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Composition Dependence of Viscosity in Binary Silicate Melts Using Double Exponential Function

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Development of a model for estimating the viscosity of a molten silicate is important because viscosity plays an important role in high-temperature processes. However, there is still much controversy with regard to the type of equation that is appropriate for expressing viscosity changes with changes in composition and temperature. In the present work, the composition dependence of viscosity for molten silicates in binary systems was investigated based on a double exponential function. The relationship between the double logarithm of viscosity, which is an inverse of a double exponential function, and the composition was clarified using the available experimental data. We found that the double logarithm of viscosity is linearly related to the composition in certain composition ranges. The double exponential function derived empirically by fitting it to the experimental data shows a reasonable viscosity dependence on composition and temperature. The linear relationship between the double logarithm of viscosity and the composition can be derived by assuming that the probability function of the occurrence of flow in a binary silicate melt has a Gumbel distribution.

KEY WORDS: viscosity; silicate; binary system; double exponential function; double logarithm; Gumbel distribution.

1. Introduction

The viscosities of molten silicate slags are important in high-temperature industrial processes. Many models for estimating the viscosities of molten silicates have therefore been developed to describe their composition and temperature dependences. However, there is still much controversy with regard to the type of equation that is appropriate for expressing abrupt and complicated viscosity changes with changes in composition and temperature. Arrhenius-type¹⁾ and Weymann-type equations²⁾ have mainly been used in models to express the composition and temperature dependences of viscosity.^{3–13)}

Arrhenius-type equation: $\eta = A \cdot \exp(B/T)$ (1)

Weymann-type equation: $\eta = A \cdot T \cdot \exp(B/T)$ (2)

here η is the viscosity, T is the temperature, and A and B are constants depending on the composition, or mutually connected parameters. Some researchers^{14–19)} have reported that the temperature dependence on viscosity for several liquids can be described with a double exponential function on the basis that the relationship between $\ln \eta$ and T is not linear over the whole temperature range. Waterton¹⁴⁾ established an empirical relationship between viscosity and temperature

in the case of glasses, as shown in Eq. (3).

$$\eta = A \cdot \exp(B \cdot \exp(C/T)/T) \text{ (3)}$$

where A , B , and C are constants. This equation gives an adequate representation of the viscosity–temperature relationship for soda-lime-silica glasses. From data on the temperature dependences of viscosity for several kinds of glasses and organic solvents, Jenckel¹⁵⁾ derived Eq. (4).

$$\eta = A \cdot \exp(C/T + B \cdot \exp(C/T)/T) \text{ (4)}$$

Here, A , B , and C are constants. Equation (4) is based on the following concept. There are active molecules and inactive molecules in the system. The movement of active molecules causes viscous flow. In the range of the linear relationship between $\ln \eta$ and T , active molecules can move about in the liquid. In contrast, in the range where the viscosity depends strongly on temperature, *i.e.*, where the viscosity increases sharply, the active molecules are surrounded by inactive molecules and cannot move freely; only neighboring active molecules can move each other to cause viscous flow. Bradbury *et al.*¹⁶⁾ obtained an empirical equation for describing the relationship between viscosity and temperature in lubricating oils:

$$\eta = A \cdot \exp(B \cdot \exp(C/T)) \text{ (5)}$$

where A , B , and C are constants that fit the viscosity data for oils.

Gross and Zimmermann^{17–19)} assumed that the clustered inactive molecules were separated from one another by

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zones of activated molecules in the structure of a generalized liquid, and represented the viscosity in terms of the size of inactive clusters. By evaluating the number of molecules occupying an edge of such an inactive cluster as the cluster size based on the fraction of inactive molecules, Eq. (6) for variations in liquid viscosities with temperature was derived.

$$\eta = A \cdot \exp(B \cdot (1 - \exp(-C/T))^{1/3} / (1 - (1 - \exp(-C/T))^{1/3})) \dots\dots\dots (6)$$

A , B , and C in Eq. (6) are specific constants for each substance. This equation can be used for a wide variety of liquids such as paraffins (C_nH_{2n+2} ; $1 < n < 20$), H_2O , H_2SO_4 , P , Br_2 , 2-propanone, and n -eicosane. Recently, Hui and Zhang²⁰⁾ have tried to extend a double exponential function to develop an empirical viscosity formulation for describing the viscosity dependences on temperature and composition for natural silicate melts:

$$\eta = \exp(A + B/T + \exp(C + D/T)) \dots\dots\dots (7)$$

where A , B , C , and D are fitting parameters, and all parameters vary linearly with the mole fractions of oxide components (X_i , X_j , X_k , ...), e.g., $A = A_iX_i + A_jX_j + A_kX_k + \dots$. Although double exponential functions are used in the expression for the change in viscosity with not only temperature but also composition, it is still not unclear how the double exponential function actually describes the composition dependences of viscosity for molten silicates.²⁰⁾

