STRUCTURE AND VISCOSITY OF ALUMOSILICATE MELTS CALCULATED FROM THE THERMODYNAMIC DESCRIPTION[1]

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Abstract

Silicate systems are of fundamental importance for many metallurgical processes for the glass industry and also for many aspects of geology. In addition to knowledge of the phase relations, there are many properties of the liquid phase such as molar volume, surface tension, absorption coefficient, thermal conductivity and viscosity that are important for understanding, simulating and modeling processes involving silicate liquids. Over the past several years, through critical evaluation of all available thermodynamic and phase equilibrium data, we have developed a quantitative thermodynamic description of multicomponent silicate melts using the Modified Quasichemical Model for short-range ordering. We find that the local structure of the liquid, in terms of the bridging behavior of oxygen, calculated using our thermodynamic description allows us to link the viscosity and the thermodynamics of the silicate liquid. We can thus simultaneously calculate phase relations, thermodynamics and viscosity of the liquid over a wide composition and temperature range. In the present work we outline the model using the SiO_2-Al_2O_3-CaO-MgO that is the most important system for metallurgical applications and the SiO_2-Al_2O_3-Na_2O system that is fundamental for the glass industry as examples.

Key words: Viscosity; Thermodynamic modeling; Silicates.

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INTRODUCTION

Viscosity is a dynamic property of practical and theoretical importance. An accurate knowledge of the viscosity of a wide variety of liquid slags is indispensable for understanding, simulating and modeling metallurgical processes. Viscosity is also a fundamental parameter for the glass industry. Modeling the viscosity of silicate melts is particularly challenging as it can increase by over twenty orders of magnitude at a constant temperature on increasing the SiO_2 content. The reason for this increase is rooted in the structure of silicate melts.

Recently a number of efforts have been published that try to correlate the viscosity of silicate melts with their structure as calculated from the thermodynamic description of the melt. Zhang and Jahanshahi[1] correlate the viscosity as a function of composition to the concentration of bridging, non-bridging and free oxygen as calculated from the cell model. Kondratiev *et al*.[2] use the quasichemical model to calculate the concentrations of Si-Si Me-Si and Me-Me next nearest neighbors that correspond to the concentrations of bridging, non-bridging and free oxygens respectively. They then also attempt to correlate the viscosity as a function of composition to the concentrations of the three types of oxygen. In both cases however it is found that the correlation between the concentration of the three types of oxygen and the viscosity is not a simple linear function but quadratic and even cubic terms are required to fit the experimental viscosity data. The resulting models are cumbersome and require a large number of parameters to fit the experimental data. It must therefore be concluded that it is in fact not the concentration of bridging oxygen that determines the viscosity of silicate melts. We thus developed a simple method of characterizing the connectivity of a silicate melt based on the concept of *Q*-species. The concentrations of *Q*-species are calculated using the concentration of bridging oxygens that are obtained from the thermodynamic description of the silicate systems using the quasichemical model.[3] We find a very simple correlation between the connectivity of the silicate melt and its viscosity resulting in a physically sound model that requires very few optimizing parameters and can easily be extended into multicomponent systems. Preliminary investigations have show that the model works well for the Li_2O-Na_2O-K_2O-MgO-CaO-CrO-MnO-FeO-Fe_2O_3-CoO-NiO-ZnO-PbO-Al_2O_3-SiO_2 system and work is in progress to include B_2O_3 in the description. In the present publication we outline the principles of the model using the experimentally well established CaO-MgO-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2 systems.

THE MODEL

Viscosity of the Unaries

The viscosity η as a function of temperature is given by a simple Arrhenius equation

$$\eta = A' \cdot e^{\left(\frac{E_a}{RT}\right)} \quad \text{and} \quad \ln(\eta) = A + \frac{E_a}{RT} \quad (1,\ 2)$$

If there are experimental data available for the unary system the pre-exponential term *A* and the activation for viscous flow E_a are fitted to the experimental data and are kept fixed when optimizing the multicomponent system. If there are no experimental data available the viscosities of the unaries are optimized using extrapolated binary viscosity data.

