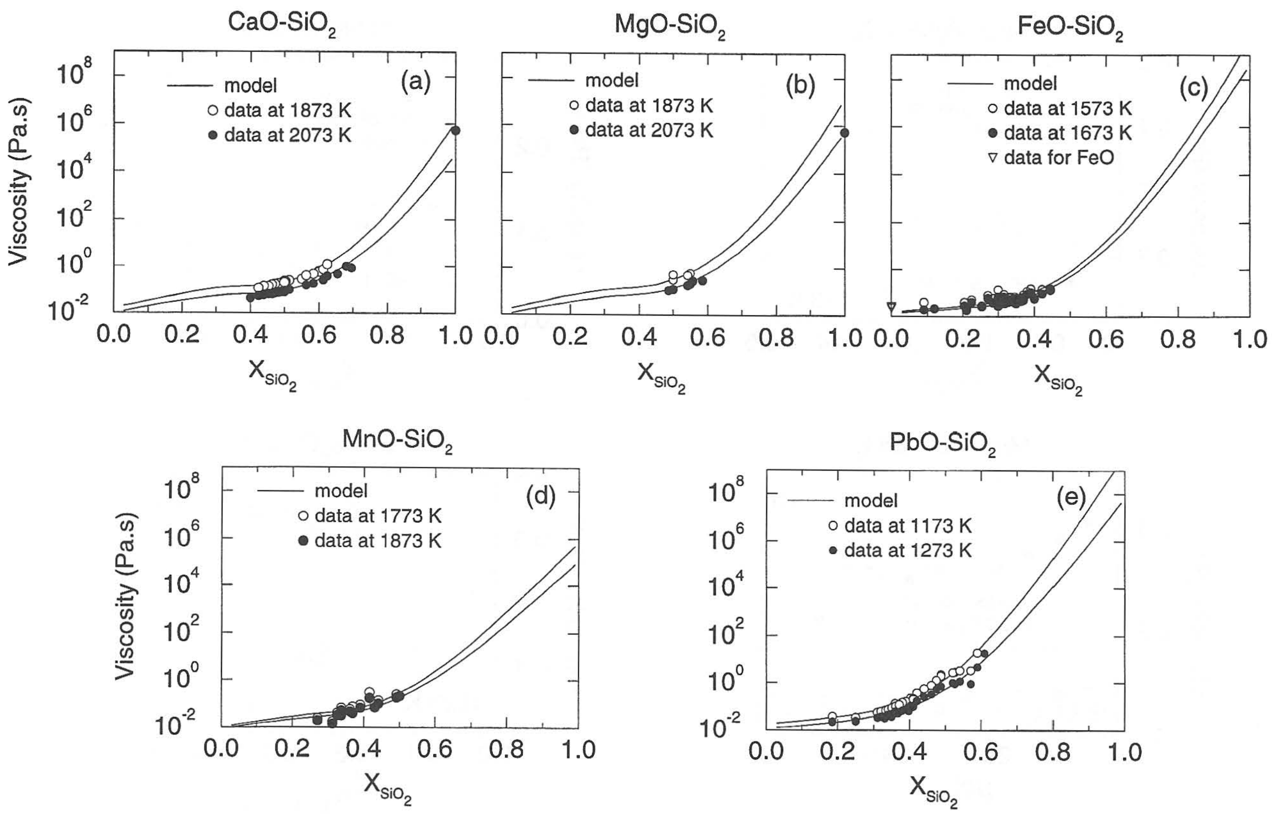

Figure 1: Composition dependence of viscosity of the binary silicate melts (a) CaO-SiO$_2$, (b) MgO-SiO$_2$, (c) FeO-SiO$_2$, (d) MnO-SiO$_2$ and (e) PbO-SiO$_2$.

If the viscosity of a binary silicate M_1O-SiO_2 is higher than that of another binary M_2O-SiO_2 for a set of X_{SiO_2}, substitution of M_2O for M_1O tends to cause viscosity to decrease. A test for the accuracy of the viscosity calculated using the present assumption would be very useful in understanding the general behaviour of viscosity in higher order systems.

