Contrib Mineral Petrol (1992) 109:295–303

Contributions to Mineralogy and Petrology

Entropy dependence of viscosity and the glass-transition temperature of melts in the system diopside-anorthite

H. Taniguchi

Science Education Institute of Osaka Prefecture, Karita 4-13-23, Sumiyoshiku, Osaka 558, Japan

Received August 10, 1990/Accepted March 24, 1991

Abstract. Viscosities of diopside-anorthite melts were measured over the wide range of temperature (near the glass-transition temperature—1580°C/1 bar) and pressure (5–20 kb/above the liquidus temperature). The measurements were carried out by the fibre-elongation method for low temperature and the counter-balanced sphere method for high temperature at 1 bar, and the sinking and floating spheres method for high temperature at high pressure. Some of the values obtained deviated slightly from those in the literature. The data on viscosity and the glass-transition temperature have been interpreted on the basis of the configurational entropy theory, by which temperature and compositional effects on viscosity were explained well. The configurational entropies at the glass-transition temperature of magmatic silicate melts are almost constant if we use an average molecular weight (amw) or "bead" as a unit; 8.0 ± 1.2 J/K · amw, 1.1 ± 0.2 cal/K · bead. The latter value coincides well with the value from the literature for organic polymers. The negative deviation from linearity of the glass-transition temperature of intermediate melts may be interpreted as the effect of the mixing entropy. The calculated glass-transition temperature-composition curve using the mixing entropy agreed well with the experimental values.

Introduction

Viscosity is one of the most important physical properties governing magmatic process in the Earth. For example, it plays an essential role in the differentiation and ascent of magma. For a better understanding of the viscous behaviour, systematic data on viscosity not only at high temperature but also at low temperature and at high pressure are indispensable.

In the present study, systematic measurements of viscosity have been made on the join diopside-anorthite under various conditions: in the glassy state near the glass-transition temperature to the stable liquid state at 1 bar, and in the stable liquid state at high pressures up to 20 kb.

Viscosity measurements at 1 bar for the diopside-anorthite join were reported by Scarfe et al. (1983) and Taniguchi and Murase (1987b) at high temperatures, and by Tauber and Arndt (1987) at low temperatures. The viscosities of the end-member melts at 1 bar were also reported by Kirkpatrick (1974), Urbain et al. (1982) and Tauber and Arndt (1986) for diopside composition, and by Cukierman and Uhlmann (1973), Urbain et al. (1982) and Hummel and Arndt (1985) for anorthite composition. The determinations at high pressures were reported by Scarfe et al. (1979) and Brearley et al. (1986) for diopside melt, and by Kushiro (1981) for anorthite melt.

This paper presents some new systematic data and contains a discussion of the entropy dependence of viscosity and the glass-transition temperature.

Experimental

Sample preparation

Present samples are those used in the previous investigations on surface tension and density (Taniguchi 1988, 1989). For the method of preparation of the original melts and the chemical composition of quenched glasses reference should be made to these papers. Though the analysed compositions are somewhat different from the nominal ones, the differences are small enough for the present purpose.

After the measurement of viscosity at high temperature, the glass fibre for the measurement at low temperature was made from the melt in a platinum crucible using a pyrex glass rod. The fibre was annealed first at the glass-transition temperature (T_g) + 15°C for 30 min, and then annealed to $T_g - 200$°C at the rate of 0.33°C/min.

The glass powders used for the high pressure measurements were made from the quenched glass.

Measurement at low temperature

Figure 1 shows the apparatus used for the viscosity measurements at low temperature (the glassy state to the supercooled liquid state near T_g) by the fibre elongation method (Watanabe and Koyama 1957). This apparatus consists of four main parts: electrical furnance, quartz glass tube, differential transformer and weight. By this

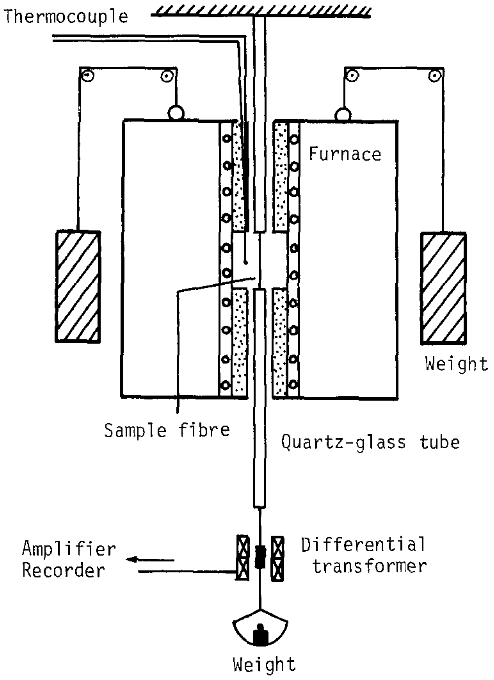

Fig. 1. Schematic diagram of the apparatus for the measurement of low-temperature viscosity (the fibre elongation method) at 1 atm

method, we can measure the viscosity in the range of $10^8 - 10^{15}$ poise (Watanabe and Koyama 1957). In the present experiments, however, we eliminated the values below 10^9 poise, because of the poor response of the electrical furnace to the temperature change; it was impossible to attain the desired temperature in a given duration of measurements.

Viscosity was calculated using the following equation.

$$\eta = \frac{1}{3} \cdot \frac{mgl}{\frac{dl}{dt} \cdot \pi r^2} \tag{1}$$

where η is the viscosity coefficient (poise), m is the load (g), g is the gravitational constant, r is a radius of the fibre (cm), l is a fibre length (cm) and dl/dt is the rate of elongation (cm/s). The length of the sample fibre is about 2 cm and its radius about 0.03 cm. The experimental errors of the measurement are estimated to be less than ± 0.1 on a logarithmic scale.

