Viscosity-temperature relationships in the system $Na_2Si_2O_5$-$Na_4Al_2O_5$

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Abstract—The viscosity-temperature relationships of five melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$ (5, 10, 20, 30 and 40 mole percent $Na_4Al_2O_5$) have been measured in air, at 1 atm and 1000–1350°C with a concentric cylinder viscometer. All the melts on this join of constant bulk polymerization behave as Newtonian fluids, in the range of shear rates investigated, and the melts exhibit Arrhenian viscosity-temperature relationships.

Isothermal viscosities on this join initially decrease and then increase with increasing mole percent $Na_4Al_2O_5$. The minimum viscosity occurs near 20 mole percent $Na_4Al_2O_5$ at 1000°C and moves to higher $Na_4Al_2O_5$ content with increasing temperature.

The observation of a viscosity minimum along the join Na_2Si_2-O_5-$Na_4Al_2O_5$ is not predicted based on earlier viscosity data for the system Na_2O-Al_2O_3-SiO_2 (RIEBLING, 1966) or based on calculation methods derived from this and other data (BOTTINGA and WEILL, 1972). This unexpected behavior in melt viscosity-temperature relations emphasizes the need for a more complete data set in simple silicate systems.

Previous spectroscopic investigation of melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$ offer a structural explanation for the observed viscosity data in terms of a disproportionation reaction involving polyanionic units. Macroscopically, the viscosity data may be qualitatively reconciled with the configurational entropy model for viscous flow (RICHET, 1984).

INTRODUCTION

THE DEVELOPMENT OF a quantitative, structurally based relationship between the composition and viscosity of aluminosilicate melts is dependent on a fundamental understanding of the mechanism of viscous flow in such melts. The ternary system Na_2O-Al_2O_3-SiO_2 is a relatively well-investigated system in terms of both viscosity (RIEBLING, 1966, HUNOLD and BRUCKNER, 1979) and structure (TAYLOR and BROWN, 1979; MCMILLAN *et al.*, 1982; NAVROTSKY *et al.*, 1982; SEIFERT *et al.*, 1982). This system also pertains to two important compositional parameters in the petrochemistry of rocks of the granitic and felsic alkaline associations, namely the Al/(Al + Si) and alkali/aluminum ratios. Along joins of constant SiO_2 content, aluminum-saturated melts [Na/Al (molar) = 1] have higher viscosities and activation energies of viscous flow than either aluminum-oversaturated (peraluminous) or aluminum-undersaturated (peralkaline) melts (RIEBLING, 1966, HUNOLD and BRUCKNER, 1979).

Previous studies of the viscosity and structure of melts along the join $NaAlO_2$-SiO_2 have provided an important insight into the effect of the substitution of aluminate for silicate tetrahedra on the viscosity of fully polymerized melts. The effect of this substitution on the viscosity of depolymerized melts, however, remains uninvestigated. Melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$ and SiO_2-$NaAlO_2$ are parallel in molar projection (Fig. 1). They have constant bulk polymerization (NBO/T) values equal to 1 and 0, respectively. NBO/T represents the ratio of nonbridging oxygens to tetrahedrally coordinated cations and the method of calculation of NBO/T has been discussed by MYSEN *et al.* (1982). Thus, the join $Na_2Si_2O_5$-$Na_4Al_2O_5$ provides a useful basis for comparison with the join $NaAlO_2$-SiO_2 be-

cause these joins represent the substitution NaAl ⇌ Si in depolymerized and polymerized melts, respectively.

EXPERIMENTAL

The compositions investigated in this study lie along the compositional join $Na_2Si_2O_5$-$Na_4Al_2O_5$, denoted NS-NA (Fig. 1). This study presents viscosity-temperature relationships for melts of composition (mole percent) $NS_{95}NA_5$, $NS_{90}NA_{10}$, $NS_{80}NA_{20}$, $NS_{70}NA_{30}$ and $NS_{60}NA_{40}$, abbreviated NSNA5, NSNA10, NSNA20, NSNA30 and NSNA40, respectively, in the following discussion.

