

Surface Tension of Compositions in the Systems PbO-B₂O₃ and PbO-SiO₂

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The surface tension of a series of compositions ranging from 0 to 100 percent of PbO in the system PbO-B₂O₃ and of compositions ranging from 0 to 35 percent of SiO₂ in the system PbO-SiO₂ was measured by a modification of the anchor ring method. The volatility and changes in composition of members of each system upon heating were found to be related to the surface tension and its change with composition. Some correlation between the temperature coefficient of surface tension and expansivity was noted.

I. Introduction

Commercial glasses in general are quite complex as they are formed from several oxides. The effect of varying the percentage of any one of these oxides relative to the percentage of the others is quite complicated. By systematically studying glasses formed from simpler systems of oxides, simpler relations between changes in composition and their effect on the properties of the glasses can be expected and, from such results, we can hope to reach a better understanding of the condition of matter called glass.

The oxides PbO, B₂O₃, and SiO₂ are of such great importance in the manufacture of many glasses, glazes, and enamels, that studies of systems of these components are of real interest in several fields of ceramics. For this reason, this study was made on the two-component systems, PbO-B₂O₃ and PbO-SiO₂. The study consisted of measuring the surface tensions of melts at different temperatures and with different compositions. Some tests were also made on volatilization and expansion.

II. Preparation of Melts and Methods of Test

The compositions investigated were prepared by melting, in platinum crucibles, the requisite amounts of H₃BO₃, PbO, and SiO₂ of the purity used for optical glasses. The weight of the melts ranged between 300 and 500 g. They were stirred with a platinum rod and, when they seemed

homogeneous, were poured into iron molds. About half of the PbO-B₂O₃ glasses were analyzed by a triple evaporation with HF and H₂SO₄ for PbO both before and after the surface tension determinations. It was found that if the time for making the surface tension determination was kept relatively short, say 3 or 4 hours, the change in composition was negligible. As the time seldom exceeded 4 hours, the remaining compositions were not reanalyzed after test.

The method [1]¹ of measuring surface tension was that of finding the maximum pull exerted on a small thin-walled platinum cylinder when its lower edge was in contact with the molten glass. In this method, a correction factor is necessary because of the finite thickness of the walls of the platinum cylinder.

The following equation was deduced by Verschaffelt [2] for this case:

$$\sigma = \frac{F}{4\pi R} \left[1 - \left(2.8284 + 0.6095 \sqrt{\frac{h}{R}} \right) \frac{\delta}{\sqrt{hR}} + \left(3 + 2.585 \sqrt{\frac{h}{R}} + 0.371 \frac{h}{R} \right) \frac{\delta^2}{hR} \right], \quad (1)$$

where

σ = surface tension in dynes/cm

$h = F/\pi R^2 \rho g = W_{\max}/\pi R^2 \rho$

F = maximum force exerted on the cylinder = gW_{\max}

2δ = thickness of cylinder

ρ = density of glass

¹ Figures in brackets indicate the literature references at the end of this paper.

R = mean radius of the cylinder

W_{\max} = maximum pull (in grams) exerted on the cylinder.

The correction factor V is the expression within the brackets. To simplify the cumbersome calculations involved, the following expansion of V was made. Thus

$$V = 1 - \frac{2.8284\delta}{\sqrt{hR}} = \frac{0.6095\delta}{R} + \frac{3\delta^2}{hR} + \frac{2.585\delta^2}{R\sqrt{hR}} + \frac{0.371\delta^2}{R^2} \quad (2)$$

For a given size ring, R , δ , and π are known constants, and V , containing in addition to these constants terms $1/h$ and $1/\sqrt{h}$, is a quadratic in $1/\sqrt{h}$. As $1/\sqrt{h}$ is equal to known constants times $(\rho/W_{\max})^{1/2}$, V is a quadratic in $(\rho/W_{\max})^{1/2}$.

A series of ρ/W_{\max} values was selected and the corresponding V 's were calculated. Figure 1 shows the curve obtained using $R = 1.26$ cm and $\delta = 0.0076$ cm. The required V can be read directly from the curve when ρ and W_{\max} are known. The surface

