Surface tension of PbO-B$_2$O$_3$ and Bi$_2$O$_3$-B$_2$O$_3$ glass melts

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The surface tensions of xPbO-$(100 - x)$ B$_2$O$_3$ ($x = 30$–80 mol%) and xBi$_2$O$_3$-$(100 - x)$ B$_2$O$_3$ ($x = 0$–100 mol%) melts were measured using the ring method over the temperature range 973 to 1373 K. The compositional and temperature dependences of surface tension were investigated. Addition of PbO and Bi$_2$O$_3$ to B$_2$O$_3$ increased the surface tensions of their respective PbO-B$_2$O$_3$ and Bi$_2$O$_3$-B$_2$O$_3$ melts. The surface tension showed a maximum at 60 mol% PbO in the PbO-B$_2$O$_3$ melts and at 70–80 mol% Bi$_2$O$_3$ in the Bi$_2$O$_3$-B$_2$O$_3$ melts. The temperature coefficient of surface tension was examined on the basis of its relationship to the structure, and it was suggested that the temperature coefficient of surface tension decreases with an increasing content of four-coordinated boron.
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1. Introduction

Surface tension is an important property of glass as it is a crucial factor affecting the working conditions of glass production and its applications [1, 2]. For example, in the process of glass melting, the surface tension plays important roles in controlling the homogeneity of glass melt and bubble elimination from glass melt. In addition, in the process of glass powder sintering, surface tension is a key factor affecting the wettability and the penetration of glass into a substrate.

PbO-containing glasses are characterised by a broad glass forming region and low thermal properties. They have been used for optical glass and electronic material such as the sealing glass for hybrid IC (integrated circuit). However, the development of Pb-free glass has recently become necessary, in order to meet environmental demands resulting from concern over the toxicity of Pb [3]. Bi$_2$O$_3$-containing glasses have been mainly studied for use as optical device materials [4, 5]. They have attracted considerable attention as candidates for Pb-free glass, since they have low thermal properties that are comparable to those of Pb-containing glass [6]. Consequently, there is a need to measure and compare the fundamental properties of PbO- and Bi$_2$O$_3$-containing glass melts for the development of Pb-free glass and for the production of high quality glass. There are several reports on the surface tensions of PbO-containing glass melts [7–9]. In contrast, there are few reports on the surface tension of Bi$_2$O$_3$-containing glass melts. In this respect, it is very important to measure the surface tensions of PbO-B$_2$O$_3$ and Bi$_2$O$_3$-B$_2$O$_3$ glass melts.

The objectives of this study were (i) to measure the surface tension of PbO- and Bi$_2$O$_3$-B$_2$O$_3$ melts, (ii) to investigate the compositional and temperature dependences of surface tension.

2. Experimental
2.1. Preparation of sample for measurement

Both the PbO and Bi$_2$O$_3$ contents for the compositions of the PbO- and Bi$_2$O$_3$-B$_2$O$_3$ systems were selected to range from 30 to 80 mol% on the basis of the glass forming region [6], and the Bi$_2$O$_3$ content was expanded to cover the whole compositional range (0–100 mol%) in order to obtain a better understanding of the melt. The batches of samples were prepared by mixing the appropriate amounts of reagent grade PbO, Bi$_2$O$_3$, and B$_2$O$_3$. Each batch was melted in Pt crucibles for 30 min in air at 1073–1473 K, and was then poured into a graphite mold. These samples obtained by melting and cooling

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were then pulverised using an alumina mortar and pestle until the particle size was reduced to below 5 mm. This procedure was repeated until there was 0.3–0.4 kg of each sample.

