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Prediction of viscosity in the two-phase range of a ternary glass-forming system

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In order to predict the viscosity of liquid and correlation between equilibrium and the glass state, the theory for composite materials and suspensions was applied to an appropriate composition range of a ternary glass-forming system where one liquid and one crystal are in a state of equilibrium. According to the results the theoretical calculation showed good agreement with the measurement within the validity of the theory. The viscosity behaviour of both results was discussed from the viewpoint of the physicochemical structure of liquid and it was suggested that glass reflects latently some characteristics of the state of equilibrium.

1. Introduction

According to several studies on composite materials [1, 2], it may be possible to predict properties, for example, the density, elastic properties and field properties of two-phase solid materials, using the relationships between the properties and the structure. A relationship also exists for the viscosity of a suspension which consists of solid particles and liquid [3, 4]. The values calculated by these relationships showed on the whole good agreement with those of experimentally determined properties.

In spite of the assumption that glass is a homogeneous amorphous state, it tries to be an energetically stable state, especially during heating owing to its thermodynamic metastable state. The so-called liquid–liquid immiscibility or phase separation and crystallization could be a transitional stage to achieve this stable state because many glasses have been shown to contain two-phase or multiphase (sub)-microstructures which reflect latently the constitutional phase relations according to the corresponding equilibrium phase diagram. On the basis of the concept for the above composite materials, properties such as the density and elastic properties of various phase-separated glasses have also been predicted using similar relationships to those of composite materials [5, 6]. The results showed that the relationships fit the experimental data for several glass systems fairly well.

According to phase diagrams corresponding to glass-forming systems, there are many two-phase regions where one liquid and one crystal are in a state of equilibrium. If this two-phase region is assumed to be a suspension, it may be possible that the theory for the viscosity of a suspension can be applied to this region and thus to predict the viscosity and correlation between equilibrium and the glass state. In the recent studies [7, 8], the present author and co-workers reported results of a viscosity calculation for two simple binary glass-forming systems. The results were compared with experimental values and demonstrated reasonable agreement upto a solid-phase concentration of 50 vol %.

In the present work, this relationship was further investigated for some ranges of a ternary glass-forming system where one liquid and one crystal are also in a state of equilibrium.

2. Theory of the viscosity of two-phase systems

According to classical studies [9–11] on the viscosity of dilute suspensions consisting of two phases, most relationships between the viscosity of the fluid and the volume fraction of the dispersed solid phase have the following equation form:

$$\frac{\eta_{\mathrm{eff}}}{\eta_{\mathrm{l}}} = (1 + mC_{\mathrm{D}})^n \tag{1}$$

where η_{eff} is the effective viscosity of suspension with volume concentration C_{D}, of solid phase, η_{l} is the viscosity of liquid without solid phase and C_{D} is the volume fraction of solid phase in suspension. m and n are empirical constants.

On the basis of the semiempirical analogy between the equations governing field properties and flow properties, namely transport properties, Saeltzer and Schulz [3, 4] have developed the following equation for the effective viscosity of suspensions:

$$\log\left(\frac{\eta_{\mathrm{eff}}}{\eta_{\mathrm{l}}}\right) = -\left(\frac{1-\cos^2\alpha}{F} + \frac{\cos^2\alpha}{1-2F}\right)\log(1 - C_{\mathrm{D}}) \tag{2}$$

In this equation, F is the shape factor of dispersed spheroidal particles in suspension and a function of the axial ratio, a/b, of spheroidal particles having the same shape but not the same size. Ondracek [2], using a spheroidal model, found that, for cylindrical platelets ($a/b \approx 0$), $F = 0$, for spherical particles ($a/b \approx 1$), $F = \frac{1}{3}$ and, for cylindrical fibres ($a/b \approx \infty$), $F = \frac{1}{2}$. α is the mean orientation angle of the spheroid or, in other words, the angle between the symmetry axis, a or b, of the spheroid and the velocity gradient when an external force is applied to the suspensions. A measurement of the orientation is not possible, but in general a value of $\cos^2 \alpha = \frac{1}{3}$ is chosen, under the assumption that spheroidal particles are randomly oriented in the suspension. Accordingly, Equation 2 can be altered to

