

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

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The rheological and thermodynamic properties of silicate melts played a crucial role in the formation and the evolution of the Earth. For instance, they influenced the evolution of a plausible primordial magma ocean, and, as a result, the differentiation of the Earth mantle and crust. Further, they control the dynamic of volcanic eruptions. Because of that, modelling the viscosity or the heat capacity of silicate melts is crucial in order to model the physical processes they are involved in.

The Adam and Gibbs theory of viscous flow offers a thermodynamic framework that assumes that the viscosity η (Pa s) at a temperature T (K) of a melt can be expressed as:

$$\log(\eta) = A_e + \frac{B_e}{TS^{conf}(T)} \quad (1)$$

with A_e a pre-exponential constant related to the viscosity at infinite temperature, B_e (J mol^{-1}) a constant proportional to the potential energy barrier opposed to the cooperative rearrangement of the liquid structure and $S^{conf}(T)$ ($\text{J mol}^{-1} \text{ K}^{-1}$) the melt configurational entropy. With expressing $S^{conf}(T)$ as the sum of the residual entropy of the glass and of the variation in melt configurational heat capacity, it is possible to link existing thermodynamic and viscosity data for melts with various chemical composition, *e.g.*, SiO_2 , $\text{NaAlSi}_3\text{O}_8$ or $\text{CaAl}_2\text{Si}_2\text{O}_8$. Further, it also is possible to describe the viscosity variation induced by mixing Ca and Mg or Na and K in silicate melts, under the assumption that such mixing produces an ideal excess entropy of mixing.

An interesting point in the Adam and Gibbs framework is that it assumes that viscous flow occurs through the cooperative re-arrangement of molecular sub-regions in the melt. From high temperature ^{29}Si NMR and Raman spectroscopy data, it actually is known that viscous flow occurs because of the cooperative exchange of oxygen atoms between tetrahedral SiO_2 units, allowing their motions. Therefore, it is tempting to link such structural knowledge to heat capacity and viscosity data through the use of equation 1.

In this communication, it is shown that such link is possible. By expressing the residual entropy of the glass as the sum of partial molar entropies of tetrahedral SiO_2 units, with known quantities from ^{29}Si NMR spectroscopy, and of a semi-ideal mixing of Na and K, it is possible to model the variations of the configurational entropy with chemical composition. The model reproduces the variations of the viscosity of melts with a standard deviation of 0.2 log unit in the $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$ ternary system, for SiO_2 contents between 60 and 100 mol% SiO_2 . Such model opens new pathways in order to build semi-empirical viscosity models that provide structural, thermodynamic and rheological information about silicate melts.