2.2. Measurement method

The surface tension (γ) was measured using the ring method [10, 11]. The principle of the ring method is to measure the maximum force (W_{max}) necessary to detach a circular ring from the surface of a melt. The surface tension was determined using the equation

$$\gamma = \frac{W_{max}}{4\pi R_0(1 + \alpha \Delta T)} \frac{g}{} S \qquad (1)$$

where g is the acceleration due to gravity (9.8 m/s^2), R_0 is the radius of the ring at room temperature, α is the thermal expansion coefficient of the ring, and ΔT is the temperature difference between the measuring temperature and room temperature. The obtained values were corrected using the empirical correction factor (S), known as Harkins and Jordan's correction factor [10], to increase the accuracy. S is an empirical correction factor that is a function of W_{max}/ρ (ρ is the density of melt). In this work, an empirical relationship between S and W_{max}/ρ was determined by measuring the surface tension and density of several molten salts (PbCl$_2$, KNO$_3$, NaCl, KCl, NaNO$_3$, K$_2$SO$_4$, and Na$_2$SO$_4$). This relationship was

$$S = 0.772 + 0.255 \times 10^6 \frac{W_{max}}{\rho} \qquad (2)$$

Details of the apparatus and the measurement procedure have been given elsewhere [11]. A Pt/Pt-13 wt% Rh thermocouple was used to control the temperature of the furnace to within ±1 K, and an additional thermocouple that was almost in contact with the crucible (Pt-10 wt% Rh, 70 mm in diameter and 35 mm in height) containing the melt was used to measure the temperature of the melt. The sample for measurement was remelted and then maintained at the highest measurement temperature for 1 h before starting the measurements. In this work, the highest temperature was fixed at 1373 K to prevent the vaporization of PbO, Bi$_2$O$_3$, and B$_2$O$_3$. The temperature range was from 250 to 400 K. The measurements were made at 50 K intervals during the cooling cycle, until the melt was either too viscous to yield reliable values or until crystallization occurred. The maximum force exerted on the ring (made of Pt-10 wt% Rh-0.16 wt% ZrO$_2$ alloy wire, with ring radius 7.165 mm and wire diameter 0.5 mm) was measured using a strain gauge. Ten measurements were taken for each point by repeating the contact and detachment of the ring from the same melt.

After the measurements, the compositions of the samples were determined using X-ray fluorescence. The differences between analyzed and batch compositions were within about 1.0 mol% PbO or Bi$_2$O$_3$. The overall error of this method was estimated to be within ±1.0% of the surface tension value. The standard de- viation of the mean (*SDOM*) for the ten repeated load measurements had a maximum of 1.42 and this value of *SDOM* corresponds to ±0.34% of the surface tension values. The errors due to the density value in the correction factor (S), the thermocouple and the strain gauge were estimated to be ±0.61%, ±0.01% and ±0.01%, respectively.

3. Results and discussion
3.1. Surface tension data
3.1.1. PbO-B$_2$O$_3$ melts

The surface tensions of the xPbO-$(100 - x)$ B$_2$O$_3$ binary system (x = 30–80 mol%) are shown as a function of temperature in Fig. 1, and are summarised in Table I. The surface tension increased with increasing PbO content, showing a maximum at 60 mol% PbO, and then decreased on further addition of PbO. The pure B$_2$O$_3$ showed a low surface tension value, and for this fact, the explanation by Scholze [12] is generally accepted. It states that the low surface tension of B$_2$O$_3$ is attributed to the parallel arrangement of the three-oxygen-coordinated BO$_3$ (triangular planar structure) at the surface of the melt, which leads to a weak bonding force perpendicular to the surface.

