THE EFFECT OF CaO ON THE VISCOSITY OF PbO-SiO$_2$ MELTS

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ABSTRACT

The effect on the viscosity of lead silicate melts by the addition of CaO was measured using a rotating cylinder technique at temperatures between 1000 and 1437 K. The effect of CaO addition was determined by maintaining a constant PbO:SiO$_2$ mole ratio and adding lime. Powder X-ray diffraction was used to confirm that the melt was homogeneous and did not contain crystals from solid phase saturation.

The measured viscosities of lead silicate are in good accord with those of other workers and the composition range studied has been extended slightly. The viscosity-temperature dependence of PbO-SiO$_2$, and CaO-PbO-SiO$_2$ melts were described using a simplified Weymann equation.

At a constant mole fraction of silica, the viscosities of CaO-PbO-SiO$_2$ melts are greater than that of PbO-SiO$_2$ melts. The increase in viscosity of melts containing CaO is attributed to the difference in strength of the interaction between the cation species (Ca and Pb) and oxygen containing anions.

1. INTRODUCTION

Viscosity is one of the important properties of slags that can play a significant role in the dynamics of smelting and refining processes. Viscosity can influence mass transfer in the slag and hence affect reaction kinetics, influence the ease of controlling foams and influence the stability of emulsions as well as determining the tapping conditions.

Numerous studies have been made into measuring the viscosity of metallurgical slags and many binary and ternary systems have been extensively studied and the measurements compiled into reference texts[1,2]. Even though the viscosity behaviour measured experimentally for most silicate melts can be described using the Weymann equation[3-5], there is still a limited understanding of the mechanism for viscous flow in silicate melts. For example, the Weymann equation is based on a "hole" model and movement of simple atoms, which is clearly not a true description of silicate melts which contain mixtures of anions of varying complexity such as rings and chains and at varying concentrations[6].

It has long been recognised that the melt structure has a major influence on viscosity and other transport properties[7,8] and various attempts have been made to correlate some of the viscosity parameters to the melt structure[9-11] using physical descriptions of the structure such as; as the degree of polymerisation (NBO/T), silicate chain lengths, optical basicity and the fractions of the three types of oxygen in the melt (N_O^0, N_O^-, N_O^{2-}). The latter approach, correlating the composition dependence of viscosity to the structural parameters[12], appears to give a reasonable description of the behaviour of a wide range of silicate melts[13].

In order to advance understanding of the effect of structure and other factors such as cation-anion interactions and compound formation on transport properties, research on the melt structure and measurement of the transport properties are needed. The literature on the structure of silicate glasses using diffraction techniques, Raman spectroscopy and Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) is expanding rapidly and reviews detailing the findings are available[14,15]. Stebbins *et al.*[16,17] have calculated viscosities from MAS-NMR studies using the determined exchange frequencies of sodium and potassium silicate melts. Although the absolute values depended on interpretation, the calculated viscosities were less than one order of magnitude away from the experimental measurements, which were around 10^7 Pa·s at the temperatures of interest (800-900 K). Even though these viscosities are much higher than those of practical metallurgical interest, understanding of the relationship between structure and the movement of species in melts and viscosity is advancing.

The results of viscosity measurements in silicate systems can be very variable and dependent on the measurement technique and procedure. In a recent study[5], the viscosity of a high temperature standard reference material (SRM), a Li_2O-Al_2O_3-SiO_2 slag with low levels of Na_2O, K_2O, FeO_x, MgO, CaO, P_2O_5, MnO and carbon was measured in several laboratories. The scatter in the measurements was greater than 50%[2]. The scatter was attributed to reactions between the slag and the container and bob, or errors in temperature measurement. The scatter was significantly reduced by using inert containers and components (e.g. Pt, Mo). The study [*sic*] concluded that experimental uncertainties of only 10% could be achieved by careful calibration of viscometers with high and low temperature materials.

In the present study, results of viscosity measurements in the PbO-SiO_2 and CaO-PbO-SiO_2 systems are presented. The work was aimed at examining the relative effect of CaO on the viscosity of PbO-SiO_2. An inert crucible and bob were used. The bob was calibrated at low temperature and the experimental technique validated at high temperature using a sample of SRM slag.