In this paper the discussions on the modelling results are concentrated on the representation of the experimental finding on the effect of different cation species on viscosity. It is considered that this kind of discussion may provide a useful guide in control of practical operations.

Figures 2(a)-(d) show the effect of substitution of one type of metal oxide by another on viscosity at set silica concentrations for four ternary silicate systems. The fits to these experimental data by the present model are shown as solid lines in the figures. The experimental data on three of these systems were measured as mole fraction, while the data on the MnO-FeO-SiO$_2$ and one set for the CaO-MgO-SiO$_2$ were as weight percentage. It should be mentioned that the effect of the substitution can be examined in a more systematic way if the silica content of the systems was in mole fraction. In this case the substitution can be considered as exchange of M_1^{2+} and M_2^{2+} in the melts, and the structure regarding the silicate anions is not expected to be much different.

In the CaO-MgO-SiO$_2$ system (Figure 2(a)) the data by Licko and Danek at X_{SiO_2}= 0.5 [24] show that the substitution of MgO for CaO tends to increase viscosity. The data by Machin et al. [38] were measured at fixed weight percentage of SiO$_2$. The effect of MgO can not be examined directly, as the ratio of (pct CaO)/(pct MgO) varies, X_{SiO_2} decreases and this drop in silica mole fraction may well

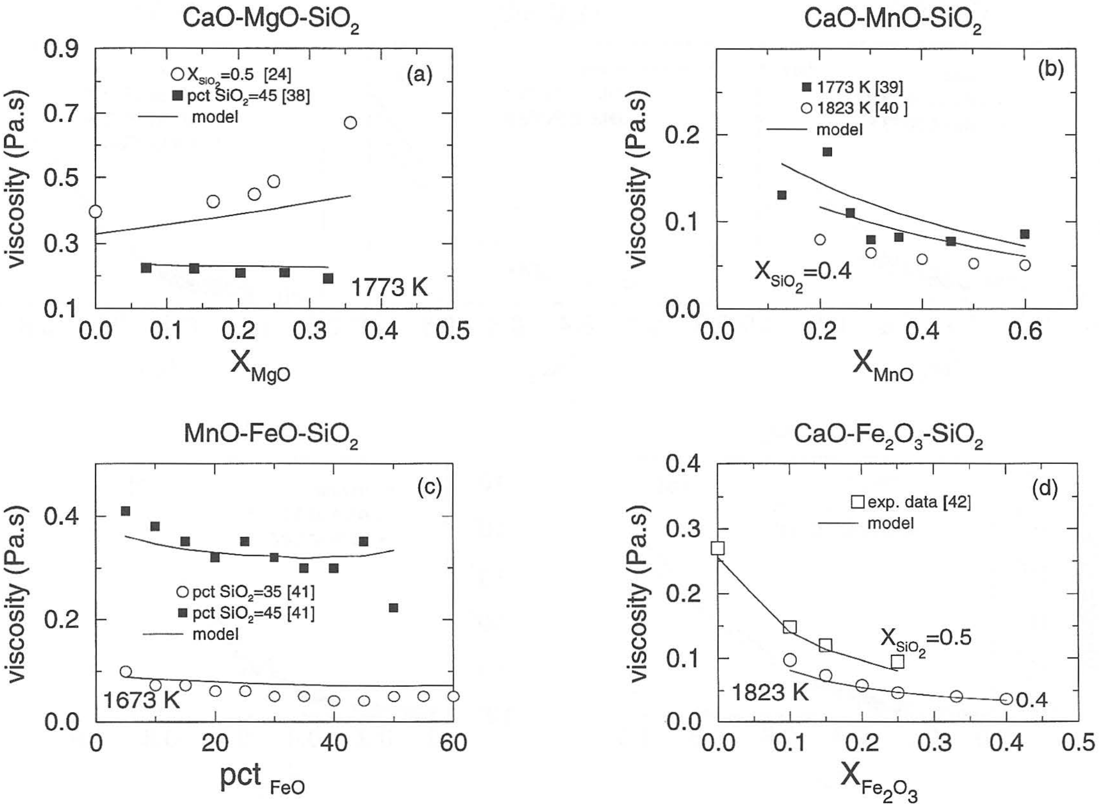

Figure 2: Comparison between the calculated viscosity values and experimental data on the effect of substitution of one oxide for another for (a) CaO-MgO-SiO$_2$, (b) CaO-MnO-SiO$_2$, (c) MnO-FeO-SiO$_2$ and (d) CaO-Fe$_2$O$_3$ - SiO$_2$ systems.

overweigh the effect of the substitution.