Characterization of the structure of the SiO_2 network

The Si^{4+} ions in silicate melts are always tetrahedrally bonded to four oxygen ions. On adding SiO_2 to basic MeO or Me_2O oxides the melt consists mainly of Me^{2+}, Me^{+}, O^{2-} and SiO_4^{4-} ions. Above the orthosilicate composition ($Me_2^{2+}SiO_4$) the SiO_4^{4+} tetrahedra start to polymerize first forming dimers, then trimers then even longer chains and rings. Eventually the rings and chains coalesce forming a three dimensional network. The structural change taking place in the SiO_2 network is best characterized by the concept of Q^i-species.[4] In the Q^i-notation the superscript *i* denotes the number of bridging oxygens per Si-ion. In pure SiO_2 all four oxygens surrounding each Si-ion are bridging oxygens. Thus the fraction of Q^4-species is 1. A Si-ion in a chain would be a Q^2-species as two of its four surrounding oxygens are bridging oxygens. The concentrations of Q^i-species in a melt (in situ measurement) or in a quenched glass can be determined using Raman spectroscopy or nuclear magnetic resonance (NMR) measurements as these spectra reveal the bonding characteristics of the Si-ion. Fig. 1 shows the experimentally determined fractions of Q^1, Q^2 and Q^3 for the CaO-SiO_2 system using Raman spectroscopy.[5] The quasichemical model[3] calculates the number of Me-Me, Me-Si and Si-Si second nearest neighbor pairs separated by an oxygen. The oxygen thus corresponds to the bond between the pairs. A Me-Me pair is separated by an O^{2-} anion a Me-Si pair is separated by a O^- singly bonded to one Si and a Si-Si pair is separated by an oxygen bridge. Thus the model calculates the fraction of free oxygen, broken bridges and bridged oxygen for any composition and therefore also the average number of bridging oxygens per Si-ion. We calculate the fractions of Q^i-species by applying a binomial distribution to the fraction of bridging oxygens per Si-ion.

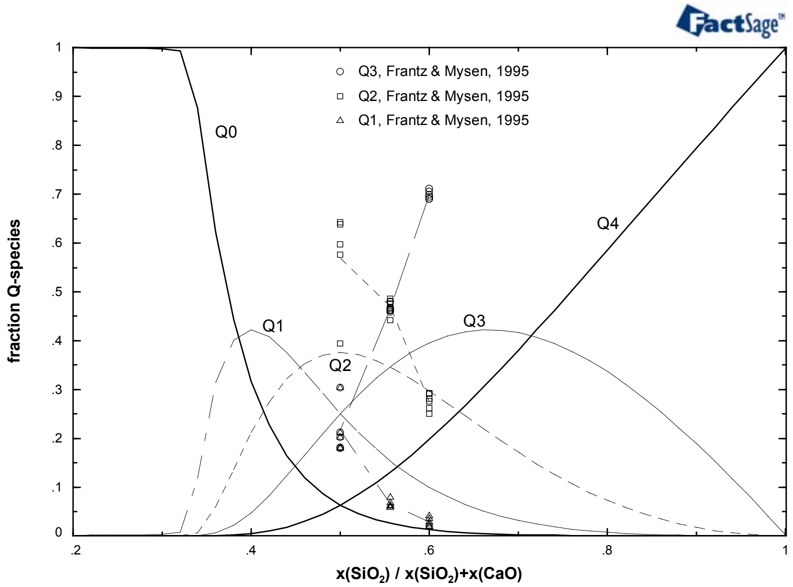

Figure 1. Calculated concentrations of *Q*-species compared to experimental values. The lines through the experimental points are to guide the eye.

For example if from the quasichemical model we calculate the fraction of bridging oxygens per Si-ion to be 0.6, then the number of non-bridging and free oxygens will be 0.4. The probability that this Si-ion will be a Q^0-species (i. e. be surrounded only be free oxygens or broken bridges) is then 0.4^4 the probability that it is a Q^1-species (i. e. one of its four surrounding oxygens is a bridging oxygen) is $4 \cdot 0.6 \cdot 0.4^3$ the probability that it is a Q^2-species is $6 \cdot 0.4^2 \cdot 0.6^2$ and so on. By a similar method we define a Q-species that we call "super Q^4" or Q^{S4}. This is a Q^4-species that is bonded exclusively to four other Q^4-species. The difference between Q^4 and Q^{S4} we call "Q^4 rest" or Q^{R4}. Q^{R4} thus comprises all the Q^4-species that are bonded to at least one Q^i-species that is not a Q^4. The assumption we are making in calculating the fractions of Q^i-species is that the bonds are statistically distributed. This might however not be the case as a certain Q^i-species could be statistically favored compared to the others. Figure 1 compares the calculated concentration of Q-species with the experimentally determined values from Frantz and Mysen.[5] It can be seen that there is at least a qualitative agreement between the calculated and experimentally determined curves, but our assumption of statistically distributed bonds might be an oversimplification. It must however also be mentioned that the experiments do not give absolute concentrations of the Q-species, but relative intensities of the spectra.

