

Quantitative links between microscopic properties and viscosity of liquids in the system $\text{SiO}_2\text{--Na}_2\text{O}$

Michael J. Toplis*

CRPG-CNRS, BP20, F-54501 Vandoeuvre-lès-Nancy, France

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Abstract

The Adam–Gibbs theory of structural relaxation is presented in terms of the microscopic parameters controlling viscous flow; $\Delta\mu$, the energy barrier hindering rearrangement of a single silicate monomer, and z^* the number of monomers that must simultaneously overcome their barrier in order for a change in configuration to occur. Independent viscosity, calorimetric and spectroscopic data for glasses and melts in the system $\text{SiO}_2\text{--Na}_2\text{O}$ are used to show that z^* at the glass transition has a value of approximately 10 for all of the compositions considered and that microscopic energy barriers are on the order of several tens of kJ per mole of silicon. Furthermore, the variation of configurational entropy of glasses in the system $\text{SiO}_2\text{--Na}_2\text{O}$ has been determined from the viscosity and calorimetric data. It is concluded that a stable melt complex with a stoichiometry close to $\text{Na}_2\text{Si}_3\text{O}_7$ exists and that medium range order plays an important role in determining the configurational entropies, although the details are unclear. Overall, a self-consistent picture of the quantitative links between microscopic and macroscopic properties is determined for this simple system, providing an encouraging first step towards a fully generalisable predictive model for silicate melt viscosity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $\text{SiO}_2\text{--Na}_2\text{O}$; Microscopic properties; Silicate melt viscosity

1. Introduction

The ability to predict the viscosity of silicate melts as a function of composition and temperature is essential for modelling magmatic processes such as convection in crustal magma chambers or explosive volcanism, as well as determining the viability of an increasing number of industrial processes in-

volving silicate melts. The importance of a predictive model in the Earth sciences was recognised by Bottinga and Weill (1972) and Shaw (1972) who proposed empirical equations valid at temperatures well above the glass transition. Although these equations have proven to be extremely useful, they predict Arrhenian behaviour of viscosity as a function of temperature whereas it has become increasingly clear that over large temperature ranges viscosity is generally non-Arrhenian (see Richet and Bottinga, 1995). Understanding the microscopic origins of this behaviour is an important step towards a predictive model for shear viscosity of molten silicates that

* Tel.: +33-3-83-59-42-12; fax: +33-3-83-51-17-98.
E-mail address: mtoplis@crpg.cnrs-nancy.fr (M.J. Toplis).

requires integrating physical property measurements and information available from spectroscopic and calorimetric studies. Although most melts of geological interest are chemically complex with at least 10 oxide components, one must initially consider simple systems in order to understand the underlying structure–property relations. The system $\text{SiO}_2\text{--Na}_2\text{O}$ is particularly suitable for this purpose as there are numerous viscosity data (e.g. Knoche et al., 1994; Poole, 1948; Bockris et al., 1956), calorimetric data (Richet et al., 1984), spectroscopic studies of glasses (e.g. Brawer and White, 1975; Brandriss and Stebbins, 1988) and in-situ studies at high temperature (Stebbins et al., 1995; Mysen and Frantz, 1994), as well as computer simulations of melt structure and dynamics (Soules, 1979; Zotov and Keppler, 1998). Furthermore, compositions along this join cover the range of polymerisation state observed in natural silicate liquids.

2. The Adam–Gibbs relaxation theory

2.1. The link between viscosity and configurational entropy

The Adam and Gibbs (A–G) theory (Adam and Gibbs, 1965; Richet, 1984; Bottinga and Richet, 1996) relates viscosity to the configurational entropy of the liquid through the equation:

$$\ln \eta = A_e + B_e / TS_{c(T)} \quad (1)$$

where η is the viscosity, $S_{c(T)}$ is the configurational entropy of the liquid at absolute temperature T , and A_e and B_e are constants, independent of temperature but dependent on composition (note that the suffix *e* is used to denote that calculated values of viscosity are on a \ln_e scale rather than \log_{10}). Eq. (1) is of interest because if the ‘configurational’ contribution to the liquid heat capacity (C_p^{conf}) can be estimated, then the configurational entropy of the liquid can be calculated at any temperature using Eq (2):

$$S_{c(T)} = S_{c(T_g)} + \int_{T_g}^T \frac{C_p^{\text{conf}}}{T} dT \quad (2)$$

