Shear viscosities of galliosilicate liquids

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ABSTRACT

The shear viscosities of 19 galliosilicate and related liquids have been measured using the concentric cylinder method. Nine of the liquid compositions lie in the NaO-GaO-SiO$_2$ system, eight liquids correspond in composition to $X$Ga$_i$Si$_{3-i}$O$_8$ (where $X$: Cs, Rb, K, Na, Li, Ba, Sr, and Ca), and five liquids are Li silicates related by the exchange of Al, Ga, and Fe. The measurements were performed at 1 atm of air pressure in the temperature range of 1700–900°C and a viscosity range of $10^{-3}$–$10^5$ dPaS. The rotation rates ranged from 0.5 to 100 rpm.

All melts exhibited Newtonian viscosities. The viscosities of the $X$Ga$_i$Si$_{3-i}$O$_8$ liquids decrease in the order Cs > Rb > K > Na > Li and Ba > Sr > Ca. Increasing SiO$_2$ content in liquids on the SiO$_2$-NaGaO$_2$ join (NaGaSiO$_4$, NaGaSi$_2$O$_6$, Na$_2$Ga$_2$Si$_2$O$_7$) results in increasing viscosity. The exchange of Ga$_2$O$_3$, for Na$_2$O along the 75 mol% SiO$_2$ isopleth (Na$_2$Si$_2$O$_5$, Na$_2$Ga$_2$Si$_2$O$_7$, NaGa$_2$Si$_2$O$_7$, Na$_2$Ga$_2$Si$_2$O$_7$, Ga$_2$Si$_2$O$_3$) yields a viscosity maximum at NaGaSi$_2$O$_6$. Comparison with viscosity data for aluminosilicate, ferrosilicate, and borosilicate liquids indicates that viscosities decrease in the order aluminosilicate > galliosilicate > ferrosilicate > borosilicate. Recent heat of solution measurements on NaXSi$_3$O$_8$ glasses (where $X$: Al, Fe, Ga, and B), in molten Pb$_2$B$_2$O$_5$ at 973 K indicate that the degree to which glasses are stabilized increases in the order Al > Ga > Fe > B (DeYoreo et al., 1990). Thus a correlation can be made between liquid viscosity and glassy heat of solution that is similar to that previously noted for the alkali exchange in aluminosilicate melts of the formula $X$Al$_2$Si$_3$O$_8$ (where $X$: alkali). Galliosilicate liquids have been used as structural analogues of the aluminosilicates. The composition-dependence of their viscosities is analogous to the aluminosilicates with the difference that the glass transition occurs at much lower temperatures in galliosilicate liquids. These results confirm galliosilicate liquids as useful analogues for aluminosilicate liquids in studies where the high viscosities of the latter may prevent experimental determination of certain relaxed liquid properties.

INTRODUCTION

Viscosity is possibly the most diagnostic property of a liquid. It has been demonstrated recently that the time scale of relaxation associated with viscous flow closely matches the mean lifetime of individual Si-O bonds in silicate liquids (Liu et al., 1988). Farnan and Stebbins (1990) have recently calculated viscosity from $^2$Si NMR relaxation time data. The relaxation behavior of silicate liquids can be approximated from the ratio of viscosity to elastic modulus, i.e., the Maxwell relation (e.g., Angell and Torrell, 1983). The relative composition and temperature invariance of the elastic modulus yields the approximation that viscosity is a linear measure of the time scale of bond exchange that dominates high-temperature melt kinetics and defines the glass transition (Dingwell and Webb, 1989).

Fundamentally then, viscosity is a measure of melt dynamics, but the dynamics themselves must correlate with the strength of bonds and distribution of cations in silicate melts. One source of information on the static structure of silicate melts is the relative enthalpies of silicate glasses. Relative enthalpies of silicate glasses are available for a wide range of compositions from the systematic studies of Navrotsky and coworkers using lead borate solution studies (e.g., Roy and Navrotsky, 1984). A recent comparison of relative heats of solution of Na aluminosilicate, galliosilicate, ferro-, and borosilicate glasses (DeYoreo et al., 1990) provides data that enable comparison with the present shear viscosity data.