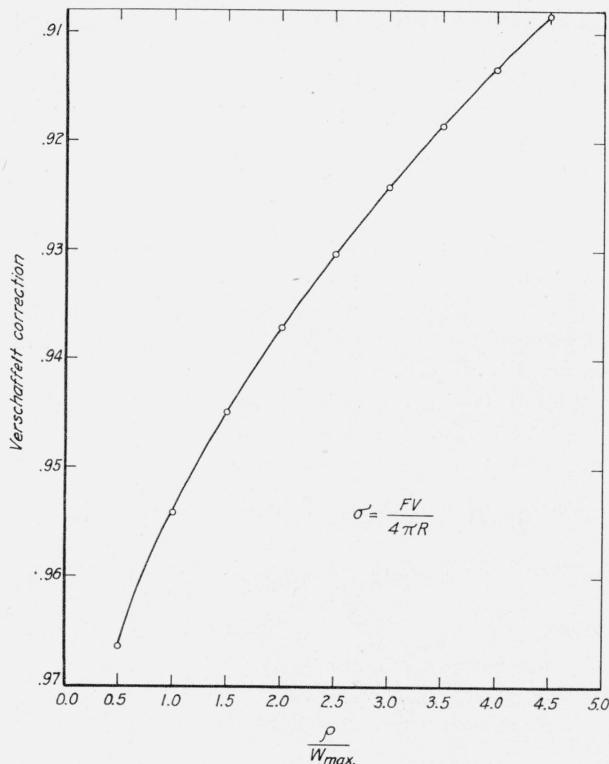


FIGURE 1. Verschaefelt correction versus ρ/W_{\max} .

These corrections were computed for a cylinder of mean radius 1.26 cm and of wall thickness 0.0162 cm. Correction V is used in the surface tension equation $\sigma = FV/4\pi R$.

tension can now be computed from the relation $\sigma = FV/4\pi R$.

It was considered sufficiently accurate to calculate a V factor for each glass at one temperature only, usually $1,000^\circ$ C, and to apply it to the proper $F/4\pi R$ value. The value of $F(1-V)/4\pi R$ was then subtracted from each of the $F/4\pi R$ values obtained at other temperatures.

The densities of the $\text{PbO-B}_2\text{O}_3$ glasses at room temperature were computed from the formula [3]

$$D = \frac{(\text{PbO})^2}{1,600} + 2,$$

where

D = density

PbO = weight percentage of PbO in the glass.

These densities were corrected to the desired temperature by use of available expansion data [3]. Above the interferometer softening point, the expansivity was assumed to be three times that at lower temperatures. The densities, expansivities, and interferometric softening points of some PbO-SiO_2 glasses are available in the literature [4, 5, 6].

III. Results and Discussion

1. The System $\text{PbO-B}_2\text{O}_3$

(a) Phase Equilibrium Relations

Figure 2 shows the phase equilibrium diagram [3] of the system $\text{PbO-B}_2\text{O}_3$. The broad features that may be noted are 1, the two-liquid area extending from about 9 to 43 percent of PbO ; 2, the flat maximum at about 61 percent, the

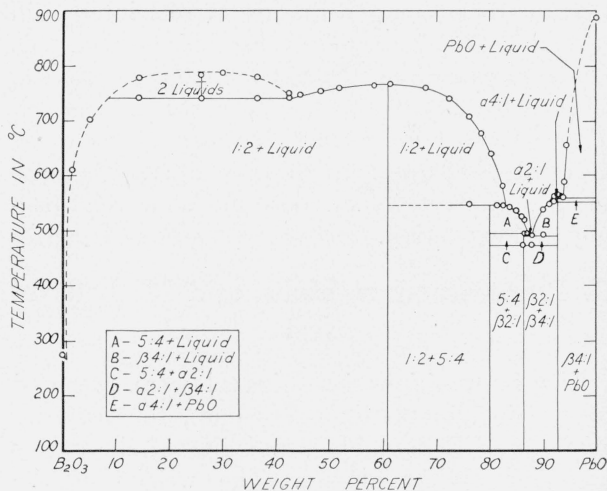


FIGURE 2. Phase equilibrium diagram of the system $\text{PbO-B}_2\text{O}_3$ [3].

lead diborate composition; 3, the steep slope of the liquidus curve at about 83 percent; and 4, the liquidus temperature being below 800° C for all compositions containing less than 95 percent of PbO.

(b) Surface Tension Data

Table 1 gives the values obtained for surface tension. Figure 3 shows a plot of the surface tension at 900° C versus percentage of PbO. In the composition region from 0 to about 40 percent

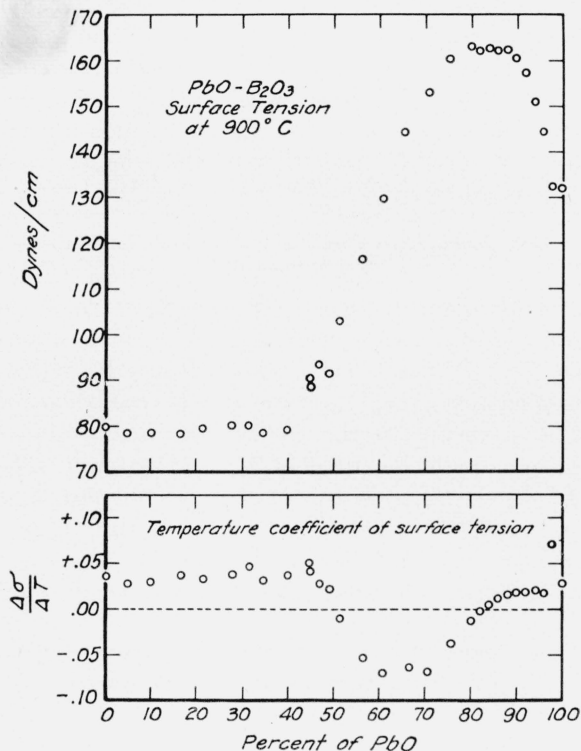


FIGURE 3. Surface tension and temperature coefficient of surface tension of the compositions in the system PbO-B₂O₃ at 900° C.

