

# VISCOSITY OF POTASSIUM BORO-SILICATE SYSTEM IN GLASSY AND MOLTEN STATES.

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## Abstract

The viscosity of potassium boro-silicate system was measured in both the glassy and molten states to know the network forming ability of boron trioxide in a silicate network. A new method, round ended tube penetration/rotation method, was developed for the continuous measurement of the viscosity from the glassy to molten state

The reliability of the new method was tested by the measurements covering the glassy to molten states of boron trioxide up to 1250K and compared with the previous studies. The agreement was reasonable with the previous data.

The viscosities of potassium meta- and di-silicates containing boron trioxide up to 60 and 50 mole %, respectively, and potassium tetra-silicate and potassium tetra-borate pseudo-binary system were measured. General scheme of the relationship between viscosity and composition are similar to that of the sodium boro-silicate system but the potassium boro-silicate system has much stronger tendency to crystallization than that of the sodium boro-silicate system. Consequently, the comparison of the viscosity between both systems could not be done precisely.

## 1. Introduction

It is well known as the borate anomaly<sup>1)</sup> that the viscosity of the alkali-borate melt decreases not monotonously with increasing alkaline oxide content but indicates a maximum around a certain composition. Main reason of this phenomenon is attributed to the change of coordination number of oxygen with boron atom from three to four. Does this nature of boron atom keep in another system; such as boro-silicate system where a silicate network is prevailing? From this point of view, the viscosity of sodium boro-silicate was measured in both the glassy and molten states<sup>2)</sup>. A small maximum of the viscosity was found around the  $\text{Na}_2\text{O} \cdot \text{SiO}_2$ -50mol%B<sub>2</sub>O<sub>3</sub> composition both in the glassy and molten states. However, it could not be observed such behavior in more acidic  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ -B<sub>2</sub>O<sub>3</sub> system where the viscosity decreased with increasing B<sub>2</sub>O<sub>3</sub> content. This may be shown the four fold oxygen-coordinating boron can not be contributed to the increase of the viscosity in the silicate system, except the basic composition where the three dimensional silicate network is not so prevailing.

To confirm this situation, similar measurement is attempted in the potassium boro-silicate system. A parallel plate creep/rotating viscometer<sup>3)</sup> was not applicable to this study, though it was successively applied to the sodium boro-silicate system in both the glassy and molten states<sup>4)</sup>. Since the some samples of potassium boro-silicate system were strongly deliquescent, the sound cylindrical sample, which is necessary for the parallel plate viscometer, could not be prepared. Thus, the new method, which does not need any shaping process of the sample, must had been developed.

Imaging a honey pot taken out from a refrigerator. At first, honey is enough hard and does not pierce a stick. But little while after, the stick will be pierced into honey and be able to rotate in the honey pot when the temperature reaches to room temperature. If this process can be described quantitatively, it may be applied to the viscosity measurement. According to this idea, our new viscometer was developed. The viscosities of boron trioxide and of the potassium boro-silicate systems were measured by this new method. In the following text, the principle of the method, the outline of the viscometer and its application to boron trioxide and the potassium boro-silicate systems are described.

## 2. Method of measurement

Two methods are combined to extend the measuring range of the viscosity from the glassy to molten states. A penetration method is applied to the glassy state measurement and a rotating method is used for the viscosity measurement of molten state.

### 2-1 Penetration method

The method is based on the work of Douglas et al.<sup>5)</sup> They proposed the following equation for a sphere penetration into an infinite medium having the viscosity  $\eta$ .

$$\eta = (3/32)(Mgt / (2r)^{1/2} l^{3/2}), \quad (1)$$

where, M is a weight applied to a penetrating sphere, l is penetrating depth during a time t, r is a radius of the sphere and g is the acceleration of gravity.