Although there have been several studies published on the viscosity of PbO-SiO_2[18-22], there have been few studies on the CaO-PbO-SiO_2 system[20,23]. These studies show that substitution of CaO for PbO increases viscosity, however the composition and temperature range covered was narrow. This work extends the data and will be used in the development and validation of a structurally related viscosity model for multi-component slags containing lead oxide.

2. EXPERIMENTAL

The experimental apparatus to measure the viscosity of liquids at high temperature is shown in Figure 1. The slag was heated in a $MoSi_2$ element vertical tube furnace with a Eurotherm programmable temperature controller which maintained temperatures to ± 1 K. A pythagorus work tube of 95 mm outer diameter with water-cooled brass end caps was used to isolate the crucible. A Pt-13%Rh crucible (67 mm diameter, 70 mm high) containing lead silicate melt of mass 600 g was supported in the hot zone on a ceramic platform cast onto an inverted closed one end alumina tube. The melts were prepared from laboratory reagent grade lead oxide, silica and

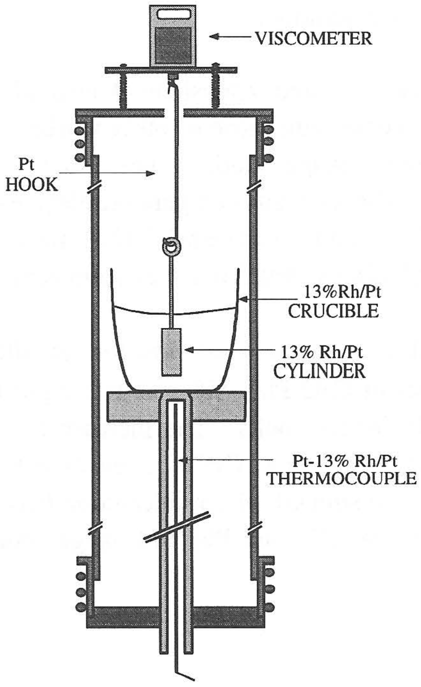


Fig. 1. Viscosity apparatus

analytical reagent grade calcium carbonate. Temperature measurements were made with a Pt-13%Rh/Pt thermocouple located in the support tube with the tip in thermal contact with the crucible bottom. The thermal gradient in the stagnant melt was measured by immersion of an alumina sheathed Pt-13%Rh/Pt thermocouple into the slag. The temperature variation in the slag was determined as ± 3 K.

A Brookfield DVII+ viscometer was positioned above the work tube on a plate which was connected to a brass flange on the water-cooled end cap by three threaded studs. The threaded studs permitted vertical positioning and levelling of the viscometer. The brass flange had a 40 mm aperture to allow air ingress and connection of a concentric Pt-13%Rh cylinder (12 mm diameter, 30 mm high with a shaft of 3 mm diameter and 100 mm high) to the viscometer with two platinum extension rods. The geometry also permitted a clear view of the melt surface at 1073-1273 K through a prism or mirror. A slight negative pressure through a filter was applied at the top end cap to collect lead fume.

The viscometer bob was calibrated against liquids of known viscosity at 298 K (0.05, 0.102, 0.485, 0.97, 4.80, 12.4 and 30.8 Pa·s). A 250 ml beaker containing the standard was placed in a water bath at a constant temperature of 298 K. The spindle constant was determined by fully immersing the cylinder to a depth of 10 mm in the standard and then measuring the torque at several rotation speeds. The effect of thermal expansion of the Pt-Rh cylinder at 1073-1473 K on the spindle constant was considered negligible. The contribution of the shaft to the spindle constant is also small and a 2 mm displacement from the calibrated depth contributes only a 0.5% contribution to the uncertainty.

The immersion depth in the melt was established by lowering the spindle into the melt until the top surface was just submerged. The spindle was then lowered a further 10 mm to the desired depth. The torque was then measured at several rotation speeds with either 100 or 200 readings collected at each speed over 5 minutes. Measurement of the torque after a small temperature change (less than twenty five degrees) showed that twenty minutes was sufficient time to regain thermal equilibrium.