Modeling the viscosity of binaries without SiO_2 or Al_2O_3

The viscosities of MeO-MeO, MeO-Me_2O and Me_2O-Me_2O binary liquids are modeled to vary linearly as a function of mole fractions according to

$$\ln(\eta) = x_{\mathrm{MgO}}\left(A_{\mathrm{MgO}} + \frac{E_{a,\mathrm{MgO}}}{RT}\right) + x_{\mathrm{CaO}}\left(A_{CaO} + \frac{E_{a,\mathrm{CaO}}}{RT}\right) \qquad (3)$$

or

$$\ln(\eta) = x_{\mathrm{MgO}} \ln(\eta_{\mathrm{MgO}}) + x_{\mathrm{CaO}} \ln(\eta_{\mathrm{CaO}}) \qquad (4)$$

Modeling the viscosity of MeO-SiO_2 binaries

In our model we assume that the viscosity of pure SiO_2 has two contributions, η^* that is the hypothetical viscosity of SiO_2 if it would not form a network. This would correspond to a liquid consisting of only SiO_4^{4-} tetrahedra with no bridging oxygen. In addition there is a contribution to the viscosity, η^E due to the formation of the SiO_2 network. The sum of the two contributions $\eta^* + \eta^E$ is equal to the viscosity of pure SiO_2. The viscosity of basic silicate liquids up to the orthosilicate composition are again modeled to vary linearly as a function of mole fractions as

$$\ln(\eta) = x_{\mathrm{MeO}} \ln(\eta_{\mathrm{MeO}}) + x_{\mathrm{SiO_2}} \ln(\eta^*_{\mathrm{SiO_2}}). \qquad (5)$$

The value of η^* is identical for all binary silicate liquids. Above the orthosilicate composition the viscosity starts increasing due to the formation of a SiO_2 network. We characterize the formation of the network using the Q^{S4}-species and Q^{R4}-species defined above. For certain binaries such as Na_2O-SiO_2 and K_2O-SiO_2 the viscosity increases sharply almost proportional to the Q^{S4}-species indicating that the contribution to viscosity of all other Q^4-species is negligible, for other systems there is a varying influence of the other Q^4-species leading to a more gradual viscosity increase.

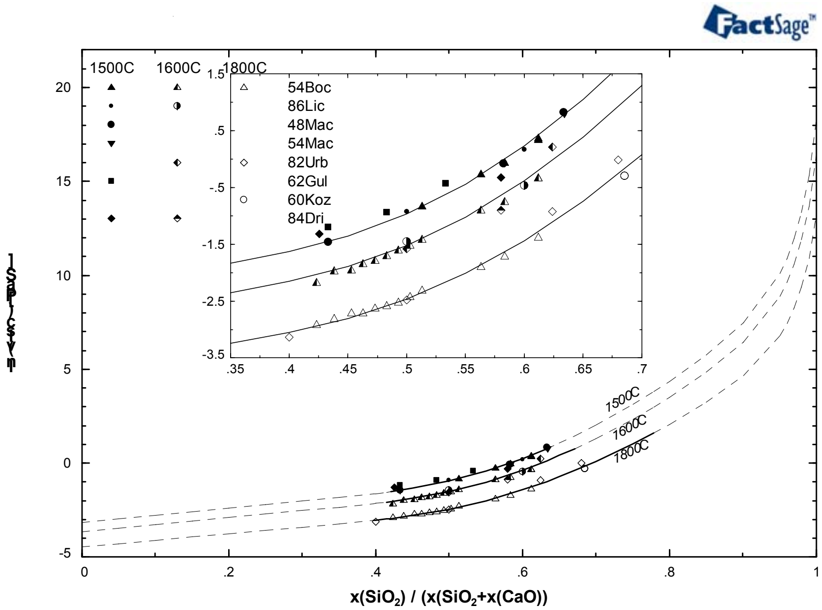

Figure 2. Calculated viscosity compared to experimental data for the CaO-SiO_2 liquid phase. The dashed lines are below the liquidus temperature.