If the penetration rate,  $dl/dt$ , is observed, then the viscosity can be determined from eq.2;

$$\eta = (3/16)(Mg / (2rl)^{1/2}(dl / dt)). \quad (2)$$

In this study, a round ended tube was used instead of a sphere as shown in Fig.1. Since the sample is contained in a relatively small crucible, and then the condition as an infinite medium is never fulfilled. Thus, the correction for a counter flow of glass sample through an annular part between tubes is necessary during the penetration of the tube. For this purpose, a resistance caused by a flow in an annular tube is taken into account.

$$V = (\pi / 8\eta)(P / l)(b^4 - a^4 - (b^2 - a^2)^2 / \ln(b / a)) \quad (3)$$

where, V is a flow volume per unit time, P is a pressure, b and a are the inner radius of the outer tube and the outer radius of the inner tube, respectively.

If we assume the applied force, Mg, is a sum of the forces resulting from the penetration and the annular flow, we can derive the following equation using the fact that the penetrated volume of the tube is equal to V in eq.3.

$$\eta = (Mg / (dH/dt)) / (7.54247(a \cdot l)^{1/2}(H_0/H) + 8b^2 l / C), \quad (4)$$

$$C = (b^4 - a^4 - (b^2 - a^2)^2 / \ln(b / a)), \quad (4')$$

where,  $H_0$  and  $H$  are the sample height at the initial and at a time  $t$ , respectively. The factor  $(H_0/H)$  is introduced as a normalizing factor for a longitudinal deformation of the sample, under the assumption that the sample has enough height at the initial stage of the deformation for the application of eq.1.

## 2-2 Round ended tube rotation method

In the rotating cylinder method, the torque,  $T_q$ , exerted on the inner cylinder by the rotation of the outer cylinder, is expressed as

$$T_q = (2\pi\eta L\omega)(r_1^2 r_2^2 / (r_1^2 - r_2^2)) \quad (5)$$

where,  $L$  is an immersion length of the inner cylinder,  $\omega$  is an angular velocity of the rotating crucible and  $r_1$  and  $r_2$  are the radius of outer and inner cylinder, respectively.

This equation can be transformed for the present measurement, whose geometry is shown in Fig.1, as follows;

$$T_q = (2\pi\eta\omega)(G_1 + G_2 + G_3) \quad (6)$$

$$\left. \begin{aligned} G_1 &= L(r_1^2 r_2^2 / (r_1^2 - r_2^2)) \\ G_2 &= \int_{r_1-r_2}^{r_1} (b^2 r_2^2 / (b^2 - r_2^2)) dz \\ G_3 &= \int_0^{r_2} (b^2 a^2 / (b^2 - a^2)) dz \end{aligned} \right\} (6')$$

where,  $dz$  denotes a small division of the height.

Equation (6') can be solved analytically under a suitable assumption on the shape of the tube end, such as a hemisphere. In this study, however, a numerical calculation is taken for the evaluation of the values based on the actual shape of the tube end.

From eq.6, we can determine the viscosity of the molten sample by the measurement of the torque exerted on the inner tube by the crucible rotation. However, the touching of the tubes on their bottom will produce some additional quantities of the torque when the crucible rotates. Thus, the touching effect of two tubes was tested by the measurements using standard reference oils at room temperatures. Typical results are shown in Fig.2, for example. Measurements were carried out with the apparatus shown in Fig.3. Figure 2(a) shows the regression of the torque respect to the revolution speed. If we take the gradient of the torque respect to the revolution speed,  $N$ , we obtain the fairly well correlation between the oil viscosity and the viscosity calculated by eq.6, based on the observed value of  $dT_q / dN$ . This fact may be reflected that the kinetic friction between two tube ends is almost independent of the revolution speed. Thus, the viscosity can be determined by the round ended tube rotation method on the basis of the theoretically derived equation, if we use the regressed gradient of the torque respect to the revolution speed, instead of the individual value of the torque measured at any revolution speed.