Measurement at high temperature

The counter balanced sphere method (Murase and McBirney 1973) was used for the measurements at high temperature (the melt in the stable liquid state and in supercooled liquid state near the liquidus temperature). The apparatus used for the measurements is the same as that for surface tension measurement (Taniguchi 1988) except for the platinum bob (10 mm in diameter). We can measure the melt viscosity below 10^5 poise by this method (Murase and McBirney 1973). It is very difficult, however, to obtain a precise value below 10 poise (Takahashi and Tanioka 1966), and thus the values below 10 poise were eliminated. Viscosity was calculated using the following equation:

$$\eta = \frac{K \cdot (W - W_0)}{\frac{dx}{dt}} \tag{2}$$

where K is the constant (poise · cm/g · s), W is the weight (g), W_0 is the weight for balance (g) and dx/dt is the rate of withdrawing the sphere (cm/s). The calibration has been done using the standard glass NBS-710 prepared by the US National Bureau of Standards. The experimental errors are estimated to be less than ± 0.05 on a logarithmic scale.

Measurement at high pressure

High pressure measurements were made with the sinking and floating spheres method of Fujii and Kushiro (1977) in a solid-media, piston-cylinder apparatus at the Institute for Study of the Earth's Interior, Okayama University. Following Fujii and Kushiro (1977), we can evaluate both density and viscosity by a single run based on Stokes' law. Thus, both values could be determined simultaneously using a SiC sphere (sinking sphere) and a BN sphere (floating sphere). The melt density at high pressure and the conditions of measurement have already been reported (Taniguchi 1989). Under each set of temperature-pressure conditions, more than two runs were made. Unfortunately, a sphere of SiC or BN was sometimes lost when the charge was polished. To save the information from the remaining sphere, the same expression of Stoke's law by Fujii and Kushiro (1977) was not used for viscosity calculation. The viscosity has been determined from the following expression using the density data:

$$\eta = \frac{2}{9} \cdot \frac{a^2 g \Delta\rho}{\frac{dx}{dt}} \tag{3}$$

where $\Delta\rho$ is the density difference (g/cm^3) between the sphere and melt, a is the radius (cm) of the sphere and dx/dt is the settling velocity (cm/s) of the sphere. In this expression, the time lag for movement of the sphere is assumed to be negligible (Taniguchi 1989). The apparent value of viscosity thus obtained was corrected by the Faxen correction (Shaw 1963; Kushiro 1976) to obtain the real value. The number of viscosity data obtained under the same conditions is larger than 4, and the average standard deviation is 0.03 on a logarithmic scale.

Results

Viscosity at 1 bar

The experimental results at high temperatures ($T \geq 1100°C$) are given in Table 1. The data for diopside melt are quoted from the paper by Scarfe et al. (1983), because the viscosity of this melt is so low that reasonable values could not be obtained by the present method. The present values for *Di*64*An*36 melt agree well with the previous data by Scarfe et al. (1983) and Taniguchi and Murase (1987b) within 2.5% error, whereas the values for anorthite melt are somewhat higher (within 7%), compared with those in the literature (Urbain et al. 1982; Scarfe et al. 1983).

The experimental results at low temperatures ($T < 1000°C$) are also given in Table 1. Compared with the results reported by Tauber and Arndt (1986) for diopside melt, the present values agree with them within 2.5% error, whereas the values of Kirkpatrick (1974) are systematically lower by 4%. On the other hand, the values for anorthite melt in the present study are systematically higher by 6% compared with the data of Hummel and Arndt (1985). The reasons for these discrepancies have not been clarified yet; however, this does not affect the later discussion. Table 2 gives the coefficients of the VFT

Table 1. Viscosities at 1 atm

T	$\log \eta$					
°C	Di100	Di80	Di64	Di40	Di20	An100
1600	0.465[a]	—	—	—	—	—
1580	—	—	—	—	—	1.68
1550	0.559[a]	—	—	1.33	1.48	—
1540	—	—	—	—	—	1.77
1500	0.678[a]	—	1.17	1.55	1.75	1.99
1450	0.821[a]	1.13	1.36	1.70	1.95	2.17
1400	0.992[a]	1.28	1.56	1.86	2.25	2.48
1375	1.086[a]	—	—	—	—	—
1350	—	1.51	1.76	2.16	—	—
1345	—	—	—	—	—	2.76
1300	—	1.84	2.03	2.44	—	3.17
1250	—	2.16	2.32	2.80	—	—
1200	—	2.52	2.67	3.24	—	—
1150	—	—	3.19	—	—	—
1100	—	—	3.62	—	—	—
953	—	—	—	—	—	9.4
925	—	—	—	—	—	10.1
900	—	—	—	—	9.4	11.3
875	—	—	—	—	10.3	12.5
850	—	—	—	—	11.6	—
845	—	—	—	—	—	13.9
840	—	—	—	9.9	—	—
825	—	9.2	9.4	—	12.4	—
800	—	10.1	10.6	11.3	13.8	—
795	9.6	—	—	—	—	
780	10.1	—	—	—	—	—
775	10.2	11.0	11.6	13.0	—	—
750	11.1	12.1	12.8	14.1	—	—
730	—	13.3	14.0	—	—	—
725	12.6	—	—	—	—	—
700	13.3	—	—	—	—	—

η, Poise; composition: mol%

[a] Scarfe et al. (1983)

Table 2. Coefficients of the VFT-type viscosity equation

	A	B	To	r^2
Diopside	− 4.880	6318	357	0.999
Di80An20	− 4.022	5126	434	1.000
Di64An36	− 3.372	4504	472	0.999
Di40An60	− 2.945	4405	494	0.999
Di20An80	− 3.352	5083	504	1.000
Anorthite	− 3.323	4910	562	0.999

$\log \eta = \mathrm{A} + \mathrm{B}/(\mathrm{T} - \mathrm{To})$: VFT equation;
To: °C, r, coefficient of correlation

equation (Vogel-Fulcher-Tammann equation; Fulcher 1925; Hummel and Arndt 1985) for data at 1 bar.