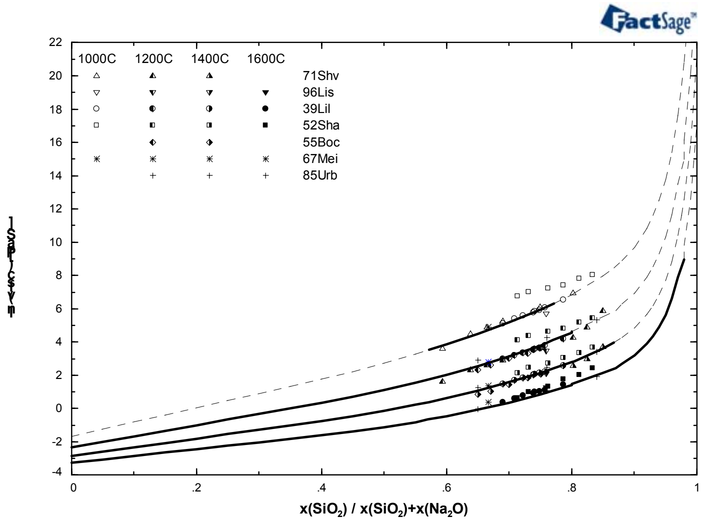

Figure 3. Calculated viscosity compared to experimental data for the Na_2O-SiO_2 liquid phase. The dashed lines are below the liquidus temperature.

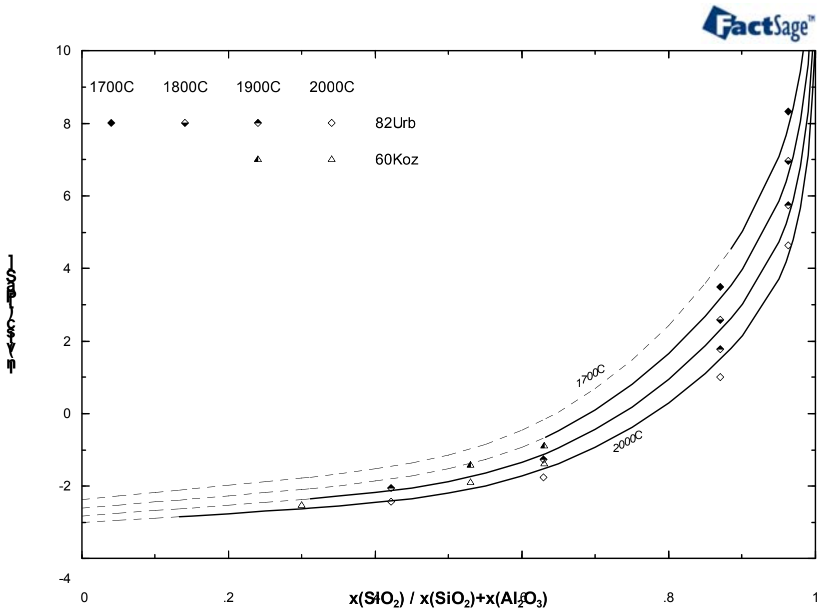

Figure 4. Calculated viscosity compared to experimental data for the Al_2O_3-SiO_2 liquid phase. The dashed lines are below the liquidus temperature.

These contributions are bunched together as arising from the concentration of all other Q^4-species that are not Q^{S4} (i. e. the Q^{R4}-species defined above) and are characteristic for every binary system. The viscosity of a binary MeO-SiO_2 system is thus given as

$$\ln(\eta) = x_{\mathrm{MeO}} \ln(\eta_{\mathrm{MeO}}) + x_{\mathrm{SiO_2}} \ln\left(\eta^{*}_{\mathrm{SiO_2}}\right) + x_{Q^{S4}} \ln\left(\eta^{E}_{\mathrm{SiO_2}}\right) + x_{Q^{R4}}\, x_{\mathrm{MeO}} \ln\left(\eta_{MeO-SiO_2}\right) \qquad (6)$$

The values of $\ln\left(\eta^{*}_{\mathrm{SiO_2}}\right)$ and $\ln\left(\eta^{E}_{\mathrm{SiO_2}}\right)$ are common for all binary liquids and their sum is equal to the viscosity of pure SiO_2. The value of $\ln\left(\eta_{MeO-SiO_2}\right)$ is characteristic for every binary and varies linearly as a function of x_{MeO} and is the only true binary parameter required to model the binary systems. The value of this parameter is optimized using the experimental data shown in Figures 2-4.