In the present work, therefore, we systematically investigated changes in viscosity with composition in the SiO_2 - M_xO_y system with the assumption that the viscosity varies as a double exponential function of composition in order to clarify the potential of double exponential functions to adequately represent the composition dependences of viscosity in silicate melts. In addition, a statistical approach was used to try to understand the relationship between viscosity and double exponential functions.

2. Viscosity Data for Binary Silicate Melts

The viscosity data for the binary silicate melts used in this study are summarized in **Table 1**. The targeted binary silicate systems are SiO_2 - MgO ,²¹⁻²³⁾ SiO_2 - CaO ,²²⁻²⁵⁾ SiO_2 - SrO ,²¹⁻²³⁾ SiO_2 - BaO ,²¹⁻²³⁾ SiO_2 - Li_2O ,²¹⁾ SiO_2 - Na_2O ,^{21,26)}

SiO_2 - K_2O ,^{21,26)} SiO_2 - Al_2O_3 ,^{23,27)} and SiO_2 - PbO .²⁸⁻³⁰⁾ The composition ranges, temperature ranges, and numbers of data are shown in the table.

3. Results

In this study, the relationship between viscosity and composition was evaluated using the double logarithm of viscosity instead of the double exponential function for composition, since the inverse of a double exponential function is a double logarithm. First, the temperature dependence of viscosity for a pure SiO_2 melt was examined to confirm the temperature dependence of viscosity using a double exponential function. The relationship between the double logarithm of viscosity and the inverse of temperature is shown in **Fig. 1**.³¹⁻³⁷⁾ The double logarithm of viscosity has a reasonable proportional relationship with the inverse of temperature. This shows that a double exponential function would be suitable for describing the viscosity variations in a pure SiO_2 melt with temperature as previously reported.¹⁴⁻²⁰⁾ The double logarithm of viscosity in several binary silicate systems is plotted against the inverse of temperature in **Fig. 2**. The relationship between the double logarithm of viscosity and the inverse of temperature shows a linear relation in all systems. As well as pure SiO_2 , therefore, a double exponential function would be applied to express the temperature dependence of viscosity in binary silicate melts. **Figures 3–11** show the relationship between the double logarithm of

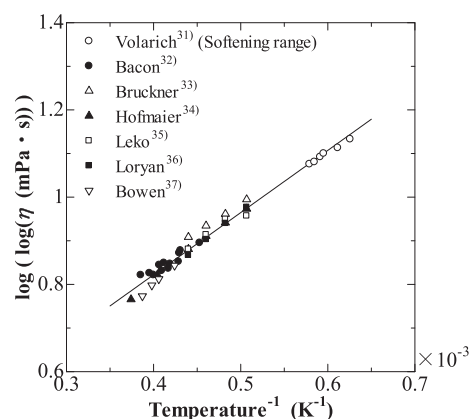


Fig. 1. Viscosity of pure SiO_2 .

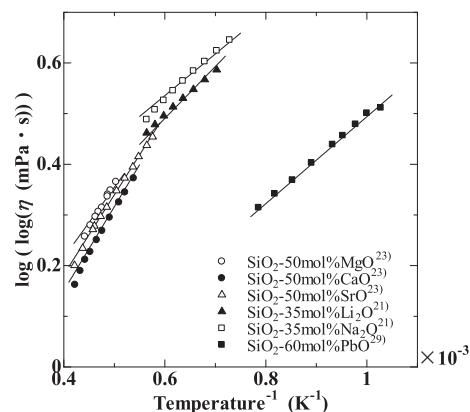


Fig. 2. Temperature dependence of viscosity of binary silicate melts.