where $S_{c(T_g)}$ is the configurational entropy of the melt at the glass transition temperature. In the case of silicate melts it has been demonstrated by Richet et al. (1986) that C_p^{conf} is adequately approximated by $C_p^{\text{liquid}(T)} - C_p^{\text{glass}(T_g)}$ even though this is demonstrably not the case for certain organic glasses studied by Goldstein (1976). Indeed, it should be noted that the A–G theory cannot account for the temperature dependence of viscosity of all liquids (Goldstein, 1969). However, several convincing lines of evidence suggest that Eq. (1) may be successfully applied to molten silicates (see also Richet and Bottinga, 1995; Bottinga and Richet, 1996). Firstly, viscosity data may be successfully fitted to Eqs. (1) and (2), if A_e , B_e , and $S_{c(T_g)}$ are treated as adjustable parameters. This is even the case for compositions such as titanosilicates that have ‘anomalous’ variations of C_p^{conf} as a function of temperature (Bouhifd et al., 1999). Secondly, absolute values of $S_{c(T_g)}$ calculated from viscosity data are in excellent agreement with values determined independently from appropriate calorimetric cycles of isochemical crystals, liquids and glasses (Bottinga et al., 1995). Furthermore, Eq. (1) predicts that if configurational entropy of a melt is constant (i.e. fixed melt structure) then the temperature dependence of the ‘isostructural’ viscosity will be Arrhenian with a gradient $B_e/S_{c(T_f)}$, where T_f is the fictive temperature of the melt (the temperature at which the isostructural viscosity line intersects the equilibrium viscosity curve, Fig. 1). This gradient will be different from that of the equilibrium viscosity curve because the temperature dependence of configurational entropy no longer has to be taken into account. For the case of window glass where ‘isostructural’ viscosities have been measured (Bottinga and Richet, 1996), the measured gradient for melts of known fictive temperature is that predicted by Eq. (2), providing strong independent support for the validity of the A–G theory. Although such ‘isostructural’ measurements are not possible at viscosities lower than 10^{13} Pa s because relaxation of the structure to equilibrium is too rapid, the difference between the hypothetical isostructural viscosity and the equilibrium viscosity is therefore a qualitative measure of the temperature-dependent structural changes in the melt, as discussed below.

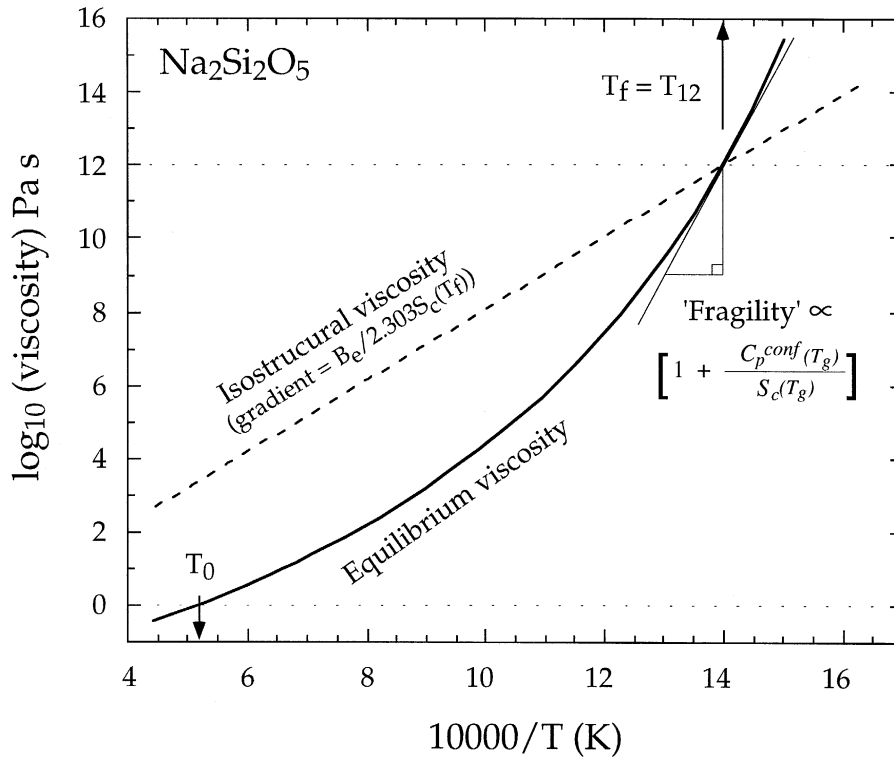


Fig. 1. Equilibrium viscosity curve for $\text{Na}_2\text{Si}_2\text{O}_5$ (thick solid line) and other parameters of interest that may be defined in terms of the Adam–Gibbs parameters (see text for details). The equation shown for ‘fragility’ uses the definition of Angell (1991) and was derived by Toplis et al. (1997).

