

## Derivation of the temperature dependent constants for $\text{KAlO}_2$ and $\text{NaAlO}_2$ in a viscosity predictive model for high aluminosilicate melts

Martin Korsgaard, Martin Pind, Peter Møller Sørensen and Henriette Sie Woldum

Department of Chemistry, Aalborg University, Aalborg (Denmark)

Mette Solvang

Department of Production, Aalborg University, Aalborg (Denmark)

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The compositional dependence of the viscosity was studied for two high aluminosilicate melt series:  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (NCAS) and  $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (KNCAS). The viscosity and the glass transition temperature were measured by concentric cylinder viscometry and differential scanning calorimetry, respectively. This work discusses the viscosity predictive model set up by Bottinga and Weill. The temperature dependent constant,  $D$ , defining the relative impact of each component on the viscosity, was derived for the compositional range from 35 to 45 mol%  $\text{SiO}_2$  for  $\text{KAlO}_2$  and  $\text{NaAlO}_2$ , respectively. With the newly derived  $D$ -values, a good agreement was achieved between measured and predicted values.

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### 1. Introduction

Mineral wool production, traditionally, relies on locally available rocks and slag. Some variations in the chemical compositions are commonly accepted as long as the basic melt and glass properties are maintained. The melt viscosity is one of the parameters that have to be within rather narrow limits to ensure good process conditions. Therefore, predictive viscosity models are commonly used. The stone wool industry often applies the viscosity model set up by Bottinga and Weill [1] (the BW model). The model is valid for a broad range of chemical compositions, and it still appears to be one of the most accurate models for the prediction of melt viscosity, even thirty years after it was published. However, for melts with a silica content between 35 and 45 mol% data is limited, and the calculation of viscosity relies, to some extent, on analogous assumptions.

The BW model [1] is based on the assumption that each component of the melt contributes to a change in the viscosity ( $\eta$ , where the viscosity is calculated in  $10^{-1}$  Pa s using equation (1)), according to the amount of the component in the melt:

$$\ln \eta = \sum (X_i \cdot D_i) \quad (1)$$

where  $X_i$  is the molar fraction of the component, and  $D_i$  is a temperature dependent constant for a given component. The  $D$ -values from (1) were found by fitting the model to a set of viscosity data for different melts. The data set consists

of 2440 data points collected over the years and covers the temperature range from 1473 to 2073 K with 50 K intervals.

The  $D$ -values are given for various intervals of the  $\text{SiO}_2$  content. The number of  $D$ -values at the lowest  $\text{SiO}_2$  content of 35 to 45 mol% is limited. The  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  are missing; in fact,  $D$ -values for  $\text{KAlO}_2$  are missing in all the  $\text{SiO}_2$  intervals. Even though directions for application of  $D$ -values for neighbouring  $\text{SiO}_2$  intervals are given [1], better documentation for high aluminosilicate melts containing  $\text{Na}^+$  and  $\text{K}^+$  is desired.

The purpose of the present paper is to derive new temperature dependent constants, to be included in the BW model. This is done by studying melts containing  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . All the studied melts are high aluminosilicate melts with a low content of  $\text{SiO}_2$  (37.3 mol%). Viscosity measurements of these melts provide a set of  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  for temperature intervals of 25 K according to the method used in [1].

Establishing these  $D$ -values can improve the applicability of the BW model and contribute to the understanding of the effect of  $\text{Na}^+$  and  $\text{K}^+$  on the viscosity of high aluminosilicate melts.

