Effects of $^{10}B/^{11}B$ Isotopic Substitution on Shear Relaxation in Supercooled B_2O_3 Liquid: A Validation of the Elastic Model of Viscous Flow

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Abstract

The effect of atomic mass in terms of its zero-point vibrational energy, on molar volume, glass transition temperature T_g and viscosity is studied in glassy and supercooled B_2O_3 liquid using boron isotope substitution. The molar volume decreases and T_g and isothermal viscosity increase on substitution of lighter ^{10}B isotope with the heavier ^{11}B isotope. These effects are argued to be a manifestation of the higher zero-point vibrational energy of the lighter isotope, which along with the anharmonicity of the potential well, results in a longer equilibrium inter-atomic distance and larger mean-square displacement with respect to that for the heavier isotope. The isotope effect on viscosity is increasingly enhanced as temperature approaches T_g, which is shown to be consistent with the prediction of the elastic models of viscous flow and shear relaxation.

Isotopic substitution in a material has been shown to result in clear changes in the equilibrium thermodynamic and kinetic behavior in materials including their molar volume, vapor pressure, melting point, specific heat and even glass transition temperature T_g [1-14]. For example, the well-known volume isotope effect (VIE) in hydrocarbons results from the quantum-mechanical effect of mass on the vibrational amplitude of the isotope atom [13,14]. The quantum mechanical effect of a higher zero-point vibrational energy, in combination with the anharmonicity of the potential well, results in a longer equilibrium bond length for the lighter isotope and consequently in a larger molar volume. On the other hand, transport properties such as the self-diffusion coefficient D of an atom is expected to be influenced by its mass m via the attempt frequency or the escape rate of the atom from its potential well, which is inversely proportional to $\sqrt{m}$ [15-18]. Therefore, $D \sim 1/\sqrt{m}$, and the heavier isotope is expected to have a slower diffusivity compared to its lighter counterpart.

The scaling between D and m has been utilized in the literature to investigate the possibility of cooperative hopping of groups of atoms in supercooled metallic melts by measuring the self-diffusivity of different isotopes in these melts [19-22]. These studies defined the isotope-effect parameter E such that [19]: $E = \frac{\frac{D_1}{D_2} - 1}{\sqrt{\frac{m_2}{m_1}} - 1}$, where the subscripts 1 and 2 refer to the different isotopes of an element. Therefore, if the scaling relation $D \sim 1/\sqrt{m}$ is valid then $E = 1$ for diffusivity controlled by single-atom hopping events. Indeed, E was measured to be ~ 1 in ordinary liquids at high temperature [22]. However, E was reported to be an order of magnitude lower than 1 in some supercooled multicomponent alloy melts [19-21]. This deviation of E from unity was explained to be a consequence of collective hopping of a group of atoms, excluding the tracer atom, with an effective mass $M >> m$ [19]. Therefore, $D \sim 1/\sqrt{m + M}$ and since the effect of the isotope mass m in Eqn. 1 is now weakened, it gives rise to $E << 1$. However, the universality of this result in glass-forming liquids has not been widely validated due primarily to the experimental challenges associated with such measurements.

Here we report the results of a study on the isotope effect on molar volume, T_g and viscosity η of an archetypal network glass-forming liquid, B_2O_3. High-precision viscosity, density and T_g measurements are carried out on nearly isotopically pure $^{10}B_2O_3$ and $^{11}B_2O_3$ to estimate the temperature dependence of the isotope-effect parameter $E^*(T)$, where the latter is defined as:

$$E^* = \frac{\frac{D_1}{D_2}}{\sqrt{\frac{m_2}{m_1}}} \tag{1}$$

The viscosity η of these liquids is used as a surrogate of diffusivity in Eqn. 1, as D and η are related through the celebrated Stokes-Einstein (S-E) relation: $D = \frac{k_B T}{6\pi a\eta}$, where k_B is the Boltzmann constant, T is temperature and a is the size of a diffusing unit. The analysis of $E^*(T)$ is shown to provide a unique way to interrogate the quantum-mechanical vs. classical effects of isotopic substitution on the transport properties in supercooled liquids.