Gallium has been used as a structural analogue for Al in several studies of the properties and structure of silicate liquid and glass (e.g., Fleet et al., 1984; Henderson et al., 1985; Matson and Sharma, 1985; Dickinson and Hess, 1986; Sherriff and Fleet, 1990). The present study illustrates some of the similarities in properties of galliosilicates and aluminosilicates. However, one important difference is the lower viscosities of the galliosilicates that reduce the temperatures required for several types of experimental investigations of melt properties.

EXPERIMENTAL METHOD

Eight of the compositions used in this study are based on a stoichiometry given by the general formula
temperatures in the range of 1700-900 °C in air, were remelted stepwise into the viscometry crucibles. The 75-ml crucibles. These batches were subsequently broken from these crucibles with a hammer, and the chips removed from the batch furnace and allowed to cool in viscometry crucibles. The remainder of the batches were weighed into 500-ml plastic bottles and mixed by agitation. The carbonate and oxide powders were kept in standards were diopside (Ca), orthoclase (K), albite (Na,Al) and synthetic MgGaO₃ spinel (Ga), Fe₂O₃ (Fe), albite (Al) and synthetic glasses CSFSI (Cs), RFSI (Rb), BFSI (Sr), CaCO₃ (Ca). The shear viscosities were measured at 1 atm and at temperatures in the range of 1700-900 °C in air, using the concentric cylinder method. The apparatus is that described in previous work (Dingwell, 1989a, 1989b). The viscometry furnace is a box furnace with MoSi₂ heating elements. The viscometry crucibles and spindle, fabricated from Pt₈₀Rh₂₀, are identical to those described by Dingwell and Virgo (1988). The viscometer heads are Brookfield models HBTD and RVTD (with full-scale torques of 5.75 × 10⁻¹ and 7.20 × 10⁻² Nm, respectively. The measurements of viscosity are relative. The values of torque are converted to viscosity values based on a family of viscosity-torque calibration curves obtained from viscosity measurements of Deutsche Glastechnische Gesellschaft standard DGG1. The precision of these measurements is ±2.5% at 2σ. The calibration using viscosity standards yields an accuracy of ±5% at 2σ.

The rotation rates vary with spindle and viscosity of the sample between 0.5 and 100 rpm. In general, the method employed here results in higher shear rates for the determination of lower viscosity data. For any individual determination, a range of about 0.67 orders of magnitude in rotation speed, and therefore shear rate, is accessible within a reasonable error range. No shear-rate dependence of viscosity was observed. The Newtonian viscosities resulting from this observation are consistent with the proposal that the time scale of structural relaxation for melts of these viscosities is much shorter than the inverse of the experimental strain rate. Thus we are measuring what may be usefully defined as liquid rather than glassy properties.

Measurements were made starting with the highest temperatures and reducing the control temperature in steps of 50, 25, or 20 °C until an instrumental or sample limit was reached. The last measurement was always a reoccurrence of the highest temperature determination. No difference was observed between first and last viscosity determinations, indicating that no compositional or instrumental drift took place during the viscometry determinations.

The oxidation state of the Fe-bearing liquids was determined on small dip-quenched samples with ⁵⁷Fe Mössbauer spectroscopy using the method described in Dingwell (1989b).

After viscometry, the samples were cooled in the viscometry furnace, removed, and remelted in the batch furnace. They were allowed to pour into a 75-cm³ Pt₈₀Au crucible in the batch furnace or poured onto a stainless steel plate upon removal from the batch furnace. The experimental products were analyzed with a Cameca SX 50 electron microprobe using wavelength dispersive analysis. The operating conditions were accelerating voltage of 15 kV, a sample current of 15 nA on brass, a defocused beam diameter of 30 μm and count times of 20 s. The standards were diopside (Ca), orthoclase (K), albite (Na,Al), synthetic MgGaO₃ spinel (Ga), Fe₂O₃ (Fe), albite (Al) and synthetic glasses CSFSI (Cs), RFSI (Rb), BFSI (Sr), SFS2 (Sr) (Dingwell, 1989b). The results are in Table 1.

### Table 1. Glass analyses (wt%)

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*Li₂O (theoretical), see text for operating conditions. Averages of 10 analyses. Fe⁴⁺/Fe³⁺ ratio obtained using ⁵⁷Fe Mössbauer spectroscopy.