The surface tensions of pure B$_2$O$_3$ and PbO melts [8] increased with increasing temperature. That is, the temperature coefficient of surface tension (dγ/dT) has a positive sign. Addition of PbO to B$_2$O$_3$ caused the sign of dγ/dT to change from positive to negative. The surface tensions of melts with 30 and 40 mol% PbO showed a bending with increasing temperature. For the dγ/dT of pure B$_2$O$_3$ melt, Scholze [12] explained that the positive dγ/dT is attributed to the disruption of the orientation of BO$_3$ groups at the surface by the increasing temperature; and that the low surface tension of
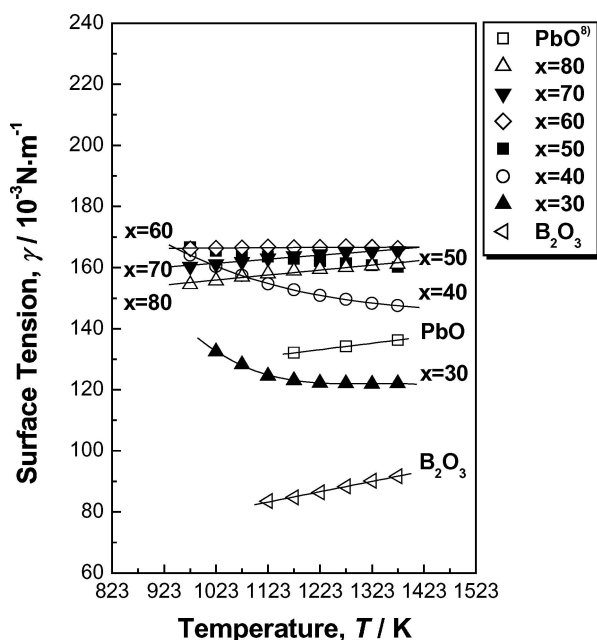

Figure 1 Surface tension of xPbO-$(100 - x)$ B$_2$O$_3$ melts as a function of temperature. The symbol x gives the PbO content in each composition. The straight line was fitted to data using the least squares method. The PbO data was from the report by Ito *et al.* [8].

TABLE I Properties of PbO-B$_2$O$_3$ melts

PbO content (mol%)	Surface tension value (10^{-3} Nm^{-1}) at each temperature (K)									Temp. Coefficient[a], dγ/dT/ 10^{-3}/Nm^{-1}/K^{-1}	Volume expansion coeff.[b] /10^{-6} K^{-1}
	973	1023	1073	1123	1173	1223	1273	1323	1373		
30	–	132.5	128.2	124.6	123.1	122.3	122.1	121.9	122.1	0.0163	248.3
40	164.1	160.4	157.4	154.7	152.8	150.9	149.6	148.3	147.6	0.0132	228.8
50	166.6	165.4	164.1	163.6	162.8	162.1	161.4	160.8	160.2	0.0008	200.5
60	166.2	166.4	166.5	166.8	166.6	166.7	166.9	166.7	166.4	−0.0154	140.4
70	160.4	161.3	162.0	163.1	163.8	164.5	165.1	165.2	165.5	−0.0249	126.9
80	154.5	155.7	157.0	158.0	158.9	159.5	160.1	160.6	161.1	0.0017	106.8

[a]The temperature at which the coefficient of surface tension was calculated is 1273 K.
[b]The range of temperature from which the volume expansion coefficient was calculated is 1123 to 1273 K.

TABLE II Properties of Bi$_2$O$_3$-B$_2$O$_3$ melts

Bi$_2$O$_3$ content (mol%)	Surface tension value (10^{-3} Nm^{-1}) at each temperature (K)									Temp. Coefficient[a], dγ/dT/ 10^{-3}/Nm^{-1}/K^{-1}	Volume expansion coeff.[b] /10^{-6} K^{-1}
	973	1023	1073	1123	1173	1223	1273	1323	1373		
0	–	–	–	83.5	84.8	86.4	88.3	90.2	91.7	0.0336	107.7
10	–	78.9	80.3	82.6	84.2	86.1	88.1	90.0	91.3	0.0367	117.8
20	–	77.7	78.6	81.7	84.2	86.2	87.9	89.3	90.3	0.0386	225.1
30	–	142.4	141.0	140.4	139.0	138.4	138.8	139.4	140.2	0.0046	208.3
40	–	190.0	186.6	183.8	181.5	179.8	177.6	175.4	173.3	−0.0460	163.8
50	214.8	213.0	211.4	209.6	208.2	206.9	205.5	203.7	200.9	−0.0326	160.3
60	221.0	220.6	220.0	220.1	219.6	218.4	217.5	215.2	212.3	−0.0193	150.0
70	227.4	227.8	227.9	227.6	227.1	226.2	224.6	222.8	219.6	−0.0180	127.5
80	–	227.1	227.0	226.6	226.1	225.6	225.4	224.2	223.3	−0.0107	130.8
90	–	223.6	223.3	222.4	221.9	221.2	220.5	219.2	218.4	−0.0152	118.0
100	–	–	–	217.1	216.1	215.6	214.8	213.1	211.7	−0.0207	113.0