The B_2O_3 glasses with ^{10}B:^{11}B isotopic ratios of 96:4, 50:50 and 2:98 were prepared from 96% ^{10}B isotope-enriched and 98% ^{11}B isotope-enriched B_2O_3 reagents (Cambridge Isotope Laboratory). The thermophysical properties of fully connected network liquids such as B_2O_3 are known to be critically dependent on the structural water content. Therefore, in order to prepare dry B_2O_3 glasses, these reagents or their mixtures were calcined at 773 K for 24 hours in a Pt-Au crucible and subsequently melted at 1473 K for 24 hours followed by quenching in air. All glass samples were immediately stored in a glove box until further experimentation. The T_g of these glasses was measured using differential scanning calorimetry (DSC) (Mettler Toledo DSC1). The

DSC temperature was calibrated against the melting points of In and Zn, both of which were measured to be within ± 0.9 K of the reported values in the literature. For each glass composition, approximately 15 to 25 mg of sample was taken in hermetically sealed Al pans. The samples were heated at a rate of 10 K/min under a nitrogen atmosphere to 633K to erase any thermal history, cooled down to 373K and then reheated to 723K at the same rate. The T_g was determined as the onset of the endothermic glass transition signal during reheating (Figure 1). Each reported T_g value is an average of 4 to 6 separate measurements on different samples, which resulted in an error bar of ± 2 K (Figure 2a). These values are found to be comparable with that (~ 554 K) obtained on the basis of volumetric measurements on a dry B_2O_3 glass with natural isotopic abundance by Macedo and coworkers, which was prepared by bubbling dry nitrogen gas through the melt for 16 h at 1573 K [23]. Density of all glasses was measured after annealing at T_g for 30 minutes to erase quenching related thermal history. Annealed samples of mass ranging between 0.50 g and 0.65 g were taken in air-tight glass vials and quickly transferred to a gas expansion pycnometer (Micromeritics AccuPyc II 1340), which was used to measure density at 20°C using helium (6N purity) as the displacement gas; each reported density value is an average of measurements on 5 different samples with 10 consecutive measurements on each sample. Such a procedure resulted in an error bar of ± 0.003 g/cm^3 for density (Figure 2b). The density of a B_2O_3 glass with natural isotopic abundance (Figure 2b), prepared and measured following the same protocol as the isotopically enriched samples, was found to be (1.806 g/cm^3), consistent with that (1.8025 g/cm^3) reported by Macedo et al. on an anhydrous B_2O_3 glass [23].

High-precision viscosity data with a relative error of ~ 7% (± 0.03 log units) were obtained on the isotopic end members i.e. the 96% ^{10}B and the 98% ^{11}B isotope-enriched B_2O_3 liquids. Viscosity of these liquids was measured using a parallel plate rheometer (MCR302, Anton-Paar) under an environment of flowing dry nitrogen gas. The temperature of the sample was controlled by a convection oven. The glass samples were heated above the softening point to reach a viscosity of ~10^5 Pa·s and trimmed between the two plates to form a sandwich-like geometry with a gap of ~ 1 mm. Viscosity measurements were carried out under steady shear for $\eta < 10^8$ Pa.s, corresponding to T > 600 K. At each desired measurement temperature, the sample was subjected to a steady shear rate $\dot{\gamma}$ using the upper plate (8 mm diameter, stainless steel), while the non-removable lower plate (25 mm diameter, stainless steel) remained stationary. The corresponding stress response from the sample was recorded using a torque transducer and the Newtonian viscosity η was calculated as the ratio of stress and strain rate at various shear rates $\dot{\gamma}$ ranging between 0.01 s^{-1} and 1 s^{-1} at each temperature. On the other hand, η in the range ~$10^{9.0}$-$10^{11.3}$ Pa·s was measured using creep test with the same rheometer setup. In the creep test, the strain was recorded as a function of time while the sample was kept under a constant shear stress τ. In this test as the viscous response of the liquid reaches a steady state at long times, the strain increases linearly with time and the gradient of this region yields the strain rate $\dot{\gamma}$. The viscosity could then be obtained from the relation: $\eta = \frac{\tau}{\dot{\gamma}}$. Each reported η value is an average of 5 to 6 separate measurements on different samples, collected during both heating and cooling, which was necessary to ensure reproducibility and a low relative error of ± 0.03 log units for η. The viscosity measurement methodology outlined above was validated by comparing the viscosity of a B_2O_3 glass with natural isotopic abundance (see supplementary section), prepared following the same protocol as the isotopically enriched samples, with that reported by Napolitano et al. for anhydrous B_2O_3 liquid [24]. The good agreement between the density and viscosity data for natural abundance B_2O_3 glass and liquid obtained here with those reported by Macedo and coworkers

[23,24] confirms the anhydrous nature of the samples and validates the measurement methodology adopted in the present study.