XₓGaSiO₄ (where X is Cs, Rb, K, Na, Li, Ba, Sr, Ca). Seven of the compositions lie in the NaₓO-Ga₂O₃-SiO₂ system. Five of these are on the NaₓSiO₄-Ga₂SiO₃ join (NaₓSiO₄, NaₓGaₓSiₓO₄₋ₓ, NaₓGa₂O₃, NaₓGaₓSiₓO₄₋ₓ, GaₓSiO₃) and three are on the SiO₂-NaGaO₂ join (NaₓGaₓOₓ, NaₓGa₂O₃, NaₓGaₓO₄). Six of the compositions are Li silicates involving the exchange of Fe, Ga, and Al [Li(Ga,Fe,Al)Si₃O₈]. These compositions were chosen to permit comparison with existing shear viscosity data for aluminosilicate and ferrosilicate melts of equivalent stoichiometry (Riebling, 1966; Hunold and Brückner, 1980; Urbain et al., 1982; Dingwell, 1989b), with low temperature data of Lapp and Shelby (1986a, 1986b) and Piguet and Shelby (1985), and with the heat-of-solution data of DeYoreo et al. (1990). The starting materials for the preparation of glasses were CS₂O (99.9%), Rb₂CO₃ (99%), K₂CO₃ (99%), Na₂CO₃ (99%), Li₂CO₃ (99%), Ga₂O₃ (99.9%), BaCO₃ (99%), SrCO₃ (99%), CaCO₃ (99%), Fe₂O₃ (99%), Al₂O₃ (99%), and SiO₂ (99.9%). The carbonate and oxide powders were kept in an oven at 200 °C prior to use. Powder mixtures equivalent to 100 g of dehydrated and decarbonated melt were weighed into 500-ml plastic bottles and mixed by agitation for approximately 5 min. The mixed powders were loaded stepwise into a 75-ml Pt₈₀Au crucible and melted directly at temperatures from 1200 to 1700 °C. Some of the batches were removed rapidly from the batch furnace and poured directly from the 75-ml crucibles into the viscometry crucibles. The remainder of the batches were removed from the batch furnace and allowed to cool in the 75-ml crucibles. These batches were subsequently broken from these crucibles with a hammer, and the chips were remelted stepwise into the viscometry crucibles.
Fig. 1. (a) The viscosity-temperature relationships of alkali galliosilicate liquids of $X$Ga$_2$Si$_2$O$_5$ stoichiometry. Data for $X$: Cs, Rb, K, Na, and Li. (b) The viscosity-temperature relationships of alkaline earth galliosilicate liquids of $X$Ga$_2$Si$_2$O$_5$ stoichiometry. Data for $X$: Ba, Sr, and Ca. (c) The viscosity-temperature relationships of sodium galliosilicate liquids along the 75 mol% SiO$_2$ isopleth; Na$_2$O, Ga$_2$O$_3$, SiO$_2$. Data for $X$: 0.00, 0.25, 0.50, 0.75 and 1.00. (d) The viscosity-temperature relationships of sodium galliosilicate liquids on the SiO$_2$-NaGaO$_2$ join. Data for NaGa$_2$Si$_2$O$_7$, NaGa$_2$Si$_3$O$_8$, and NaGa$_2$SiO$_4$. (e) The viscosity-temperature relationships of lithium silicate liquids of the stoichiometry Li(Al,Fe,Ga)Si$_2$O$_5$. 
Table 2. Viscosity data (log₁₀η, in dPaS)

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Note: Viscosity data are accurate to ±5% (2σ).

RESULTS AND DISCUSSION

The results of the viscometry determinations are presented in Table 2 and Figures 1a-1e. The viscosities of the galliosilicate melts are Arrhenian, within error, over the present experimental temperature range. Thus the temperature dependence of the liquid viscosities can be described using

\[ \log_{10} \eta = a + b/T \]  

where a and b are constants. Table 3 contains the values of a and b obtained for the present liquids. The viscosities range in value from \(10^{13}\) to \(10^7\) poises. The viscosities and activation energies of these high temperature data decrease through the alkali galliosilicates in the order Cs > Rb > K > Na > Li. The viscosities of the alkaline earth galliosilicates decrease in the order Ba > Sr > Ca with constant activation energy.