[a]The temperature at which the coefficient of surface tension was calculated is 1273 K.
[b]The range of temnerature from which the volume exnansion coefficient was calculated is 1123 to 1273 K.

pure B$_2$O$_3$ melt at the lower temperature resulted from the orientation of BO$_3$ groups at the surface. For the dγ/dT of pure PbO melt, Ito *et al.* [8] reported that the positive dγ/dT can be attributed to the breakdown of its network-like structure by the increased temperature. The relationship between dγ/dT and PbO content will be discussed in the later section on the temperature coefficient of surface tension.

3.1.2. Bi$_2$O$_3$-B$_2$O$_3$ melts

The surface tensions of the x Bi$_2$O$_3$-(100 − x) B$_2$O$_3$ binary system ($x = 0$–100 mol%) are shown as a function of temperature in Fig. 2, and are summarised in Table II. The surface tension stayed constant with increasing Bi$_2$O$_3$ content up to 20 mol% Bi$_2$O$_3$, and then increased sharply beyond this region, up to 70–80 mol% Bi$_2$O$_3$. It then decreased again on further addition of Bi$_2$O$_3$. The dγ/dT of Bi$_2$O$_3$ had a negative sign (the general tendency of normal liquids) and the addition of Bi$_2$O$_3$ to B$_2$O$_3$ caused the sign of dγ/dT to change from positive to negative.

The surface tensions in the range 0 to 20 mol% Bi$_2$O$_3$ have almost the same values as that of pure B$_2$O$_3$, and this can be explained by the two-liquid region in the phase equilibrium diagram of the Bi$_2$O$_3$-B$_2$O$_3$ binary system [13] shown in Fig. 3. The range over which the surface tension is constant in Fig. 2 is in accord with that of the two-liquid region in Fig. 3. From this, it can
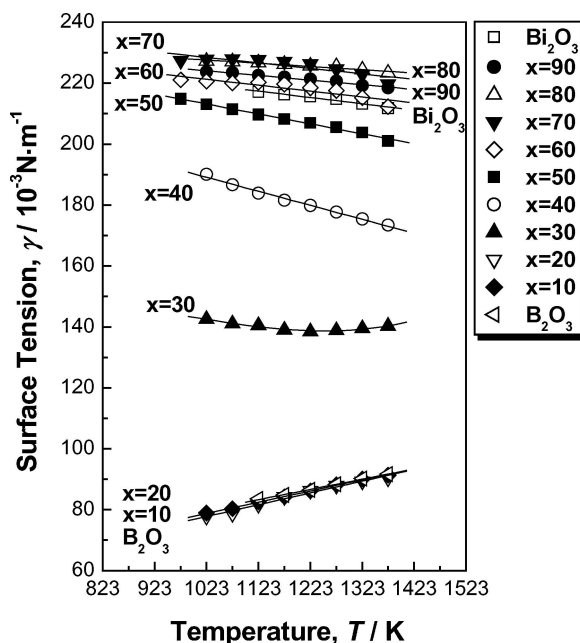

Figure 2 Surface tension of xBi$_2$O$_3$-(100 − x) B$_2$O$_3$ melts as a function of temperature. The symbol x gives the Bi$_2$O$_3$ content in each composition. The straight line was fitted to data using the least squares method.