The variation in molar volume and T_g with the isotopic composition for these B_2O_3 glasses are shown in Figure 2. The molar volume shows a small monotonic decrease with increasing ^{11}B:^{10}B ratio, consistent with a shorter ^{11}B-O bond length compared to the ^{10}B-O bond length, as expected from the VIE discussed above (Figure 2a). Compared to the heavier ^{11}B isotope, the higher zero-point energy of the lighter ^{10}B isotope responsible for the VIE, should also result in a larger vibrational and possibly relaxational mean-square displacement $<u^2>$ [25]. The elastic models of viscous flow and shear relaxation predict that the shear relaxation timescale τ_{shear} is a function of $<u^2>$ such that at any temperature T, the shear relaxation time is given by [25-28]:

$$\tau_{shear}(T) \sim \exp\left(\frac{C}{<u^2(T)>}\right) \qquad (2)$$

where C is a temperature independent constant. This relation in Eqn. 2 implies that a larger $<u^2>$ would lead to a shorter τ_{shear}. Since glass transition in liquids corresponds to a constant τ_{shear} on the order of ~ 100s, T_g is then expected to increase with decreasing fraction of the lighter ^{10}B isotope as it would result in a decrease in the ensemble-averaged value of $<u^2>$. This expectation is indeed borne out in Figs. 1 and 2b, where T_g shows a small but systematic increase with increasing ^{11}B:^{10}B ratio in B_2O_3 glass.

It is important to note at this point that τ_{shear} is related to the shear viscosity η according to the Maxwell relation as: $\tau_{shear} = \eta/G_\infty$, where G_∞ is the glassy shear modulus [29]. Therefore, following the same line of argument as above, one would predict from Eqn. 2 that the isothermal viscosity of $^{11}B_2O3$ would also be higher than that of $^{10}B_2O_3$, and this difference in viscosity will increase with progressive lowering of temperature as the quantum-mechanical effect will be enhanced. The variation in η(T) with the isotopic composition for the two isotopic end-member B_2O_3 liquids with 96% ^{10}B and 98% ^{11}B are shown in Figure 3 and the temperature dependence of the ratio of isothermal viscosities R for these liquids is shown in Figure 4. The data in Figures 3 and 4 are consistent with the predicted behavior as mentioned above and the isothermal viscosity of the ^{11}B-rich liquid becomes increasingly higher than that of the ^{10}B-rich liquid, upon lowering of temperature. It may be noted that if a difference in $<u^2(T)>$ is the sole contributor to the observed viscosity difference in Figure 4, then the $<u^2>$ for the ^{10}B-rich liquid needs to be only ~ 2% higher than that for the ^{11}B-rich liquid in order to explain the largest viscosity difference ($10^{11.28}$ vs. $10^{10.99}$ Pa.s) observed at the lowest temperature of measurement. A closer look at Figure 4 reveals that the viscosity ratio R rapidly increases below ~ 575 K, which is likely a manifestation of the increasing importance of the quantum-mechanical effect of isotopic mass on $<u^2>$. Therefore, as the temperature exceeds 575 K, the thermal energy of the system becomes the dominant factor in determining the transition rates between the metabasins in the energy landscape rather than the difference in the zero-point vibrational energy induced by the mass difference between the two B isotopes in B_2O_3 liquid. However, the reason behind the relatively abrupt nature of the rise of R below ~ 575 K remains unclear at this point. It is also important to note that R reaches a plateau value of ~ 1.1 ±0.1 at T >675 K. Although it can be argued that an R value of ~ 1.1 ±0.1 is indistinguishable from 1 within the experimental uncertainty, the rather small spread of ±0.04 in its average value in the temperature range 675 K to 750 K suggests that the departure of R from 1 may be real.