Table 1. Viscosity data for molten binary silicates: composition ranges, temperatures, and numbers of data.

| System | Composition range | Temperature (K) | Date number | Reference |
|---------------------|----------------------------------|-----------------|-------------|-----------|
| SiO_2 - MgO | $0.414 \leq X_{MgO} \leq 0.651$ | 1823–2073 | 56 | 21–23) |
| SiO_2 - CaO | $0.3 \leq X_{CaO} \leq 0.6$ | 1723–2073 | 158 | 22–25) |
| SiO_2 - SrO | $0.254 \leq X_{SrO} \leq 0.503$ | 1823–2073 | 43 | 21–23) |
| SiO_2 - BaO | $0.2 \leq X_{BaO} \leq 0.5$ | 1773–2073 | 49 | 21–23) |
| SiO_2 - Li_2O | $0.2 \leq X_{Li_2O} \leq 0.55$ | 1423–1923 | 61 | 21) |
| SiO_2 - Na_2O | $0.15 \leq X_{Na_2O} \leq 0.44$ | 1373–2023 | 154 | 21, 26) |
| SiO_2 - K_2O | $0.108 \leq X_{K_2O} \leq 0.414$ | 1373–2023 | 135 | 21, 26) |
| SiO_2 - Al_2O_3 | $0.5 \leq X_{Al_2O_3} \leq 0.8$ | 1973–2373 | 48 | 23, 27) |
| SiO_2 - PbO | $0.35 \leq X_{PbO} \leq 0.75$ | 923–1573 | 172 | 28–30) |

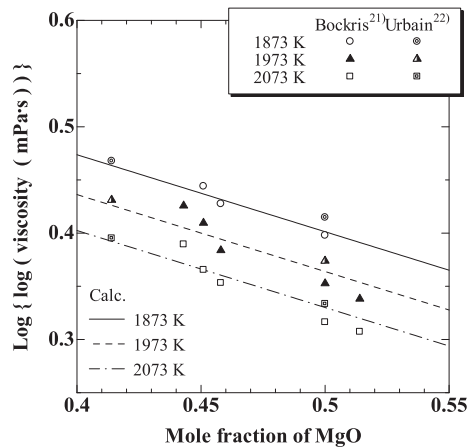


Fig. 3. Viscosity of SiO₂-MgO melt. Lines are calculated based on Eq. (8).

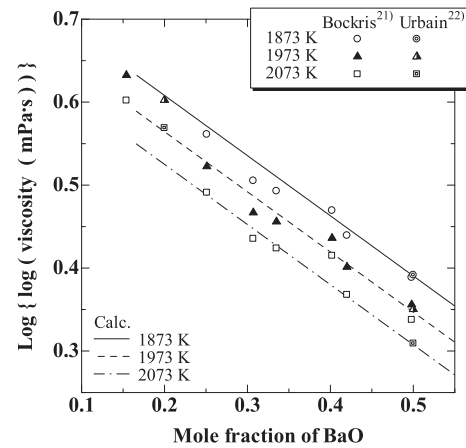


Fig. 6. Viscosity of SiO₂-BaO melt. Lines are calculated based on Eq. (8).

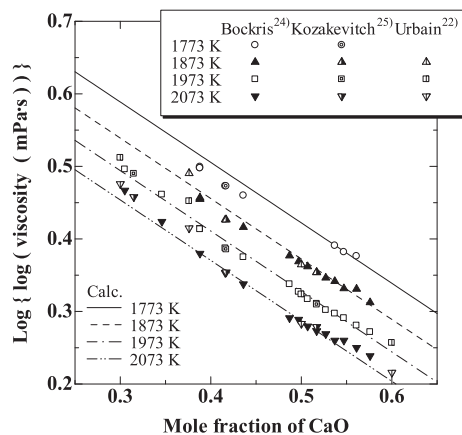


Fig. 4. Viscosity of SiO₂-CaO melt. Lines are calculated based on Eq. (8).

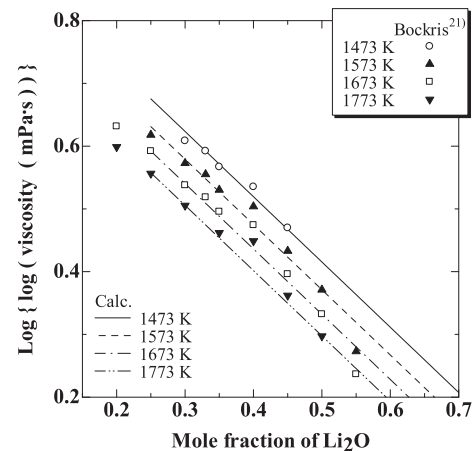


Fig. 7. Viscosity of SiO₂-Li₂O melt. Lines are calculated based on Eq. (8).

