Adam-Gibbs theory and the prediction of glass transition temperatures: the join $Na_2Si_2O_5$-$NaAlSi_2O_6$

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The viscosity of silicate melts is a parameter of extreme importance, not only in the Earth sciences, but also in a number of applied disciplines such as glass, and steel making. Empirical predictive models of melt viscosity proposed in the geological literature (e.g. Bottinga and Weill 1972), have been shown to be reliable at temperatures well above the glass transition, but these models do not take good account of non-Arrhenain behaviour, and extrapolation to temperatures close to the glass transition can lead to significant errors in estimated viscosity. In contrast to these empirical approaches, various attempts have made to quantitatively link viscosity to some structural property of the melt. Of these, the Adam-Gibbs theory (Adam and Gibbs, 1965) which considers viscosity to be related to the configurational entropy of the melt, has been shown to be particularly successful in accounting for non-Arrhenian variations of viscosity of molten silicates with temperature (Richet, 1984; Bottinga *et al.*, 1995). Despite this fact, the Adam-Gibbs (A-G) theory has not yet been used in a predictive sense, due to highly non-linear variations of the A-G parameters (A_e, B_e, temperature independent constants, $S_c(T_g)$, the configurational entropy at the glass transition) as a function of composition, even along simple pseudo-binary joins, (e.g. $CaSiO_3$-$MgSiO_3$, Neuville and Richet, 1991).

Compositional dependence, and parameterisation of the A-G parameters

As discussed by Toplis (1998), consideration of the A-G theory shows that non-linearities in the A-G parameters are to be expected due to the presence of terms involving the configurational entropy. However, the ratio of parameters B_e and $S_c(T_g)$ should show simpler variations as a function of composition, because terms involving the configurational entropy cancel out. The expression for the ratio $B_e/S_c(T_g)$ is:

$$Be/Sc(Tg) = z^*(Tg)\ \Delta\mu/k \qquad (1)$$

where $z^*(T_g)$ is the size of the rearranging domains at the glass transition (i.e. the number of particles per domain), $\Delta\mu$ is the average height of the potential energy barriers to viscous flow, and k is Boltzmann's constant. Toplis (1998) evaluated the variations of the ratio $B_e/S_c(T_g)$ for a number of simple silicate and aluminosilicate compositions. It was found that $B_e/S_c(T_g)$ shows simple compositional variations, directly proportional to those which may be qualitatively expected for the height of the potential energy barrier to viscous flow, suggesting that $z^*(T_g)$ may be a constant for all compositions. Based upon these observations a parameterisation of the variations in $B_e/S_c(T_g)$ was proposed within the physical framework of equation 1, assuming that $z^*(T_g)$ is a constant. In this parameterisation each viscous flow mechanism has an associated value of $B_e/S_c(T_g)$. Endmember values were determined for mechanisms involving K, Na, Ca and Mg as network modifying cations, as well as for the mechanism occurring in pure SiO_2, and that involving aluminate tetrahedra (i.e. that occurring in fully polymerised aluminosilicates).

$Na_2Si_2O_5$-$NaAlSi_2O_6$ join

Even though many of the important endmember values of $B_e/S_c(T_g)$ have been determined, extension of this analysis to melts of geological relevance requires a better understanding of the variation of $B_e/S_c(T_g)$ for compositions where more than one viscous flow mechanism occurs. In particular, data is missing for compositions where both network modifying cations and aluminate tetrahedra occur. The join $Na_2Si_2O_5$-$NaAlSi_2O_6$, with a constant silica content of 67 mol%, is ideally suited for this purpose. Viscous flow for $Na_2Si_2O_5$ may be expected to occur exclusively through a mechanism involving network modifying sodium, whereas viscous flow in $NaAlSi_2O_6$ will be dominated by a mechanism involving aluminate tetrahedra. Viscosity data for compositions along the join $Na_2Si_2O_5$-$NaAlSi_2O_6$ have been combined with calorimetric data to estimate the variation of $B_e/S_c(T_g)$ along this join, shown in Fig. 1.

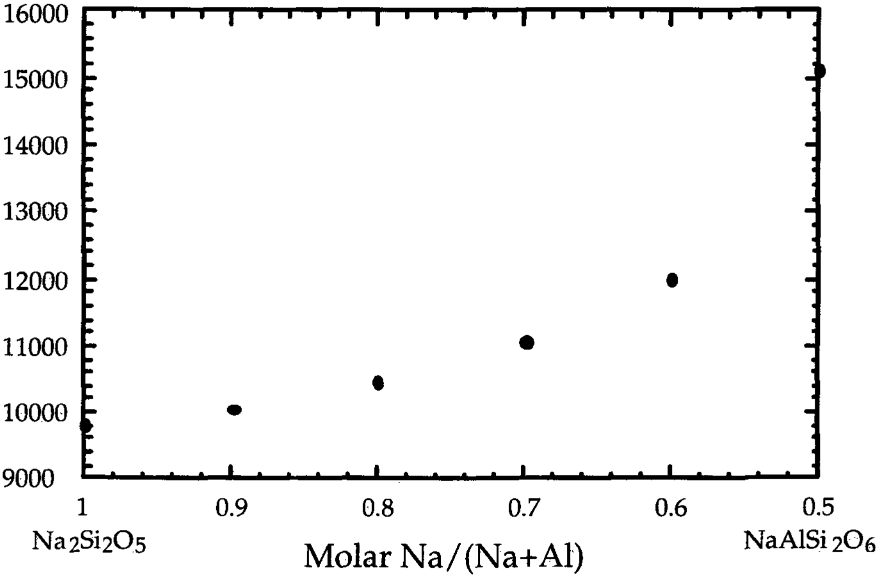

FIG. 1. Variation of $B_e/S_c(T_g)$ along the join $Na_2Si_2O_5$-$NaAlSi_2O_6$.

One observes that the ratio $B_e/S_c(T_g)$ shows a smooth variation between the endmember values, implying that the average energy barrier to viscous flow of intermediate compositions is some simple combination of those of the endmembers. However, this intermediate variation is non-linear, showing little change as a function of Na/(Na+Al) for depolymerised compositions, and the greatest change close to the metaluminous join. This may be qualitatively understood by the fact that for intermediate compositions the lower energy mechanism is favoured (i.e. that involving network modifying sodium). Further analysis is clearly required to explain the details of this intermediate variation in terms of the microscopic mechanisms leading to viscous flow.

Concluding remarks

If it is assumed that the glass transition temperature (T_g) occurs when viscosity reaches a value of 10^{12} Pa s it may be simply shown that:

$$T_g = [B_e/S_c(T_g)][1/(12 - A_e] \tag{2}$$

Therefore, calculation of T_g requires estimation of the ratio $B_e/S_c(T_g)$ and A_e, the latter term having an approximately constant value of -2.5 ± 1 (Toplis, 1998). The smooth variation of $B_e/S_c(T_g)$ observed along the join $Na_2Si_2O_5$-$NaAlSi_2O_6$ supports the idea that parameterisation of this ratio in terms of the average potential energy barrier to viscous flow represents a promising framework for the prediction of glass transition temperatures, which may in time be applied to more complex geological melts. Although calculation of the whole viscosity curve using the A-G theory requires knowledge of the absolute value of $S_c(T_g)$ rather than just the ratio $B_e/S_c(T_g)$, calculated glass transition temperatures may be combined with existing models for viscosities in the range $10-10^5$ Pa s (e.g. Bottinga and Weill, 1972), interpolation providing the whole viscosity curve, and thus also an estimate of the departure from Arrhenian behaviour.

References

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