$$\log\left(\frac{\eta_{\text{eff}}}{\eta_l}\right) = \frac{3F - 2}{3F(1 - 2F)} \log(1 - C_D) \qquad (3)$$

and this equation is valid for the concentration range $0 < C_D < 0.65$ in which the agglomeration of spheroidal particles does not occur. In comparison with Equation 1, the constants m and n can be expressed as follows: $m = -1$, $n = (3F - 2)/3F(1 - 2F)$. By using Equation 3 for the salt–glass (particle and fibre forms) suspensions, Saeltzer and Schulz [4] found fairly good agreement between experimental values and predicted data.

As a first approach to viscosity evaluation for a binary glass-forming system, in earlier work [7, 8] the Na_2O–SiO_2 glass-forming system as shown in Fig. 1 was considered and its viscosity in the equilibrium state at 1400 °C was calculated using Equation 4, under the assumption that the solid phase (in this case tridymite is the solid phase) is spherical, i.e., $F = \frac{1}{3}$:

$$\eta_{\text{Tri}} = \eta_l (1 - C_{\text{Tri}})^{-3} \qquad (4)$$

where η_{Tri} is the effective viscosity of the materials containing two phases (liquid + tridymite) with the volume concentration, C_{Tri}, of the tridymite phase at 1400 °C, and η_l is the experimentally determined viscosity of liquid with composition 17.9 vol% Na_2O–82.1 vol% SiO_2 at 1400 °C. The results in Fig. 1 show up to 50 vol% tridymite, giving approximate agreement between experimental and calculated values.

3. Measurement and calculation of the viscosities in a ternary system

As a ternary system, Na_2O–Al_2O_3–SiO_2, which has the main components of commercial alkali aluminosilicate glasses, was selected [12] and the (31-x) mol% K_2O–1.15x mol% Al_2O_3–(69–0.17x) mol% SiO_2 glass-forming system [13] was investigated in detail. x was taken in the range from 0 to 14.4. The phase diagram is shown in Fig. 2 as a quasibinary system, 31 mol% K_2O–69 mol% SiO_2–leucite (16.6 K_2O–16.6Al_2O_3–66.6SiO_2 or K_2O–Al_2O_3–4SiO_2). The investigated temperatures, 1000 and 1200 °C, where liquid and leucite coexist are also indicated by open arrows in this figure.