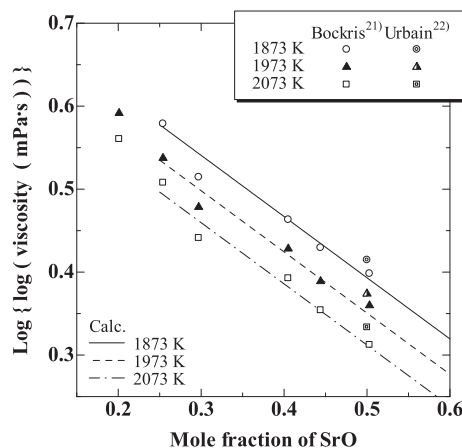


Fig. 5. Viscosity of SiO₂-SrO melt. Lines are calculated based on Eq. (8).

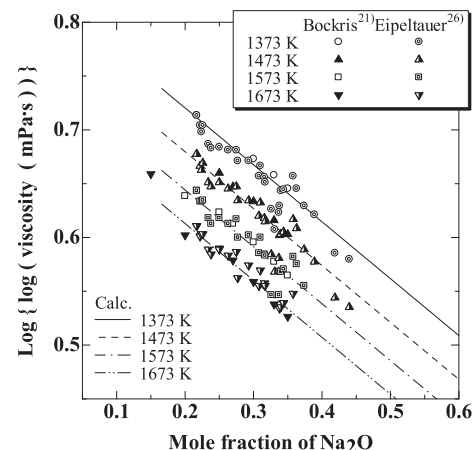


Fig. 8. Viscosity of SiO₂-Na₂O melt. Lines are calculated based on Eq. (8).

viscosity and composition in molten binary SiO₂-M_xO_y systems (M_xO_y = MgO, CaO, SrO, BaO, Li₂O, Na₂O, K₂O, Al₂O₃, or PbO). In the alkaline-earth-metal silicate melts (SiO₂-M_xO_y; M_xO_y = MgO, SrO, BaO) except for the SiO₂-CaO melt, it is difficult to discuss the composition dependence of the viscosity because of the small numbers of data and narrow composition ranges as shown in Figs. 3, 5, and 6. In contrast, the SiO₂-CaO system in Fig. 4 shows a linear relationship between the double logarithm of viscosity and

the content of CaO in this composition range at each temperature as shown by the data on the composition-dependent viscosity of this system reported by Bockris *et al.*²¹⁾ The amounts of data available for alkali-metal silicate melts (SiO₂-M_xO_y; M_xO_y = Li₂O, Na₂O, K₂O) are relatively high compared with those available for alkaline-earth-metal silicate melts. The double logarithm of viscosity has a linear relationship with composition as seen in Figs. 8 and 9,

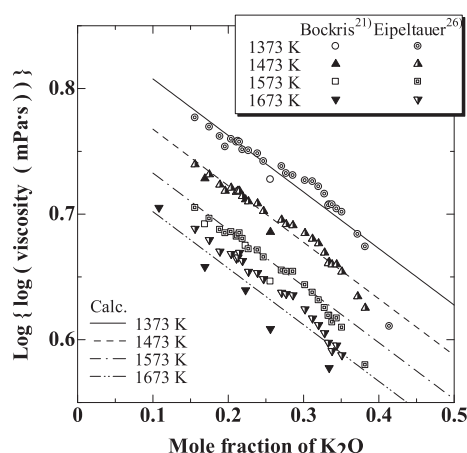


Fig. 9. Viscosity of $\text{SiO}_2\text{-K}_2\text{O}$ melt. Lines are calculated based on Eq. (8).

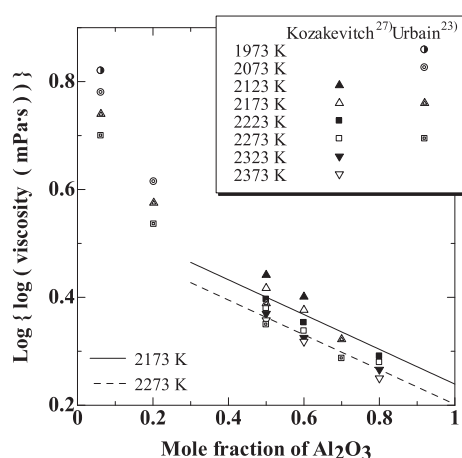


Fig. 10. Viscosity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ melt. Lines are calculated based on Eq. (8).