Figure 2 shows the overall viscosity-temperature relations, the T_g (Taniguchi and Murase 1987b) and the liquidus temperature (Yoder 1976). We can point out two characteristics. The first is that the viscosity does not change linearly when plotted against the reciprocal of temperature, i.e. the Arrhenius relation is not valid in the present system. The second is that the viscosity at T_g is not a constant value but a function of composition; it ranges from 12 to 14 on a logarithmic scale.

Viscosity at high pressure

The experimental results at high pressures for diopside, *Di*64*An*36 and anorthite melts are given in Table 3. The values for diopside and anorthite melts at 1 bar were calculated from the data given by Urbain et al. (1982), because they gave the experimental values under temperature conditions at which the present high pressure meas-

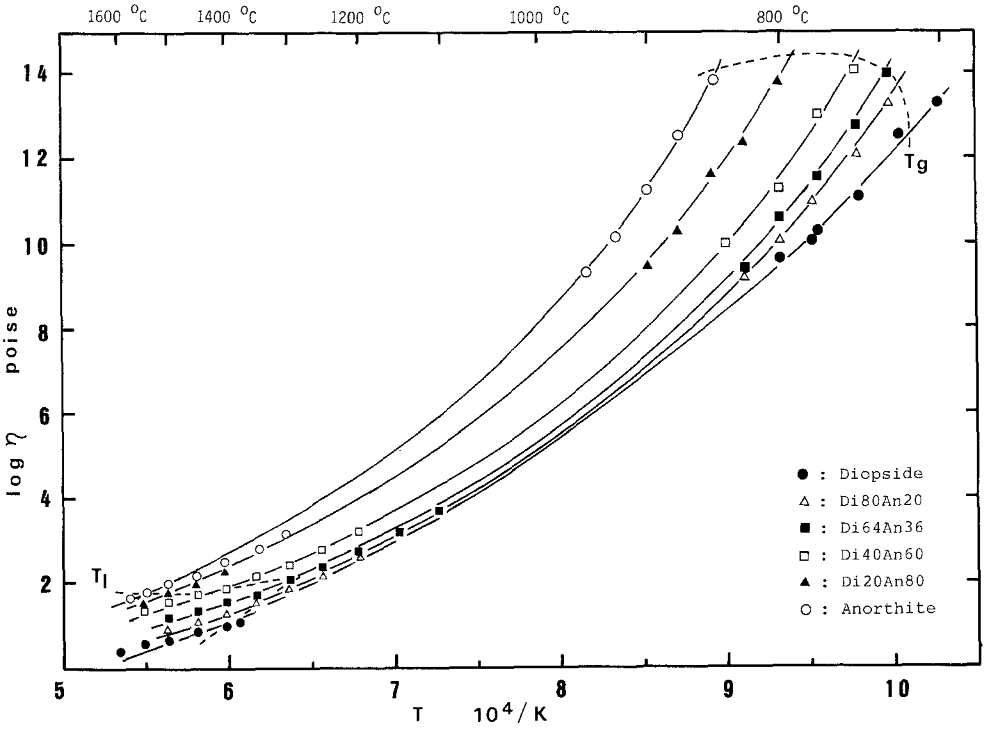

Fig. 2. Viscosity-temperature relations at 1 atm. *Solid curves* are calculated using the VFT equation listed in Table 2. The *broken lines* indicate the glass-transition temperature (T_g) and the liquidus temperature (T_1)

Table 3. Viscosities at high pressures

		log η					
	T			P	Kb		
	°C	0.001	5	7.5	10	15	20
Diopside	1550	0.62[a]	0.55 ± 0.10	—	—	—	—
	1650	0.38[a]	0.36 ± 0.02	—	0.34 ± 0.02	0.44 ± 0.04	—
	1800	0.07[a]	0.06 ± 0.02	—	0.05 ± 0.02	0.19 ± 0.03	0.23 ± 0.01
Di64An36	1400	1.56	1.41 ± 0.01	—	1.54 ± 0.04	—	—
	1500	1.17	—	—	0.95 ± 0.06	1.02 ± 0.02	—
	1650	0.75	—	—	0.55 ± 0.01	0.64 ± 0.02	0.72 ± 0.08
Anorthite	1650	1.22[a]	1.22 ± 0.03	1.25 ± 0.01	1.20 ± 0.06	—	—
	1800	0.76[a]	0.89 ± 0.02	—	0.67 ± 0.01	0.54 ± 0.01	0.77 ± 0.06

η, Poise, composition: mol%

[a] Estimated value based on the data of Urbain et al. (1982)

urements were made. The viscosity at 1650°C/1 bar for *Di64An36* melt was estimated from the present values.

The viscosities of diopside melt at high pressures have been reported by Scarfe et al. (1979) at 1640°C and by Brearley et al. (1986) at 1600°C using the sinking and floating spheres method. Although they used the same technique as was used to obtain the present measurements, their values were much larger than the present values. For example, Scarfe et al. (1979) indicate that the viscosity of melt at 1640°C/15 Kb is about 1.0 on a logarithmic scale, whereas the present measurement at 1650°C/15 kb is 0.44 ± 0.04. Though the reasons for this discrepancy are not clear, there are two possibilities. Firstly the viscosity of this melt is too low for the method to be used, and secondly there is a difference between materials used for the moving sphere. The present values for anorthite melt at 1650°C agreed well with the values given by Kushiro (1981) within experimental error.