An alternative approach in the analysis of the temperature dependence of R is to consider the classical effect of isotope mass m on viscosity. As noted earlier, classically $D \sim 1/\sqrt{m}$, and according to the S-E relation $D = \frac{k_B T}{6\pi a \eta}$. Moreover, previous high-temperature ^{11}B nuclear magnetic resonance line shape and spin-lattice relaxation studies indicated that the diffusive motion of B atoms is closely linked to the shear relaxation of B_2O_3 [30]. Therefore, under the assumption that the size of the diffusing unit a in this liquid does not depend on the makeup of the B isotope, the isotope-effect parameter E^* in Eqn. 1 can be written in terms of viscosity as: $E^* = \frac{\eta_2/\eta_1}{\sqrt{m_2/m_1}}$, where the subscripts 1 and 2 refer to ^{10}B and ^{11}B isotopes, respectively. The $E^*(T)$ for the B_2O_3 liquids with 96% ^{10}B and 98% ^{11}B liquids can thus be calculated (Figure 5) with the approximation that these liquids are isotopically pure i.e. $m_1 = 10$ and $m_2 = 11$. Not surprisingly, such a calculation yields $E^*(T)$ that has a temperature dependence that is quite similar to that of $R(T)$ as $m_1 \approx m_2$. The value of $E^*(T)$ increases from ~ 1.1 at the highest temperatures to ~ 1.9 as glass transition is approached (Figure 5). Such a positive departure of E^* from 1 may originate from a breakdown of the S-E relation in the supercooled state, a phenomenon that has been reported in recent studies on a wide variety of glass-forming liquids and is now considered to be a hallmark of glass transition [31-35]. This breakdown of the S-E relation is manifested in a supercooled liquid in the form of an enhancement in D relative to η, as the latter increases rapidly on cooling such that the quantity $D\eta/T$ continues to increase instead of staying constant [31-35]. It is now widely accepted that this breakdown is linked to the appearance of dynamical heterogeneities in a supercooled liquid and its enhancement on cooling as the glass transition is approached [32-35]. It has been found empirically that in the region of the breakdown a fractional S-E relation holds well such that: $D \sim \left(\frac{T}{\eta}\right)^{\xi}$, where ξ typically ranges between 0.50 and 0.95 [34]. Consequently, the expression for E^* given above can be rewritten as: $E^* = \frac{(\eta_2/\eta_1)^{\xi}}{\sqrt{m_2/m_1}}$. Indeed, a value of $\xi = 0.35$ results in $E = 1$ at all temperatures $T > 575$ K, though we note that this value of ξ is significantly smaller than those typically observed for the enhancement of translational diffusivity and is more typical of the low ξ values reported for the enhancement of rotational diffusivity in molecular liquids (Figure 5) [34]. Moreover, below this temperature E^* starts to rise, showing a behavior similar to that of R as discussed above (Figure 4).

In summary, the isotopic substitution of B atoms results in relatively subtle but clear changes in the atomic packing in B_2O_3 glass and in the shear relaxation behavior of the corresponding supercooled liquid. These effects can be attributed to the difference in the zero-point vibrational energy between the lighter ^{10}B and heavier ^{11}B isotopes. The substitution of ^{10}B with ^{11}B results in a higher T_g and isothermal viscosity of B_2O_3 liquid, which when taken together, provide strong evidence in favor of the elastic models of shear relaxation of deeply supercooled glass-forming liquids.

SUPPLEMENTARY MATERIAL

See supplementary material for a comparison between the temperature dependence of viscosity of B_2O_3 liquid with natural isotopic abundance determined in the present study, and that reported in the literature for anhydrous B_2O_3 liquid.