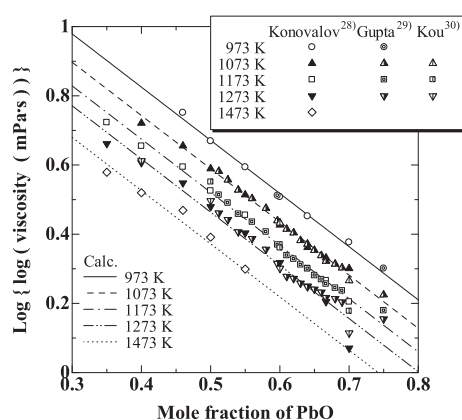


Fig. 11. Viscosity of $\text{SiO}_2\text{-PbO}$ melt. Lines are calculated based on Eq. (8).

although there are variations among the data. In contrast, the amount of data for the $\text{SiO}_2\text{-Li}_2\text{O}$ system is too small to show the dependence of viscosity with composition. There is no linear relationship between the double logarithm of viscosity and composition in the aluminosilicate melt ($\text{SiO}_2\text{-Al}_2\text{O}_3$) in Fig. 10. Konovalov *et al.*²⁸⁾ and Gupta *et al.*²⁹⁾ have reported large amounts of viscosity data over wide composition and temperature ranges for the binary SiO-PbO melt (Fig. 11). At each temperature, the double

logarithm of viscosity shows a linear relationship with the PbO content in the composition range. These results show that the double exponential function can describe the composition dependence of viscosity in certain composition regions in some binary silicate systems with a linear relationship.

4. Discussion

4.1. Composition Region where a Linear Relationship Describes the Double Exponential Function

We found that the double logarithm of viscosity shows a reasonable linear relationship with the inverse of temperature in a pure SiO_2 melt; the viscosity is also linearly related with the composition at each temperature in some of the binary silicate systems. However, there is a problem with these two findings. The viscosity of a pure SiO_2 melt extrapolated from the linear relationship based on the binary silicate data is not consistent with the data for a pure SiO_2 melt. For example, the value extrapolated from the linear relationship at 1873 K in the $\text{SiO}_2\text{-CaO}$ system in Fig. 4 is about 0.8 for the double logarithm of viscosity, but the estimated value at 1873 K for pure SiO_2 is about 1 as shown in Fig. 1. The extrapolated value from the data at 1373 K in the $\text{SiO}_2\text{-K}_2\text{O}$ system in Fig. 9 is about 0.85, but is estimated to be about 1.3 from the data for pure SiO_2 . The extrapolated value for the $\text{SiO}_2\text{-PbO}$ system at 973 K in Fig. 11 and the value derived for pure SiO_2 are about 1.4 and 1.7, respectively. These differences mean that the composition region where a linear relationship can be applied is limited. Here, we investigate the width of the composition range in which a linear relationship applies by considering the relationship between the composition of the complex oxide in the binary silicate system and the structure of the silicate melt, and the effect on the viscosity.

It is well known that viscosity variations of silicate melts are largely attributed to the structural features of the melt. In particular, it is emphasized that the three-dimensional random network structure of a silicate melt, which consists of bonded SiO_4^{4-} units, causes abrupt variations in viscosity. These SiO_4^{4-} units are connected with each other through bridging oxygen atoms, *i.e.*, the vertex oxygens in tetrahedral structures of SiO_4^{4-} units. When a basic oxide such as CaO or Na_2O is added to pure SiO_2 in a binary silicate system, the network structures are partially cut off by oxygen ions from the basic oxide. This cutting-off of the network structure causes a corresponding decrease in the viscosity of the silicate melt. In contrast, because the complex oxide is a crystalline solid, the constituent anions and cations are arranged in an orderly, repeating arrangement extending in all three spatial dimensions. Although a melt and a crystalline complex oxide are in different states (liquid or solid), when discussing viscosity it is reasonable to suppose that the characteristics of the solid reflect those of the liquid to some degree, especially in the case of a compound with congruent melting, which predicts that the bonds between anions and cations are strong. From this viewpoint, the silicate melt no longer maintains its network structure at the composition where the first complex oxide with congruent melting appears in the solid state in a binary silicate system when an oxide is added to pure SiO_2 . It is well known that