In Figure 2(b) both sets of experimental data at 1773 K by Segers et al. [39] and 1823 K by Kawahara et al. [40] show that substitution of MnO for CaO in the CaO-MnO-SiO$_2$ system causes viscosity to decrease at silica content of X_{SiO_2}=0.4.

Viscosity in the MnO-FeO-SiO$_2$ system has been measured by Adolf and Myslivec [41] at four different temperatures of 1573, 1623, 1673 and 1723 K and composition range from 5 to 45 pct SiO$_2$ and 5 to 95 pct FeO with an increment of 5 pct for each component. Iso-viscosity contours with a minimum in the centre were observed inside the liquid region. The contours suggest that the liquid viscosity in this ternary system decreases first with increasing silica content in the (Fe,Mn)O-rich region (X_{SiO_2}<0.3). At around X_{SiO_2}=0.3 viscosity reaches a minimum. When X_{SiO_2}>0.3, increasing silica content causes viscosity to increase, consistent with the general behaviour of viscosity for most silicate melts. The present model provides reasonable fit to the upper parts of the iso-viscosity contours, but is unable to reproduce the lower parts. This is because the model was developed mainly to describe the general behaviour of viscosity in regard to the structural change of the silicate anions and network. For melts with low silica content (X_{SiO_2}<0.3), the model predicts continuous decrease in viscosity with decreasing silica content. Detailed discussion on the model results for this system can be found in Ref [11]. In Figure 2(c) the effect of substitution of FeO for MnO at a constant pct SiO$_2$ is shown. It can be said that replace of MnO by FeO causes viscosity to decrease. However, the viscosity curves up with increasing pct FeO. This is because during the replacement, X_{SiO_2} increases as well. The effect of SiO$_2$ overrides that of

FeO.

In Figure 2(d) the experimental data [42] show that the substitution of Fe_2O_3 for CaO in the CaO-Fe_2O_3-SiO_2 at a fixed X_{SiO_2} tends to decrease viscosity. The calculated viscosity values using the present model in Figures 2(a)-(d) show that the agreement to the experimental data are very good. Not only are the fits close, more importantly, the effect of different cation species can be represented correctly.

In Figure 3.(a) and (b) the effect of different metal oxides on viscosity was compared by equal amount of addition to the melts for the FeO-M(Ca,Mg)O-SiO_2 and PbO-M(Ca,Mg)O-SiO_2 systems. The experimental results [34, 43] in Figures 3(a) and (b) show that the addition of metal oxides to the melts causes viscosity to decrease. These melts started from a fixed ratio of Fe/Si or Pb/Si. When more metal oxides are added to the melts, silica content drops which is the main reason for the decrease in viscosity. However, as can be seen, CaO and MgO are not as effective as PbO or FeO in reducing viscosity. Again the results from the present model provide a good representation of the experimental findings.

Figure 4(a)-(c) show the effect of addition of Fe_2O_3 and substitution of MgO for CaO on viscosities in the CaO-MgO-Fe_2O_3-SiO_2 system. The experimental data by Drissen et al. [44] were obtained for melts with three different starting ratio of $(X_{CaO}+X_{MgO})/X_{SiO_2}$. The results show that, firstly, the addition of Fe_2O_3 to melts with a fixed ratio of $(X_{CaO}+X_{MgO})/X_{SiO_2}$ causes viscosity to decrease, and secondly, the substitution of MgO for CaO causes viscosity to increase slightly. The decrease of viscosity with increasing Fe_2O_3 content is due to decrease in silica content of the melts. It can be seen that the fit of the present model to the experimental data is close and the present model can represent the effect of different metal oxides on viscosity.