Two compositional joins were examined in the interval 35 to 45 mol%  $\text{SiO}_2$ . The melts are depolymerized, and the ratio of nonbridging to tetrahedrally coordinated oxygen (NBO/T) is equal to 1. The first join, called the NCAS series, contains six melts with a constant amount of  $\text{SiO}_2$  (37.3 mol%) and  $\text{Al}_2\text{O}_3$  (14.7 mol%), whereas the amounts of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  were changed throughout the melt series to increase the ratio  $2\text{Na}/(2\text{Na}+\text{Ca})$  from 0 to 0.42. The

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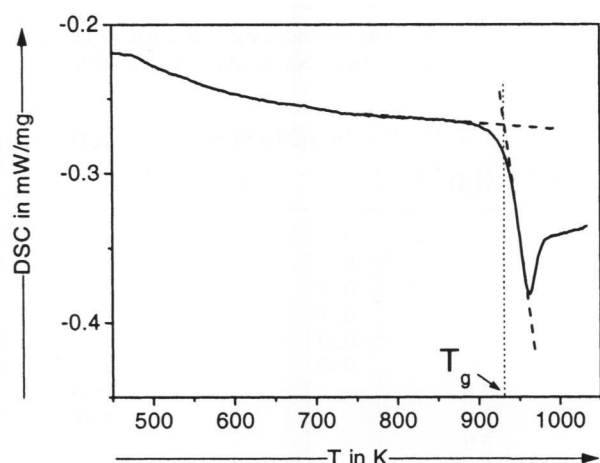


Figure 1. The heat flow rate versus temperature showing the determination of  $T_g$ .

viscosities of the NCAS melt series were measured, and  $D$ -values for  $\text{NaAlO}_2$  were found by fitting the model to the obtained viscosity data. The second join, called the KNCAS series, contains five melts with a constant amount of  $\text{SiO}_2$  (37.3 mol%),  $\text{Al}_2\text{O}_3$  (14.7 mol%) and  $\text{CaO}$  (39.9 mol%), whereas the amounts of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  were changed throughout the series to increase the ratio  $\text{K}/(\text{K}+\text{Na})$  from 0 to 1. This was done in order to establish the  $D$ -values for  $\text{KAlO}_2$  with the same method as for  $\text{NaAlO}_2$ .

## 2. Experimental methods

The high aluminosilicate melts from the NCAS and KNCAS melt series were synthesized from the analytical chemicals  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in a Pt-crucible at 1773 K for 4 h. Subsequently, the melts were quenched on a brass disc at room temperature. The chemical compositions were analysed by X-ray fluorescence spectroscopy (XRF) (Philips 1404, Eindhoven (Netherlands)).

Shear viscosities in the range from 1823 K to the temperature of crystallization were measured at 25 K intervals in air atmosphere using concentric cylinder viscometry (ccv) (Paar Physica, Physica Rheolab MC 1, Stuttgart (Germany)). The main parts of the viscometer are a 30 mm long Pt80Rh20 cylinder with a 16 mm diameter, including conical ends, and a 70 mm high Pt80Rh20 crucible with a 22 mm diameter. A speed of rotation of approximately 40 rpm was maintained throughout the measurements. Viscosity measurements continued for one hour at each temperature.

The glass transition temperature ( $T_g$ ) was determined by differential scanning calorimetry (DSC), (Jupiter, NETZSCH STA 449 C, Cell, Selb (Germany)), using heating and cooling rates of 10 K/min.  $T_g$  was defined as the onset temperature of the heat flow rate versus the temperature curve (figure 1). The dimensions of the glass samples were  $(5 \times 5 \times 1) \text{ mm}^3$ .

## 3. Results

Table 1 displays the chemical compositions of the melts. Figures 2 and 3 show the viscosity-temperature relationship for the two melt series NCAS and KNCAS, respectively. The viscosities cover the range from 0.3 to 13 Pa s and are summarized in tables 2 and 3. Figure 2 shows that, for the NCAS melt series, there is no pronounced compositional dependence of the viscosity except for NCAS 0, which has a slightly lower viscosity, at a certain temperature, than the other melts. Figure 3 shows the viscosity-temperature relationship for the KNCAS melt series. At a certain temperature, the viscosity increases with increasing substitution of  $\text{K}^+$  for  $\text{Na}^+$ .

The  $T_g$  values are given in table 4.  $T_g$  decreases almost linearly as the  $2\text{Na}/(2\text{Na}+\text{Ca})$  ratio increases for the NCAS melt series. For the KNCAS melt series an increase in the  $\text{K}/(\text{K}+\text{Na})$  ratio leads to a nonlinear increase of  $T_g$ .