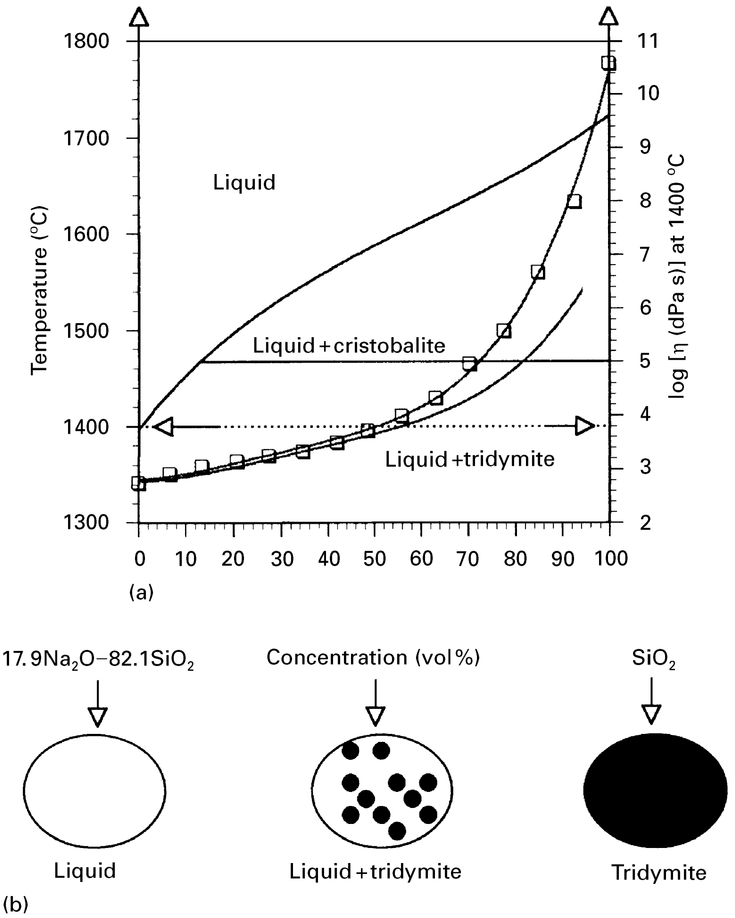

Figure 1 (a) Na_2O–SiO_2 phase diagram on the SiO_2-rich side above 1300 °C, showing the experimental viscosity curve (□) in the glass state and the calculated viscosity curve (——) in the equilibrium state (liquid + tridymite) at 1400 °C. (b) Hypothetical microstructures at various volume concentrations of tridymite in the equilibrium state at 1400 °C.

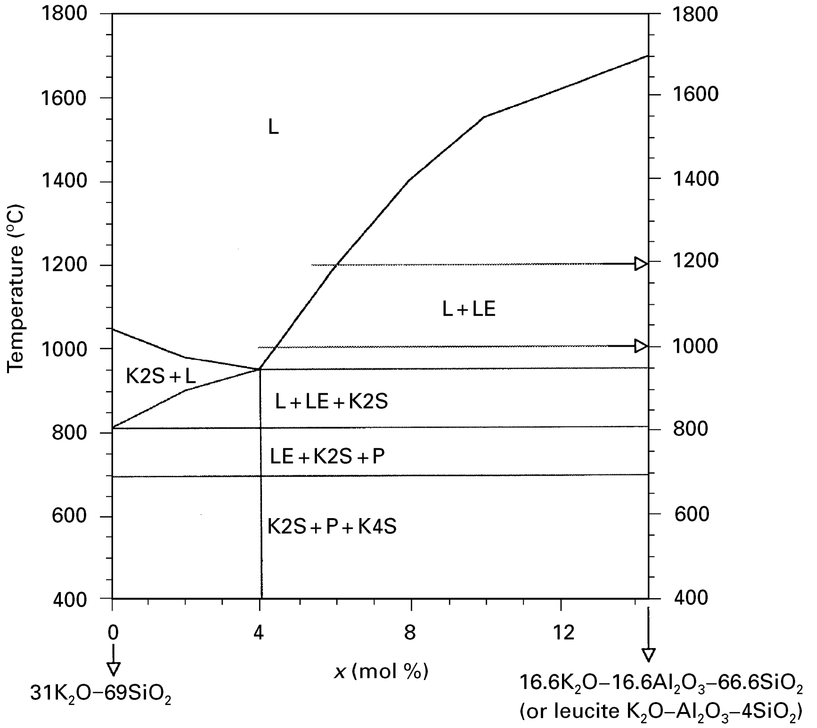

Figure 2 Quasibinary phase diagram of the (31-x)K_2O–1.15$x$$Al_2O_3$–(69–0.17$x$)$SiO_2$ system. L, liquid; Le, leucite (K_2O–Al_2O_3–4SiO_2); K2S, K_2O–2SiO_2; K4S, K_2O–4SiO_2; P, potash feldspar (K_2O–Al_2O_3–6SiO_2).

3.1. Glass preparation and viscosity measurement

Eight glasses with $x = 4.4$–11 were prepared from high-purity quartz sand, commercial reagent grade K_2CO_3 and $Al(OH)_3$. A batch for producing about 200 g of glass was melted in a Pt–5 wt % Au crucible at 1450–1700 °C for 4–10 h depending upon the composition. The bubble-free homogeneous glass melts were poured into a Pt–30 wt % Rh crucible to measure the viscosity. For the compositions with $x > 11$ it was difficult to produce a homogeneous glass owing to their high melting temperature.