Modeling the viscosity of systems with Al_2O_3: the charge compensation effect

Al^{3+}-ions can behave in profoundly different ways in a silicate melt depending on the overall composition. When added to pure silica melt Al_2O_3 has a basic character and breaks the oxygen bridges of the pure silica network thereby substantially decreasing the viscosity as seen in figure 4. When equimolar amounts of MeO or Me_2O and Al_2O_3 are added some of the two Al^{3+}-ions can enter the liquid network in the tetrahedral coordination substituting for Si^{4+}-ions and can thus act as network formers. The two missing charges are compensated by the Me^{2+}-ion or two Me^{+}-ions that enter a mesh of the network and stay close to the Al^{3+}-ions. Due to this effect, also known as the charge compensation effect there is a maximum in the viscosity when the molar ratio of Al_2O_3:MeO or Me_2O is one as seen in Figures 5 and 6.

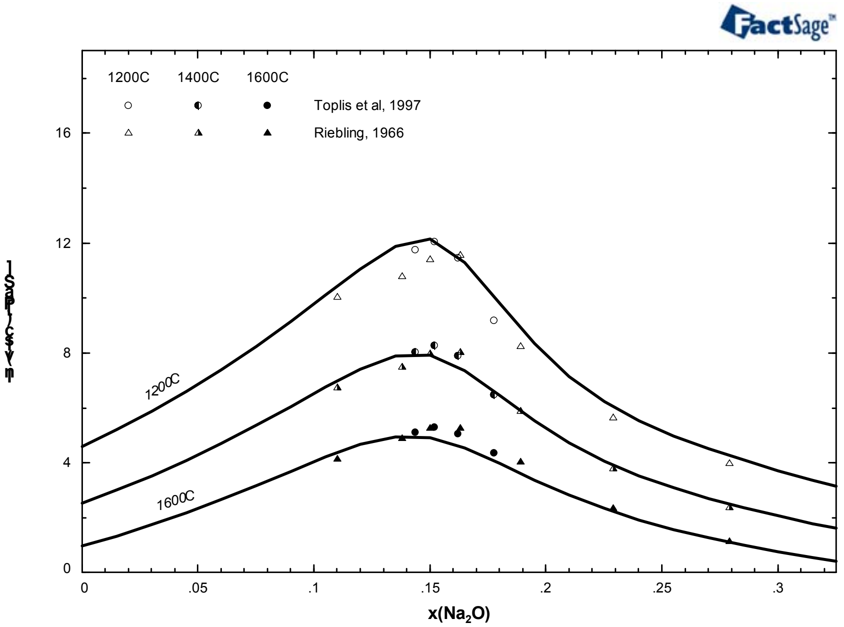

Figure 5. Calculated viscosity compared to experimental data for the Na_2O-Al_2O_3-SiO_2 liquid phase at 67.5 mol% SiO_2.

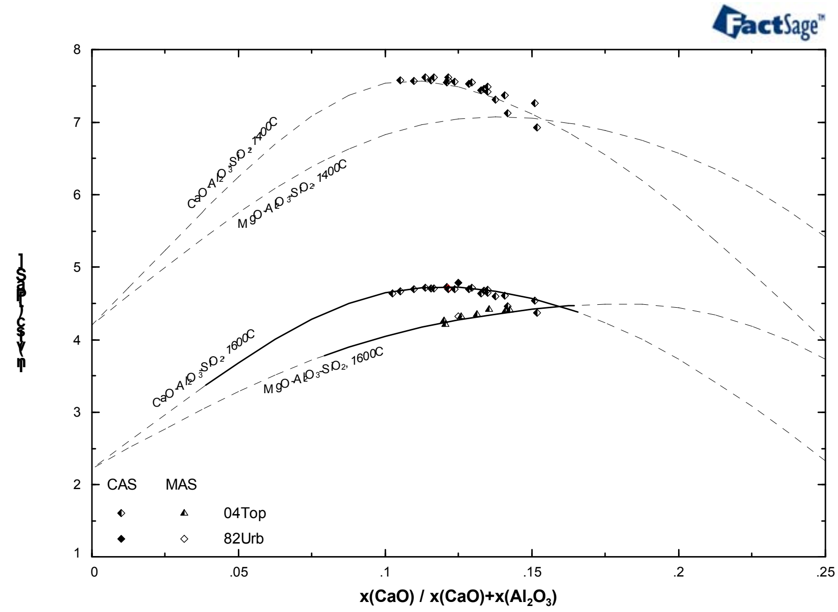

Figure 6. Calculated viscosity compared to experimental data for the CaO-Al_2O_3-SiO_2 and MgO-Al_2O_3-SiO_2 liquid phase at 75 mol% SiO_2.