## 4. Modelling with the BW model

In the BW model, each component in the melt has a unique contribution to the viscosity. A component is defined as a structural unit in the melt structure. The structural units are primarily  $\text{SiO}_2$  tetrahedra, but also  $\text{Al}_2\text{O}_3$  forms tetrahedral units when charge balancing cations are present. Other structural units are network-modifying cations in the form of oxide units such as  $\text{CaO}$  and  $\text{Na}_2\text{O}$  [1 and 3].

If more than one charge balancing cation is available, their willingness to combine with  $\text{Al}^{3+}$  is defined by the following order  $\text{K}^+ > \text{Na}^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Mn}^{2+}$ . This order corresponds to that of structural stability of aluminosilicate melts as discussed below. Due to this order the amount of  $\text{KAlO}_2$  is calculated first, then  $\text{NaAlO}_2$ , and so forth.

The contribution to the viscosity from each component is an empirically determined  $D$ -value times the molar ratio of the component (equation (1)). The  $D$ -value defines the impact the component has on the viscosity. A component with a high  $D$ -value has a larger contribution to the viscosity than a component with a small or even negative  $D$ -value.

In the BW model, data are grouped according to the amount of  $\text{SiO}_2$  (35 to 45, 45 to 55, 55 to 65, 65 to 75, 75 to 81 mol%) in the melts. Therefore, each  $\text{SiO}_2$  interval has a set of  $D$ -values for each component and each temperature. In the  $\text{SiO}_2$  interval of 35 to 45 mol%,  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  are not available. Bottinga & Weill recommend using the  $D$ -values for  $\text{NaAlO}_2$  from the neighbouring  $\text{SiO}_2$  interval (45 to 55 mol%) for both  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ . However, estimates of  $D$ -values for both  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  have been based upon the results of this study (table 5).

The  $D$ -values given in [1] are listed for a certain temperature with steps of 50 K. In order to calculate model viscosities at 25 K intervals, the  $D$ -values as a function of  $1/T$  were linearly extrapolated to cover temperatures in between (table 5). The difference between the measured and the modelled viscosity was minimized by altering the  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ , respectively. The  $D$ -values for  $\text{NaAlO}_2$  were found using the viscosity data from the NCAS series,

Table 1. Compositions of the melts analysed by XRF given in mol%. In the KNCAS series the numbers, e.g. 2-6, correspond to the approximate mol% of K<sub>2</sub>O and Na<sub>2</sub>O, respectively. The sample NCAS 8 was used as the pure Na-bearing end member in the KNCAS series.

melt	oxide content in mol%					2Na/(2Na+Ca)	K/(K+Na)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O		
NCAS 0*	37.3	14.7	47.9	—	—	0	—
NCAS 4	36.9	15.3	43.6	4.2	—	0.09	—
NCAS 8	37.3	15.0	39.4	8.3	—	0.16	0
NCAS 12	37.3	14.9	35.3	12.5	—	0.26	—
NCAS 16	37.1	14.9	31.4	16.6	—	0.35	—
NCAS 20	37.3	14.4	28.2	20.1	—	0.42	—
KNCAS 2-6	36.9	14.9	40.0	6.2	2.0	—	0.33
KNCAS 4-4	37.0	15.1	39.6	4.4	3.8	—	0.46
KNCAS 6-2	37.4	14.7	40.0	2.1	5.9	—	0.73
KNCAS 8-0	36.3	15.2	40.6	0.2	7.6	—	1.0

\* Values are from [2].