3.3. Effect of Different Cations on Viscosity

Suginohara and coworkers [45] have studied the effect of addition of a third oxide to the PbO-SiO_2 systems on surface tension, density, viscosity, electrical conductivity and liquidus temperature. A linear correlation between these properties and the radius of the added metallic ion was found. The effect of addition of the third element can be described by effectiveness of the cations in reducing viscosity as all the measurements started from the melts with the same ratio of X_{PbO}/X_{SiO_2}. It was

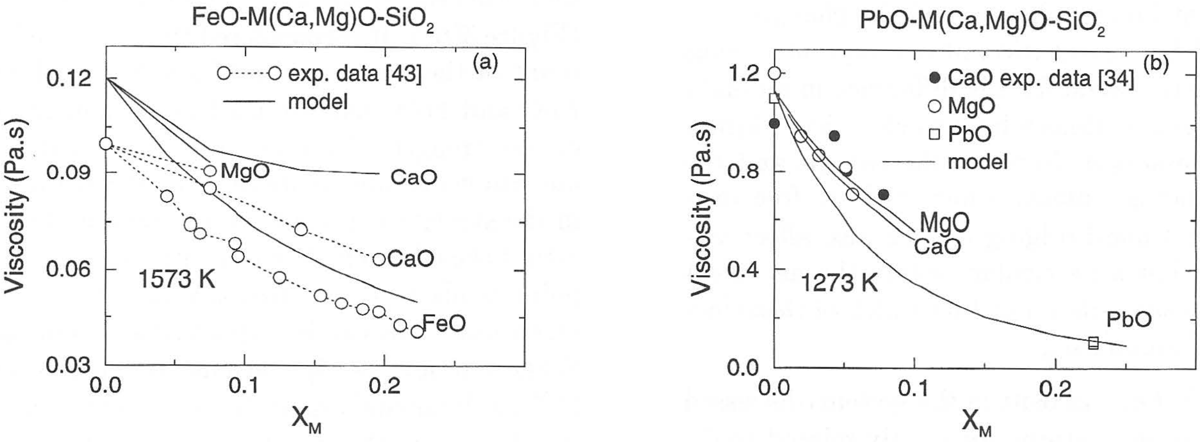

Figure 3: Comparison between the calculated viscosity values and experimental data on the effect of addition of different metal oxide for (a) FeO-M(Ca,Mg)O-SiO_2 (melts with an initial ratio of Fe/Si=2.9) and (b) PbO-M(Ca,Mg)O-SiO_2 (melts with an initial ratio of X_{SiO_2}/X_{PbO}=1.13) systems.