Figure 3 gives the experimental results for these three melts. Although the present results for diopside melt are not in good agreement with the published data, the tendency of viscosity change with pressure is similar in each case, i.e. the viscosity increases with increasing pressure above 10 kb.

Discussion

Many theories and equations have been proposed to describe the relations between viscosity and temperature, pressure and composition of liquids. In the field of geological science, the Arrhenius and the VFT equations (Fulcher 1925; Hummel and Arndt 1985) have been used frequently to describe the viscosity–temperature relation; however, there are essential weak points for the application of these equations to magmatic silicate melts. For example, the Arrhenius equation does not predict precisely the viscous behaviour of most magmatic silicate melts except for SiO_2 and albite melts in a wide temperature range (glassy to stable liquid states). Although the VFT equation reproduces more exactly the experimental values in the wide temperature range, the physical meaning of the equation is not clear.

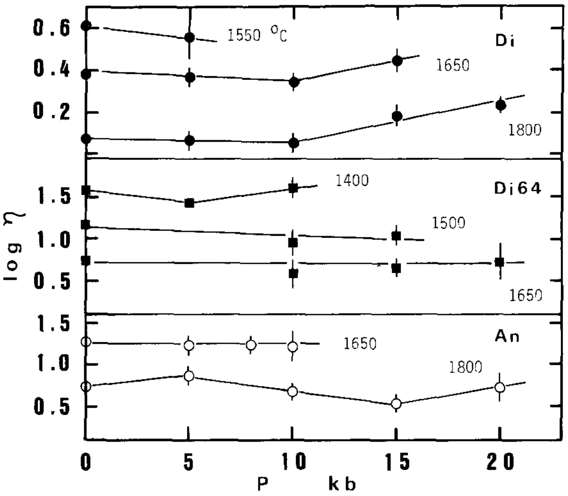

Fig. 3. Viscosity-pressure relations of diopside, Di64An36 and anorthite melts. For the values at 1 atm, see the text

Therefore an equation which accounts for the viscous behaviour of magmatic silicate melts should fulfil both the theoretical and experimental aspects. Two representative theories, the free volume theory (Cukierman and Uhlmann 1973) and the configurational entropy theory (Richet 1984, 1986) have been employed recently. The validity of the latter has been confirmed gradually, whereas the former has been almost rejected (Richet 1984; Hummel and Arndt 1985).

In the following section, the validity of the configurational entropy theory will be discussed on the basis of the experimental data.

Temperature effect on viscosity

The configurational entropy theory is based on the assumption that the viscosity is proportional to the number of attainable configurations in a system, and the configurational entropy is the measure of that number. The basis of this theory has been established by Adam and

Gibbs (1965), and its application to magmatic silicate melts has been attempted by some researchers, for example, by Tauber and Arndt (1987) for the present system, by Tauber and Arndt (1986) and by Richet (1986) for diopside melt, and by Richet (1984) and Hummel and Arndt (1985) for anorthite melt.

In the present discussion, I will give a brief outline of the application of this theory to the present melt system and some new related evidence.

The basic equation based on this theory (Adam and Gibbs 1965; Richet 1984) is:

$$\log \eta = A_e + \frac{B_e}{T \cdot S_{c(T)}} \tag{4}$$

where A_e and B_e are constants, T is the absolute temperature and $S_{c(T)}$ is the configurational entropy calculated from the following equation:

$$S_{c(T)} = S_{c(\bar{T})} + \int_{\bar{T}}^{T} \frac{\Delta C_p}{T} dT \tag{5}$$

where ΔC_p is the configurational heat capacity; the difference of heat capacities between the glassy state at the fictive temperature $\bar{T}$ and the melt at the temperature $T \cdot S_{c(\bar{T})}$ is the configurational entropy at the fictive temperature, and is given by the following equation (Richet 1984):

$$\begin{aligned} S_{c(\bar{T})} = S_{cc} &+ \int_{0}^{T_f} \frac{C_{pc}}{T} dT + \Delta S_f \\ &+ \int_{T_f}^{\bar{T}} \frac{C_{pl}}{T} dT + \int_{\bar{T}}^{0} \frac{C_{pg}}{T} dT \end{aligned} \tag{6}$$

where T_f and ΔS_f are the temperature and entropy of fusion of the crystal; S_{cc} is the configurational entropy of the crystal; C_{pc}, C_{pl} and C_{pg} are the heat capacities of the crystalline, liquid and glassy phases of the substance. If the fictive temperature data are not available, we use T_g or the temperature at which the viscosity is 10^{13} poise instead of real $\bar{T}$ (Richet 1984).

For diopside and anorthite compositions, the parameters necessary for the calculation have been reported by Richet (1984, 1986) as listed in Table 4. If Eq. 4 is applicable to the present melt system, we can expect a linear relation between $log\,\eta$ and the reciprocal of $T \cdot S_{c(T)}$. Since we do not have the parameters of the intermediate melts, we must make two assumptions; the first is that the additivity of heat capacities holds for the melts:

$$C_{p(DiXAnY)} = X \cdot C_{p(Di)} + Y \cdot C_{p(An)} \tag{7}$$

where X and Y are the mole fractions of *Di and An*, respectively, $C_{p(Di)}$, $C_{p(An)}$ and $C_{p(DiXAnY)}$ are the heat capacities of *Di* , *An* and *DiXAnY* melts, respectively. The additivity of heat capacity of silicate melts has already been confirmed (Stebbins et al. 1984; Richet 1987). The second is that $S_{c(\bar{T})}$ is an adjustable parameter.