The charge compensation effect has a substantial influence on the viscosity of the melts but has only a small influence on the thermodynamic properties of the SiO_2-Al_2O_3-MeO systems and is thus modeled using ternary interaction parameters in the current thermodynamic database without considering the variable coordination states of Al^{3+}. Therefore the thermodynamic description can not be used to predict the maximum in viscosity directly.

In this work we model the charge compensation effect by introducing the following equilibrium constants for the formation of tetrahedrally coordinated Al^{3+} in the liquid phase:

$$\mathrm{CaO} + \mathrm{Al_2O_3} = \mathrm{CaAl_2O_4}, K = \frac{[\mathrm{CaAl_2O_4}]}{[\mathrm{CaO}][\mathrm{Al_2O_3}]}, \Delta G_{CaAl2O4} = -RT\ln(K) \tag{7}$$

$$\mathrm{NaO_{1/2}} + \mathrm{AlO_{3/2}} = \mathrm{NaAlO_2}, K = \frac{[\mathrm{NaAlO_2}]}{[\mathrm{NaO_{1/2}}][\mathrm{AlO_{3/2}}]}, \Delta G_{\mathrm{NaAlO_2}} = -RT\ln(K). \tag{8}$$

The $NaSiO_2$ and $CaAl_2O_4$ or $MgAl_2O_4$ clusters, that each correspond to one or two tetrahedrally coordinated network forming Al^{3+}-ions respectively, are then assumed to have the same effect on the viscosity as if they were one or two Si^{4+}-ions. This idea is realized by assuming the viscosity in the SiO_2-Al_2O_3-MeO liquid varies linearly as a function of $x(\mathrm{MeO}) / (x(\mathrm{MeO}) + x(\mathrm{Al_2O_3}))$ for constant SiO_2 content, but the effective composition is displaced to higher SiO_2 content by the number of $NaAlO_2$ or twice the number of $MeAl_2O_4$ clusters formed according to the reactions above. The values of ΔG are optimized in order to reproduce the experimentally determined viscosity and can vary as functions of composition and/or temperature.

Optimization of viscosity parameters

While optimizing the viscosity parameters great care was taken to evaluate and assess the reliability of the experimental data. One important criterion turned out to be whether the experiment was conducted below the liquidus temperature or not. Often it is observed that the measured viscosity shows a strong deviation from Arrhenius behavior at low temperatures. The most likely explanation for this is that the sample started to crystallize while the viscosity was being measured. This tendency is particularly pronounced for compositions with low viscosity. We consequently rejected all experimental data that were measured more than 25ºC below the liquidus temperature as calculated from the FactSage oxide database. We give no numerical values for the viscosity parameters as the work is ongoing and the values might still change.

The viscosity of the unaries

The viscosity of pure Al_2O_3 and SiO_2 were fitted to the parameters A_{Al2O3}, A_{SiO2}, $E_{a,\mathrm{Al2O3}}$ and $E_{a,\mathrm{SiO2}}$ of the Arrhenius equation using the experimental data of Urbain.[6,7] Due to the extremely high melting temperatures of CaO and MgO and the reactivity of Na_2O no viscosity measurements exist. The viscosity parameters were thus obtained by extrapolating the viscosity data in the binary systems.

The viscosity of the binaries

The viscosity parameters A^{*}_{SiO2} and $E^{*}_{a,SiO2}$ of unassociated SiO_2 is optimized using all binary data simultaneously. The parameters for the excess viscosity are given as the difference between the parameters for the hypothetical viscosity of unassociated SiO_2 and the parameters for the experimentally determined pure SiO_2,

$$A^{E}_{SiO2} = A_{SiO2} - A^{*}_{SiO2},\ E_{a,SiO2} = E_{a,\ SiO2} - E^{*}_{a,\ SiO2}. \qquad (9)$$