2.2. Derivation in terms of microscopic properties

In order to derive Eq. 1, Adam and Gibbs (1965) considered the microscopic parameters controlling structural relaxation time. They thought of the melt as composed of ‘subsystems’, which upon sufficient fluctuation in enthalpy can rearrange into an alternative configuration independent of their environment. Structural relaxation is proportional to the probability of a subsystem being able to adopt a new configuration and is thus a thermally activated process. The energy barrier of this process is defined by: (1) $\Delta\mu$, the energy barrier hindering the rearrangement of a single element, for example a monomer segment in a polymeric glass, and (2) z^* , the ‘size’ of the subsystems, defined as the minimum number of monomer segments that must simultaneously overcome their individual energy barrier. The resulting expression

for viscosity is (Adam and Gibbs, 1965; Bottinga and Richet, 1996):

$$\ln \eta = A_e + z_{(T)}^* \Delta \mu / kT \quad (3)$$

where η is the viscosity, T is absolute temperature, A_e is a constant independent of temperature but dependent on composition, and k is Boltzmann’s constant. In this expression the energy barrier per monomer segment is considered to be independent of temperature, whereas the minimum size of subsystems permitting a change in configuration ($z_{(T)}^*$) changes as a function of temperature. This derivation in terms of microscopic parameters whose physical reality is not proven is one of the weaknesses of the theory as viscous flow in general may not always occur through microscopic mechanisms with well-defined energy barriers. This fact is most likely at the origin of the failure of the A–G theory to

account for the temperature dependence of the viscosity of all classes of liquids (Goldstein, 1969). However, current understanding of viscous flow in silicate melts (e.g. Stebbins, 1995) suggests that in this case well-defined microscopic mechanisms do exist, thus explaining the general success of the A–G theory in accounting for the temperature dependence of melt viscosity for this class of liquid.

If it is accepted that the notions of ‘energy barrier’ and ‘size of subsystems’ have some physical reality in the case of silicate melts, then the two equivalent forms of the A–G theory, expressed by Eqs. (1) and (3), show that at a given temperature the microscopic and macroscopic parameters are related by the equation:

$$B_e/S_{c(T)} = \Delta\mu z_{(T)}^*/k. \quad (4)$$

Because the ratio $B_e/S_{c(T_g)}$ can be calculated from viscosity and calorimetric data as described above, this information may be used to learn something about the relative variations of $\Delta\mu$ and/or z^* as a function of composition (e.g. Toplis, 1998). It is the aim of this contribution to extend this idea and quantify absolute values of $\Delta\mu$ or z^* for compositions along the join $\text{SiO}_2\text{--Na}_2\text{O}$.

3. Variation of the ratio $B_e/S_{c(T_g)}$ in the system $\text{SiO}_2\text{--Na}_2\text{O}$

Many viscosity measurements have been performed in the system $\text{SiO}_2\text{--Na}_2\text{O}$, particularly at temperatures well above the glass transition. In the present study we have chosen to use only the viscosity data of Knoche et al. (1994) because the range of silica content is one of the widest, and viscosity measurements were performed over very large temperature ranges on exactly the same compositions. The high temperature values are in good agreement with data from the literature, and the low temperature data are in excellent agreement with those of Poole (1948), with the exception of the most sodium rich composition, for which the older measurements of viscosity are considerably lower, potentially due to the highly hygroscopic nature of these compositions. The viscosity data of Knoche et al. (1994) were fitted to Eqs. (1) and (2), with A_e , B_e and $S_{c(T_g)}$ as adjustable parameters, using the calorimetric

data of Richet et al. (1984) for C_p^{conf} . The glass transition temperature was defined as the 10^{12} Pa s viscosity isokom, an assumption supported by calorimetric measurements performed on silicate melts at laboratory cooling rates (Richet and Bottinga, 1995).

The calculated ratio $B_e/S_{c(T_g)}$ is approximately constant for SiO_2 contents less than 67 mol%, but increases markedly with increasing silica content (Table 1, Fig. 2). In order to attribute these variations to changes in $\Delta\mu$ and/or $z_{(T_g)}^*$ (Eq. 4), one must consider how the energy barrier to viscous flow may be expected to vary along the join $\text{SiO}_2\text{--Na}_2\text{O}$.

Based upon computer simulations and spectroscopic evidence it has been proposed that in the presence of non-bridging oxygens (NBO) viscous flow in silicate melts occurs through the formation of five coordinated silicon (Soules, 1979; Stebbins, 1991). For SiO_2 contents ≤ 67 mol% each silicate tetrahedron has, by stoichiometry, an average of at least 1 NBO, therefore the energy barrier to viscous flow may be expected to be constant in this range. For pure SiO_2 the microscopic mechanism responsible for viscous flow is poorly known. It must differ from that in depolymerised melts because there are few if any NBO, and its activation energy may be

Table 1
Summary of Adam–Gibbs parameters

	A_e^a	B_e^a , J/gfw	$S_{c(T_g)}$, J/gfw K	$B_e/S_{c(T_g)}$
SiO_2^b	–3.34	230 200	5.10	45 140
$\text{Na}0.15^c$	–5.87	315 100	12.22	25 775
$\text{Na}0.2^d$	–4.29	235 650	9.83	23 970
$\text{Na}0.25^c$	–4.08	172 300	7.36	23 395
$\text{Na}0.3^c$	–4.04	164 500	7.12	23 105
$\text{Na}0.33^d$	–3.99	179 525	7.95	22 572
$\text{Na}0.35^c$	–4.39	183 675	8.03	22 865
$\text{Na}0.4^c$	–5.37	200 250	8.72	22 961
$\text{Na}0.45^c$	–6.02	195 150	8.47	23 053

gfw = gram formula weight.