The starting materials for viscosity determinations were glasses prepared from reagent grade Na_2CO_3, Al_2O_3 and purified quartz sand. Mixtures of the sodium carbonate, alumina and quartz equivalent to a decarbonated weight of 50 g were ground under alcohol in an agate mortar for 3 hours and then decarbonated at 800°C overnight. The decarbonated samples were fused at 1350°C for 3 hours in a 25 cm³ Pt crucible. Prior to viscosity determinations, fused samples were poured from the Pt crucible into the $Pt_{80}Rh_{20}$ crucibles used for viscosity determinations and stirred with a $Pt_{80}Rh_{20}$ spindle for 1 hour at 1350°C resulting in homogeneous, bubble-free melts.

Viscosities were measured at 1 atm in the temperature range 1350–1000°C with the concentric cylinder method. The samples were contained in cylindrical $Pt_{80}Rh_{20}$ crucibles (5.1 cm long, 2.56 cm inner diameter, 0.1 cm wall thickness) in a SiC-heated vertical tube furnace (Fig. 2). Temperatures were monitored during viscosity runs with a $Pt_{90}Rh_{10}$ thermocouple (calibrated against the melting of Au at 1064°C) in ceramic insulation. The thermocouple was recessed into a 0.2 cm vertical groove in the firebrick cradle adjacent to the sample crucible (Fig. 2). In addition, the sample temperature was checked by immersing a shielded (in platinum tubing) $Pt_{90}Rh_{10}$ thermocouple in the melt at the high and low temperature extremes of each viscosity run. There was a reproducible 5°C difference between the temperatures recorded by the permanent and immersed thermocouples due to a radial temperature gradient outside the crucible. There were no significant (>1°C) temperature gradients inside the sample crucible. The vertical temperature profiles from immersion and furnace thermocouples are shown in Fig. 2. The temperatures reported in this study are accurate to ±2°C.

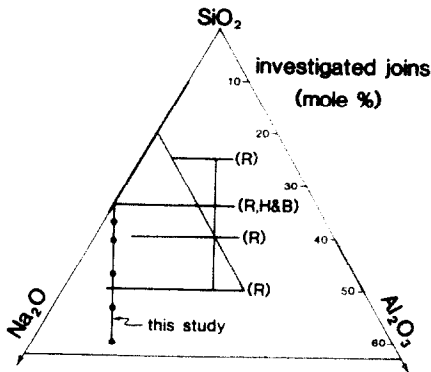FIG. 1. Starting compositions for this study and previously investigated joins in the system Na_2O-Al_2O_3-SiO_2. [(R) = RIEBLING, 1966; (H&B) = HUNOLD and BRUCKNER, 1979]. The diagram is in mole percent.

Viscosities were measured with a Brookfield RVTD viscometer head. This viscometer head drives a spindle at a range of constant speeds (0.5 to 100 rpm) and digitally records the torque exerted on the spindle by the sample. The $Pt_{80}Rh_{20}$ spindle used in this study has the cross-section of a cylinder (1.44 cm diameter, 3.32 cm length) with 45° conical ends to reduce end effects and a 0.24 cm diameter stem.

The spindle and head were calibrated for viscosity measurement with the NBS SRM 711 Lead-silica glass for which the viscosity-temperature relationship is accurately known. The precision and accuracy of viscosity data are based on the observed precision during replicate measurements of the standard glass SRM 711. Six determinations of the viscosity of SRM 711, each involving re-occupation of the temperature setting and removal and reinsertion of the measuring spindle gave a standard deviation (1σ) equal to 1.5%. The precision of determinations is quoted at $\pm3\%$ (2σ). The accuracy of determinations is taken as the sum of the uncertainties from standard and sample determinations, equal to $\pm6\%$ (2σ).