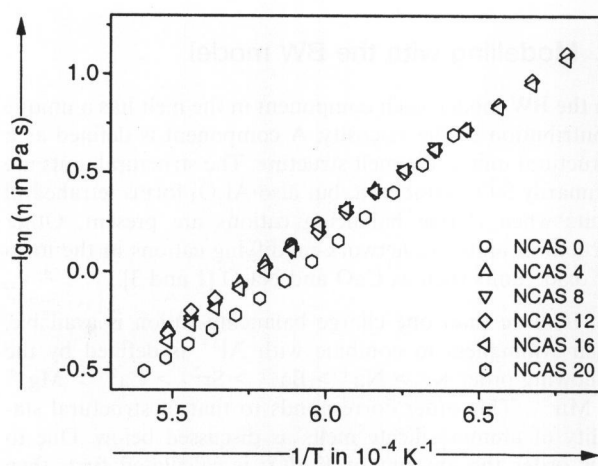


Figure 2.  $\lg \eta$  as a function of  $1/T$  for the NCAS series.

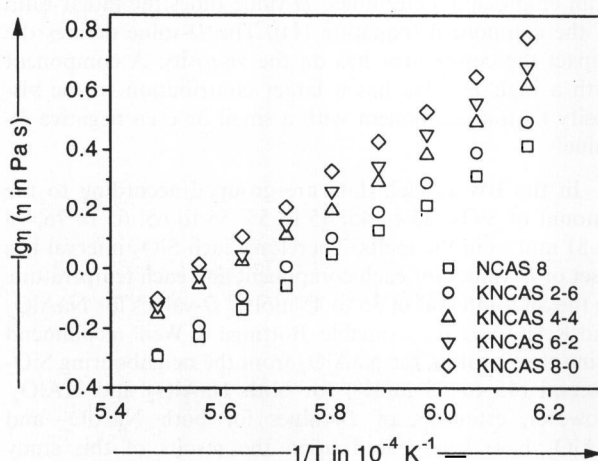


Figure 3.  $\lg \eta$  as a function of  $1/T$  for the KNCAS series.

and the  $D$ -values from [1], listed in table 5. The  $D$ -values for  $\text{KAlO}_2$  were found using the viscosity data from the KNCAS series, the  $D$ -values given in [1], and the estimated  $D$ -values for  $\text{NaAlO}_2$  (table 5).  $D$ -values for components given in [1] are reasonably accurate because they are based on a comprehensive data set.

Table 2. Viscosities  $\eta$  for melt series NCAS 0 measured by concentric cylinder viscometry at various temperatures  $T$ . Values are from [2].

$T$ in K	$\eta$ in Pa s
1849	0.31
1825	0.37
1801	0.43
1776	0.51
1776	0.60
1752	0.73
1728	0.90
1704	1.13
1679	1.44
1655	1.89
1631	2.52
1607	3.47
1583	4.94

The application of the new  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  for prediction of the viscosity was tested on a melt with the following composition (in wt%): 31.3  $\text{SiO}_2$ , 20.3  $\text{Al}_2\text{O}_3$ , 0.6  $\text{TiO}_2$ , 10.3  $\text{FeO}$ , 20.5  $\text{CaO}$ , 8.3  $\text{MgO}$ , 3.0  $\text{Na}_2\text{O}$ , 3.2  $\text{K}_2\text{O}$  and 0.5  $\text{MnO}$ . The viscosity was measured by GLAFO, Växjö (Sweden). Figure 4 shows the measured viscosity, the viscosity predicted when including the new  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ , the viscosity predicted using the  $D$ -values for  $\text{NaAlO}_2$  from the  $\text{SiO}_2$  interval 45 to 55 mol% (which is the neighbouring  $\text{SiO}_2$  interval) for both  $\text{KAlO}_2$  and  $\text{NaAlO}_2$ , for the remaining components the  $D$ -values are from the  $\text{SiO}_2$  interval 35 to 45 mol% (a method suggested in [1]), and finally the viscosity predicted without including  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ . Figure 4 shows that it is not reasonable to predict the viscosity without including the  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ . Furthermore, the  $D$ -values derived for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  were found to be reasonable, since the predicted viscosities were in good agreement with the measured ones.

## 5. Discussion

The ability for a cation to charge-balance an alumina tetrahedron is determined by the field strength. Ions with high

Table 3. Viscosities for various melt series NCAS and KNCAS measured by concentric cylinder viscometry at various temperatures  $T$ .