be expected that the upper layer of melt in the two-liquid region consists of almost pure B$_2$O$_3$ melt. The behaviour of the surface tension in the two-liquid region can be explained by Gibbs' adsorption rule [14, 15]. According to this rule [14, 15], the component with
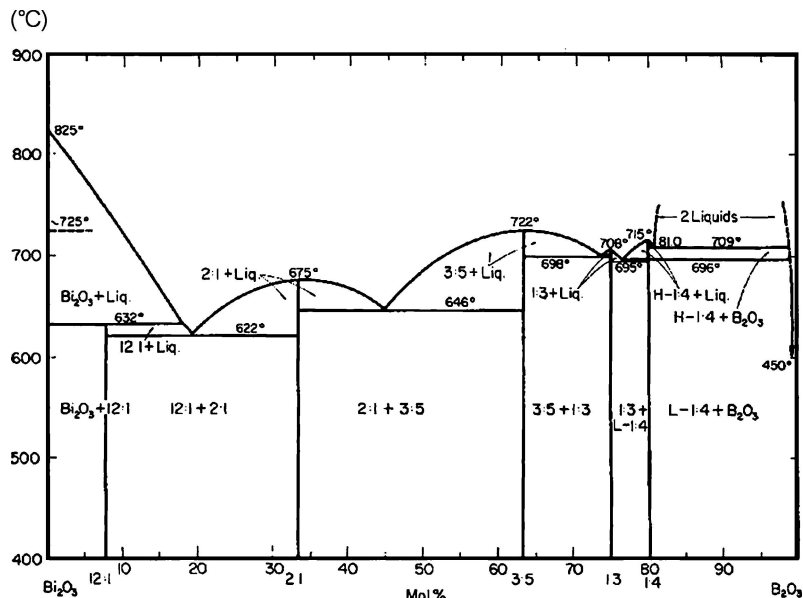
Figure 3 Phase equilibrium diagram [13] for the Bi_2O_3-B_2O_3 system.

lower surface tension will concentrate at the surface of a melt in order to reduce the surface tension of the system, and the component with higher surface tension will concentrate in the inner part of the melt. On the basis of Gibbs' adsorption rule [14, 15], it would be expected that the surface layer of the melt in the two-liquid region consists almost entirely of B_2O_3 melt, due to the large difference between the surface tensions of pure B_2O_3 and Bi_2O_3 melts. Besides the surface tension difference between pure Bi_2O_3 and B_2O_3 melts, the large density difference between the two single components may account for the behavior of the surface tension in the two-liquid region of the Bi_2O_3-B_2O system. Therefore, despite the increasing content of Bi_2O_3, which has a higher surface tension than B_2O_3, the surface tension stays almost constant in the two-liquid region.

3.1.3. Surface tension comparison

In order to identify the effects of PbO and Bi_2O_3 on the surface tensions of their borate melts, the surface tensions of PbO- and Bi_2O_3-B_2O_3 melts at 1273 K were compared with those of R_2O-B_2O_3 (alkali borates) [16] melts, as shown in Fig. 4. The existence of the two-liquid regions in the PbO-B_2O_3 melts (up to 25 mol%) [17] and the Bi_2O_3-B_2O_3 melts (up to 20 mol%) makes it difficult to compare their surface tensions with those of the R_2O-B_2O_3 melts. However, if the surface tensions of the PbO-B_2O_3 melts are compared with those of the Bi_2O_3-B_2O_3 melts, it is seen that Bi_2O_3 has a larger surface tension contribution to its system than PbO does. For R_2O-B_2O_3 systems, Shartsis *et al.* [16] reported that in the high alkali region (above 30 mol% R_2O), the order of the surface tension contribution is the same as that of its ionic potential (z/r, z: valence and r: ionic radius), that is, Li^+ (1.35) > Na^+ (0.98) > K^+ (0.66) as shown in Table III [18]. Based on the above report, the larger surface tension contribution of Bi_2O_3 in comparison to that of PbO can be explained
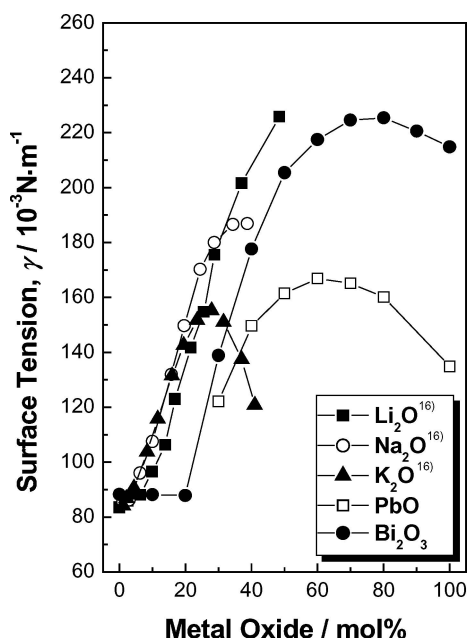