Table 4. Thermodynamic parameters of diopside and anorthite melts for the calculation based on the configurational entropy theory

Composition	T_g K	$S_c(T_g)$ J/mol·K	$C_{pg}(T_g)$ J/mol·K	C_{pl} J/mol·K
$CaMgSi_2O_6$	1005	24.3	257.6	334.6
$CaAl_2Si_2O_8$	1160	36.8	329.5	$400.77 + 20.242 \times 10^{-3} T$

Tg, Calorimetric glass-transition temperature
Data sources: Richet (1984, 1986), Richet and Bottinga (1984)

Figure 4 shows an example of the calculations. It is clear that there exists almost perfect linearity between $log\,\eta$ and $1/T \cdot S_c$. The linear relations for other melts along the present join are also observed. Thus the temperature effect on viscosity in the wide temperature range can be suitably explained by the configurational entropy theory.

Glass-transition temperature and configurational entropy

The parameters for Eq. 4 determined by the least squares method are given in Table 5. The first two lines for diopside and anorthite indicate the values using $\bar{T}$ (calorimetric T_g) and $S_{c(\bar{T})}$ reported by Richet (1986). For the other lines, the dilatometric (Taniguchi and Murase 1987b) was used for $\bar{T}$, and $S_{c(\bar{T})}$ was regarded as an adjustable parameter. One of the important results shown in this table is that the values of $S_{c(T_g)}$ ($= S_{c(\bar{T})}$) are similar to each other. This may suggest that the melts at T_g are in an iso-configurational entropy state.

The glass-forming liquids at the glass-transition temperature were assumed to be in an iso-viscous state, but this assumption was rejected by Fox and Flory (1950). Instead of the iso-viscous state, they claimed that the glass-transition occurred at an equal free volume state. Shimha and Boyer (1962) pointed out that for many organic polymers the free volume ($\Delta\alpha \cdot T_g$, where $\Delta\alpha$ is the difference in the cubic thermal expansion coefficients above and below T_g) is a constant value around 0.11. However, it has been already proved that the free volume is not a constant value for many melts such as phosphate,

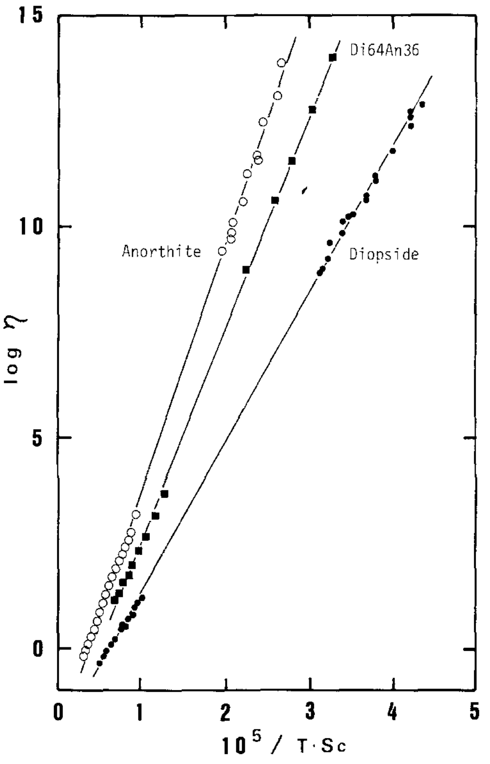

Fig. 4. The relations between viscosity and $1/T \cdot Sc$

borate and alkali-silicate (Suzuki and Abe 1981). In the case of magmatic melts, including the diopside-anorthite system, it was also shown by Taniguchi and Murase (1987a) that the free volume at T_g was not constant but a clear function of composition; the free volume decreased with increasing degree of polymerization. Adam and Gibbs (1965), on the other hand, suggested that the glass-transition occurred when the configurational entropy reached at a universal critical value. This was proven previously for many organic polymers, *Se* and B_2O_3 by Bestul and Chang (1964). They showed that the critical value is about 0.8 ± 0.2 cal/K · bead, where the "bead" means the simplest molecular unit defined by Wunderlich (1960). The present data and those in the literature are summarized in Table 6, to confirm the constant configurational entropy at T_g for magmatic silicate melts. If we use the gram-formula-weight as a unit, it is clear that the entropy, $S_c(\bar{T})$, is not a constant value. For example, the value for $Na_2Si_4O_9$ melt is about ten times that for SiO_2 melt. If we use the average molecular weight or "bead" (in this case, oxygen ion) as a unit, the constancy of those values are obvious. The average value $S_{c(\bar{T})} = 1.1 \pm 0.2$ cal/bead · K is almost comparable to the value for organic substances reported by Bestul and Chang (1964). Thus we can conclude that the glass transition occurs at the constant configurational entropy state in magmatic silicate melts as in the organic substances, although they have different structures.

Table 5. Coefficients of the viscosity equation based on the configurational entropy theory

Di (mol%)	Number of data set	$\bar{T}$ (K)	$Sc(\bar{T})$ (J/mol · K)	Ae	Be (10^5J/mol · K)	1σ
100	37	1005	24.3	− 2.092 ± 0.037	3.469 ± 0.025	0.23
0	43	1160	36.8	− 2.049 ± 0.025	5.786 ± 0.033	0.17
100	37	993	31.0[a]	− 2.579	4.687	0.17
80	11	993	33.1[a]	− 2.929	5.516	0.07
64	30	1007	27.8[a]	− 2.115	4.471	0.13
40	12	1021	27.3[a]	− 1.657	4.466	0.11
20	9	1071	29.8[a]	− 1.855	5.041	0.10
0	43	1115	27.1[a]	− 1.704	4.692	0.15

Average $Sc(\bar{T})$: 29.4 ± 2.2 J/mol · K

[a] For the calculation, $Sc(\bar{T})$ is regarded as an adjustable parameter

Table 6. The glass-transition temperature and the configurational entropy at *Tg*