For each sample, the viscosity measurements were made at the highest temperature and then at successively lower temperatures. Thermal equilibrium was monitored with a chart recording of the sample viscosity during the decreasing tem-
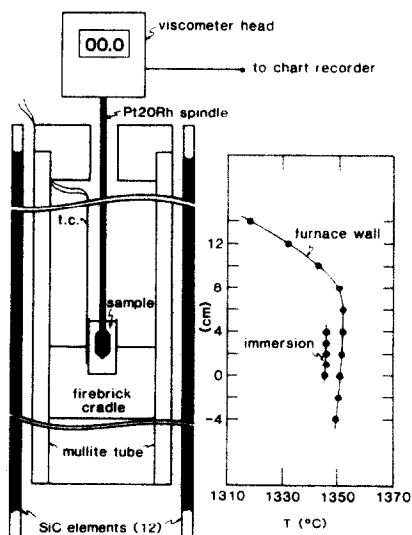

FIG. 2. The experimental apparatus used in the present study. (schematic except for vertical scale)

Table 1. Analysed melt compositions.

SAMPLE	Na_2O	Al_2O_3	SiO_2	Total
NSNA5	35.1	2.8	62.4	100.3
	(35.30)	(2.77)	(61.93)	
NSNA10	36.4	5.7	57.6	99.7
	(36.35)	(5.67)	(57.98)	
NSNA20	38.7	10.6	50.3	99.6
	(38.96)	(10.68)	(50.36)	
NSNA30	39.0	15.8	43.3	98.1
	(41.26)	(15.66)	(43.07)	
NSNA40	42.1	20.5	36.7	99.3
	(42.70)	(20.70)	(36.60)	

Analysts: J. Marinenko,H. Smith,USGS,Reston, VA. Na & Al by ICP, Si by gravimetry. (precision: elements less than 10% equals 2-10% rel.; elements greater than 10% equals 1-2% rel., SiO_2 equals 0.1% abs.) Numbers in brackets are stoichiometric compositions.

perature steps of approximately 50°C. One hour was sufficient for thermal equilibration of the sample over each 50 to 100°C temperature decrease. At the termination of each viscosity run, a high temperature viscosity measurement was redetermined to check for instrumental drift during a run. No drift was observed for any of these samples.

Torque measurements were made over a range of shear rates (*i.e.*, rotation speeds) for each sample. In all cases, the viscosities obtained were independent of shear rate. Samples were poured from the crucibles at the termination of each run and analysed by inductively coupled plasma for Na_2O and Al_2O_3 and by gravimetry for SiO_2. Glass homogeneity was checked by microprobe analysis of several chips of each glass. The chemical analyses are presented in Table 1.

RESULTS

The results of the viscosity determinations are presented in Table 2 and are plotted *versus* reciprocal absolute temperature in Fig. 3. All compositions exhibit viscosity-temperature relationships that may be fitted, within error, to the Arrhenius relationship,

$$\log_{10} \eta = \log_{10} \eta_0 + E_\eta/2.303RT \qquad (1)$$

where η is the viscosity at temperature T, $\log_{10}\eta_0$ is the pre-exponential or frequency factor, R is the gas constant and $E\eta$ is the activation energy of viscous flow. The Arrhenius parameters, $\log_{10}\eta_0$ and $E\eta$ are included in Table 2. The viscosity of sodium disilicate melt (denoted NS in text and Fig. 3) in the temperature range of this study has been investigated by several workers and the results of studies by LILLIE (1939), MEILING and UHLMANN (1967) and FONTANA and PLUMMER (1979) are included in Fig. 3 along with a least squares fit to all the sodium disilicate data. It is evident from the data in Fig. 3 that the viscosity-temperature relationships of melts on the join NS-NA exhibit a decreasing bulk viscosity with increasing NA content to composition NSNA20 and an increasing bulk viscosity beyond this composition. The activation energies $E\eta$ of the melts (as defined by the slopes in Fig. 3) are constant (within error) from sodium disilicate to NSNA20 and then increase to NSNA40. The frequency factors ($\log_{10}\eta_0$; vertical intercepts in Fig. 3) decrease from NSNA5 to NSNA40. The isothermal viscosities along the NS-NA join obtained by 50°C interpolations of the data of Table 2 (Fig. 4) show a minimum near NSNA30 at 1350°C. This minimum moves towards

Table 2. Viscosity data and derived Arrhenian parameters.

