Molecular structure, configurational entropy and viscosity of silicate melts: Link through the Adam and Gibbs theory of viscous flow

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ABSTRACT

The Adam and Gibbs theory depicts the viscous flow of silicate melts as governed by the cooperative re-arrangement of molecular sub-systems. Considering that such subsystems involve the silicate Q^n units (n = number of bridging oxygens), this study presents a model that links the Q^n unit fractions to the melt configurational entropy at the glass transition temperature T_g, $S^{conf}(T_g)$, and finally, to its viscosity η. With 13 adjustable parameters, the model reproduces η and T_g of melts in the Na_2O-K_2O-SiO_2 system (60 ≤ [SiO_2] ≤ 100 mol%) with 1σ standard deviations of 0.18 log unit and 10.6°, respectively.

The model helps understanding the links between the melt chemical composition, structure, S^{conf} and η. For instance, small compositional changes in highly polymerized melts generate important changes in their $S^{conf}(T_g)$ because of an excess of entropy generated by mixing Si between Q^4 and Q^3 units. Changing the melt silica concentration affects the Q^n unit distribution, this resulting in non-linear changes in the topological contribution to $S^{conf}(T_g)$. The model also indicates that, at [SiO_2] ≥ 60 mol%, the mixed alkali effect has negligible impact on the silicate glass Q^n unit distribution, as corroborated by Raman spectroscopy data on mixed Na-K tri- and tetrasilicate glasses. Such model may be critical to link the melt structure to its physical and thermodynamic properties, but its refinement requires further high-quality quantitative structural data on silicate and aluminosilicate melts.

1. Introduction

Silicate melts are important material for both Earth and material sciences. Indeed, they played a crucial role in the geologic history of the Earth, being important carriers of heat and matter between the Earth mantle, crust and surface. For instance, the dynamic and thermodynamic properties of the silicate melt composing the Earth primordial magma ocean, present right after Earth accretion, controlled the magma ocean evolution, and, as a result, the differentiation of the Earth mantle and crust [1]. Nowadays, we observe the influence of the viscosity η of magmas on the dynamic of volcanic eruptions, through the effects of η on magma mobility, degassing behavior and probability to fragment [2,3]. Therefore, as the magma chemical composition dictates the melt thermodynamic and rheological properties [4–6], it is heavily correlated to volcanic eruptive styles. In addition, silicate melts are the source of glass and glass ceramic materials that are produced in the industry and used in a broad variety of technological applications. As a result, understanding how the intimate links between melt composition and

molecular structure dictate melt physico-chemical properties is a corner stone for Earth and Material sciences.

The viscosity η of silicate melts is a complex function of the temperature T, the melt chemical composition X, and the pressure P. T and X strongly affect η, leading to changes of several orders of magnitude (Fig. 1). P has a much smaller importance [7–9]. As a result, existing models aiming at predicting the viscosity of silicate melts mostly rely on linear or non-linear relationships between X, T and η [4,10–14], with some exceptions that also try to take into account the effect of P [15]. Linear models focus on predicting η at high temperature, for $10^0 < \eta < 10^6$ Pa s. Indeed, in this narrow range, η variations can be approximated as being linear as a function of T and X [e.g., [4,10]]. For $\eta > 10^6$ Pa s, the X-T-η relationship becomes strongly non-linear, and, hence, prevents the use of such linear models. The viscosity of natural molten rocks frequently is higher than 10^6 Pa s during eruptive processes. As a result, several models from the geoscience community, such as for example those of Giordano et al. [13] and Hui and Zhang [12], link X, T and η with using a parametrization of the Tammann-Vogel-Fulcher equation $\log \eta = A + B / (T - C)$, where A, B and C are fitting parameters that can be expressed as complex non-linear functions of melt composition. Such models can allow successful predictions within the X-T-η domain they were constrained. However, they have poor extrapolation
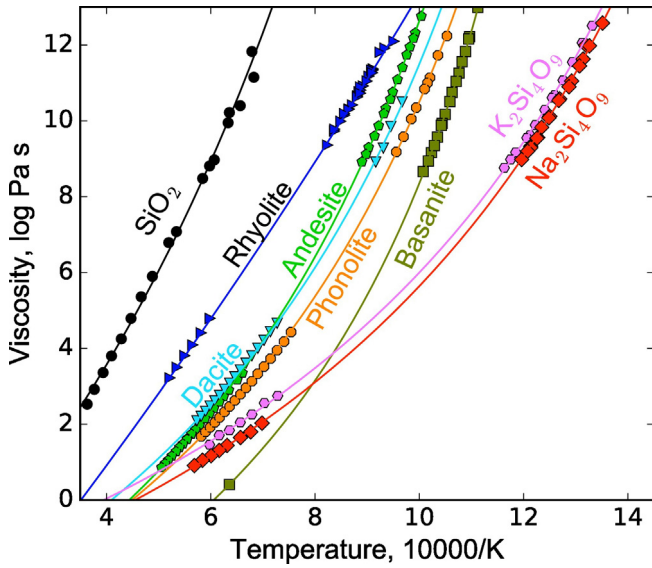
Fig. 1. Viscosity (log Pa s) of various silicate melts as a function of the inverse of temperature (10,000/K). Origin of the data are: SiO_2 from [6,74]; Rhyolite from [120]; Dacite from [121]; Andesite from [122]; Phonolite from [123,124]; Basanite from [125]; $K_2Si_4O_9$ and $Na_2Si_4O_9$: see Table 2.