^aNote that the suffix e is used to denote that calculated values of viscosity are on a \ln_e scale rather than \log_{10} (conversion factor 2.303).

^bParameters calculated using the viscosity data of Hetherington et al. (1964) for temperatures below 1600 K, and the calorimetric data of Richet et al. (1982).

^cParameters calculated using the viscosity data of Knoche et al. (1994) and the model of Richet et al. (1984) for values of C_p^{conf} . Na_x corresponds to $x\text{Na}_2\text{O}:(1-x)\text{SiO}_2$ (molar).

^dData taken from Richet (1984).

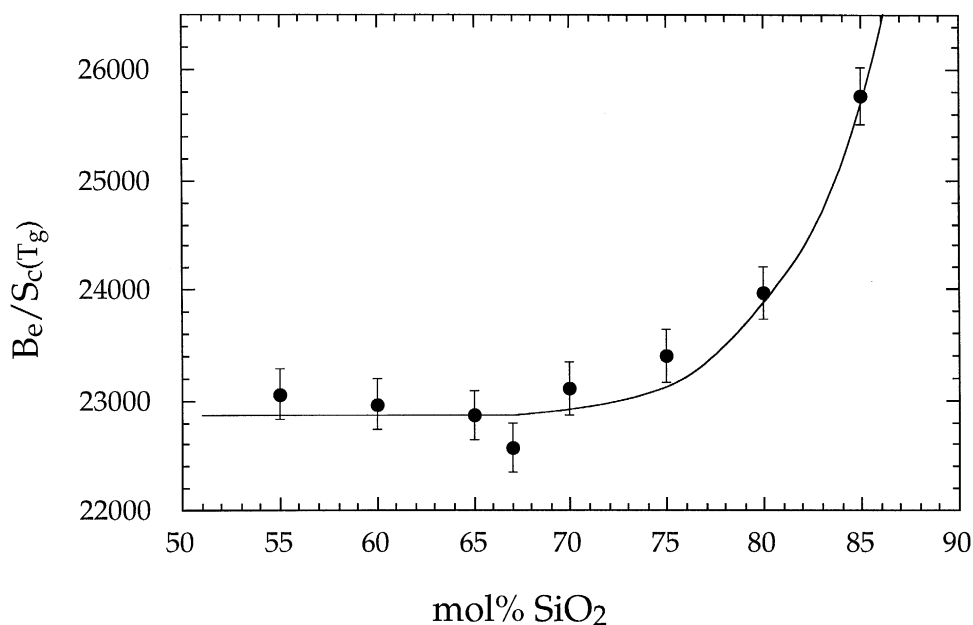


Fig. 2. Variation of the ratio $B_e/S_{c(T_g)}$ along the join $\text{SiO}_2\text{--Na}_2\text{O}$, calculated using values shown in Table 1. Error bar represents $\pm 1\%$.

expected to be greater. Above 67 mol% SiO_2 an increasing proportion of viscous flow events may occur through this alternative mechanism as pure SiO_2 is approached and the average height of the energy barrier to viscous flow should therefore increase. The fact that $B_e/S_{c(T_g)}$ shows the same variation as that expected for $\Delta\mu$ as a function of silica content would imply that $z_{(T_g)}^*$ shows little or no variation as a function of composition. Data from a number of other simple silicate systems have also been used to infer that $z_{(T_g)}^*$ is approximately independent of composition (Toplis, 1998) and it was proposed that z^* might be the limiting factor determining the glass transition at fixed cooling rate.

4. Absolute values of $\Delta\mu$ and $z_{(T_g)}^*$

Different methods may be used to estimate absolute values for $z_{(T_g)}^*$ or $\Delta\mu$ as described below. It should be noted that values for $z_{(T_g)}^*$ and $\Delta\mu$ are not independent but are linked through Eq. (4) for a known value of $B_e/S_{c(T_g)}$. Furthermore, it should be kept in mind that $z_{(T_g)}^*$ may be independent of composition.