The viscometer was also calibrated at high temperature with the SRM slag supplied by Hoogovens RL. The measurement protocol outlined by the authors of the SRM study was adopted[5]. The agreement between the measured viscosities and the recommended values were well within the quoted experimental uncertainties. The determined viscosity-temperature dependence was:

$$\log \eta /(\mathrm{Pa\cdot s}) = -8.07 \pm 0.02 + \log T + (8100 \pm 40)\, T^{-1}$$

and the recommended relationship[5] was:

$$\log \eta /(\mathrm{Pa\cdot s}) = -8.12 \pm 0.02 + \log T + 8127\, T^{-1}$$

The temperature range studied for the PbO-SiO_2 and CaO-PbO-SiO_2 melts depended on the PbO content of the melt and the upper temperature was restricted by the lead volatility. Gram samples of the slag were collected by quenching on a cold steel dip rod at several temperatures for chemical analysis by ICP-AES and for XRD confirmation of homogeneity. After measurement at the maximum temperature, the viscosity was re-measured at lower temperatures to confirm there were no significant differences due to composition changes. After completion of a series of measurements and while the melt was at a high temperature, $CaCO_3$ was added to the melt. The lime was mixed into the melt using the viscometer bob. The melt was then stirred for 20 minutes by the viscometer bob and then the melt was cooled to above the expected liquidus and stirred overnight. The next series of measurements were performed and the procedure continued until it was apparent that the added CaO was not dissolving.

3. RESULTS

The viscosity of PbO-SiO_2-CaO melts was studied at three SiO_2:PbO mole ratios of 1.6, 1.1, and 0.69, where the initially targeted mole fractions of SiO_2 were 0.4, 0.5 and 0.6. The measured torque was linearly proportional to the rotation speed and could be extrapolated to the origin. This implies that the homogeneous melts obeyed Newtonian behaviour over the measured rotation speed range. As discussed earlier, the temperature and composition range of the measurements was dictated by the formation and nucleation of solid phases and by PbO volatilisation at higher temperatures. The highest temperature at which viscosity measurements were made in this work was 1437 K. ICP-AAS analysis of the samples collected during each viscosity experiment showed no significant change in SiO_2:PbO ratio.

The lower temperature depended on the liquidus temperature, although the phenomena of super-cooling observed with PbO-SiO_2 melts[22] was also observed to occur for PbO-SiO_2-CaO melts. In these systems, super-cooling of the order of 50 degrees was observed, with solid phase formation often occurring after collecting a sample on a cold steel rod. This caused localised chilling and nucleation of a solid phase.

Figure 2 shows the powder X-ray diffraction pattern of a quenched sample collected from a PbO-SiO_2 melt where the mole fraction of SiO_2 (X_{SiO2}) was 0.6 and the temperature was 1081 K. The pattern is typical of the glassy samples collected and there is a broad low intensity peak consistent with the behaviour of non-crystalline materials. In Figure 3, the XRD pattern from a melt collected at 1183 K with a "bulk" calcium oxide mole fraction

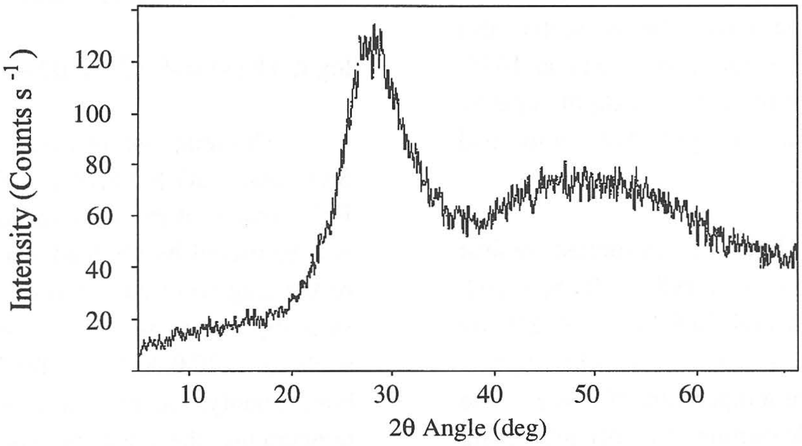


Fig. 2.Powder XRD pattern of a PbO-SiO_2 melt (X_{SiO2} = 0.6) quenched from 1081 K.