the three dimensional network are totally fractured at the composition of 66.6 mol% oxide (alkaline oxide and alkaline earth oxide) in binary silicate systems when considering SiO_4^{4-} as a unit anion. On the other hand, Bockris *et al.*²¹⁾ mentioned that the three dimensional network bonding can disappear at the composition less than 66.6 mol% oxide by postulating the existence of discrete anions like $(\text{Si}_3\text{O}_9)^{6-}$, $(\text{Si}_6\text{O}_{15})^{6-}$, $(\text{Si}_9\text{O}_{21})^{6-}$ and $(\text{Si}_{12}\text{O}_{27})^{6-}$, which are larger than SiO_4^{4-} . The theory suggested by Bockris *et al.* supports the structural change described in the present work. It is therefore expected that there will be large variations in the composition-dependent viscosities associated with structural changes in a silicate melt in a composition between pure SiO_2 and a complex oxide with congruent melting closest to that of pure SiO_2 . The complex oxides with congruent melting points closest to that of pure SiO_2 in each binary $\text{SiO}_2\text{--M}_x\text{O}_y$ system are summarized in Table 2;³⁸⁾ these are $2\text{MgO}\cdot\text{SiO}_2$, $\text{CaO}\cdot\text{SiO}_2$, $\text{SrO}\cdot\text{SiO}_2$, and $\text{BaO}\cdot 2\text{SiO}_2$ for the alkaline-earth-metal silicate group, $\text{Li}_2\text{O}\cdot\text{SiO}_2$, $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$, and $\text{K}_2\text{O}\cdot 4\text{SiO}_2$ for the alkali-metal silicate group, $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ in aluminosilicate, and $\text{PbO}\cdot\text{SiO}_2$ in the $\text{SiO}\text{--PbO}$ system. These results suggest that the stoichiometric proportion of the complex oxide depends on the system, and even in the same group the stoichiometric proportions are different. In addition, it is found that the SiO_2 content of a complex oxide increases down the group in both the alkaline-earth-metal silicates and alkali-metal silicates. Based on the above assumption that there are great variations in the composition dependences of viscosities between pure SiO_2 and complex oxides, a shift in the stoichiometric proportion of a complex oxide means a shift in the composition, at which the composition dependence of the viscosity changes significantly, in the same silicate group. This shift can be observed in the composition dependence of activation energy for viscous flow in binary silicate melts as shown in Fig. 12.³⁹⁾ The activation energy for viscous flow decreases with adding the alkali-metal oxides and the alkaline-earth-metal oxides. Concerning the composition dependence of the activation energy, Mackenzie made a common curve drawn by a solid line in each silicate group, *i.e.* the alkaline-earth-metal silicates or alkali-metal silicates. In the alkali-metal silicates, it is noticed that there is a difference between the

trends of activation energy change with composition for alkali-metal silicates when looking at the composition dependence of activation energy in each alkali-metal oxide in greater detail. The trend of activation energy change with composition for each alkali-metal silicate is expressed as a dashed-two dotted line in $\text{SiO}_2\text{--Li}_2\text{O}$ system, a dashed-dotted line in $\text{SiO}_2\text{--Na}_2\text{O}$ system or a dashed line in $\text{SiO}_2\text{--K}_2\text{O}$ system. Here, the composition dependence of the activation energy significantly changes in $\text{SiO}_2\text{--K}_2\text{O}$ system at the higher SiO_2 content than in $\text{SiO}_2\text{--Na}_2\text{O}$ system. And the significant change occurs in $\text{SiO}_2\text{--Na}_2\text{O}$ system at the higher SiO_2 content than in $\text{SiO}_2\text{--Li}_2\text{O}$ system. This order is in good agreement with the order of complex oxides with a congruent melting closest to pure SiO_2 in the alkali-metal silicates ($\text{K}_2\text{O}\cdot 4\text{SiO}_2 > \text{Na}_2\text{O}\cdot 2\text{SiO}_2 > \text{Li}_2\text{O}\cdot\text{SiO}_2$). On the other hand, it is difficult to mention the trend in the alkaline-earth-metal silicates because of the narrow range of composition for activation energy data in each system. At this stage, however, it is impossible to decide exactly which composition shows a large change in the composition dependence of viscosity in each binary system. We therefore simply assume that the composition dependence of the viscosity changes at the medium composition between pure SiO_2 and the complex oxide with a congruent melting point closest to pure SiO_2 , and a linear relationship between the double logarithm of viscosity and composition is available in the range between this medium composition and pure M_xO_y ($\text{M}_x\text{O}_y = \text{MgO}, \text{CaO}, \text{SrO}, \text{BaO}, \text{Li}_2\text{O}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{Al}_2\text{O}_3$, or PbO) in each binary $\text{SiO}_2\text{--M}_x\text{O}_y$ system. Table 2 shows this composition range for each system.