4.1. A lower limit for $z_{(T_g)}^*$

The fact that the A–G equation can account for the temperature dependence of silicate melt viscosities in the range $10^0\text{--}10^{12}$ Pa s (Bottinga et al., 1995) implies that $z^* > 1$ over this range, a value less than one having no physical meaning. Rearranging Eq. (4) implies that the product $[S_{c(T)} \times z_{(T)}^*]$ is independent of temperature. Therefore, comparing the temperatures of the 10^{12} and the 10^0 Pa s isokoms (T_{12} and T_0 , respectively, see Fig. 1) it may be shown that:

$$z_{(T_{12})}^*/z_{(T_0)}^* = S_{c(T_0)}/S_{c(T_{12})}. \quad (5)$$

For sodium disilicate the viscosity is 10^0 Pa s at 1926 K. At this temperature the configurational entropy of the liquid is 23.4 J/mol, compared to 7.95 J/mol when the viscosity is 10^{12} Pa s. Using these values and Eq. (5), a ratio $z_{(T_{12})}^*/z_{(T_0)}^*$ of approximately 3 is calculated. Assuming that $z_{(T_0)}^*$ has a lower limit of 1 therefore implies that $z_{(T_{12})}^*$ has an absolute lower limit of 3, in turn implying an absolute upper limit for $\Delta\mu$ of 60 kJ/mol (Eq. (4)). It is

also of note that z^* is not markedly temperature dependent showing a variation of only a factor of three from the glass transition to almost 2000 K.

4.2. Using spectroscopically determined enthalpies of formation

If the intermediate species responsible for viscous flow can be identified, then spectroscopic techniques may be used to constrain their enthalpies of formation. For example, below 67 mol% SiO₂ it may be assumed that formation of five coordinated silicon Si^V represents the energy barrier to viscous flow, as discussed above. Using NMR spectroscopy to determine the concentration of Si^V in glasses quenched at different rates, and thus of different fictive temperature, Stebbins (1991) estimated the enthalpy of formation of five coordinated silicon to be 20 ± 10 kJ/mol. Assuming a value for $\Delta\mu$ of 20000 and applying Eq. (4) to data for sodium silicates with less than 67 mol% SiO₂ (noting that per mole, Boltzmann's constant in Eq. (4) becomes R , the gas constant) a value for $z_{(T_g)}^*$ of 9.5 is calculated. The lower limit for $z_{(T_g)}^*$ is 6 (for $\Delta\mu = 30$ kJ/mol) and the upper limit 19 (for $\Delta\mu = 10$ kJ/mol).

Another constraint on the magnitude of $z_{(T_g)}^*$ is given by Raman spectra of a series of pure SiO₂ glasses of different fictive temperatures which show a prominent 'defect' band (D2) at 606 cm⁻¹ (Geissberger and Galeener, 1983). The structural origin of this band has been the subject of controversy, but several lines of evidence suggest that it is due to a breathing mode of three-membered silicate rings (e.g. Kubicki and Sykes, 1993). In turn, the formation/destruction of such structures as a function of temperature may be responsible for viscous flow. The fictive temperature dependence of the intensity of the D2 defect band is described by an activation energy of 38.6 kJ/mol (Geissberger and Galeener, 1983) that if combined with the value of $B_c/S_{c(T_g)}$ for SiO₂ of 45140 (Table 1) gives a calculated value for $z_{(T_g)}^*$ of 9.5 ± 0.5 , in excellent agreement with the estimate for depolymerised compositions.

If subsystems consist of approximately 10 'activated' tetrahedra, and enthalpy barriers per silicon are on the order of several tens of kJ per mole (as also suggested by measured enthalpies of Q-

species exchange in alkali silicate melts: Brandriss and Stebbins, 1988; Mysen and Frantz, 1994), Eq. (3) therefore provides a simple explanation for the apparent paradox between the low values of enthalpy proposed for the microscopic changes of melt structure and the 'macroscopic' activation energies of viscous flow (the tangent to a plot of $\ln\eta$ vs. $1/T$) that are typically several hundred kJ/mol.

4.3. Using the spread in relaxation time

An entirely independent estimate of $z_{(T_g)}^*$ may be made based upon the consideration of relaxation time in the glass transition range. If structural relaxation is controlled by a single process with fixed relaxation time, τ , then following a perturbation of the liquid, the value of property P (e.g. volume) as a function of time, t , should vary according to Eq. (6a) as the system returns to equilibrium (e.g. Scherer, 1990):

$$(P_t - P_\infty)/(P_0 - P_\infty) = \exp(-t/\tau) \quad (6a)$$

where P_0 is the initial value (at time = 0), P_∞ is the equilibrium value (at infinite time) and P_t is the value at time t . However, real data do not generally follow Eq. (6a), which is interpreted to suggest that there exists a range of relaxation times (Scherer, 1990). One way of describing relaxation data is to fit them to the Kohlrausch–Williams–Watt stretched exponential equation:

$$(P_t - P_\infty)/(P_0 - P_\infty) = \exp(-t/\tau)^\beta \quad (6b)$$

The constant β tends towards zero as the range of relaxation time increases. Within the framework of A–G theory this spread may be related to the distribution of subsystem 'sizes'. As the average subsystem size gets larger the range in size may also be expected to increase, thus $z_{(T_g)}^*$ and β may be related. Indeed, Hodge (1997) has shown that for a wide range of glass-forming polymers there exists a correlation between $z_{(T_g)}^*$ and β that may be described by the equation

$$\beta = 1 - 0.3 \log_{10} z_{(T_g)}^* \quad (7)$$

Values of β derived for silicate systems include 0.75 for SiO₂ and 0.67 for a depolymerised potassium

silicate (Richet and Bottinga, 1984), thus values for $z_{(T_g)}^*$ predicted by Eq. (7) are in the range 7 to 13, consistent with estimates described above.

4.4. Physical size of heterogeneities

Several lines of evidence, such as light and neutron scattering experiments (Moynihan and Schroeder, 1993; Duval et al., 1990) or the temperature interval of the glass transition as defined from heat capacity measurements (Donth, 1982), imply the existence of heterogeneities in simple glasses. The existence of such heterogeneities is consistent with the postulate of Adam and Gibbs (1965) that liquids contain discrete subsystems, and their physical size should therefore be proportional to $z_{(T_g)}^*$. In cases where the size of such ‘cooperatively rearranging regions’ has been determined, a surprisingly constant linear dimension (or ‘correlation length’) of 1–2 nm is obtained for a number of inorganic glasses (e.g. Moynihan and Schroeder, 1993; Donth, 1982). In the case of the silicate ‘crown glass’ considered by Donth (1982) the cooperatively rearranging regions were calculated to contain 35 tetrahedra. For the case of pure SiO₂ (Duval et al., 1990) a sphere of diameter 2 nm will contain approximately 90 SiO₂ tetrahedra, a similar number to that calculated for more depolymerised crown glass. These values are somewhat higher than those of $z_{(T_g)}^*$ inferred above, but this is to be expected given that scattering is caused by regions whose average density varies from the mean. The ‘activated’ tetrahedra (e.g. five coordinated silicon in the case of depolymerised melt) will form the core of a locally dense region, but the overall extent of the density anomaly may be expected to be greater. Taking this fact into account, it may be concluded that the physical sizes of heterogeneities determined from scattering experiments are perfectly consistent with 10 or so activated tetrahedra in silicate glasses. It is also of note that the analysis presented in Section 4.1 predicts that the volume of the rearranging regions (proportional to $z_{(T)}^*$) only varies by a factor of 3 over temperature intervals in excess of 1000 K. Therefore, the linear dimension of such regions only varies by a factor of 1.4, suggesting that it will be very difficult to measure differences in z^* directly using scattering data.

5. Configurational entropies of glasses

At the present time Eq. (3) cannot be used as the basis for a predictive model of melt viscosity because it is impossible to measure the temperature dependence of z^* above T_g . On the other hand, Eq. (1) has the great practical advantage that the temperature dependence of configurational entropy is related to heat capacity, a macroscopic property that may be readily measured and for which predictive models already exist for simple silicates (Richet and Bottinga, 1985). Therefore, if values for $S_{c(T_g)}$ can be predicted as a function of composition, then configurational entropies can be calculated at all temperatures (Eq. (2)). Furthermore, if values for $S_{c(T_g)}$ are known, and $B_e/S_{c(T_g)}$ may be predicted from values of $z_{(T_g)}^*$ and $\Delta\mu$, then the absolute value of B_e may be calculated. Configurational entropy also affects the ‘fragility’ (see Angell, 1991) of silicate melts (Fig. 1), and is an important parameter controlling phase equilibria, thus relating configurational entropy to melt structure is of considerable practical importance. However, there is a general lack of data for $S_{c(T_g)}$, because of the difficulties and limitations of obtaining $S_{c(T_g)}$ by purely calorimetric techniques (Bottinga et al., 1995). The use of viscosity data and the A–G theory is a relatively simple alternative method of estimating configurational entropies of silicate glasses that may be applied to all compositions and not only those for which a stable mineral exists (Richet and Bottinga, 1995).