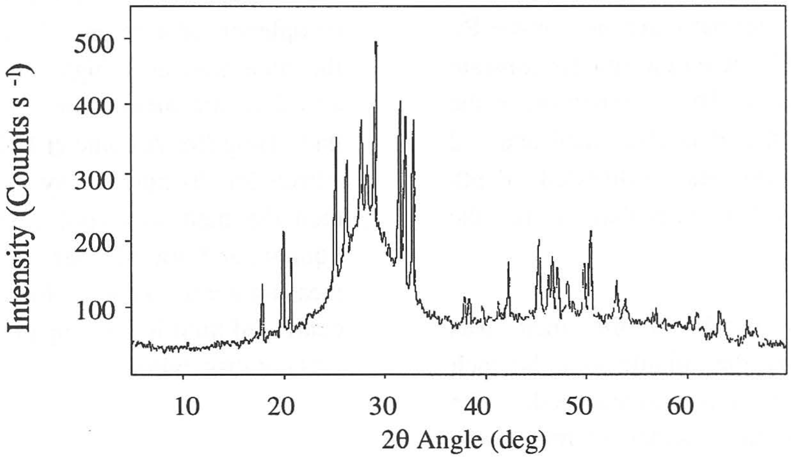


Fig. 3.Powder XRD pattern of a CaO-PbO-SiO_2 (SiO_2:PbO = 1.1, X_{CaO}= 0.11) melt quenched from 1183 K.

(X_{CaO}) of 0.11, had a broad peak and well defined small peaks indicating that the melt contained a crystalline phase and is no longer homogeneous. A similar XRD pattern was observed from a sample from the same experiment at 1350 K indicating that the melt contained two phases over the practical measurement range. The primary phase of the melt identified was $Ca_2Pb_3Si_3O_{11}$. The primary phases and the observed saturation limits of this study were in accord with the recently revised phase diagram of Jak *et al.*[24].

As discussed earlier, the Weymann equation has been found to be the most appropriate to describe the viscosity behaviour of silicate slags. The simplified Weymann equation is:

$$\eta = A_w \cdot T \cdot e^{E_w/RT}$$

where E_W is the activation energy for viscous flow, R is the gas constant, and A_W is a pre-exponential term. The results of this study are presented in Figure 4(a)-(c) and the mole fraction ratio of SiO_2:PbO is constant in each figure. Even though there is a slight curvature observed for some melts where the viscosity has been measured over a wide temperature range, when the measurement uncertainty is considered these melts all followed Weymann behaviour.

4. DISCUSSION

4.1 PbO-SiO₂ system

Measurements on lead silicate were performed for two reasons. It provides a good reference point for determining the effect of CaO on viscosity and there is also little viscosity data at silica mole fractions above 0.5 compared with other compositions. The composition dependence of viscosity at 1273 K of PbO-SiO_2 binary melts examined in this study and from other studies[19-22] are shown in Figure 5.

The viscosity data of the present study and that of Urbain[21] were interpolated by a curve fit to