T(°C)	$\log_{10}\eta$	T(°C)	$\log_{10}\eta$	T(°C)	$\log_{10}\eta$	T(°C)	$\log_{10}\eta$	T(°C)	$\log_{10}\eta$
1350	1.63	1330	1.59	1345	1.46	1314	1.51	1348	1.55
1300	1.78	1280	1.75	1287	1.64	1229	1.85	1315	1.65
1255	1.96	1235	1.92	1240	1.82	1178	2.06	1294	1.78
1200	2.14	1185	2.11	1190	2.00	1130	2.27	--	--
1150	2.34	1140	2.30	1142	2.20	1076	2.53	--	--
1105	2.55	1085	2.55	1095	2.41	1029	2.78	--	--
1055	2.78	1035	2.76	1048	2.66	979	3.07	--	--
1008	3.02	995	2.93	995	2.93	--	--	--	--
E_η	37.3±0.7		38.4±1.2		38.3±1.6		42.7±0.7		49.1±3.0
PF	-3.4±0.1		-3.7±0.2		-3.7±0.2		-4.4±0.1		-5.1±0.4

E_η is the arrhenian activation energy, PF is the pre-exponential factor. Temperatures are ± 2°C; viscosities are ± 6% at 2 std. dev.

higher sodium disilicate content with decreasing temperature.

DISCUSSION

Previous work

Discussion of these data is facilitated by comparison with the results of previous investigations of melt viscosities in the system Na_2O-Al_2O_3-SiO_2 (as indicated in Fig. 1). RIEBLING (1966) measured the viscosities of melts along joins of constant SiO_2 content, constant Na_2O content and constant Na/Al ratio. The only other join of constant bulk polymerization (NBO/T = 0) that has been investigated in this system is SiO_2-$NaAlO_2$ (RIEBLING, 1966). No viscosity minima have been observed along previously investigated binary joins in the system Na_2O-Al_2O_3-SiO_2 and there is no indication from the pre-existing data base that a minimum in viscosity would occur on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$.

In this regard it is important to note that all the data of RIEBLING (1966) and HUNOLD and BRUCKNER (1979) are for melts containing at least 50 mole % SiO_2. With the new data presented in this study it is tempting to speculate on the possibility of a viscosity minimum on the join SiO_2-$NaAlO_2$.

Considering the limited composition range of previous data it is not surprising that the calculation method of BOTTINGA and WEILL (1972) (based on the data of RIEBLING, 1966 and others) does not predict a viscosity minimum on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$. Figure 4 compares the calculated and measured viscosities for the join $Na_2Si_2O_5$-$Na_4Al_2O_5$. Good agreement is found for sodium disilicate to NSNA30. The calculations fail for NSNA40. This discrepancy at NSNA40 is probably due to the lack of data for $NaAlO_2$-bearing melts in the compositional interval of mole fraction SiO_2 = 0.35–0.45, as noted by BOTTINGA and WEILL (1972).