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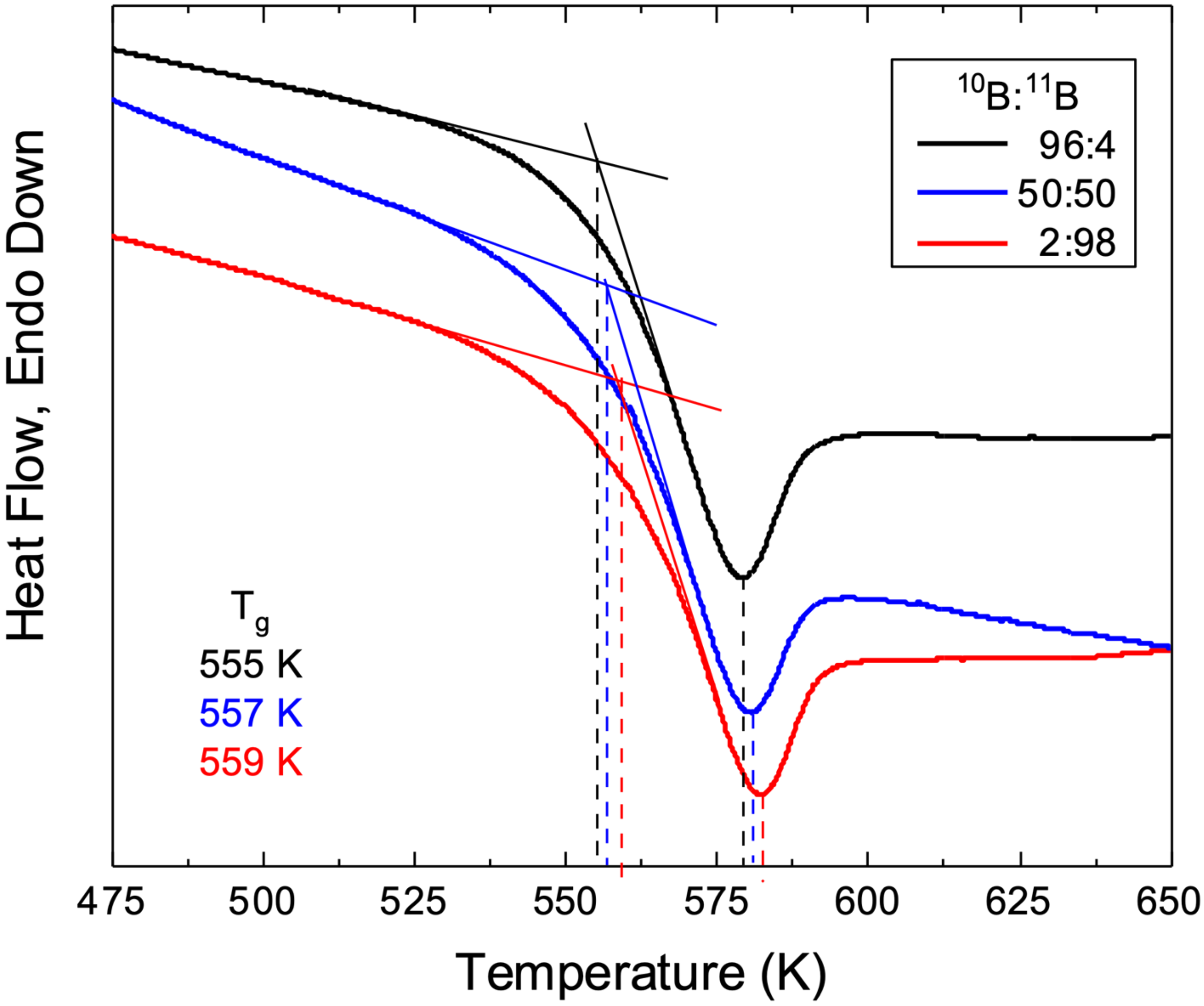

Figure 1. Representative DSC scans obtained at a heating rate of 10K/min for B_2O_3 glasses with different isotopic composition across glass transition. Scans from top to bottom correspond to 96% (black), 50% (blue) and 2% (red) ^{10}B. Vertical dashed lines show locations of onset and peak of T_g endotherms. T_g values obtained from endotherm onset are listed in the inset.

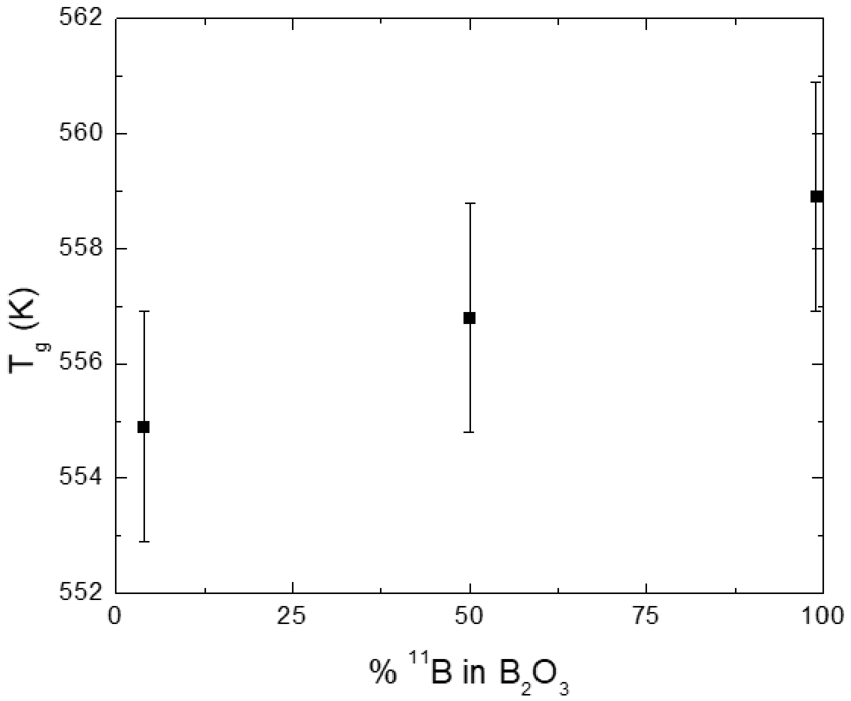

Figure 2a. T_g of B_2O_3 glasses with different isotopic composition expressed as a function of relative fraction of ^{11}B isotope.