$T$ in K	$\eta$ in Pa s								
	NCAS 4	NCAS 8	NCAS 12	NCAS 16	NCAS 20	KNCAS 2-6	KNCAS 4-4	KNCAS 6-2	KNCAS 8-0
1823	0.49	0.51	0.47	0.48	0.44	0.51	0.71	0.75	0.79
1798	0.58	0.59	0.57	0.63	0.54	0.64	0.88	0.95	1.03
1773	0.70	0.73	0.71	0.73	0.65	0.81	1.06	1.11	1.28
1748	0.85	0.88	0.84	0.86	0.82	1.01	1.30	1.41	1.61
1723	1.07	1.12	1.05	1.06	1.01	1.27	1.57	1.83	2.13
1698	1.37	1.35	1.28	1.31	1.29	1.56	1.97	2.22	2.68
1673	1.76	1.64	1.63	1.58	1.69	1.95	2.42	2.85	3.39
1648		2.06	2.06	2.00	2.07	2.46	3.13	3.63	4.42
1623		2.60	2.53	2.52	2.55	3.13	4.16	4.79	5.99
1598			3.29	3.18	3.27				
1573			4.30	4.11	4.16				
1548				5.28	5.26				
1523				6.99	6.82				
1498				9.31	8.89				
1473				12.73	11.90				

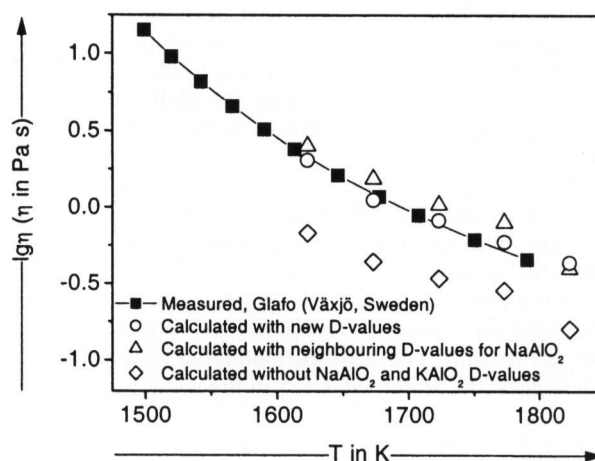
Table 4. Glass transition temperatures measured with DSC, where heating and cooling rates of 10 K/min were used.

melt series	$T_g$ in K
NCAS 0	1075
NCAS 4	1025
NCAS 8	992
NCAS 12	961
NCAS 16	933
NCAS 20	906
KNCAS 2-6	997
KNCAS 4-4	1008
KNCAS 6-2	1028
KNCAS 8-0	1054

 Table 5.  $D$ -values for the BW model for the components  $\text{KAlO}_2$  and  $\text{NaAlO}_2$  found by a least squares fit to the viscosity data, valid for the  $\text{SiO}_2$  interval 35 to 45 mol%. Using the  $D$ -values derives the viscosity in  $10^{-1}$  Pa s.  $D$ -values for  $1/2\text{CaAl}_2\text{O}_4$  are from [1]. (There appears to be a misprint in the  $D$ -value for CaO at 1723 K given in [1], which is seen clearly when  $D$ -values for CaO are compared versus temperature. Therefore, the  $D$ -value has been changed from 0.71 to  $-0.71$  in this work.)

$T$ in K	$D$ -values					
	$\text{KAlO}_2$	$\text{NaAlO}_2$	$1/2\text{CaAl}_2\text{O}_4$	CaO	$\text{Na}_2\text{O}$	$\text{SiO}_2$
1623	10.55	5.43	2.70	0.39	-4.93	4.43
1648	9.71	4.82	2.43	0.12	-4.97	4.30
1673	9.00	4.50	2.16	-0.16	-5.00	4.17
1698	8.77	4.30	2.09	-0.44	-5.02	4.04
1723	8.65	4.12	2.01	-0.71	-5.03	3.90
1748	7.89	3.70	2.47	-0.94	-5.07	3.79
1773	7.23	3.52	2.93	-1.17	-5.11	3.67
1798	8.49	4.43	3.09	-2.33	-5.16	3.54
1823	9.45	5.27	3.25	-3.48	-5.20	3.41

field strength polarize the bridging oxygens, thereby they weaken the network-forming bonds and destabilize the overall structure of the melt. Cations with low field strength