In order to clarify the potential of linear relationships based on the double logarithm of viscosity and composition, we investigated the applicability of the empirical Eq. (8) to viscosity for binary silicate melts in the composition ranges shown in Table 2.

$$\log(\log \eta) = A + B \cdot X_{\text{M}_x\text{O}_y} + C/T \quad \text{..... (8)}$$

where A , B , and C are specific constants for each binary silicate melt. This equation was derived based on the facts that the double logarithm of viscosity shows a reasonable linear relationship with the inverse of temperature in binary silicate melts, and, in addition, it is linearly related to the composition at each temperature in some binary silicate systems

Table 2. Complex oxide with congruent melting point closest to that of pure SiO_2 in each binary system, composition range satisfying a linear relationship, number of target data, and error.

| System | Complex oxide | Composition range (linear) | Data number | Δ (%) |
|---------------------------------------|---|--|-------------|--------------|
| $\text{SiO}_2\text{--MgO}$ | $2\text{MgO}\cdot\text{SiO}_2$ | $1/3 \leq X_{\text{MgO}} \leq 1$ | 56 | 8.6 |
| $\text{SiO}_2\text{--CaO}$ | $\text{CaO}\cdot\text{SiO}_2$ | $1/4 \leq X_{\text{CaO}} \leq 1$ | 158 | 13.4 |
| $\text{SiO}_2\text{--SrO}$ | $\text{SrO}\cdot\text{SiO}_2$ | $1/4 \leq X_{\text{SrO}} \leq 1$ | 40 | 13.6 |
| $\text{SiO}_2\text{--BaO}$ | $\text{BaO}\cdot 2\text{SiO}_2$ | $1/6 \leq X_{\text{BaO}} \leq 1$ | 46 | 21.3 |
| $\text{SiO}_2\text{--Li}_2\text{O}$ | $\text{Li}_2\text{O}\cdot\text{SiO}_2$ | $1/4 \leq X_{\text{Li}_2\text{O}} \leq 1$ | 55 | 17.6 |
| $\text{SiO}_2\text{--Na}_2\text{O}$ | $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ | $1/6 \leq X_{\text{Na}_2\text{O}} \leq 1$ | 143 | 18.4 |
| $\text{SiO}_2\text{--K}_2\text{O}$ | $\text{K}_2\text{O}\cdot 4\text{SiO}_2$ | $1/10 \leq X_{\text{K}_2\text{O}} \leq 1$ | 128 | 21.4 |
| $\text{SiO}_2\text{--Al}_2\text{O}_3$ | $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ | $3/10 \leq X_{\text{Al}_2\text{O}_3} \leq 1$ | 32 | 16.1 |
| $\text{SiO}_2\text{--PbO}$ | $\text{PbO}\cdot\text{SiO}_2$ | $1/4 \leq X_{\text{PbO}} \leq 1$ | 172 | 15.4 |

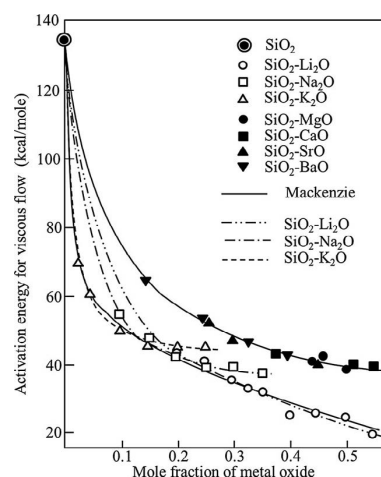


Fig. 12. Activation energy for viscous flow in binary silicate melts.³⁹⁾

Table 3. Parameters A , B and C in the equation: $\log(\log \eta) = A + B \cdot X_{M_xO_y} + C/T$. Units of η and T are mPa·s and K, respectively.