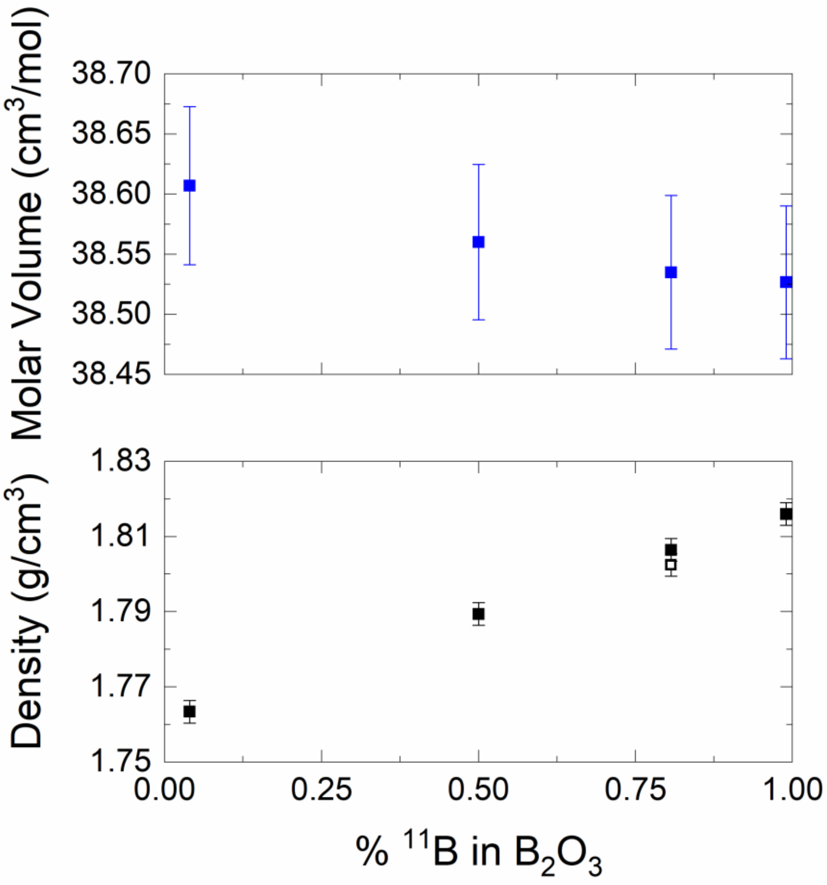

Figure 2b. Density (bottom panel) and molar volume (top panel) of B_2O_3 glasses with different isotopic composition expressed as a function of relative fraction of ^{11}B isotope. The density of a glass with natural isotopic abundance (80.1% ^{11}B) prepared in this study (filled square) is compared with that reported on dry B_2O_3 glass (open square) by Macedo et al. [23]. Error bars for molar volume data are obtained by propagating errors from density measurements.