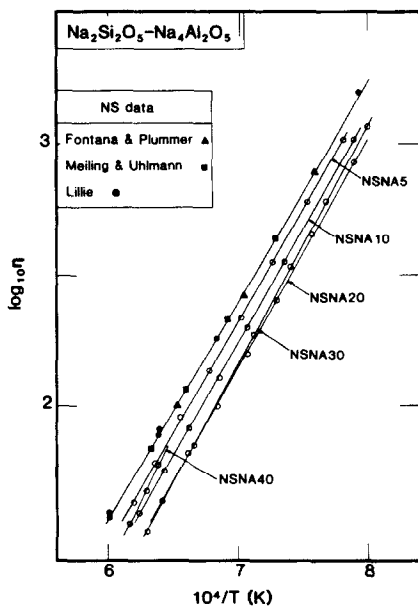FIG. 3. Viscosity-temperature relationships for melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$. Sodium disilicate data are from FONTANA and PLUMMER (1966) (triangles), MEILING and UHLMANN (1967) (squares) and LILLIE (1939) (solid circles).
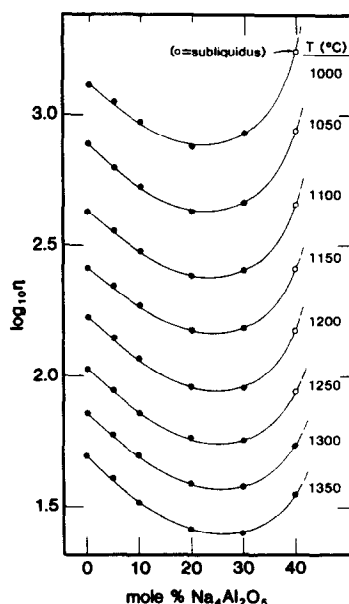
FIG. 4. Isothermal viscosities of melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$. (Solid circles represent interpolations at 50°C intervals, open circles represent extrapolations.)

More significant for the present study, however, is the observation that the BOTTINGA and WEILL (1972) method does not reproduce the smooth trend of melt viscosity reported in this study (Fig. 5, inset). Again, BOTTINGA and WEILL (1972) anticipate such difficulties due to the fact that their method was based on a variation of the logarithm of viscosity with composition fitted over discrete composition ranges. The compositions of this study vary greatly in silica content and thus highlight the discontinuities observed when using the BOTTINGA and WEILL (1972) method over large ranges of silica content.

Melt structure

Melts on the join SiO_2-$NaAlO_2$ consist of a continuous three-dimensional network of silicate and aluminate tetrahedra with each tetrahedrally coordinated Al charge balanced by a neighbouring Na atom (TAYLOR and BROWN, 1979; NAVROTSKY et al., 1982; SEIFERT et al., 1982). Accordingly, the observation of decreasing viscosity and activation energy with decreasing SiO_2 content along this join has been interpreted in terms of a decrease in the average strength of bridging bonds that must be broken for viscous flow in these melts (MYSEN et al., 1980). Viscosity and activation energy decrease strongly from SiO_2 to $3SiO_2 \cdot NaAlO_2$ (albite), but activation energies decrease only slightly from $3SiO_2 \cdot NaAlO_2$ (albite) to $SiO_2 \cdot NaAlO_2$ (nepheline).

Melts on the joins $Na_2Si_3O_7$-$NaAlSi_3O_8$ (RIEBLING, 1966), $Na_2Si_2O_5$-$NaAlSi_2O_6$ (RIEBLING, 1966; HUNOLD and BRUCKNER, 1979) and Na_2SiO_4-$NaAlSiO_4$ (RIEBLING, 1966) (all at constant SiO_2 content) exhibit increasing viscosity and activation energy with increasing Al content. These rapid increases in viscosity and activation energy results from polymerization of the melt structure due to the transfer of sodium atoms from network-modifying coordination of silicate tetrahedra to network-stabilizing coordination of aluminate tetrahedra (SEIFERT et al., 1982). Structural interpretation of the role of aluminate tetrahedra in determining the viscosity of melts along these joins is, however, com-

plicated by the fact that bulk polymerization (NBO/ T) and Al/(Al + Si) are varying simultaneously.

In contrast, melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$ maintain a bulk polymerization of NBO/T = 1 regardless of aluminum content. Based on the variation of viscosity with composition on the parallel (in molar projection, Fig. 1) join $NaAlO_2$-SiO_2, a continuous decrease in bulk viscosity with increasing aluminum might be expected. In fact, the viscosity and activation energy of melts on the join sodium disilicate-sodium dialuminate do not vary in a manner consistent with the simple replacement of silicate by aluminate tetrahedra. Instead, the minimum in viscosity (Fig. 3) and the increase in activation energy (Table 2), with increasing $Na_4Al_2O_5$ content may result from a structural reorganization of the aluminosilicate anions in response to the chemical exchange, $NaAl \rightleftharpoons Si$.