Composition	$\bar{T}$ (K)	$Sc(\bar{T})$ (J/mol · K)	$Sc(\bar{T})^a$ (J/amw · K)	$Sc(\bar{T})^b$ (J/bead · K)	Data source
SiO_2	C: 1480	5.1	5.1	2.6	R
$NaAlSi_3O_8$	C: 1100	36.8	9.2	4.6	R
$NaAlSi_2O_6$	V: 1053	23.07	7.7	3.9	R
$KAlSi_3O_8$	V: 1200	28.3	7.1	3.5	R
$CaAl_2Si_2O_8$	C: 1160	36.8	9.2	4.6	R
$CaMgSi_2O_6$	C: 1005	24.3	6.1	4.1	RB
$Na_4Si_3O_8$	V: 682	39.00	7.8	4.9	R
$Na_2Si_2O_5$	V: 714	23.86	8.0	4.8	R
$Na_2Si_3O_7$	V: 742	32.91	8.2	4.7	R
$Na_2Si_4O_9$	V: 753	49.16	9.8	5.5	R
(Na, K) S_3, x = 0.28	V: 719	40.31	10·1	5.8	R
(Na, K) S_3, x = 0.53	V: 707	37.81	9.5	5.3	R
(Na, K) S_3, x = 0.82	V: 712	35.59	8.9	5.1	R
$K_2Si_3O_7$	V: 754	32.99	8.3	4.7	R
$CaMgSi_2O_6$	D: 993	31.0	7.8	5.2	PS
$Di_{80}An_{20}$	D: 993	33.1	8.3	5.2	PS
$Di_{64}An_{36}$	D: 1007	27.8	7.0	4.1	PS
$Di_{40}An_{60}$	D: 1021	27.3	6.8	3.6	PS
$Di_{20}An_{80}$	D: 1071	29.8	7.5	3.9	PS
$CaAl_2Si_2O_8$	D: 1115	27.1	6.8	3.4	PS

Average $Sc(\bar{T})^a$: 8.0 ± 1.2 J/amw · K; $Sc(\bar{T})^b$: 4.5 ± 0.8 J/bead · K

[a] For the calculation, average molecular weight M is used; $M = \Sigma Ni \cdot Mi$, where Ni is molecular fraction of component oxide MiOj and Mi is molecular weight of MiOj

[b] For the calculation, "bead" is used as a unit; in this case, bead is an oxygen ion

C, Calorimetric glass transition temperature; D, dilatometric glass transition temperature; V, the temperature at which the viscosity is 13 on log scale

(Na, K) S_3: xNa_2O $(1 - x)K_2O$ $3SiO_2$, Di: $CaMgSi_2O_6$, An: $CaAl_2Si_2O_8$ R, Richet (1984); RB, Richet and Bottinga (1984); PS, present study

Composition effects on viscosity and on the glass-transition temperature

The application of the configurational entropy theory to the composition effect on viscosity has been done for the first time by Richet (1984) for the join $Na_2Si_3O_7$–$K_2Si_3O_7$, followed by Hummel and Arndt (1985) and Tauber and Arndt (1987) for the melts of plagioclase and of the diopside-anorthite system, respectively.

According to them, the mixing of ions at constant temperature and pressure results in an increase in configurational entropy and thus in a decrease in viscosity of intermediate compositions. Figure 5 shows two examples of the compositional effect on viscosity at lower and higher temperatures. As in the cases of $Na_2Si_3O_7$–$K_2Si_3O_7$ (Richet 1984) and albite-anorthite (Hummel and Arndt 1985), the present system also shows the negative deviation from linearity, and the deviation decreases with increasing temperature as already pointed out by Tauber and Arndt (1987). For application of the theory, we need the mixing entropy of the present system, based on the two-lattice mixing model of Weill et al. (1980) used by Tauber and Arndt (1987). Following this model, the mixing entropy of intermediate melts along the diopside-anorthite join is given by the equation:

$$\Delta_m S^{tl} = -RX\ln\left\{\frac{4X}{(2-X)^2(1+X)^2}\right\} - RY\ln\left\{\frac{16Y^2}{(1+Y)^4(2-Y)}\right\} \qquad (8)$$

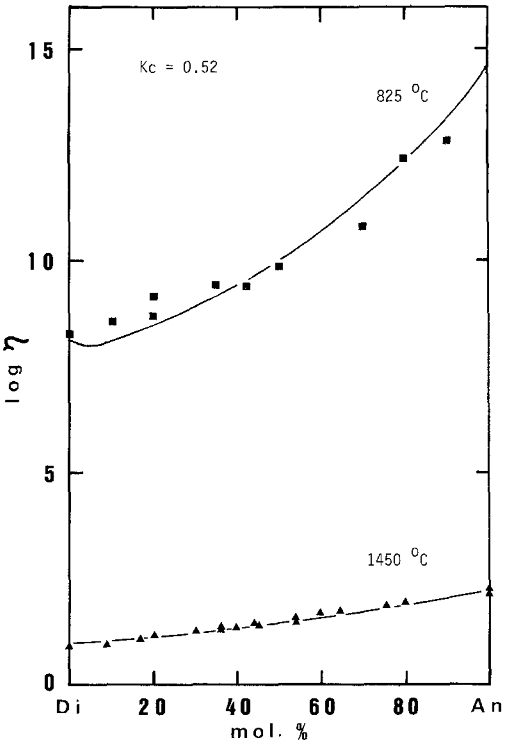

Fig. 5. Viscosity-composition relations at 825 (± 5)°C and 1450°C. The *lines* indicate the results of calculation using mixing entropy by the two-lattice model with the correction factor $Kc = 0.52$

where $\Delta_m S^{tl}$ is the mixing entropy based on the two-lattice model, and R is the gas constant. The viscosity of intermediate melt at a constant temperature is given using the parameters of end-member melts by the following expression:

$$\log\eta = X\cdot\log\eta_{T,Di} + Y\cdot\mathrm{lon}\,\eta_{T,An} \qquad (9)$$

where

$$\log\eta_{T,Di} = A_{e(Di)} + \frac{B_{e(Di)}}{T\cdot(S_{c(T)} + \Delta_m S)} \qquad (10)$$

and

$$\log\eta_{T,An} = A_{e(An)} + \frac{B_{e(An)}}{T\cdot(S_{c(T)} + \Delta_m S)} \qquad (11)$$