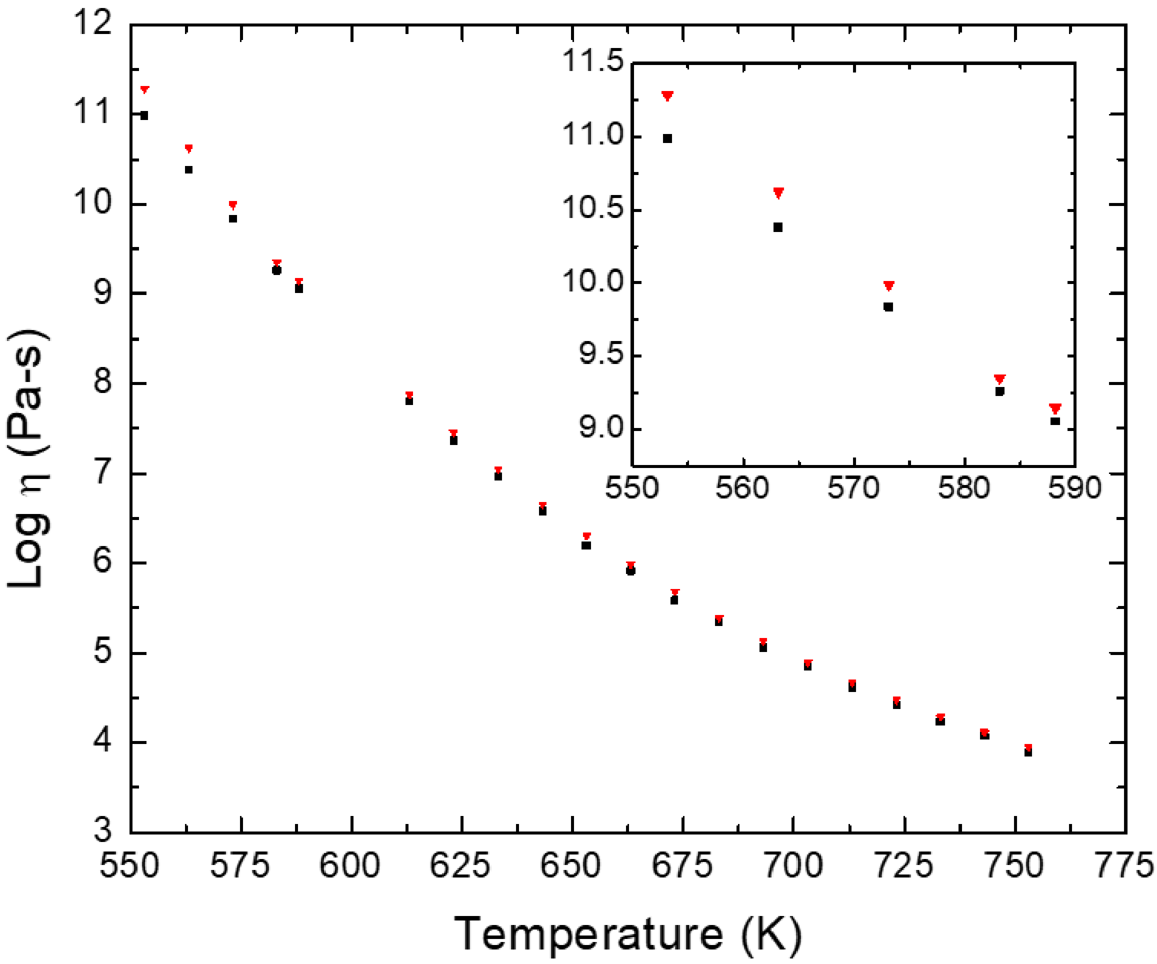

Figure 3. Temperature dependence of shear viscosity of B_2O_3 liquids with 2% (red triangles) and 96% (black squares) ^{10}B. Inset is a magnified view of viscosity variation near glass transition. Experimental error bars for viscosity (± 0.03 log units) and temperature (± 1K) are within the size of the symbols.