 Figure 4.  $\lg \eta$  as a function of the temperature for the melt with the following composition (in wt%): 31.3  $\text{SiO}_2$ , 20.3  $\text{Al}_2\text{O}_3$ , 0.6  $\text{TiO}_2$ , 10.3  $\text{FeO}$ , 20.5  $\text{CaO}$ , 8.3  $\text{MgO}$ , 3.0  $\text{Na}_2\text{O}$ , 3.2  $\text{K}_2\text{O}$  and 0.5  $\text{MnO}$ . The figure shows the measured viscosity, the viscosity predicted when including the new  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ , the viscosity predicted using the neighbouring  $D$ -values for  $\text{NaAlO}_2$  to calculate for both  $\text{NaAlO}_2$  and  $\text{KAlO}_2$  (as suggested in [1]) and, finally, the viscosity predicted without including  $D$ -values for  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ .

affect the network forming bonds less strongly than cations with high field strength. The result is that cations with low field strength will create a less perturbed structure with stronger bonds. The mobility of structural units decreases, thereby the resistance of the melt to flow increases, and hence also the viscosity [3 and 4]. Cations can therefore be listed according to their charge-balancing ability in the following order  $\text{Cs} \approx \text{Rb} > \text{K} > \text{Na} > \text{Li} \approx \text{Ba} > \text{Pb} > \text{Sr} > \text{Ca} > \text{Mg}$  [5]. This order is in agreement with the allocation given in [1] based on viscosity data, and it also reflects the increasing ability of the cation to compete with the  $\text{Al}^{3+}$  or  $\text{Si}^{4+}$  for bonding to bridging oxygen [3].

In the low viscosity range, no dramatic change in viscosity was demonstrated for the NCAS melt series when

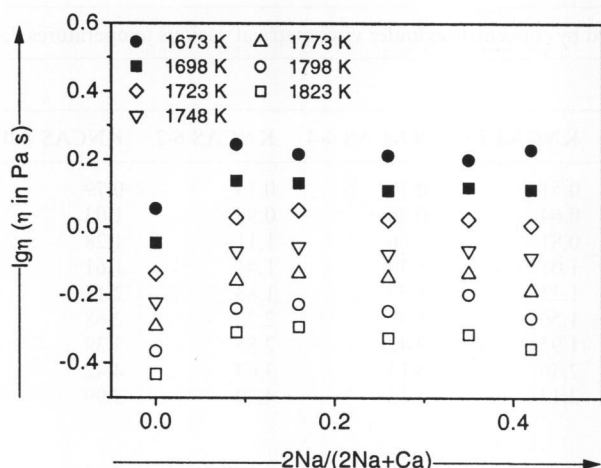


Figure 5. Isothermal plot of  $\lg \eta$  as a function of the  $2\text{Na}/(2\text{Na}+\text{Ca})$  ratio.

substituting  $2\text{Na}^+$  for  $\text{Ca}^{2+}$  as seen in figure 5. However, the slight increase in viscosity (at a given temperature) from melt NCAS 0 to NCAS 4 is a response to the initial substitution of  $\text{Na}^+$  for  $\text{Ca}^{2+}$ , because the ability of  $\text{Na}^+$  to charge-balance for Al tetrahedrons is higher than that of  $\text{Ca}^{2+}$ . The charge-balancing by  $\text{Na}^+$  instead of  $\text{Ca}^{2+}$  may stabilize the melt structure and thereby increase the viscosity. Both melt NCAS 16 and melt NCAS 20 contain more  $\text{Na}^+$  than required for charge-balancing  $\text{Al}^{3+}$ , and the excess  $\text{Na}^+$  acts as modifying ions. Figure 2 shows that substitution of two network modifying  $\text{Na}^+$  for one network modifying  $\text{Ca}^{2+}$  does not influence the viscosity-temperature relationship. The network modifying  $2\text{Na}^+$  plays the same role as the modifying  $\text{Ca}^{2+}$  in the melt.