abilities, and further lack a strong physical background. From the glass science community, other models have been proposed and are based on different ways to link X, T and η, with using, for instance, the MYEGA [see [14,16] and references cited therein] or the Avramov-Milchev [see [15,17,18] and references cited therein] equations. The latter models are based on different theories of the viscous flow of silicate melts, and, hence, have the advantage to have a physical background. A discussion of such theories is out of the scope of the present study, such that we refer the reader to those publications, and to the other theories listed in [19] for instance, for further documentation. In all cases, all the above cited models have achieved variable success in linking X, T and η. However, up to this date and to the knowledge of the authors, none has linked spectroscopic observations of the structure of silicate melts to their thermodynamic and rheological properties. The establishment of such model can allow improving our knowledge, understanding and prediction abilities of the structure and the properties of silicate melts.

In such context, the Adam and Gibbs theory of relaxation of liquids [20] provides a useful framework that allows relating η (Pa s) to the melt configurational entropy $S^{conf}(T)$ (J mol^{-1} K^{-1}) [5]:

$$\log(\eta) = A_e + \frac{B_e}{T S^{conf}(T)}, \tag{1}$$

with A_e a pre-exponential term corresponding to a high-temperature viscosity limit, B_e (J mol^{-1}) a constant proportional to the potential barrier opposed to the cooperative rearrangement of the liquid structure and T the melt temperature (K). This theory successfully relates the viscosity of silicate melts to their measurable thermodynamic properties [5,21]. Indeed, in Eq. (1), $S^{conf}(T)$ is equal to:

$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^{T} \frac{C_p{}^{conf}}{T} dT, \tag{2}$$

with

$$C_p{}^{conf}(T) = C_{pl}(T) - C_{pg}(T_g). \tag{3}$$

In Eq. (2), $S^{conf}(T_g)$ is the configurational entropy of the supercooled liquid at the glass transition temperature T_g. It actually corresponds to the residual entropy of the glass at 0 K that can be determined from