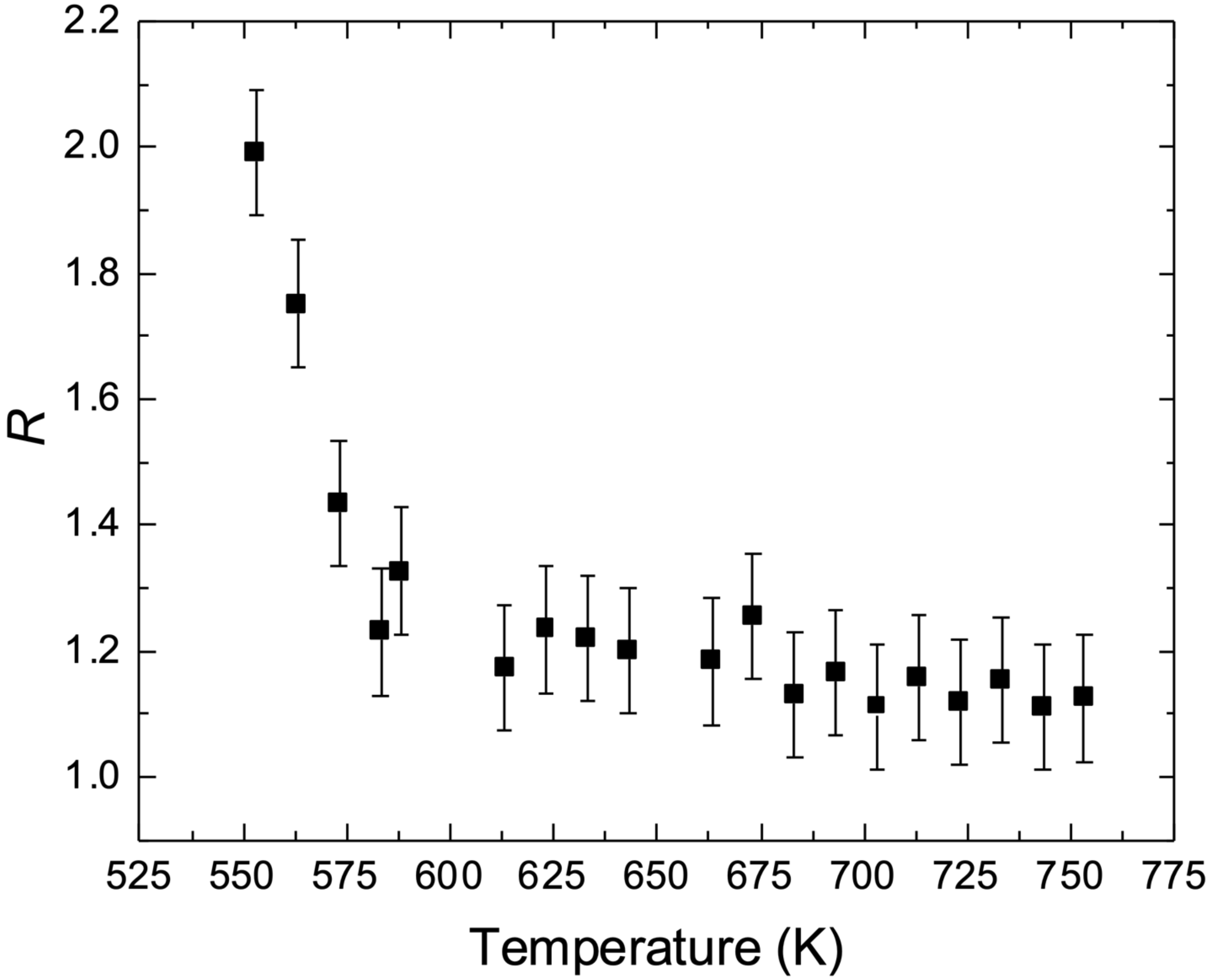

Figure 4. Temperature dependence of ratio *R* of isothermal shear viscosities of B_2O_3 liquids with 2% and 96% ^{10}B.

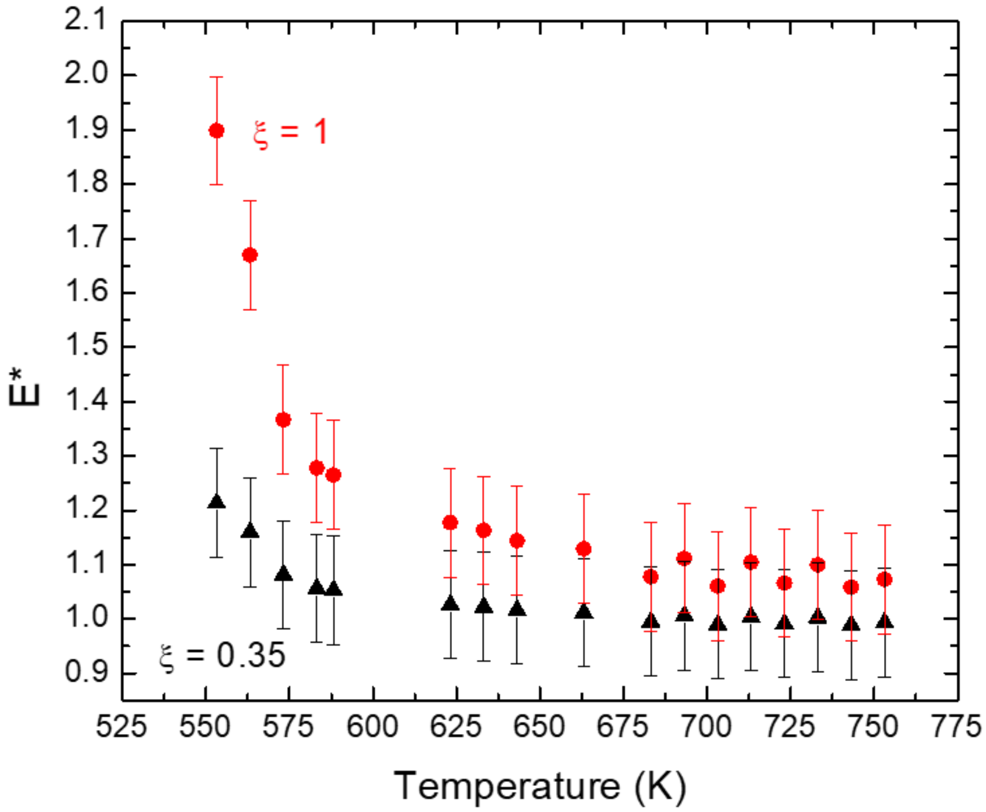

Figure 5. Temperature dependence of isotope-effect parameter E^* for B_2O_3 liquid estimated using Stokes-Einstein relation ($\xi = 1$; red circles) and fractional Stokes-Einstein relation ($\xi = 0.35$; black triangles). See text for details.