$\Delta_m S$ is the real mixing entropy. For the present calculation, the values listed in Table 5 (the first two lines) were used as the parameters in Eqs. 10 and 11. Some authors (Henry et al. 1982; Hummel and Arndt 1985) have pointed out that the two-lattice model yields too large a value of mixing entropy. According to Tauber and Arndt (1987), the real mixing entropy is given by: $\Delta_m S = K_c \cdot \Delta_m S^{tl}$, where K_c is the correction factor and is determined by the least squares method. The factor was 0.52 when calculated using 180 sets of data (Kirkpatrick 1974; Urbain et al. 1982; Scarfe et al. 1983; Hummel and Arndt 1985; Tauber and Arndt 1986; Taniguchi and Murase 1987b; present values). If we use only the present data listed in Table 1, the K_c is 0.43. The results with $K_c = 0.52$ for the relation between composition and viscosity at 825 (± 5)°C and at 1450°C show good agreement with the measured values, as shown in Fig. 5. The deviation from the linearity at 825°C is clearly larger than that at 1450°C, and it decreases with increasing temperature. This is because the mixing entropy is independent of temperature; thus the contribution of mixing entropy to the entropy terms in Eqs. 10 and 11 decreases with increasing temperature.

Figure 6 shows the relation between the dilatometric T_g and composition (Taniguchi and Murase 1987b). Although, roughly speaking, T_g can be regarded as a constant value it depends, in the strictest sense, on both the annealing condition of the sample and the rate of increasing temperature for measurement of thermal expansion. In the present case, the samples were annealed at $T_g + 15$°C for 30 min, where T_g is the glass-transition temperature roughly measured beforehand, and then they were cooled to $T_g - 200$°C at the rate of 0.33°C/min. The heating rate for the measurements was 3°C/min. Comparing the composition-T_g relation in Fig. 6 with the composition-viscosity relation at 825°C in Fig. 5, both relations are similar to one other. Now, we may assume that the reason for the similarity is due to the similar role of mixing entropy. In other words, the negative deviation from linearity for the composition-T_g relation depends on the mixing entropy. This assumption is based on the fact that the configurational entropy at T_g on the basis of average molecular weight is almost constant as shown previously. In this case, the relation should be formulated as follows:

$$S_{c(Tx)} - S_{c(T_g)} = \Delta_m S = \int_{Tg}^{Tx} \frac{\Delta C_{px}}{T}\,dT \qquad (12)$$

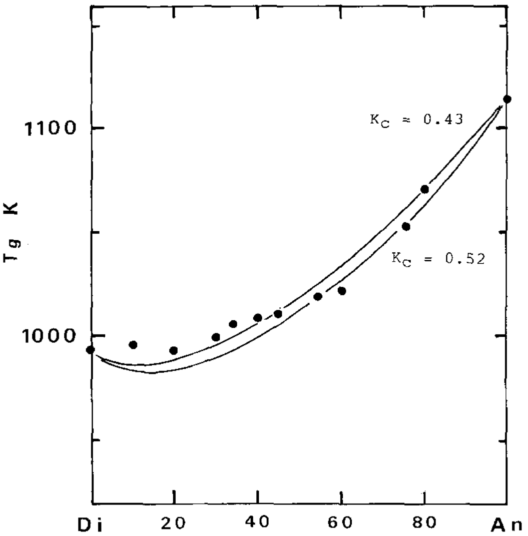

Fig. 6. Compositional dependence of the glass-transition temperature. The *lines* indicate the results of calculation using the mixing entropy with $Kc = 0.52$ and $Kc = 0.43$, respectively.

where $S_{c(Tx)}$ and $S_{c(T_g)}$ are the configurational entropy at Tx and T_g, respectively. Tx is the temperature calculated from the following linear relation:

$$Tx = X \cdot T_{g(Di)} + Y \cdot T_{g(An)} \qquad (13)$$

where $T_{g(Di)}$ and $T_{g(An)}$ are the T_g of *Di* and *An* melts, respectively. ΔC_{px} is the difference of heat capacities between liquid and glassy states near the T_g. Also in this case, we may assume the additivity between heat capacity and composition. For the calculation, the heat capacities listed in Table 4 and the T_g given by Taniguchi and Murase (1987b) were used. For the mixing entropy, the two-lattice model of Weill et al. (1980) with the correction factor K_c was employed.

The calculated T_g using Eq. 12 with the factors $K_c = 0.52$ and 0.43 are shown in Fig. 6, which shows clearly that the calculations are in good agreement with the measured values ($1\sigma/K_c$: 11.3 K/0.52, 8.0 K/0.43). Thus we may conclude that the configurational entropy at T_g for silicate melt is the universal constant value, and that the negative deviation of T_g from the linearity between T_g and composition depends only on the mixing entropy.

Acknowledgements. The author wishes to thank T. Murase and K. Yagi for their constructive comments and critical reading of an early draft of the manuscript. The author also thanks I. Kushiro, E. Ito, E. Takahashi and T. Katsura for their help in the measurements. High-pressure measurements were done while the author was a visiting scientist at the Institute for Study of the Earth's Interior, Okayama University. This study was supported by grants 01460067 to H. Taniguchi and 62103007 to I. Kushiro from the Japanese Ministry of Education, Science and Culture.