When expressed in terms of gram formula weight (gfw) of melt (Table 1), calculated values of $S_{c(T_g)}$ show a well-defined variation as a function of composition along the join SiO₂–Na₂O, with a maximum value between 85 and 100 mol% SiO₂, and a local minimum between 70 and 75 mol% SiO₂ (Fig. 3a). The fact that calculated configurational entropies pass through a maximum in the range 75–100% SiO₂ is significant because liquid compositions in this region are in a field of metastable liquid–liquid immiscibility (Haller et al., 1974). This result would therefore imply that the origin of immiscibility cannot be attributed to entropic forces, but must be due to strong non-idealities in the *enthalpy* of mixing, possibly due to strong coulombic forces between sodium atoms (e.g. McGahay and Tomozawa, 1989). It is also of note that calculated values of entropy are

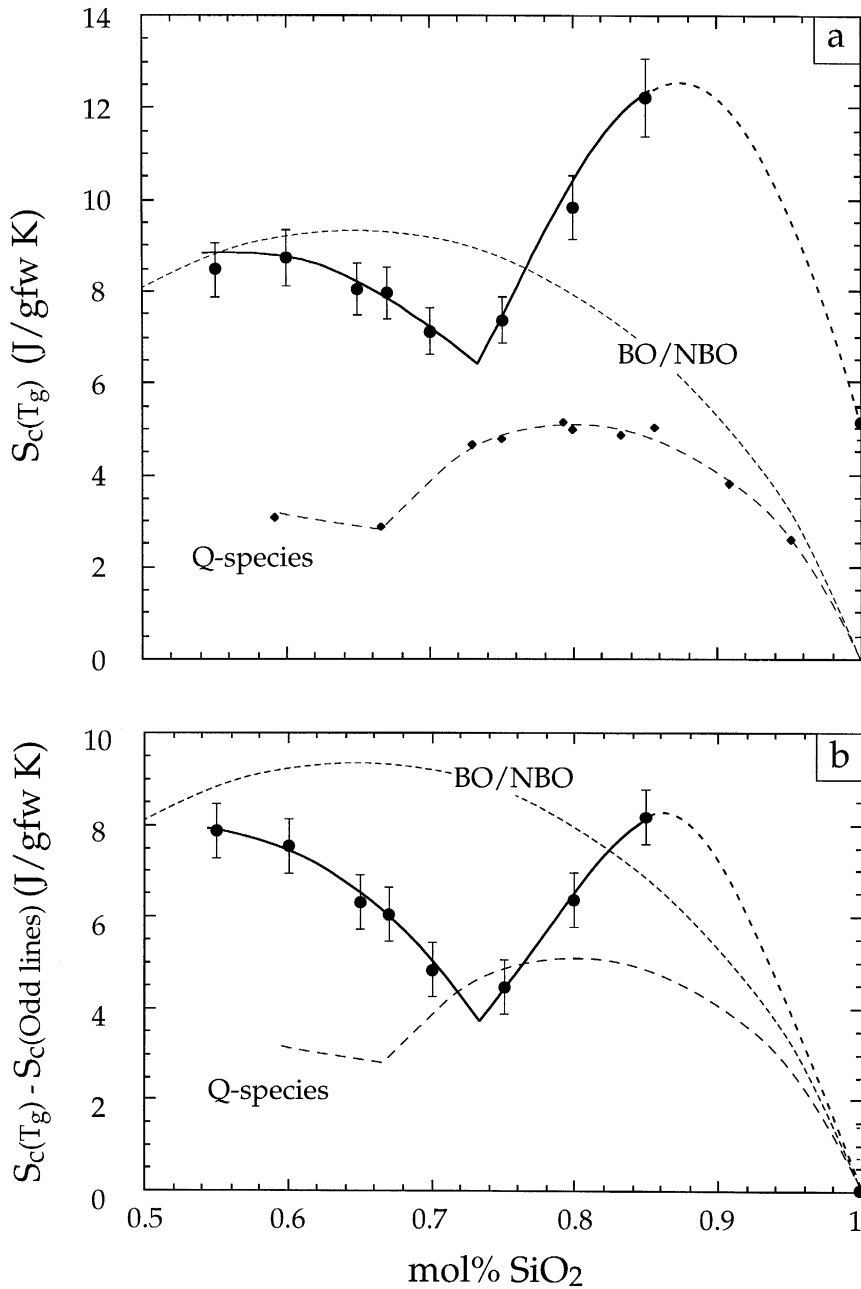


Fig. 3. (a) Configurational entropies per gfw of glasses on the join $\text{SiO}_2\text{-Na}_2\text{O}$ calculated using the A–G theory (filled circles) compared to values calculated using Eq. (8) for mixing of bridging and non-bridging oxygens (dashed line noted BO/NBO) and mixing of Q-species (data from Mysen, 1990; Mysen and Frantz, 1994). Error bar represents $\pm 8\%$. (b) Configurational entropies of glasses as in (a), but corrected for a contribution from 'odd lines' (see text for details).

greatest close to SiO_2 rather than for more depolymerised compositions where we may intuitively expect there to be greater configurational disorder.

However, this feature of Fig. 3a may be, in part, an artefact of the units chosen to represent entropy. For example, if considered per mole of silicon (tetra-

hedra) rather than per gfw, then calculated entropies would be greatest at the lowest silica content.