The parameters giving the contribution to the viscosity of the Q^4-species that are not Q^{S4} and are characteristic for each binary are optimized using selected binary data. The viscosity parameters $A_{SiO2\text{-}Al2O3}$ and $E_{a,\ SiO2\text{-}Al2O3}$ are optimized using the experimental data from Urbain *et al.*[7] and Kotzakevitch,[8] the parameters $A_{SiO2\text{-}CaO}$ and $E_{a,\ SiO2\text{-}CaO}$ are optimized using the data from Machin *et al.,*[9-12] Bockris *et al.*,[13] Kotzakevitch,[8] Gul'tyai,[14] Urbain *et al.*[7] Varshal *et al.*,[15] Drissen *et al.*[16] and Licko and Danek.[17] The parameters $A_{SiO2\text{-}MgO}$ and $E_{a,\ SiO2\text{-}MgO}$ are optimized using the data from Machin *et al.*,[9-12] Bockris *et al.*,[13] Urbain *et al.*,[7] Licko and Danek,[17] Hofmann[18] and Kawai.[19] The parameters $A_{SiO2\text{-}Na2O}$ and $E_{a,\ SiO2\text{-}Na2O}$ are optimized using the data from Shvaiko-Shvaikovskaya *et al.*,[20] Lillie,[21] Bockris *et al.*[13] and Urbain.[22] The data from Shartsis *et al.* [23] are not used as they deviate from all other sets of data.

The viscosity of the ternaries with Al_2O_3 showing the charge compensation effect

The parameters for the charge compensation are the Gibbs energy for the formation of $NaAlO_2$, $CaAl_2O_4$ and $MgAl_2O_4$ clusters ΔG_{NaAlO2}, $\Delta G_{CaAl2O4}$ and $\Delta G_{MgAl2O4}$. The Al^{3+}-ions in these clusters are assumed to be network formers and thus increase the viscosity. The more negative the value of ΔG the more Al^{3+} enters the network and the more pronounced the viscosity maximum will be at the charge compensation composition. Technically the concentration of the clusters was calculated by modeling an ideal solution of the clusters and the oxide constituents. As the ΔG of formation of the clusters becomes more negative on increasing SiO_2 content an additional negative interaction parameter between the clusters and SiO_2 was modeled making the total number of parameters necessary to model the charge compensation effect equal to two. The values of ΔG of formation of the clusters and the interaction parameter were optimized using experimental viscosity data for the SiO_2-Al_2O_3-CaO and SiO_2-Al_2O_3-MgO systems taken from Urbain *et al.*[7] and Toplis and Dingwal.[24] For the system SiO_2-Al_2O_3-Na_2O the experimental viscosity data of Toplis *et al.*[25] and Riebling[26] was used. In the present work ΔG is assumed to be constant as function of temperature.

RESULTS AND DISCUSSION

Figures 2-4 compare the calculated viscosities with the experimental measurements for the binary liquids CaO-SiO_2, Na_2O-SiO_2 and Al_2O_3-SiO_2. The dotted line corresponds to calculated viscosities below the liquidus temperature. It can be seen that the composition range for which the curves are above the liquidus temperature and experimental data is available can be very limited. For modeling it is important that the model extrapolates well into regions where the liquid is metastable and no experimental data are available. It can also be seen that the viscosity range that needs to be modeled is vast, covering over 20 orders of magnitude. For the system Al_2O_3-SiO_2 the experiments by Urbain *et al.*[7] show that the viscosity drops by over 5 orders of magnitude on the addition of a mere 8 mol% Al_2O_3 to pure SiO_2. This is a very challenging behavior to reproduce properly. Interestingly neither Zhang and Jahanshahi[1] nor Kondratiev *et al.*[2] show how their model reproduces these data.

Figure 7 compares the calculated viscosity as a function of $x(SiO_2)$ in the CaO-MgO-SiO_2 liquid for a molar ratio of CaO:MgO =1 with experimental data. Figure 8 traces the calculated viscosity in the same system as a function of $x(CaO)$ for a constant value of $x(SiO_2)$ = 0.5.