The composition dependence of the viscosities of the galliosilicate melts exhibit similarities to aluminosilicate melts of equivalent stoichiometry (e.g., Urbain et al., 1982). The relative viscosities of the alkali galliosilicates (Cs > Rb > K > Na > Li) and alkaline earth galliosilicates (Ba > Sr > Ca) match those observed for the aluminosilicates and ferrosilicates (Dingwell, 1989b). One possible difference is the relative viscosity of the Na-GaSi₂O₅ liquid vs. the Ba₂GaSiO₆ melt. The viscosities of the ferrosilicate melts decrease in the order Na > Ba (Fig. 1a of Dingwell, 1989b) but the ferrosilicate data are not extensive enough in temperature to preclude a crossover, as is observed in this study. Additionally, the ferrosilicate comparison is complicated by the differing oxidation states of the Na and Ba ferrosilicate liquids (Dingwell, 1989b). Equivalent aluminosilicate data (Urbain et al., 1982) illustrate the trend Na > Ba but data are only available at higher temperatures, where this trend would also be observed in the galliosilicate liquids (Fig. 1a). In general it appears that the relative viscosities of
TABLE 3. Arrhenius parameters

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* Including low temperature data of Lapp and Shelby (1986a). Numbers in parentheses are 1 standard error.

the alkali vs. the alkaline earth gallio-, ferro-, and aluminosilicates might be temperature-dependent, whereas there is no indication of this within the alkali or alkaline earth groups.

Figure 2 compares the viscosities of the alkali galliosilicate liquids (this study) containing 75 mol% SiO₂ at 1600 °C. Five liquids spanning the compositional range of sodium trisilicate to gallium trisilicate (Na₂O·3SiO₂·Ga₂O₃·3SiO₂) illustrate a maximum at or near the NaGaSi₃O₈ composition. This variation of viscosity at constant temperature is similar to that observed by Lapp and Shelby (1986a, 1986b) at much lower temperatures and higher viscosities. It is also similar to the variation of viscosity with composition in the equivalent aluminosilicate liquids, at high temperatures (Riebling, 1966) and low temperatures (Hunnold and Brückner, 1980). The relative viscosities of the alkali galliosilicates of XGaSi₃O₈ are also illustrated in Figure 2. These data for X = Cs, Rb, K, Na, and Li can be combined with the alkali trisilicate data (left side of Figure 2) and the Ga₂O₃·3SiO₂ data to illustrate how cation specific the relative viscosities on the trisilicate join are. The magnitude of the maximum in viscosity at or near the XGaSi₃O₈ composition depends strongly on the identity of X. A similar conclusion can be drawn from the low temperature data of Lapp and Shelby (1986b) for potassium and sodium galliosilicates on the trisilicate join.

Fig. 2. Viscosities of galliosilicate liquids containing 75 mol% SiO₂ at 1600 °C.

Fig. 3. Comparison of viscosity-temperature relationships for liquids on the join SiO₂-NaXO (where X = Al, Ga, Fe, and B). Data from this study, galliosilicates; Riebling (1966), aluminosilicates; Tait et al. (1984), borosilicates; and Dingwell and Virgo (1988), ferrosilicates.

Fig. 4. Isothermal comparison of viscosities of lithium silicate liquids at 1400 °C.
Figure 3 is a comparison of viscosities of liquids along the join SiO\textsubscript{2}-Na\textsubscript{2}O (where $T$ = Al, Ga, Fe, B). As discussed by Dingwell and Virgo (1988), the relative viscosities of these liquids may be explained in terms of the increasingly destabilizing effects of Al, Ga, Fe, and B on the strength of O-bridging bonds in the tetrahedral network structure of the liquids. The departure of the borosilicates from the trend exhibited by the gallio-, ferro-, and aluminosilicates may be related to an increasing proportion of B in trigonal coordination in liquids on the SiO\textsubscript{2}-NaBO\textsubscript{3} join with decreasing SiO\textsubscript{2} content.