### 3. Experiment

#### 3-1. Apparatus and its operation

Schematic diagram of the apparatus is shown in Fig.3. Main frame of the apparatus is the same as the previous one<sup>4)</sup>. However, the improvement had been done at several points as described as follows;

- (1) Whole the system connecting to the inner tube is suspended by string without any bearing. Thus, the better sensitivity of the torque measurement is achieved than that in the previous apparatus.
- (2) Coil and core of the displacement transducer are supported as a differential type for the reduction of the correction for the expansion of the penetration tube. The coil is supported by the reference rod from a rim of an alumina reaction tube in the furnace. The amount of the correction for the expansion of measuring system reduced to one tenth than that of the previous apparatus.
- (3) Argon stream is used as a protection atmosphere surrounding the sample.
- (4) Both reaction tube and furnace were made as separable. The penetrating tube and a supporting rod of a rotating case can be shorten by this way. This makes the alignment of the tube and the crucible to be easily adjusted.

The crucible containing the premelted sample is put into the rotating case as shown in Fig.1 and adjust the rotation to be smooth as possible (usually less than 0.5 mm in deflection). Penetration tube having diameter of 10 mm is placed on the center of the sample and loaded by a desired weight. Amount of the sample was taken about 3 to 4 cm<sup>3</sup>, which makes 25 to 35 mm sample height in the crucible. Weight applied to the penetration tube is taken as 30 to 100 g to get a proper deformation rate of the sample.

During the course of an ascending temperature process, expansion of the sample can be observed, at first. From a sudden change of the expansion, we can estimate the glass transition point. Just before the sample becomes to creep, we determine the average expansion coefficient of the sample and use it to the correction of the sample volume in the molten state. After the creep of the sample takes place, height and temperature of the sample are measured at each 30 s and the viscosity is calculated from the deformation rate. When the sample height is reduced to less than few mm, viscosity calculation is closed, because the deformation rate becomes erroneous due to the end effect of the tube.

After the melting of the sample, this is not so clear in most cases, the sample is subjected to rotate. Most of the cases, 5 levels of the revolution speed are selected to obtain the reliable regression of the torque gradient respect to the revolution speed. Near the melting point, viscosity changes tediously with the small change of temperatures. In this case, we measured the torque at only one or two levels of revolution speed to minimize the temperature effect on the viscosity. At moderate temperatures, 8 successive measurements are made to get an average value of the torque at each revolution level. All the measurements are carried out in an ascending temperature process and a few of them are carried out in a descending process, too.

#### 3-2. Samples

Guaranteed grade of boron trioxide reagent was melted in a platinum crucible at 1500K in air until bubbles could not be observed. Melt was poured onto a stainless steel

plate and crushed roughly and stored in a desiccator. The sample was weighed and premelted in the measuring crucible. Glassy sample thus prepared was served to the measurements.

The composition of the potassium boro-silicate samples is shown in Fig.4. It is selected to clarify the effect of boron oxide on the viscosities of silicate systems. Three series of the sample are chosen. Two series are characterized in a constant ratio of O/Si and in another series the amount of  $K_2O$  is kept constant. Samples were prepared from guaranteed grade of  $K_2CO_3$  and  $SiO_2$  and premelted  $B_2O_3$ . All chemicals were weighed individually and  $K_2CO_3$  was melted in a platinum crucible, at first.  $SiO_2$  was added bit by bit into  $K_2CO_3$  melt and when all amounts of silica were dissolved,  $B_2O_3$  was added in a course of lowering temperature. Melt was stirred well and poured into the measuring crucible. Finally, poured sample was melted again in the crucible to get a smooth surface of the sample.

#### 4. Results and discussion

##### 4-1. $B_2O_3$

The viscosity of  $B_2O_3$  measured in this study is shown in Fig.5 together with the previous works<sup>6~10,1,4)</sup>. All the data in molten state agree well except the work of Shartsis et al.<sup>1)</sup> whose values are little lower than the others. On the other hand, our present results in the glassy state gave significantly higher values than the other values. The curves marked by p and f denote the results calculated by eqs.(2) and (4), respectively. Since eq.(4) contains the correction for a glass flow at an annular part between crucible and penetration tube, the curve f is much plausible than the curve p. Never the less, discrepancy between curve f and the previous data can not be ignored, especially in the mid range of the glassy state measurement. Since this discrepancy clearly comes from the retardation of the deformation rate of the sample, every effort has been done to eliminate the resistance of the deformation. However, all the six measurements showed the same results in spite of many trials. In other words, the reproducibility was excellent.