References

Adam G, Gibbs JH (1965) On the temperature dependence of cooperative relaxation properties in glass-forming liquids. J Chem Phys 43:139–146

Bestul AB, Chang SS (1964) Excess entropy at glass transformation. J Chem Phys 40:3731–3733

Brearley M, Dickinson JE Jr, Scarfe CM (1986) Pressure dependence of melt viscosities on the join diopside-albite. Geochim Cosmochim Acta 50:2563–2570

Cukierman M, Uhlmann DR (1973) Viscosity of liquid anorthite. J Geophys Res 78:4920–4923

Fox TG Jr, Flory PJ (1950) Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight. J Appl Phys 21:581–591

Fujii T, Kushiro I (1977) Density, viscosity, and compressibility of basaltic liquid at high pressures. Carnegie Inst Wash Yearbook 76:419–424

Fulcher GS (1925) Analysis of recent measurements of the viscosity of glasses. J Am Ceram Soc 8:339–355

Henry DJ, Navrotsky A, Zimmermann HD (1982) Thermodynamics of plagioclase-melt equilibria in the system albite-anorthite-diopside. Geochim Cosmochim Acta 46:381–391

Hummel W, Arndt J (1985) Variation of viscosity with temperature and composition in the plagioclase system. Contrib Mineral Petrol 90:83–92

Kirkpatrick RJ (1974) Kinetics of crystal growth in the system $CaMgSi_2O_6$–$CaAl_2SiO_6$. Am J Sci 274:215–242

Kushiro I (1976) Changes in viscosity and structure of melt of $NaAlSi_2O_6$ composition at high pressures. J Geophys Res 81:6347–6350

Kushiro I (1981) Change in viscosity with pressure of melts in the system CaO–Al_2O_3–SiO_2. Carnegie Inst Wash Yearbook 80:339–341

Murase T, McBirney AR (1973) Properties of some common igneous rocks and their melts at high temperature. Geol Soc Am Bull 84:3563–3592

Richet P (1984) Viscosity and configurational entropy of silicate melts. Geochim Cosmochim Acta 48:471–483

Richet P (1986) Low-temperature heat capacity of diopside glass ($CaMgSi_2O_6$): a calorimetric test of the configurational-entropy theory applied to the viscosity of liquid silicates. Geochim Cosmochim Acta 50:1521–1533

Richet P (1987) Heat capacity of silicate glasses. Chem Geol 62:111–124

Richet P, Bottinga Y (1984) Anorthite, andesine, wollastonite, cordierite and pyrope: thermodynamics of melting, glass transition, and properties of the amorphous phases. Earth Planet Sci Lett 67:415–432

Scarfe CM, Mysen BO, Virgo D (1979) Changes in viscosity and density of melts of sodium disilicate, sodium metasilicate, and diopside composition with pressure. Carnegie Inst Wash Yearbook 78:547–551

Scarfe CM, Cronin DJ, Wenzel JT, Kauffman SA (1983) Viscosity–temperature relationships at 1 atm in the system diopside-anorthite. Am Mineral 68:1083–1088

Shaw HR (1963) Obsidian-H_2O viscosities at 1000 and 2000 bars in the temperature range 700°–900°C. J Geophys Res 68:6337–6343

Shimha R, Boyer RF (1962) General relation involving the glass temperature and coefficients of expansion of polymers. J Chem Phys 37:1003–1007

Stebbins JF, Carmichael ISE, Moret LK (1984) Heat capacities and entropies of silicate liquids and glasses. Contrib Mineral Petrol 86:131–148

Suzuki S, Abe Y (1981) The free volume of some oxide glasses at the transition temperature. J Non-Crystalline Solids 43:141–143

Takahashi K, Tanioka M (1966) Studies on the drawing sphere viscometer (in Japanese). Oyou-Butsuri 35:786–796

Taniguchi H (1988) Surface tension of melts in the system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$ and its structural significance. Contrib Mineral Petrol 100:484–489

Taniguchi H (1989) Densities of melts in the system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$ at low and high pressures, and their structural significance. Contrib Mineral Petrol 103:325–334

Taniguchi H, Murase T (1987a) Role of free volume in the viscous behavior of magma. J Jpn Assoc Mineral Petrol Econ Geol 82:189–202

Taniguchi H, Murase T (1987b) Some physical properties and melt structures in the system diopside-anorthite. J Volcanol Geotherm Res 34:51–64

Tauber P, Arndt J (1986) Viscosity-temperature relationship of liquid diopside. Phys Earth Planet Inter 43:97–103

Tauber P, Arndt J (1987) The relationship between viscosity and temperature in the system anorthite-diopside. Chem Geol 62:71–81

Urbain G, Bottinga Y, Richet P (1982) Viscosity of liquid silica, silicates and alumino-silicates. Geochim Cosmochim Acta 46:1061–1072

Watanabe M, Koyama R (1957) The relation of the viscosity of glasses to load, temperature, and time in the range 10^8–10^{13} poises, part I. J Soc Glass Tech 41:137–156

Weill DF, Hon R, Navrotsky A (1980) The igneous system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$: variation on a classic theme by Bowen. In: Hargraves RB (ed) Physics of magmatic processes. Princeton University Press, Princeton, N.J., pp 49–92

Wunderlich B (1960) Study of the change in specific heat of monometric and polymetric glasses during the glass transition. J Phys Chem 64:1052–1056

Yoder HS Jr (1976) Generation of basaltic magma. National Academy of Sciences, Washington

Editorial responsibility: I. S. E. Carmichael