calorimetry data for compositions that melt congruently [5]. At this point, we should warn the reader that the concept that glasses have a residual entropy at 0 K still is a matter of debate [see [22–24] and references cited therein]. In the case of supercooled liquids, $S^{conf}(T_g)$ is a real thermodynamic parameter that can be linked to changes in the liquid structure at T_g, as shown by several experimental studies [e.g., [25–28]]. In Eq. (3), $C_p{}^{conf}(T)$, $C_{pl}(T)$, and $C_{pg}(T_g)$ respectively are the liquid configurational heat capacity at T, the liquid heat capacity at T, and the glass heat capacity at T_g. $C_{pl}(T)$ and $C_{pg}(T_g)$ are measurable quantities, and models exist to predict them as a function of the glass and melt chemical composition [29–32]. $C_{pl}(T)$ and $C_{pg}(T_g)$, and, hence, $C_p{}^{conf}(T)$ vary linearly as a function of chemical composition. As a result, η tends to vary linearly with melt composition at high temperature because the $\int_{T_g}^{T} \frac{C_p{}^{conf}}{T} dT$ term in Eq. (2) is more important than $S^{conf}(T_g)$. At low temperatures, close to T_g, $S^{conf}(T_g) > \int_{T_g}^{T} \frac{C_p{}^{conf}}{T} dT$. In this case, as $S^{conf}(T_g)$ varies non-linearly depending on melt composition, η also is a complex function of melt composition.

With using measured heat capacity values and calorimetry-derived $S^{conf}(T_g)$ values, Richet [5] showed that Eq. (1) reproduces well the viscosity variations of SiO_2, $NaAlSi_3O_8$, $KAlSi_3O_8$ and $CaAl_2Si_2O_8$ melts. Furthermore, considering $S^{conf}(T_g)$ as an adjustable parameter, Eq. (1) can be applied to model the viscosity of various silicate melts and to determine $S^{conf}(T_g)$ [5,21,26,28,33–35]. Eq. (1) also allows modeling the viscosity depletion resulting from the mixing of K and Na in silicate melts [5] (Fig. 2), and of Ca and Mg in silicate and aluminosilicate melts [21]. To do so, $S^{conf}(T_g)$ is calculated as the sum of topological and chemical contributions [36,37]:

$$S^{conf}(T_g) = S^{topo} + S^{mix}. \tag{4}$$

The topological S^{topo} and chemical S^{mix} contributions to $S^{conf}(T_g)$ arise from the disorganized distribution of tetrahedral species with various
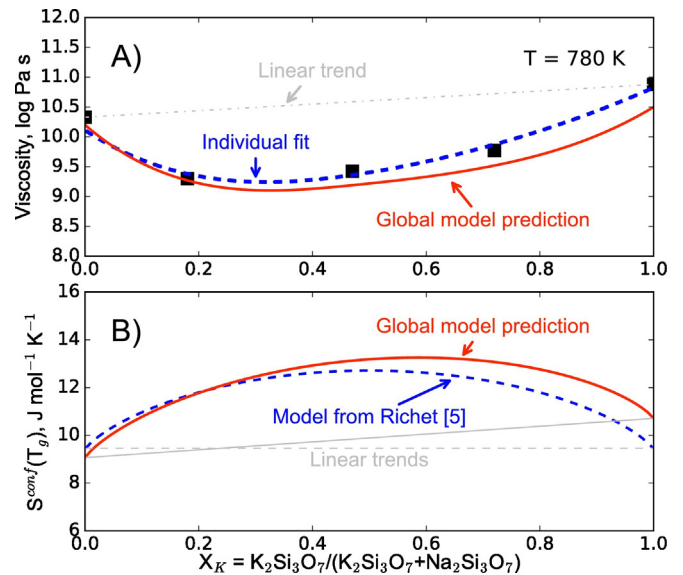
Fig. 2. A) Viscosity at 780 K and B) configurational entropy at the glass transition temperature T_g of $(Na_{(1-X_K)}K_{X_K})_2Si_3O_7$ melts, as a function of their $X_K = K/(K + Na)$ ratio. The Mixed Alkali Effect is marked by the maximum and minimum in $S^{conf}(T_g)$ and viscosity, respectively. In A), the black squares are viscosity data from [95,96], the red line is the prediction from the global model presented in this study, and the blue dotted line represents a local model obtained from an individual fit of only the $(Na_{(1-X_K)}K_{X_K})_2Si_3O_7$ melt data, with considering A_e and B_e as adjustable parameters and modeling $S^{conf}(T_g)$ as done in Richet [5]. In B), the blue dotted line shows the latter $S^{conf}(T_g)$ model, while the red line shows the prediction from the global model presented in this study. Linear trends between the endmembers are indicated by grey lines as visual guidelines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)