In order to determine the viscosities of melts the well-known rotating-cylinder method was used, in which an outer crucible is fixed while rotating an inner spindle. The crucible and the spindle consist 70 wt % Pt–30 wt % Rh alloy. The viscometer used was RV 30 (Hakke, Germany) with a measuring head. The apparatus was calibrated using Deutsche Glastechnische Gesellschaft (DGG) standard glass I in the temperature range 1450–1000 °C and a corresponding apparatus constant was determined at the immersion depth of spindle of 35 mm. The viscosity of each glass melt was measured at 1000 and 1200 °C and the measured values were analysed by computer program. For the compositions with $x > 11$ the viscosities were extrapolated.

3.2. Viscosity calculation

According to the phase diagram in Fig. 2, a range between 26.6K_2O–5.06Al_2O_3–68.2SiO_2 ($x = 4.4$) and leucite is valid for 1000 °C, and between 25K_2O–7Al_2O_3–68SiO_2 ($x = 6$) and leucite for 1200 °C. In order to calculate the viscosity of liquid containing a solid phase by Equation 3, the mole concentration of leucite must be changed to a volume concentration using the densities. The densities of the 26.6K_2O–5.06Al_2O_3–68.2SiO_2 ($x = 4.4$) and 25K_2O–7Al_2O_3–68SiO_2 ($x = 6$) liquids were measured in the glassy solid state: $d_{4.4} = 2.447\ \mathrm{g\,cm^{-3}}$ and $d_6 = 2.445\ \mathrm{g\,cm^{-3}}$. The density, d_{Leu}, of leucite was taken from the literature [14]: $d_{\mathrm{Leu}} = 2.47\ \mathrm{g\,cm^{-3}}$. The volume fraction, C_{Leu}, of leucite in the two-phase region can be calculated from

$$C_{\mathrm{Leu}} = \frac{1}{1 + (N_x M_x / d_x)(d_{\mathrm{Leu}} / N_{\mathrm{Leu}} M_{\mathrm{Leu}})} \tag{5}$$

where N_x and N_{Leu} are the mole percentages of liquid and leucite, respectively at 1000 and 1200 °C. M_x and d_x are the molecular weight and density, respectively, of the liquid with $x = 4.4$ and $x = 6$. The shape factor, F, of the leucite in the liquid phase was taken as about $\frac{1}{3}$ on the basis of microscopic observation of divitrified glasses.

Therefore, the equation for viscosity calculation can be simplified as follows:

$$\eta_{\mathrm{Leu}} = \eta_{\mathrm{l}}(1 - C_{\mathrm{Leu}})^{-3} \tag{6}$$

where η_{Leu} is the effective viscosity of the liquid with the volume concentration, C_{Leu}, of the leucite, η_{l} is the experimental viscosity of liquid (glass melt) without leucite or, in other words, liquid with $x = 4.4$ at 1000 °C and liquid with $x = 6$ at 1200 °C.

4. Results and discussion

Experimental viscosities at 1000 and 1200 °C are shown with the calculated viscosity curves in Fig. 3.