After all, we calculated the effect of the meniscus of the sample on the penetration depth of the tube. Equations (2) and (3) are derived under the assumption that the sample has a flat surface. This is true if the diameter of the crucible is large enough. However, meniscus of the sample is inevitably produced in the course of melting and freezing processes of the sample preparation. Figure 6 illustrates the penetration of the tube into the sample through the meniscus. From the condition that hatched volumes bounded by the meniscus must be equal, we can calculate the relation between the penetration depth,  $l$  and the deformation of sample height,  $\Delta H$ . Details of the calculation are given in appendix. Several results of the calculation are shown in Fig.6(b) for several cases of the meniscus depth. The curve of 0.1mm meniscus depth is effectively same as that of the flat surface.

Measured depth is about 5 mm in average for the meniscus of  $B_2O_3$  samples. We correct the viscosity of  $B_2O_3$  based on this value and give the corrected viscosity in Fig.5 by the circles marked m. Agreement with the previous works is fairly good. This suggests the importance of the correction for the meniscus of the glass sample.

##### 4-2. $K_2O$ - $SiO$ - $B_2O_3$ systems

Iso-viscosity curves of  $\text{K}_2\text{O}\cdot\text{SO}_2\text{-B}_2\text{O}_3$ ,  $\text{K}_2\text{O}\cdot 2\text{SiO}_2\text{-B}_2\text{O}_3$  and  $\text{K}_2\text{O}\cdot 4\text{SiO}_2\text{-K}_2\text{O}\cdot 4\text{B}_2\text{O}_3$  systems are shown in Figs. 7, 8 and 9, respectively. Chain line in each figure shows the liquidus estimated from the viscosity measurement. Potassium meta-silicate–borate system shown in Fig. 7 has a strong tendency to crystallization and its viscosity in glassy range is little reliable. The viscosity of this system decreases with increasing  $\text{B}_2\text{O}_3$  content and makes a minimum around 20 mole % and increases again with increasing  $\text{B}_2\text{O}_3$  content. Considering the values of the atomic ratio,  $\text{O}/(\text{Si}+\text{B})$ , three fold oxygen-coordinating boron,  $\text{BO}_3^{-3}$ , will contribute to the viscosity as the increasing component in this system. On the contrary, Fig. 8 indicates the decreasing of the viscosity in a whole region of the system irrespective of  $\text{BO}_4^{-5}$  or  $\text{BO}_3^{-3}$  formation. This is also true in Fig. 9 in which  $\text{K}_2\text{O}$  content remains constant. These facts suggest the idea on the hierarchy of the viscosity in network forming melt as follows: (1) Most high viscosity comes from the three dimensional silicate network and (2) next arises from the two dimensional borate network and (3) lower viscosity results from the two dimensional network of silicate. The validity of this hierarchy of the viscosity is not proved yet but it is worthwhile to evaluate in further studies.

Comparison of the viscosity between potassium and sodium boro-silicate systems is given schematically in Fig. 10. Liquidus lines of these systems are shown in the middle of Fig. 10. Liquidus lines of  $\text{K}_2\text{O}$  system are not sure, because they were estimated from the viscosity measurement. General shape of the liquidus lines is mostly alike each other except the peak appeared in potassium di-silicate system. This sample has a strong tendency to crystallization but is not clear whether the sample is a compound or not.