A first approach to rationalising the variation of configurational entropy as a function of composition is to consider that its source is mixing of discrete structural units. In this case, S_c may be calculated using the equation:

$$S_c = R \sum X_i \ln X_i \quad (8)$$

where X_i is the mole fraction of structural unit i and R is the gas constant. Suitable candidates for such structural units are distinct types of oxygen (e.g. bridging and non-bridging oxygens) or distinct tetrahedral sites (e.g. Q-species). However, for compositions in the system SiO_2 – NaAlSiO_4 (Toplis et al., 1997), the variation of $S_{c(T_g)}$ was inferred to be the sum of a ‘chemical’ contribution given by Eq. (8), and a ‘topological’ contribution of uncertain origin. This latter contribution may be most clearly appreciated in the case of pure SiO_2 glass that has a measured configurational entropy of 5.1 ± 0.5 J/mol K (Richet et al., 1982), whereas Eq. (8) will predict a value of zero for any definition of different oxygen or tetrahedral sites used. That SiO_2 glass has some configurational entropy is not surprising given that it is more disordered than its crystalline counterparts. One possible way to view this disorder is in terms of ‘odd lines’, closed lines threading through rings of bridging bonds containing an odd number of tetrahedra, a configuration not present in ordered crystalline phases (Rivier, 1979; Rivier and Duffy, 1982). For a covalent glass containing one mole of tetrahedrally coordinated network forming atoms (e.g. Si), and an average of x bridging bonds per network former, Rivier and Duffy (1982) calculated the configurational entropy due to odd lines to be:

$$S_{c \text{ odd lines}} = R(0.5x - 1) \ln 2. \quad (9)$$

For the case of pure SiO_2 with no dangling bonds $x = 4$, and the calculated configurational entropy is 5.8 J/mol K, very close to the measured value (Richet et al., 1982). The addition of network modifying cations such as Na will reduce the average number of bridging bonds per Si, thus Eq. (9) predicts that the contribution to S_c from odd lines will decrease to 0 when the silica content reaches 50 mol% ($x = 2$), thus accounting in part for the high values of configurational entropy near SiO_2 .

Bearing in mind a potential contribution from ‘odd lines,’ an attempt may be made to rationalise the compositional dependence of configurational entropy in terms of Eq. (8). In the case of SiO_2 – NaAlSiO_4 glasses the variation of $S_{c(T_g)}$ was found to be consistent with mixing of aluminate and silicate tetrahedra rather than different oxygen sites (Toplis et al., 1997). However, in the present case, comparison of the configurational entropies derived either directly from viscosity measurements (Fig. 3a) or corrected for a contribution from odd lines (Fig. 3b) with values estimated using Eq. (8) (for mixing of different oxygens or Q-species) does not show good agreement. In particular, neither of these mixing units reproduces the minimum in configurational entropy close to 75 mol% SiO_2 . This minimum in entropy is significant, as it implies ordering of melts of that stoichiometry (i.e. possible formation of a stable melt species). Indeed, independent evidence for a stable melt complex in this composition range is given by the fact that the silica poor limb of metastable liquid–liquid immiscibility in the system Na_2O – SiO_2 asymptotically approaches the composition $\text{Na}_2\text{Si}_3\text{O}_7$ (Haller et al., 1974). The presence of a stable melt species that does not correspond in stoichiometry to a simple Q-species suggests that order on length scales greater than a single silicate tetrahedron may be important. This is consistent with the results of computer simulations that suggest that the connectivities of Q-species are not random in sodium silicates (Zotov and Keppler, 1998), but further quantitative interpretation of Fig. 3 is not possible at the present time.

6. Conclusions

The data presented above suggest that viscosity in the system SiO_2 – Na_2O may be understood in terms of the microscopic view of viscous flow embodied in the A–G theory. This theory proposes that structural relaxation time is a function of the energy barrier for rearrangement of a single silicate monomer, and the number of monomers that must simultaneously overcome their barrier in order for a change in configuration to occur. Various independent lines of evidence suggest that at the glass transition of all composi-

tions on the join $\text{SiO}_2\text{--Na}_2\text{O}$, the subsystems consist of approximately 10 'activated' tetrahedra, and that individual enthalpy barriers are on the order of several tens of kJ per mole of silicon. However, further spectroscopic studies or numerical simulations are needed to determine the microscopic enthalpy barriers to viscous flow in more complex melts of interest to the Earth sciences. The compositional variation of configurational entropy of glasses is not found to be simply related to mixing of different oxygen or tetrahedral sites, and it is inferred that medium range order of glass structure may be important. A recent study has demonstrated the potential for using NMR spectroscopy to quantify the medium range order of silicate glasses (Glock et al., 1998), and further studies of this type may ultimately lead to a better understanding of the quantitative link between glass structure and configurational entropy.

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