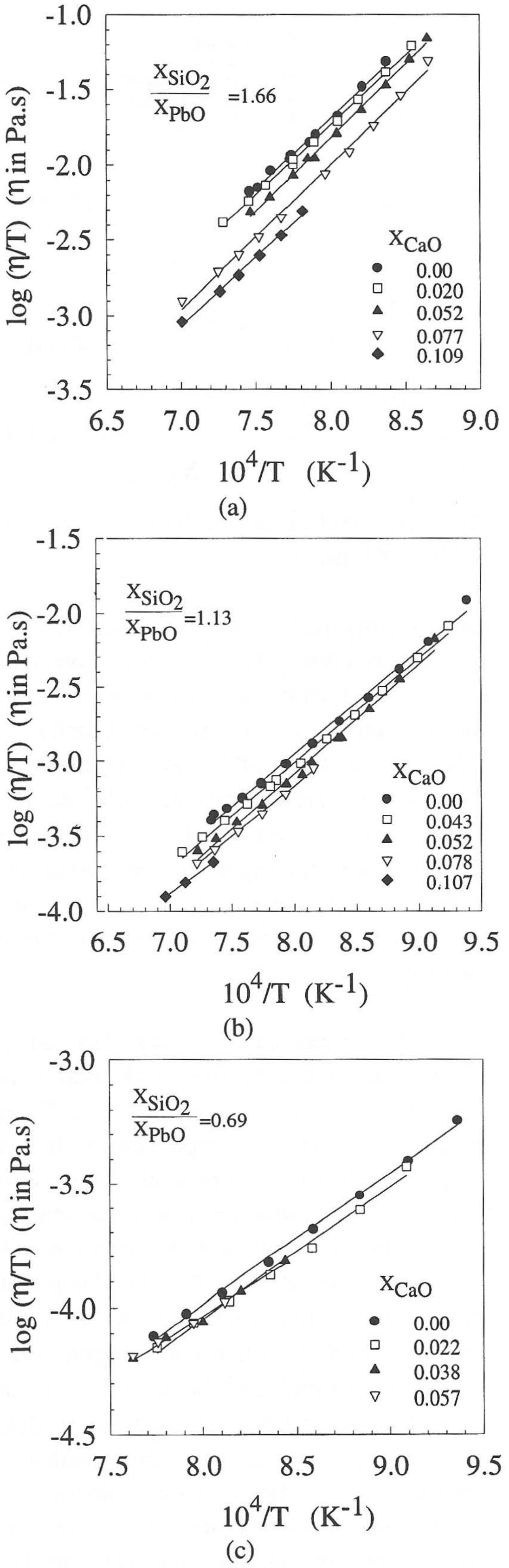


Fig. 4. Viscosity of CaO-PbO-SiO_2 melts.

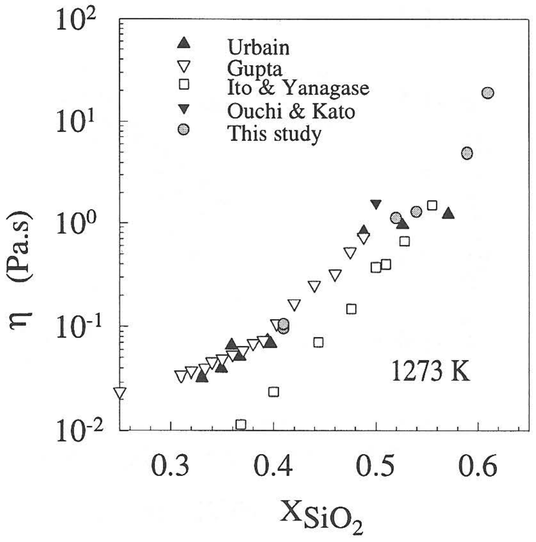


Fig. 5.Composition dependence of the viscosity of $PbO-SiO_2$ melts.

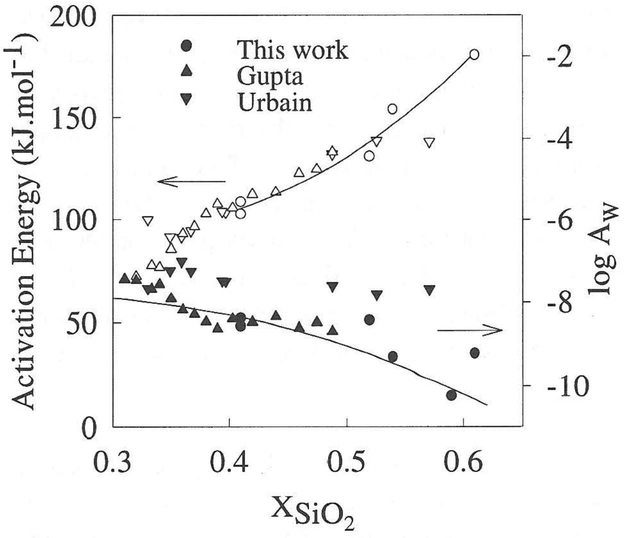


Fig. 6. Variation of E_W and A_W with composition in the $PbO-SiO_2$ binary. (Open symbols - Activation Energy (E_W), filled symbols A_W)

the data using the Weymann equation. The viscosity is relatively insensitive to the melt composition at low silica contents and increases as the silica content increases, (with significantly greater sensitivity at high SiO_2 mole fractions). This behaviour is typical of silicate melts and has been shown in many experimental studies and is believed to be related to the degree of polymerisation of the melts. As silica content increases the size of the silicate anion increases causing an increase in viscosity.