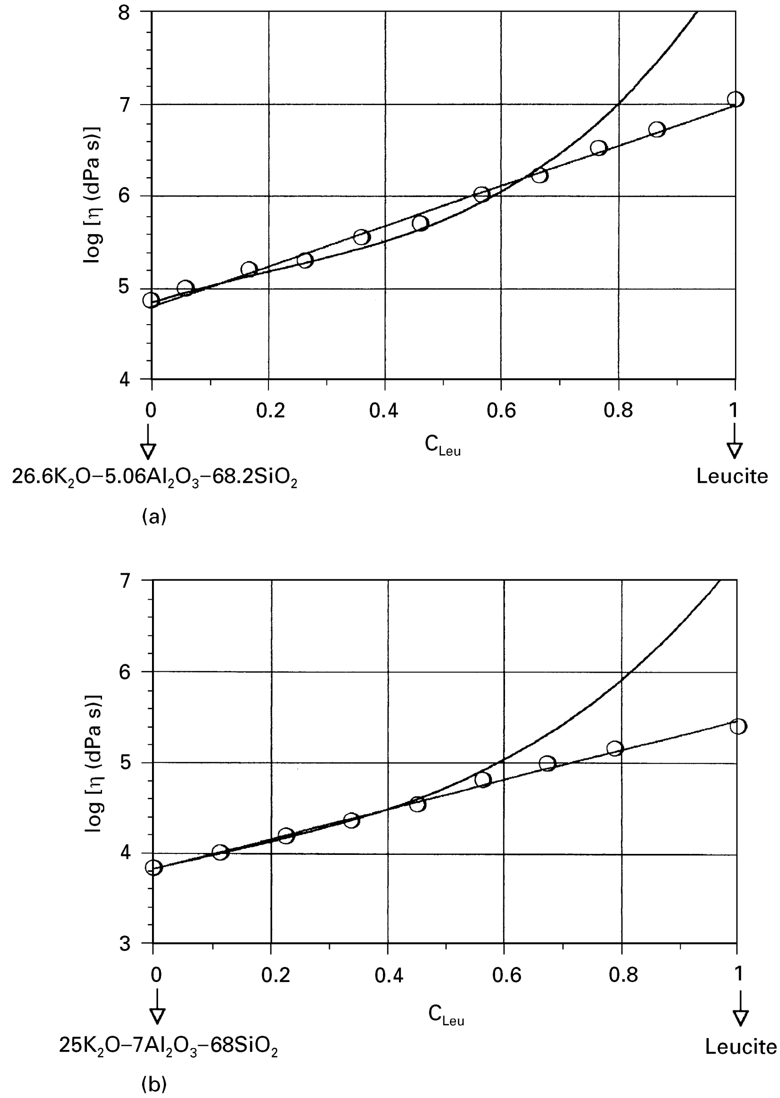

Figure 3 Measured (○) and calculated (——) viscosities of (a) the 26.6K_2O–5.06Al_2O_3–68.2SiO_2–leucite system at 1000 °C and (b) the 25K_2O–7Al_2O_3–68SiO_2–leucite system at 1200 °C.

The experimental viscosities of all glasses increase on substitution of K_2O by Al_2O_3 or, in other words, with increasing Al_2O_3 (leucite) content. This indicates that the glass network becomes rigid on introduction of Al_2O_3. From the viewpoint of the structural model for alkali aluminosilicate glass melts [15], this viscosity behaviour can be explained as follows: on introduction of Al_2O_3 into potassium silicate glass at a molar fraction $[Al_2O_3]/[K_2O] < 1$ the aluminium ion goes into tetrahedral coordination as a network former, $[AlO_4]^-$, which eliminates the non-bridging oxygen atoms. Charge neutrality of $[AlO_4]^-$ tetrahedra is maintained by the presence of potassium ions, which break up the network and create non-bridging oxygen atoms, $[\text{–O}]^-$. The elimination of the non-bridging oxygen atoms leads to connection of the network, inducing the increase in viscosity.

On the other hand the increase in the calculated viscosity of liquid containing leucite can be explained by the physical structure of the liquid. The gradual increase in leucite concentration as a solid phase induces an increase in the effective viscosity of the liquid and viscosity increases infinitely when the concentration of leucite reaches the final 100%. The calculated viscosity curves can be divided in two distinct regions compared with the experimental data. In the first region, negligible deviation occurs between calculation and experiment but, on passing through $C_{\text{Leu}} \approx 0.5$, both curves show a steep deviation, because the leucite concentration is outside of the validity of Equation 6.