In contrast to the high temperature-viscosity relationship, a pronounced decrease in  $T_g$  with increasing substitution of  $\text{Na}^+$  for  $\text{Ca}^{2+}$  was seen. This reflects a different structural response to the substitution of  $\text{Na}^+$  for  $\text{Ca}^{2+}$  in the low temperature range from that in the high temperature range.

The  $D$ -values in table 5 illustrate that the contribution of  $\text{Na}^+$  to the change in viscosity is higher than that of  $\text{Ca}^{2+}/2$ . That was to be expected because  $\text{Na}^+$  is believed to be a better charge-balancing ion than  $\text{Ca}^{2+}$  and, therefore, the contribution to the viscosity per tetrahedron must be higher for  $\text{Na}^+$  than for  $\text{Ca}^{2+}$ .

In the KNCAS melt series, the  $\text{Ca}^{2+}$ ,  $\text{Si}^{4+}$ , and  $\text{Al}^{3+}$  contents were maintained constant whereas  $\text{Na}^+$  was stepwise replaced with  $\text{K}^+$ . In this way, the different effect on the viscosity of applying either  $\text{K}^+$  or  $\text{Na}^+$  as the charge-balancing ion was observed. The effect on the viscosity due to the charge-balancing ability of the cations ( $\text{K}^+$  and  $\text{Na}^+$ ) is modest compared to the effect on the viscosity due to the low concentration of both  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  relative to the  $\text{CaO}$  concentration. However, an increase in the viscosity is expected due to the replacement of  $\text{Na}^+$  with  $\text{K}^+$ . This replacement resulted in an increase in the viscosity at a specific temperature in the high temperature range (figure 6). This suggests that  $\text{K}^+$ , in contrast to  $\text{Na}^+$ , strengthens the structural network even more when it acts as the charge-

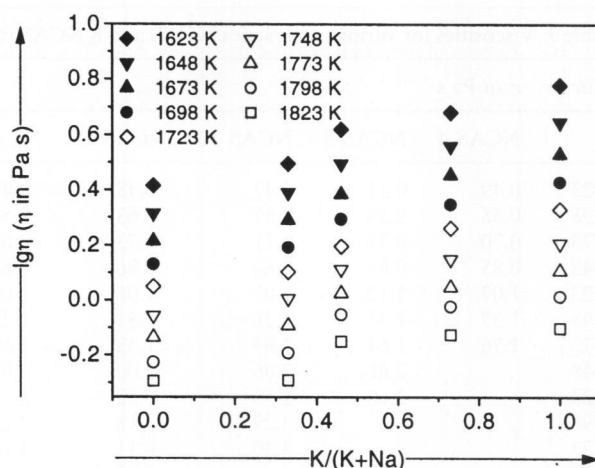


Figure 6. Isothermal plot of  $\lg \eta$  as a function of the  $\text{K}/(\text{K}+\text{Na})$  ratio.

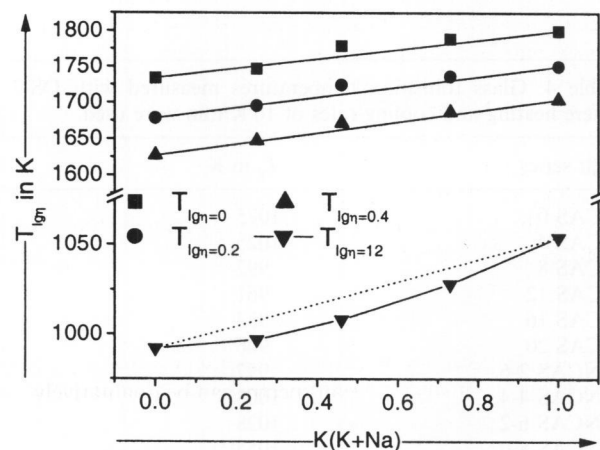


Figure 7. Compositional dependence of the 1, 1.6, 2.5 and  $10^{12}$  Pa s isokom temperature. The  $10^{12}$  Pa s isokom temperature is equal to  $T_g$  of each melt.

balancing ion. The reason is that  $\text{K}^+$  has higher field strength, causing a lower polarizing ability.