The agreement between this study and Urbain[21] and Gupta[22], who both used a rotating cylinder technique, is good. Ito and Yanagase[19] measured the effect of composition on the viscosity using an oscillating bob method. Their results are an order of magnitude lower than the other studies at low silica contents and this could possibly be attributed to the method where the damping rate of an oscillating wire is measured. At low viscosities, the background correction will be significant, and λ (the natural logarithm of the damping rate) and the associated uncertainties are squared to determine the viscosity. Furthermore this method needs density data for the viscosity calculation. The related uncertainties from density determination must contribute to the viscosity measurement uncertainty. The higher values of Ouchi and Kato[20] may be due to either using a counterbalanced sphere method or composition changes occurring during viscosity measurement. The temperature range studied was 1110 to 1538 K, and at the upper temperature, lead volatilisation may have been significant.

The constant slopes observed in Figure 4 shows that the Weymann relationship gives a good description of the temperature dependence of viscosity and that the activation energy of viscous flow (E_W) is independent of temperature over the measured temperature range. Although similar behaviour is observed if a simple Arrhenius relationship ($\eta = A \cdot e^{E/RT}$) is used, the Weymann equation is a better fit to the data. The variation of the Weymann activation energy (E_W) and the pre-exponential term (A_W) as a function of composition are shown in Figure 6. The solid lines in Figure 6 are lines of best fit to the Weymann terms determined in this study. The activation energies reported by Gupta have been recalculated over a single temperature range using the Weymann equation.

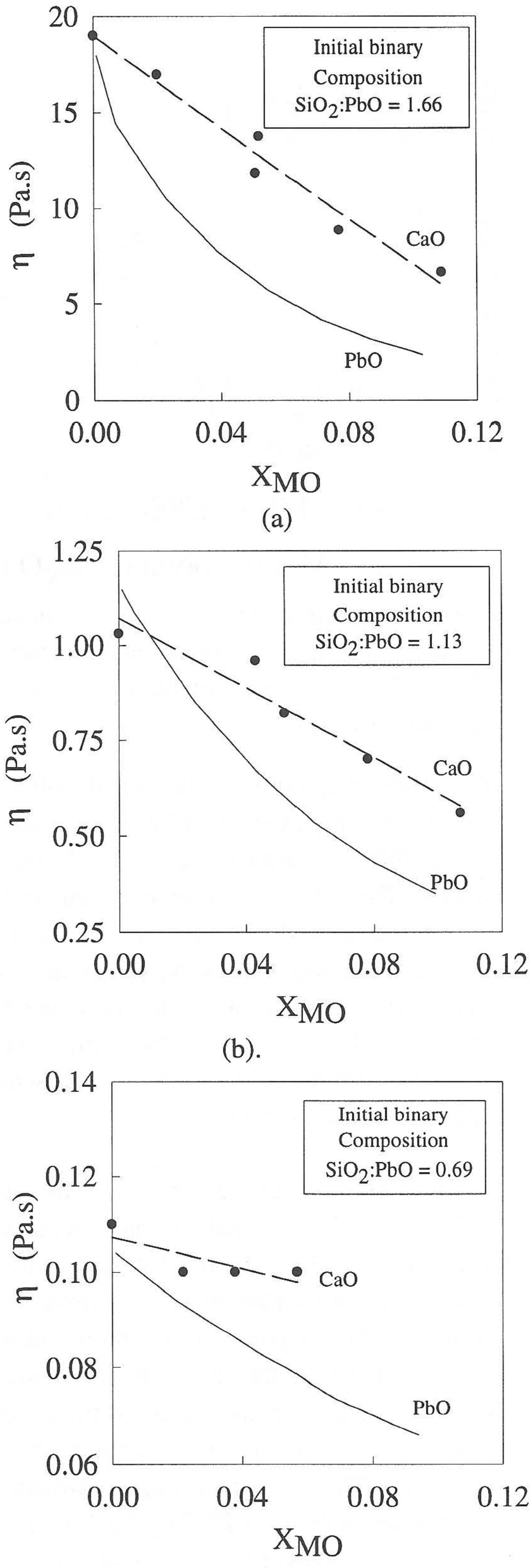
Gupta reported that plots of log η against 1/T for $PbO-SiO_2$ melts were linear only over narrow ranges in temperature and that the activation energy was temperature dependent. It would appear that this interpretation is too narrow. For melts where X_{SiO2} was greater than 0.36, least squares fitting of his reported data over the homogeneous liquid range yields regression coefficients (r^2) of greater than 0.99 for both Arrhenius and Weymann type behaviour. At lower silica contents the fit is not as good (r^2 between 0.94 and 0.98) but the measurement uncertainties are greater as the viscosities are low.