The structures of melts on the join sodium disilicate-sodium dialuminate have been investigated recently (MYSEN et al., 1985). The Raman spectra of quenched melts of sodium disilicate, NSNA5, NSNA10, NSNA20 and NSNA30 show systematic variations in the positions and relative intensity of several peaks.

MYSEN et al. (1985) used the statistical deconvolution procedure developed by SEIFERT et al. (1981) and estimates of the scattering efficiency of the Si-O symmetric stretch in ortho-, meta- and disilicate anionic units to estimate the relative proportions of anionic units in these melts. The resulting variations in polyanionic proportions were attributed to a disproportionation reaction of the type:

$$Si_2O_5^{2-} + (NaAl)_2O_5^{2-} = 2SiO_3^{2-} + 2NaAlO_2 \quad (2)$$
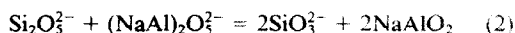
(MYSEN et al. 1985). The disilicate units of intermediate polymerization (NBO/T = 1) are disproportionated into more and less polymerized units, i.e., tecto-(NBO/T = 0) and metasilicate (NBO/T = 2) units, respectively.

RICHET (1984) has recently reviewed the configurational entropy theory of viscous flow of ADAM and GIBBS (1965) as applied to silicate melts. This theory states that there is an inverse correlation between the configurational entropy and viscosity of melts. RICHET and BOTTINGA (1984) have shown that some features of the composition-dependence and temperature-dependence of viscosity of some melt systems may be qualitatively understood in terms of the number of energetically equivalent rearrangements recorded by the configurational entropy of the melt system. In the absence of thermodynamic data for $Na_4Al_2O_5$ melt and in view of the Arrhenian behavior observed over the temperature range of this study, a quantitative evaluation of the configurational entropy theory of viscous flow is not attempted here. Low temperature viscosity data are required to constrain the configurational entropy theory parameters. Qualitatively, the position and magnitude of the viscosity minimum with respect to the endmembers is explicable in terms of the configurational entropy theory in which the contribution of
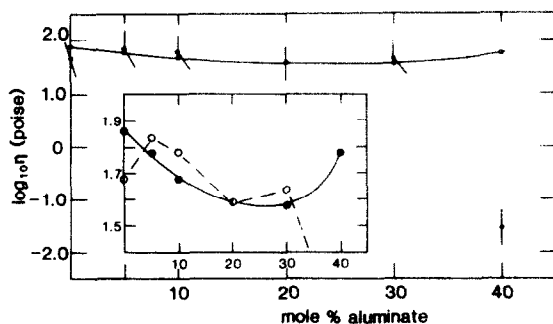

FIG. 5. Comparison of the measured (solid circles) and calculated (open circles) viscosities of melts on the join $Na_2Si_2O_5$-$Na_4Al_2O_5$. (Data at 1300°C, calculations using the method of BOTTINGA and WEILL, 1972)

the entropy of mixing becomes larger with decreasing temperature.

CONCLUSION

The viscosity-temperature relationships of melts on the join Na$_2$Si$_2$O$_5$-Na$_4$Al$_2$O$_5$ exhibit a minimum at a temperature-dependent intermediate composition. The increase in viscosity with increasing aluminate content beyond this intermediate composition is not predicted by calculation methods derived from the pre-existing data base. This failure illustrates the need for a more complete data base on the viscosities of relatively simple silicate melts.

The behavior of viscosity along the join Na$_2$Si$_2$O$_5$-Na$_4$Al$_2$O$_5$ may reflect the progress of a disproportionation reaction involving di-, meta- and tectosilicate polyanionic units. The viscosity data are qualitatively consistent with the configurational entropy theory of viscous flow.

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