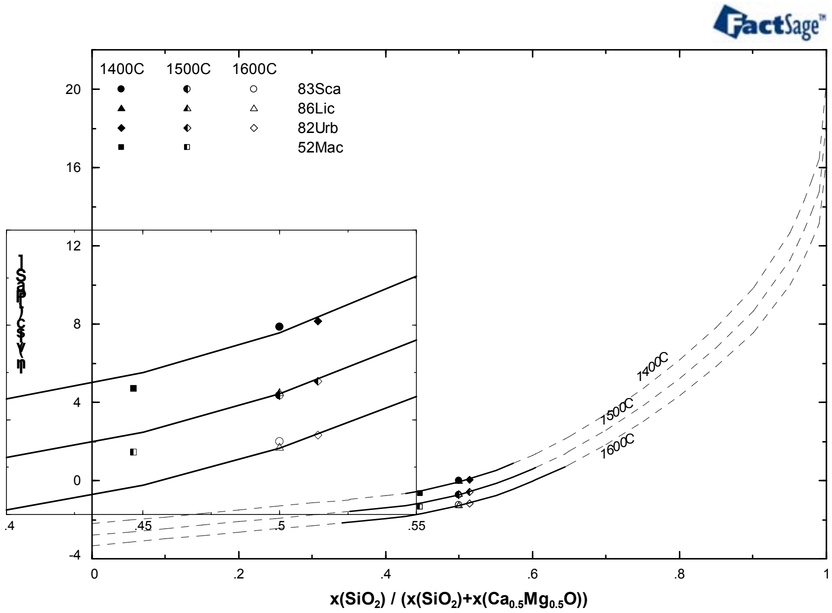

Figure 7. Calculated viscosity of the liquid phase compared to experimental data along the $Ca_{0.5}Mg_{0.5}O$-SiO_2 join. The dashed lines are below the liquidus temperature.

These figures show that the assumption that the viscosity varies linearly between CaO and MgO for constant SiO_2 and Al_2O_3 content is reasonable as the experimental data [7, 11,17,27] are reproduced to within experimental uncertainties. Figure 5 shows the viscosity in the SiO_2-Al_2O_3-Na_2O system at a constant SiO_2 content of 67.5 mol%. Figure 6 compares the viscosities in the ternary SiO_2-Al_2O_3-CaO and SiO_2-Al_2O_3-MgO liquids for a constant SiO_2 content of 75 mol% at 1400ºC and 1600ºC. In both cases the maximum in viscosity caused by the charge compensation effect is evident. The maximum is more pronounced for Na_2O than for both MgO and CaO indicating that the Na^+-ions are more effective at compensating the charges of the Al^{3+}-ions that substitute Si^{4+} in the network than the Me^{2+}-ions. This is reflected by a less negative value for the parameters $\Delta G_{MgAl2O4}$ and $\Delta G_{CaAl2O4}$ compared to ΔG_{NaAlO2}. The experimental data further show that the viscosity maximum is not strictly at the 1:1 composition and can have a different shape depending on the system. Our model reproduces both the asymmetry and the shape accurately, again indicating that the model truly reflects the structural changes taking place in the liquid that cause the viscosity maximum.

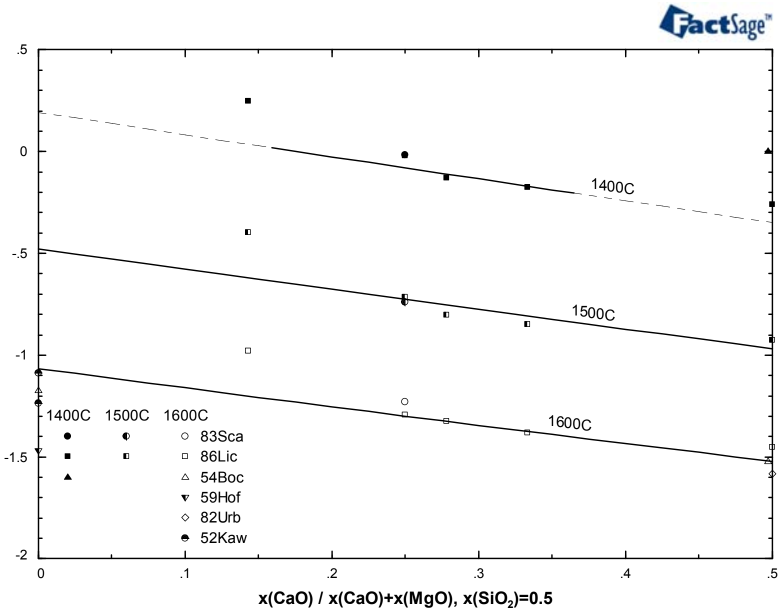

Figure 8. Calculated viscosity compared to experimental data for the CaO-MgO-SiO$_2$ liquid phase at 50 mol% SiO$_2$. The dashed lines are below the liquidus temperature.

CONCLUSIONS

A new model to predict the viscosity of multicomponent silicate liquids is presented. We try to characterize the structure of the liquid as accurately as necessary and then relate the viscosity to the structure. We find that there is a surprisingly simple link between the structure of the melt and its viscosity leading to a model in which every parameter has a clear physical meaning and is directly related to the structure of the melt. The model requires very few adjustable parameters, extrapolates well into composition regions where no experimental data are available and reliably predicts the viscosity of multicomponent liquids. We are currently testing the model for multicomponent silicate liquids with over ten components. Preliminary results are very promising.

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