There is insufficient data from this study on binary silicates to confirm the observations of Ito and Yanagase[19] of cation anion interactions and clustering at X_{SiO2} = 0.5 and 0.33 causing a viscosity discontinuity or change in slope due to compound formation. The relatively smooth variation of activation energy with composition in Figure 6 discounts the possibility of strong interactions due to clustering and compound formation.

4.2 PbO-SiO_2-CaO system

The effect of CaO on the viscosity of PbO-SiO_2 melts at 1273 K with constant SiO_2:PbO molar ratio is shown in Figures 7(a)-(c). In order to examine the effect of substitution of CaO for PbO, the effect of adding PbO or CaO from the same starting point composition on PbO-SiO_2 binary is presented. The line is calculated from the PbO-SiO_2 viscosity data and the slight difference between the experimental point and the line is due to curve fitting using all the PbO-SiO_2 data.

Addition of both CaO and PbO causes viscosity to decrease. This is mainly due to the decrease in silica content of the melts as metal oxides are added. It is well known that the reducing silica content tends to reduce viscosity of silicate melts. However, the results show that PbO is more effective in reducing viscosity than CaO. This observation is in agreement with observations of other workers. Ouchi and Kato[20] and Suginohara *et al.*[23] examined the effect of different metal oxides on the viscosity of PbO-SiO_2 melts.



(a)

(b).

(c)

Fig. 7. Effect of CaO and PbO additions to the viscosity of PbO-SiO_2 melts at 1273 K.

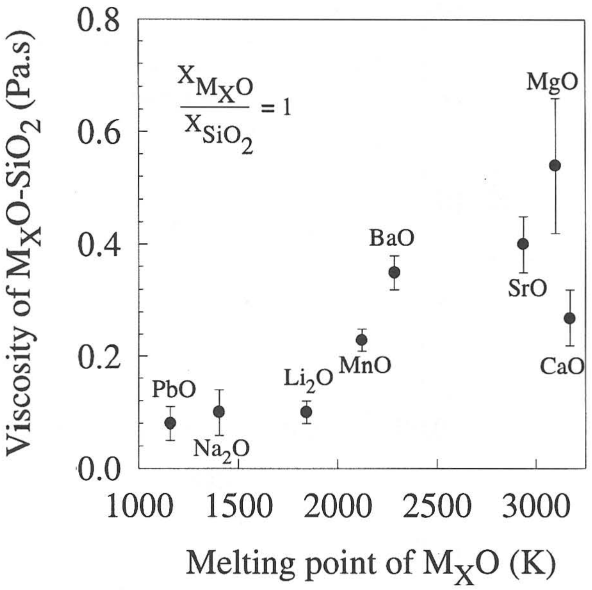


Fig. 8. Estimated viscosity of binary silicate melts at 1823 K with a silica mole fraction of 0.5[7,8,10,19,26-32]. Data extrapolated using the Weymann equation.

Although the magnitude of their results differs from those of this study, they also found that addition of CaO or PbO to a lead silicate melt decreases the viscosity. The effect of different metal oxides has also been observed in other silicate melts. For example, the study by Kucharski *et al.*[25] on the effect of the addition of CaO, MgO and FeO to Fe-O-SiO_2 slags showed that the order of effectiveness of an oxide in reducing viscosity by oxide is FeO>CaO>MgO.