Figure 4 Comparison of surface tensions with those of R_2O-B_2O_3 melts [16] at 1273 K.

by the larger ionic potential of Bi^{3+} (2.94) than of Pb^{2+} (1.69).

3.2. Temperature coefficient of surface tension (dγ/dT)

The dγ/dT values of PbO- and Bi_2O_3-B_2O_3 melts at 1273 K are shown as a function of metal oxide content (mol%) in Fig. 5. In the PbO-B_2O_3 melts, the dγ/dT decreased with increasing PbO content up to 40 mol% PbO and then increased on further addition of PbO. In the Bi_2O_3-B_2O_3 melts, dγ/dT in the two-liquid region had almost the same values as that of pure B_2O_3 melt. Beyond the two-liquid region, dγ/dT decreased with increasing Bi_2O_3 content up to 40 mol% Bi_2O_3, and then increased on further addition of Bi_2O_3. In both

TABLE III Ionic potential of each cation

Cation	Valence z	Ionic radius[a] $r/\text{Å}$	Ionic potential $(z/r)/\text{Å}^{-1}$
K	1	1.51	0.66
Na	1	1.02	0.98
Li	1	0.74	1.35
Pb	2	1.18	1.69
Bi	3	1.02	2.94

[a]The radius of each cation is reffered from the report by Shannon *et al.* [18].
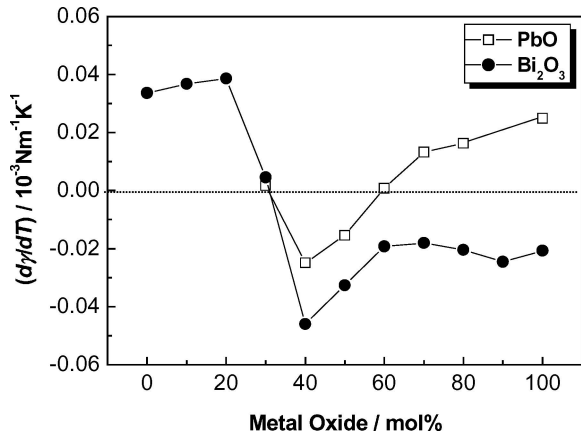
Figure 5 Temperature coefficient of surface tension in PbO-B_2O_3 and Bi_2O_3-B_2O_3 melts at 1273 K.