DeYoreo et al. (1990) have measured the heats of solution (in 2PbO·B\textsubscript{2}O\textsubscript{3} at 973 K) of glasses on the joins Na\textsubscript{2}O-SiO\textsubscript{2} (where $X$ = Ga and Fe). These results, compared for the equivalent aluminosilicates and borosilicates (Roy and Navrotsky, 1984), illustrate a trend of decreasing enthalpy of solution in the order Al $> \text{Ga} > \text{Fe} > \text{B}$. The relative viscosities of the Na\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} melts (this study; Urbain et al., 1982; Dingwell, 1989b) decrease in the same order. This positive correlation between relative enthalpy and viscosity is also observed for the substitution of alkali and alkaline earth cations in melts of the SiO\textsubscript{2}-\textit{X} \textsuperscript{2+}\textsubscript{2}O\textsubscript{3} joins (Dingwell and Virgo, 1988), and it is speculated here that heat-of-solution data for the alkali-substituted galliosilicate and borosilicate melts of the present study will also show this enthalpy-viscosity trend.

Figure 1c presents the viscosity data for Li silicate melts involving the exchange of Al, Ga, and Fe for each other. The two Ga-bearing joins, LiGaSi\textsubscript{2}O\textsubscript{6}-LiAlSi\textsubscript{2}O\textsubscript{6} and LiGaSi\textsubscript{2}O\textsubscript{6}-LiFeSi\textsubscript{2}O\textsubscript{6}, exhibit linear composition dependence of viscosities (Fig. 4). In contrast, the LiAlSi\textsubscript{2}O\textsubscript{6}-LiFeSi\textsubscript{2}O\textsubscript{6} join has a negative deviation from additivity.

Low-temperature viscosity and glass transition-temperature data for a number of the compositions of this study are available in the literature. The low-temperature viscosity data are combined with the high temperature data of this study in Figure 5. The T\textsubscript{g} data of Lapp and Shelby (1986a, 1986b) may be converted into viscosity data using relationships among relaxation time, cooling and heating rates, and viscosity (Dingwell and Webb, 1990). The resultant viscosity data are plotted in Figure 5. All the compositions exhibit non-Arrhenian behavior. The data of Figure 5 can be reduced to a simpler comparison using a plot of log\textsubscript{o} shear viscosity vs. T\textsubscript{g}/T (Angell, 1984). This yields a spectrum of curves of strong vs. fragile liquid behavior (Angell, 1984). Figure 6 is such a plot. It can be seen that the T\textsubscript{g}/T normalization reduces the temperature dependence of shear viscosity of the KGaSi\textsubscript{2}O\textsubscript{6}, NaGaSi\textsubscript{2}O\textsubscript{6}, and LiGaSi\textsubscript{2}O\textsubscript{6} to a single curve. Thus the degree of fragility of these liquids appears to be independent of the identity of the alkali cation. This can be taken to imply that the temperature-induced changes in the structural rearrangements characterizing viscous flow (recorded by the configurational entropy, according to Adam and Gibbs, 1965) in these liquids are only weakly dependent on the identity of the alkali cation. In contrast, decreasing SiO\textsubscript{2} content from 75 to 50 mol\% in the SiO\textsubscript{2}-NaGaO\textsubscript{2} system increases the fragility of the liquids. The Ga/Si ratio exerts a control on the degree of non-Arrhenian behavior. Similar observations have been made on aluminosilicate liquids (Scamehorn and Angell, 1989).

**Summary**

The viscosity-temperature relationships of galliosilicate liquids have been measured at high temperatures using the concentric cylinder method. The composition dependence of viscosities of the galliosilicate liquids are similar to those of equivalent aluminosilicates. Viscosities exhibit intermediate maxima along silica isopleths at or near the composition Ga/Na = 1. An increase in the field strength of the alkali or alkaline earth cation decreas-
es viscosity. Comparison with previously published low-
temperature viscosity data reveals that all the galliosili-
cate viscosity data are non-Arrhenian functions of tempera-
ture. Normalization of the viscosity temperature rela-
tionships to $T_g / T$ simplifies the composition depen-
dence of the viscosity data. The fragility or degree of non-
Arrhenian behavior of the galliosilicates is independent
of the identity of the alkali cation but dependent on the
Ga/Si ratio. A correlation between the heat of solution and shear viscosity noted previously for alkali and alka-
line earth exchanges may be qualitatively extended to a
comparison of gallium, iron, aluminum, and boron si-
licates. The galliosilicates should prove useful as analogue
compositions for aluminosilicate liquids whose higher
viscosities may prevent certain experimental investiga-
tions of liquid properties.

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