| System | A | B | C |
|--|---------|--------|------|
| SiO ₂ –MgO | 0.0246 | –0.724 | 1383 |
| SiO ₂ –CaO | –0.0946 | –0.833 | 1655 |
| SiO ₂ –SrO | –0.0790 | –0.738 | 1575 |
| SiO ₂ –BaO | –0.107 | –0.725 | 1612 |
| SiO ₂ –Li ₂ O | 0.240 | –1.04 | 1025 |
| SiO ₂ –Na ₂ O | 0.227 | –0.523 | 822 |
| SiO ₂ –K ₂ O | 0.263 | –0.450 | 809 |
| SiO ₂ –Al ₂ O ₃ | –0.292 | –0.322 | 1855 |
| SiO ₂ –PbO | 0.559 | –1.54 | 857 |

as mentioned above. The calculation results obtained by fitting Eq. (8) to the silicate viscosity data are shown in Figs. 2–11. The fitting parameters A , B and C obtained here are summarized in **Table 3**. The calculated lines are drawn for the composition ranges in Table 2. The fitted lines are in good agreement with the temperature dependency and the composition dependency of the experimental data for all binary systems including the SiO₂–Al₂O₃ system, which does not show any linear relationship in the composition range before the composition range is limited. The relative differences, Δ ,⁴⁰⁾ among the calculated and experimental data, as defined below, are shown in Table 2.

$$\Delta = 1/N \cdot \sum |\eta_{\text{cal}} - \eta_{\text{exp}}| / \eta_{\text{exp}} \cdot 100 \quad (\%) \quad \text{..... (9)}$$

Here, η_{cal} and η_{exp} are the calculated and measured viscosities, respectively, and N is the number of data. The relative difference, Δ , is within 20% in almost all systems, which is acceptable for prediction of viscosity, considering the reported experimental uncertainties of 30%. These results confirm that the double exponential function can represent a reasonable estimation of viscosity in molten binary SiO₂–M_xO_y systems in which the M_xO_y content is higher than the medium composition between pure SiO₂ and the complex oxide with the congruent melting point closest to that of SiO₂.

4.2. Double Exponential Function for Viscosity of Silicate Melts

A double exponential function is generally given by Eq. (10).

$$f(x) = a^{b^x} \quad \text{..... (10)}$$

Equation (11) is known as a Gumbel distribution.^{41,42)}

$$F(x) = \exp\{-\exp(-(x-A)/B)\} \quad \text{..... (11)}$$

$F(x)$ is a cumulative frequency distribution, x is a variable, and A and B are constants. The Gumbel distribution is also called the Fisher–Tippett Type I distribution of extreme values. Extreme value analysis is used in probability theory and statistics to model the distribution of the maximum, or the minimum, of a number of samples with various distributions.^{43,44)} Extreme value distributions for maximums have been used to predict river flooding, earthquakes, and other natural disaster, and maximum corrosion pit depths in mate-

rials. The Gumbel distribution in Eq. (11) can be used to determine maximum value probability distributions such as these. The distributions of minimum values have been used to investigate areas such as the strengths of materials and their reliability in engineering. Viscosity is defined as the inverse of the probability function of the occurrence of flow. Here, we assumed that the probability function is a function of the content of oxide M_xO_y in a molten binary SiO₂–M_xO_y system, and the probability function of the occurrence of flow conforms to the Gumbel distribution. The viscosity of a binary silicate melt is represented by the following equation:

$$\eta = C / F(X_{M_xO_y}) = C \cdot \exp\{\exp(-(X_{M_xO_y} - A)/B)\} \quad \text{..... (12)}$$

C is a constant. The double natural logarithm of viscosity, based on Eq. (12), is

$$\ln(\ln \eta / C) = -(X_{M_xO_y} - A)/B \quad \text{..... (13)}$$

This equation shows a linear relationship between the double natural logarithm of viscosity divided by the constant C , and the content of M_xO_y; this is quite similar to Eq. (8), which is empirically derived based on experimental data. This result means that the probability function of the occurrence of flow in a binary silicate melt in the composition range shown in Table 2 is expressed by an extreme value distribution for the maximum. This kind of estimation using a statistical or stochastic approach does not directly describe actual features of the viscosities of silicate melts. However, it is very useful for reviewing the viscosity of a molten silicate based on a statistical or stochastic approach in order to link an experimentally obtained viscosity with that estimated using a model, since such models are still controversial issues in this field.

5. Conclusions

The composition dependences of viscosity in molten silicates in binary systems were investigated based on a double exponential function. We clarified the relationship between the double logarithm of viscosity and the composition using the available experimental data. From this relationship, it was found that the double logarithm of viscosity is linearly related to composition in certain composition ranges.

We tried to derive the double exponential equation for the composition to describe the viscosity empirically using the experimental data. This equation reasonably expresses the dependence of viscosity on composition and temperature. By assuming that the probability function of the occurrence of flow in a binary silicate melt is a Gumbel distribution, it is possible to obtain the linear relationship between the double logarithm of viscosity and the composition.

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