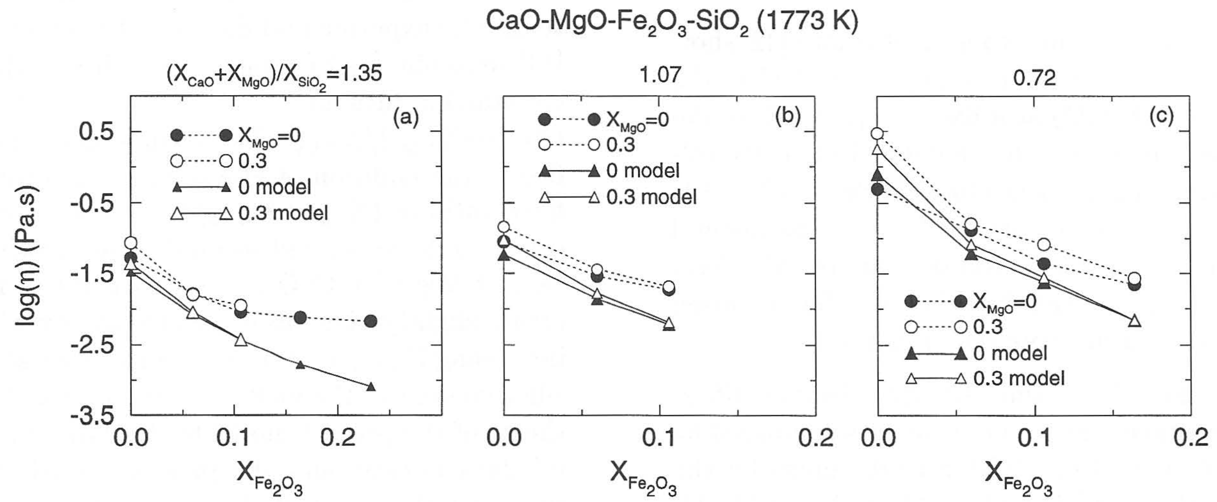

Figure 4: Comparison between the calculated viscosity and experimental data [44] for Fe_2O_3-FeO-CaO-MgO-SiO_2 system.

found that the effectiveness of divalent ions (alkali-earth cations, Zn^{2+} and Cd^{2+}) increases with increasing ionic radius, while the effectiveness of the monovalent ions (alkali cations) decreases with increasing ionic radius. In other words divalent and monovalent ions showed opposite trends.

The influence of different cations on viscosity is complicated by many factors. These include, firstly, the effect on the silicate anion structure. Some spectrometric studies on the structure of silicate melts and glasses [19, 46] have shown the structural differences among different binary silicates and the changes caused by substitution of one type of cations by others. Secondly, the difference in mobility of different cations relates to viscosity. Thirdly, the interactions between the cations and the surrounding anions, which include free oxygens and non-bridging oxygen also affect viscosity. For a particular system the net effect on viscosity will depend on which of these factors is dominating.

The effect on viscosity of the systems discussed in the present study are mostly related to divalent cations. A quantitative analysis is impossible at the present because of lack of data. However, a qualitative description of the general trend can be drawn based on the available experimental data. The results seem to suggest that the interaction between cations and anions are the dominant factor for viscosity changes in these systems. The effect on viscosity cannot simply be related to the ionic radius; for example, the sizes of Mg^{2+}, Mn^{2+} and Fe^{2+} are close, but the results in Figures 2(a), 2(b) and 3(a) show that Mn^{2+} and Fe^{2+} are more effective than Mg^{2+} in reducing viscosity, and in fact Mg^{2+} and Mn^{2+} have opposite effects on viscosity of the CaO-SiO_2 system. In the case of Ca^{2+} and Pb^{2+}, both have similar size, but the measurements show that Pb^{2+} is more effective than Ca^{2+} in reducing viscosity (Figure 3(b)). It is considered that the melting point of the metal oxides (CaO, MgO, MnO, PbO and FeO) may be used as an indication of the strength of interaction between cations and anions in silicate melts. The trend shown in the systems concerned in the present study is that the addition of oxides with high melting point tends to cause viscosity increases, and vice versa. This can be explained as following. When fractions of M_2^{2+} cations are replaced by M_1^{2+} in the melts, especially by small amount, the changes in the structure regarding silicate anions are not expected to be great, thus the difference in viscosity caused by such replacement may be attributed mainly to the difference in the strength of the M^{2+}-O^{2-} interaction. Although a direct comparison of viscosity of the binary melts studied in the present work at certain temperature is not possible, the extrapolation of model calculation for different binary systems at 1573 K suggests the viscosity of the binary silicate melts follow the same trend as the melting point of the metal oxides. The fact that the present model can represent the trend found by the experiments reasonably accurately suggests that the contribution of each type of cations is proportional to their relative amount in the melts. When one oxide with high melting point (CaO) in the $CaO-SiO_2$ binary is substituted by low melting point MnO, the viscosity value of the ternary $CaO-MnO-SiO_2$ is in between these two binaries and a linear description of such combined effect seems to be acceptable.

4. CONCLUSION

The proposed structurally related model for the calculation of viscosity of silicate shows that the model can provide accurate representation of the experimental data for binary systems. The model also provides close representation of the viscosity of higher order system not only the values, but also the effect of different metal oxides as well, by using the binary parameters. The approach taken by the present modelling study allows close examination of the general behaviour of viscosity in relation with other physical and structural properties of the components.

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