General scheme of the viscosities in the di-silicate systems resembles each other. Serious difference between them arises from the crystallizing tendency in potassium system. In meta-silicate system, the comparison over the whole composition range is difficult due to the lack of the data of molten state in the sodium system and the crystallizing tendency of potassium system. Speaking boldly, the effect of the borate addition seems to be strong in the potassium system than in sodium system since the silicate structure is more distorted by the introduction of the larger anion of potassium. However, precise discussion on the difference between sodium and potassium boro-silicate systems is a problem in future.

## 5. Conclusion

- (1) A new viscometer based on the round ended tube penetration/rotation method was developed for the simple preparation of the measuring sample. The method consists of a combination of penetration and rotating cylinder methods and covers the wide viscosity range from glassy to molten state.
- (2) The penetration method used here requires the correction for the flow of glass and the meniscus shape of the sample glass.
- (3) Viscosity of the molten sample can be calculated absolutely from the regressed gradient of the torque respect to revolution speed, instead the individual values of torque and revolution speed.
- (4) Viscosity of boron trioxide was measured continuously from glassy to molten states of 1250K without the calibration by the standard reference materials. Measured values agreed well to those of the previous works.

- (5) Viscosities of potassium boro-silicate systems were measured and compared with those of sodium systems. General scheme of the effect of borate addition was similar in both systems. However, detail comparison could not be done due to the strong tendency to crystallization in potassium system.

## 6. References

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## Appendix

Referring Fig.6(a), we calculate the penetration depth,  $l$ , as a function of the sample height change,  $\Delta H$ , under the assumption that the meniscus can be approximated by spherical cap having a radius  $R_0$  and the tube end has a shape of hemisphere.

We can classify the penetration process as follows;

- 1)  $d < d_0$  and  $l < r_2$  : For very shallow penetration.

Since the volume penetrated through the meniscus is equal to the volume filled up the meniscus, we obtain the next equation:

$$\pi d^2(R_0 - d/3) = \pi l^2(r_2 - l/3)$$

where,  $R_0 = (r_1^2 + d_0^2) / 2d_0$  is the radius of the meniscus and  $l = d + \Delta H$  is the penetration depth. Solve this equation on  $d$ , we can get the relation between  $l$  and  $\Delta H$ .

- 2) For further penetration, we have two possibilities.

- 2a)  $d < d_0$  and  $l > r_2$  : For medium depth of meniscus.

The volume equation is ;

$$\pi d^2(R_0 - d/3) = (2/3)\pi r_2^3 + \pi r_2^2(d + \Delta H - r_2).$$

From this equation, we can obtain the relation between  $l$  and  $\Delta H$  as a third order equation of  $d$ .

- 2b)  $d > d_0$  and  $l < r_2$  : For shallow meniscus.

The volume equation is ;

$$\pi d_0^2(R_0 - d_0/3) + \pi r_1^2(d - d_0) = \pi(d + \Delta H)^2(r_2 - (d + \Delta H)/3).$$

From this equation, we can obtain  $d$  as a third order equation.

3)  $d > d_0$  and  $l > r_2$  : All round parts of the tube and meniscus are filled up.

The volume equation is simply;

$$\pi d_0^2 (R_0 - d_0/3) + \pi r_1^2 (d - d_0) = (2/3)\pi r_2^3 + \pi r_2^2 (d + \Delta H - r_2).$$

From this equation, we can get the relation between  $l$  and  $\Delta H$ .

Examples of these calculations are shown in Fig.6(b).





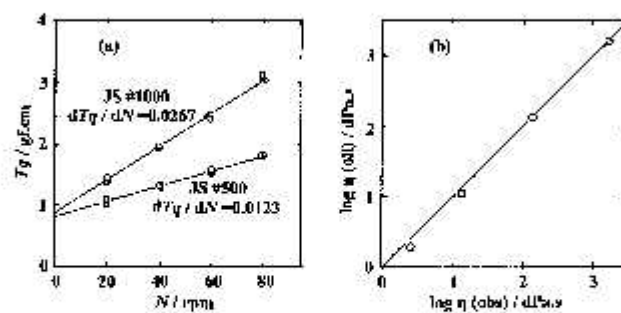


Fig. 2 : (a) Linear regression of the torque exerted on the inner tube with respect to the revolution speed of the rotary crucible. (b) Relation between the viscosity of standard reference oil and the calculated value from observed torque.