systems, $d\gamma/dT$ goes through a minimum at 40 mol% of PbO or Bi_2O_3, and the sign changes from positive to negative. A positive $d\gamma/dT$ in melt has been reported by King [19] for the silicate melts, and he proposed that the change in $d\gamma/dT$ is related to the change in the melt structure resulting from the increasing temperature. Thus, in this study, the change in the coordination number (C. N.) of boron was considered for each PbO-B_2O_3 and Bi_2O_3-B_2O_3 system. However, since there is no report on the C. N. of boron in PbO-B_2O_3 and Bi_2O_3-B_2O_3 melts, a report for a glass system at room temperature [20] was referred to. This consideration is based on the assumption that the basic structural unit of melt at high temperature is analogous to that of glass at room temperature [21]. The BO_4 fractions (the ratio of four-coordinated boron to total boron) in PbO- and Bi_2O_3-B_2O_3 glass systems are shown in Fig. 6. A comparison of $d\gamma/dT$ and the BO_4 fraction in PbO- and Bi_2O_3-B_2O_3 systems shows that the BO_4 fraction goes through a maximum near 50 mol% PbO and 30 mol% Bi_2O_3 (Fig. 6), and the $d\gamma/dT$ goes through a minimum near 40 mol% PbO and Bi_2O_3 (Fig. 5). The results obtained in the above comparison suggest that the $d\gamma/dT$ decreases with an increasing BO_4 fraction. One possible explanation for this is that the complex BO_4 unit (with high surface tension) breaks down to the simple BO_3 unit (with low surface tension) with increasing temperature. Therefore, as the content of the BO_4 unit increases, the extent of the decrease in surface tension becomes larger, that is, $d\gamma/dT$ becomes more negative.
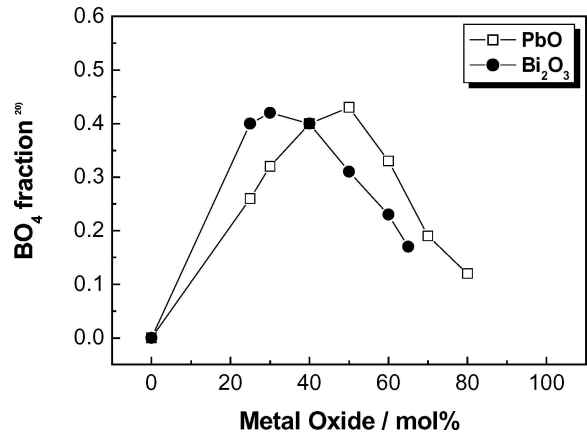

Figure 6 BO_4 fraction in PbO-B_2O_3 and Bi_2O_3-B_2O_3 glass systems at room temperature [20].

4. Conclusions

The following conclusions can be drawn from this work:

Surface tension data of PbO- and Bi_2O_3-B_2O_3 melts

(1) In the PbO-B_2O_3 melts, the surface tension increased with increasing PbO content, exhibited a maximum at 60 mol% PbO, and then decreased on further addition of PbO.

(2) In the Bi_2O_3-B_2O_3 melts, the surface tensions were constant up to 20 mol% Bi_2O_3. Beyond this region, the surface tension increased sharply, up to 70–80 mol% Bi_2O_3, and it then decreased on further addition of Bi_2O_3.

(3) In the Bi_2O_3-B_2O_3 melts, for the constant surface tension value in the two-liquid region, it was suggested that the upper layer of melt in the two-liquid region consists of almost pure B_2O_3 melt.

(4) The surface tension contribution of Bi_2O_3 to its borate system was larger than that of PbO to its borate system, and this tendency may be attributed to the larger ionic potential of Bi^{3+} (2.94) than of Pb^{2+} (1.69).

Temperature coefficient of surface tension ($d\gamma/dT$)

(1) In the PbO-B_2O_3 melts, $d\gamma/dT$ decreased with increasing PbO content up to 40 mol% PbO, and then increased on further addition of PbO.

(2) In the Bi_2O_3-B_2O_3 melts, the $d\gamma/dT$ in the two-liquid region had almost the same values as that of pure B_2O_3 melt. Beyond the two-liquid region, the $d\gamma/dT$ decreased with increasing Bi_2O_3 content up to 40 mol% Bi_2O_3, and then increased on further addition of Bi_2O_3.

(3) By considering the relationship between $d\gamma/dT$ and the BO_4 fraction in PbO- and Bi_2O_3-B_2O_3 systems, it was suggested that $d\gamma/dT$ decreases with an increasing BO_4 fraction.

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