When  $\text{Na}^+$  is stepwise replaced with  $\text{K}^+$ , a negative deviation from the linearity in  $T_{ig\eta}$  as a function of composition occurred in the high viscous range, however, not in the low viscous range (figure 7). This negative deviation is shown as the  $10^{12}$  Pa s isokom temperature, denoted as  $T_{ig\eta=12}$ .  $T_{ig\eta=12}$  is equal to  $T_g$  of each melt because the viscosity at  $T_g$  is generally assigned to  $10^{12}$  Pa s. The deviation from linearity in the high viscous range is a reflection of the mixed alkali effect. This mixing phenomenon has previously been reported in [6 to 9]. However, the mixed alkali effect for the KNCAS melt series is not as pronounced as for the glass series  $16(\text{Na}, \text{K})_2\text{O} \cdot 10\text{CaO} \cdot 74\text{SiO}_2$  (in mol%) (named in the following as the NKCS melt series) described in [7]. The mixed alkali effect vanishes with increasing temperature because the topological contribution to the configurational entropy is predominant compared to the chemical contribution [10]. The mixed alkali effect is less pronounced in the KNCAS melt series than in the NKCS melt series as a consequence of the much higher NBO/T for the KNCAS than for the NKCS melt series. Furthermore, a high content of  $\text{Ca}^{2+}$  will reduce the mixed alkali effect.

It is seen from the  $D$ -values in table 5 that  $\text{KAlO}_2$  contributes more to the viscosity of the melt than  $\text{NaAlO}_2$ . This indicates, as mentioned previously, that  $\text{K}^+$  as a charge-balancing ion with aluminium in silicate melts results in a more stable network than  $\text{Na}^+$ .

## 6. Conclusion

In the high viscous range, the substitution of  $\text{Na}^+$  for  $\text{Ca}^{2+}$  in the NCAS melt series showed a decrease in  $T_g$  with increasing  $2\text{Na}/(2\text{Na}+\text{Ca})$ . In the low viscosity range, the substitution had a less pronounced effect on the viscosity. In the KNCAS melt series, the viscosity for a specific high temperature increases with increasing  $\text{K}/(\text{K}+\text{Na})$ . The negative deviation from linearity in  $T_g$  values of the KNCAS melt series is caused by the mixed alkali effect.

For the  $\text{SiO}_2$  interval, 35 to 45 mol%,  $D$ -values for  $\text{KAlO}_2$  and  $\text{NaAlO}_2$  are derived. The  $D$ -values derived for  $\text{KAlO}_2$  are the first derived  $D$ -values for  $\text{KAlO}_2$  at all. At a specific temperature,  $D$ -values for  $\text{KAlO}_2$  were found to be higher than  $D$ -values for  $\text{NaAlO}_2$ . Likewise,  $D$ -values for  $\text{NaAlO}_2$  were found to be higher than  $D$ -values for  $1/2\text{CaAl}_2\text{O}_4$ . In conclusion, the efficiency of the charge-balancing ions is in agreement with the succession given by the field strength. By including the  $D$ -values for  $\text{KAlO}_2$  and  $\text{NaAlO}_2$ , the BW model becomes more accurate in predicting the viscosity for melts in the compositional range from 35 to 45 mol%  $\text{SiO}_2$ .

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Contact:

Mette Solvang  
Materials Research Department  
Risø National Laboratory  
Frederiksborgvej 399  
DK-4000 Roskilde  
Denmark  
E-mail: mette.solvang@risoe.dk