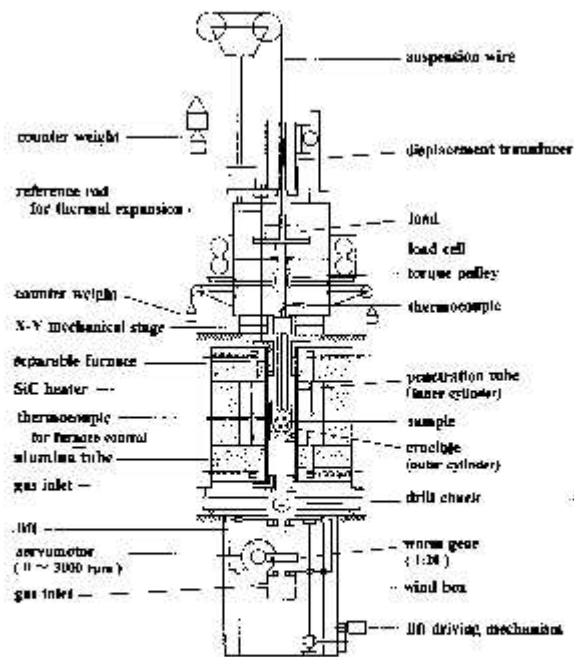


Fig. 3 Schematic diagram of the viscometer.

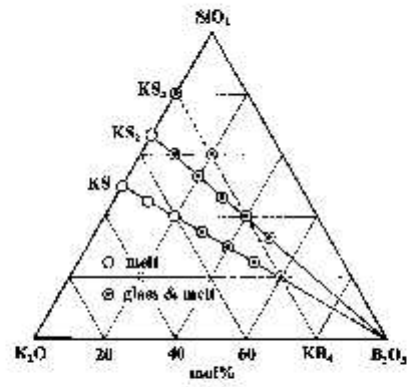


Fig. 4 Composition of the samples.  $\odot$ , measured in both glassy and molten states;  $\circ$ , measured in molten state.

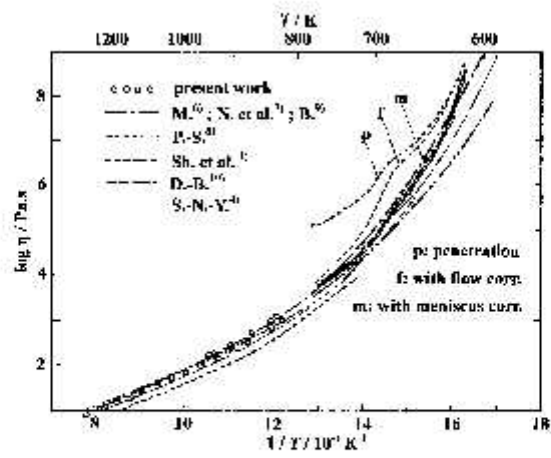


Fig. 5 Viscosity of  $B_2O_3$ . Averaged values of 4 heats for glassy range and 2 heats for molten state are shown.

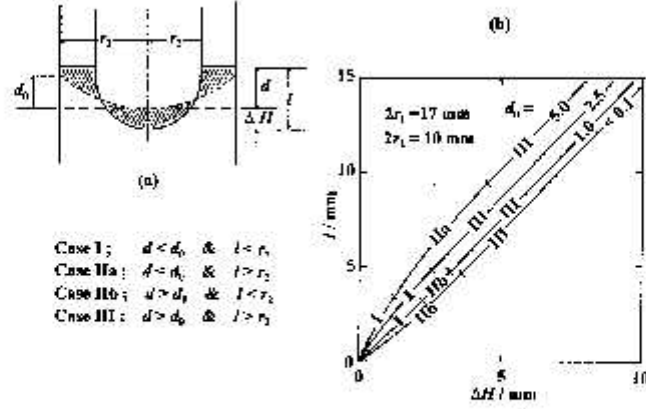


Fig. 6 (a) Effect of the thickness of the glass sample on the penetration depth of the inner tube. (b) Relation between the calculated penetration depth and the sample height under a typical measuring condition.