It is known that the increase in the viscosity of silicate melts is mainly influenced by the development of the complex network structure as the melts become richer in SiO_2. However, if we consider a melt at a given silica content, substitution of one oxide by another by a small amount is not expected to cause a great change in the structure of the silicate anions or the distribution of the silicate anion types. Therefore the change in structure from the replacement of some Pb^{2+} by Ca^{2+} in the silicate matrix is not expected to be significant. Direct confirmation of the degree of structural change is not possible due to lack of experimental evidence.

Table I shows the relative viscosity increase by substituting CaO for PbO at different X_{CaO}/X_{PbO} for melts with the same mole fraction of SiO_2 at 1273 K. It can be seen that the viscosity ratio $\eta_{PbO\text{-}SiO2\text{-}CaO}/\eta_{PbO\text{-}SiO2}$ increases with increasing X_{CaO}/X_{PbO}. If the effect of a small amount of substitution of CaO (X_{CaO} = 0.05) on the silicate structure can be considered negligable, the results show that the greater the substitution (X_{CaO}/X_{PbO}), the greater the increase in viscosity.

Table I Relative viscosity increase due to CaO (X_{CaO} = 0.05) compared to PbO-SiO_2 melts with the same silica mole fraction.

X_{SiO_2}	$\frac{X_{CaO}}{X_{PbO}}$	$\frac{\eta_{CaO-PbO-SiO_2}}{\eta_{PbO-SiO_2}}$
0.39	0.09	1.2
0.5	0.11	1.5
0.59	0.14	2.2

Viscosity modelling work carried out by the present authors[13] found that the effectiveness of oxides in reducing viscosity can be related to the melting points of the oxides. This was based on the available experimental data on viscosity for silicate systems in the CaO-MgO-MnO-FeO_x-PbO-SiO_2 system. Figure 8 shows the estimated viscosity of binary silicate melts with a silica mole fraction of 0.5 at 1823 K. It shows the average and range of the viscosity which was estimated by extrapolating the temperature dependence of the viscosity for systems where experimental data were available[7,8,10,19,26-32]. The melting point of CaO was taken from a thermodynamic assessment on the CaO-SiO_2 system[33] while the other melting points were from Barin[34]. The figure shows that, in general the viscosity increases as the metal oxide fusion temperature increases. In general, the substitution of an oxide with a high melting point for one with a low melting point at a given silica content causes the viscosity to increase and vice versa. This behaviour is also evident in calcium ferrite melts[35,36], where at constant temperature, the viscosity increases as the CaO mole fraction increases.

The difference in the effectiveness of metal oxides in reducing viscosity may be considered as the difference in strength of the interaction between cation species (Ca, Mg, Mn, Fe and Pb) and the oxygen-containing ions. The melting points of these oxides are directly related to such interaction. The higher the melting point, the stronger the interaction between the cations and oxygen ions. The melting points of CaO and PbO are 3172 K and 1159 K respectively. Such large differences in the melting points of these two oxides may explain the reason for the increase in viscosity by small amounts of substitution of CaO for PbO.

5.CONCLUSION

The viscosity of homogeneous $PbO-SiO_2$ and $CaO-PbO-SiO_2$ melts has been measured for slags with SiO_2:PbO ratios of 1.66, 1.13 and 0.69. The melts displayed Newtonian behaviour over the composition and temperature range studied. Powder X-ray diffraction of quench samples permitted detection of crystalline phases and ensured that the melts were a single phase. The experimental data for $PbO-SiO_2$ has been extended to higher silica concentrations than previously published.

The viscosity of $CaO-PbO-SiO_2$ melts are higher than $PbO-SiO_2$ with the same SiO_2 content. Due to the relatively low CaO concentrations studied, when CaO is substituted for PbO the melt "structure" should not be altered significantly. The increased viscosity of $PbO-SiO_2$ melts containing CaO is attributed to the difference in strength of the interaction between the cation species (Ca and Pb) and oxygen- containing anions.

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