The viscosity of glass melts or, in other words, the experimental viscosity, η_l, in a state of non-equilibrium has the following relationship with the concentration, C_{Leu}, of leucite:

$$\log \eta_l = 2.18 C_{\text{Leu}} + 4.87 \text{ at } 1000\,^\circ\text{C}$$

$$\log \eta_l = 1.64 C_{\text{Leu}} + 3.84 \text{ at } 1200\,^\circ\text{C}$$

The calculated viscosity, η_{Leu}, in the state of equilibrium can be expressed as a modified form of equation 6:

$$\log \eta_{\text{Leu}} = 4.87 - 3\log(1 - C_{\text{Leu}}) \text{ at } 1000\,^\circ\text{C}$$

$$\log \eta_{\text{Leu}} = 3.84 - 3\log(1 - C_{\text{Leu}}) \text{ at } 1200\,^\circ\text{C}$$

where 4.87 is $\log \eta$ of the 26.6K_2O–5.06Al_2O_3–68.2SiO_2 liquid and 3.84 is $\log \eta$ of the 25K_2O–7Al_2O_3–68SiO_2 liquid.

Considering the change in glass structure due to variation in composition, the replacement of K_2O by Al_2O_3 in the mole base theoretically induces the elimination of four non-bridging oxygen atoms and the connection of the network. The linear relation between $\log \eta_l$ and C_{Leu} reflects this physicochemical change in liquid structure. In the case of the calculated viscosity, the relationship is parabolic. As indicated above, Equation 6 is valid for the concentration range $0 < C_{Leu} < 0.65$ in which the isolation and homogeneous distribution of the leucite phase in the liquid phase is assumed. Thus, the calculated viscosity reflects only a physical change, namely, the simple change in the solid-phase concentration in the liquid structure. In spite of this difference in physicochemical approach for the liquid structure, the calculated values agree with those of experiment as shown in the first region (less than $C_{Leu} \approx 0.5$) of Fig. 3. In previous work [7, 8] such a relationship for some binary glass-forming systems has already been observed and it was also found that the calculated viscosity agreed with those of experiments for a solid-phase concentrations of up to 0.5. A theoretical explanation for this correlation is not possible at the present time. It can be suggested only that some characteristics of the equilibrium state exist latently in the glass state. There is another example of this latent property. According to the work of Sakka and Mackenzie [16], the liquidus temperature T_l, in the equilibrium state and the transition temperature, T_g, in the glass state for many inorganic glass-forming systems show an almost simple empirical relation, the so-called "two-thirds rule" ($T_g/T_l \approx \frac{2}{3}$) irrespective of composition change. At the transition temperature, most properties of glass show a dramatic change and, thus, it plays the role of the liquidus temperature or melting temperature in crystalline materials. It can be postulated that the transition temperature is the latent point of the liquidus–melting temperature.

5. Summary

The viscosities of liquid in the equilibrium state of the ternary glass-forming system, K_2O–Al_2O_3–SiO_2, were calculated using the theory for suspensions and compared with those of the glass state. For the two composition ranges investigated, $26.6K_2O$–$5.06Al_2O_3$–$68.2SiO_2$ to $16.6K_2O$–$16.6Al_2O_3$–$66.6SiO_2$ (leucite) and $25K_2O$–$7Al_2O_3$–$68SiO_2$ to $16.6K_2O$–$16.6Al_2O_3$–$66.6SiO_2$ (leucite), the viscosity was calculated on the basis of the amounts of phases (liquid and leucite) at the state of equilibrium. The viscosities of the corresponding glass melts were measured using the rotating cylinder method at 1000 and 1200 °C. By comparing the results it was found that the calculated values agree with those of experiment within the leucite concentration range up to $C_{Leu} \approx 0.5$. The increasing experimental value with increasing leucite concentration was explained by physicochemical change of the glass structure. On the other hand the increase in the calculated value was discussed using the simple physical change in liquid structure. Although this agreement up to the concentration $C_{Leu} \approx 0.5$ cannot be clarified theoretically, it has been suggested that some characteristics of equilibrium state exist latently in the glass state using another example, the relationship between the liquidus temperature and the transition temperature.

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