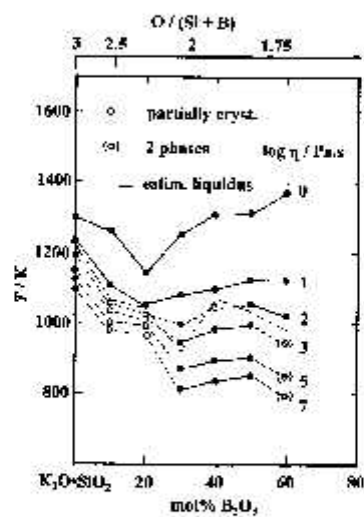


Fig. 7 Isoviscosity curves in the temperature vs. composition diagram for  $K_2O-SiO_2-B_2O_3$  system.

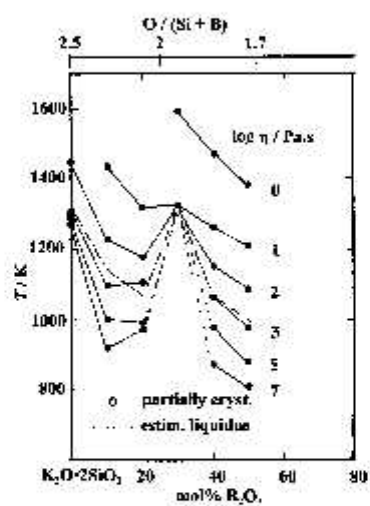


Fig. 8 Isoviscosity curves in the temperature vs. composition diagram for  $K_2O-2SiO_2-B_2O_3$  system.



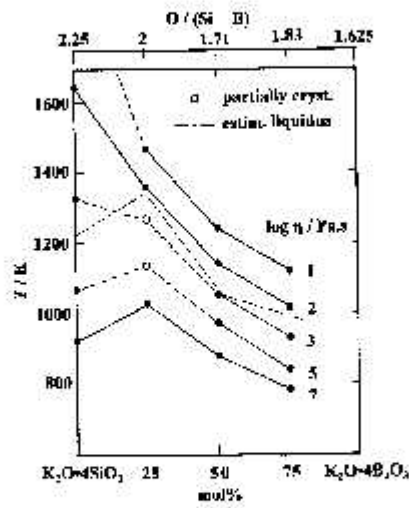


Fig. 9. Isoviscosity curves in the temperature vs. composition diagram for  $K_2O-4SiO_2-K_2O-4B_2O_3$  system.

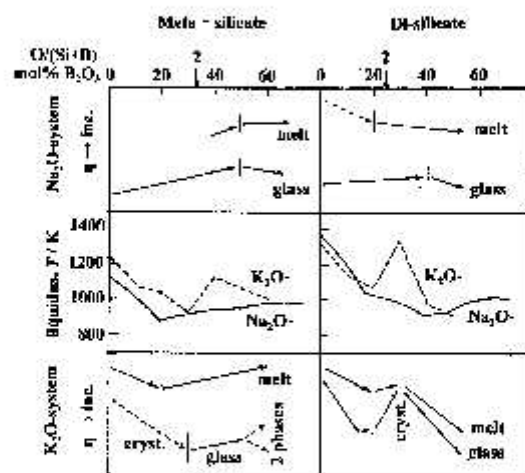


Fig.10 Comparison of the viscosity between K<sub>2</sub>O- and Na<sub>2</sub>O-SiO<sub>2</sub>-R<sub>2</sub>O<sub>3</sub> systems.