of PbO, the surface tension is almost constant. This is the region, at lower temperatures, of two immiscible liquids. However, 900° C is far above the critical solution temperature and only one liquid should exist. It is interesting to note that a large change in composition causes such a small change in surface tension. This condition may indicate that the composition of the surface layer is quite different from that of the interior of the liquid and, as the surface tension differs but little from that of pure B₂O₃, that this layer consists almost wholly of that oxide.

TABLE 1. Surface tension of compositions in the system PbO-B₂O₃

PbO	Number of tests	Surface tension (in dyn/cm) at—				
		600° C	700° C	800° C	900° C	1,000° C
Percent 0 (100 B ₂ O ₃)	2	-----	-----	75.9	79.5	83.0
4.9	1	-----	-----	75.5	78.2	-----
10.1	1	-----	-----	75.5	78.4	-----
16.6	2	-----	-----	74.5	78.2	82.1
21.6	2	-----	-----	76.1	79.4	-----
27.8	2	-----	-----	76.3	80.1	-----
31.4	2	-----	-----	75.5	80.1	-----
34.4	2	-----	-----	75.4	78.5	-----
39.9	2	-----	-----	75.4	79.1	-----
44.9	4	-----	-----	84.8	89.3	-----
47.0	1	-----	-----	90.6	93.3	-----
49.1	2	-----	-----	89.4	91.6	-----
51.3	2	-----	-----	104.0	103.0	-----
56.3	1	-----	-----	121.8	116.4	-----
60.9	1	-----	-----	136.8	129.8	-----
66.4	2	-----	159.8	150.6	144.2	-----
70.7	2	172.3	165.2	157.7	152.9	-----
75.5	2	-----	166.0	162.6	160.3	-----
80.0	2	167.6	165.7	164.3	163.0	-----
82.0	2	163.6	163.0	162.3	162.0	-----
84.1	2	161.6	162.2	162.4	162.8	-----
86.0	2	159.0	160.0	161.6	162.2	-----
88.1	2	156.8	159.1	160.6	162.2	-----
89.8	2	156.5	155.7	158.4	160.4	-----
91.1	1	151.5	152.7	155.4	157.4	-----
94.0	1	-----	-----	-----	151.0	153.1
96.0	1	-----	-----	-----	144.5	146.2
97.9	1	-----	-----	-----	132.3	139.3
100.0	1	-----	-----	-----	132.0	134.8

From about 40 to 80 percent of PbO, the surface tension rises rapidly to a flat maximum near 84 percent of PbO. Above this percentage it drops to the value for pure PbO.

The lower part of figure 3 shows a plot of the temperature coefficient of surface tension at 900° C versus composition. From 0 percent of PbO through the two-liquid region, the coefficient is positive and probably constant within the limits of experimental error. Increasing PbO beyond the two-liquid region causes the coefficient to drop and become negative. The maximum negative value occurs between 60 and 70 percent of PbO. Further increase in PbO causes the coefficient to increase to zero at about 82 percent, and from this percentage to pure PbO it is positive. The positive coefficients of pure PbO and B₂O₃ indicate that they are molecularly complex [7]. It is interesting to note that a region of negative temperature coefficients of surface tension exists in a sys-

tem whose end members have positive coefficients of surface tension.

(c) Some Effects of Heating Various Compositions

Table 2 presents data on the effect of heating various compositions. The first column gives the percentage of PbO calculated from the batch components. The second column gives the composition of the resulting glasses as found by chemical analysis. Note that the percentage of PbO found is higher than that in the first column until 80 percent is reached. Beyond this the agreement is fairly good. These results seemed interesting enough to warrant checking by prolonged heating of some of the glasses. The results are shown in the third column. Below 80 percent, heating resulted in an increase in the percentage of PbO, and above 80 percent a decrease resulted. These results can be interpreted in the light of the surface tension curve previously shown (fig. 3). From 50 to 80 percent of PbO, the surface tension increases as the percentage of PbO increases. According to the Gibbs adsorption isotherm, a substance that raises the surface tension is negatively adsorbed; its concentration is less in the surface than it is in the body of the liquid. If the intrinsic volatilities of the two end members are approximately equal, relatively less PbO than B_2O_3 will be lost and the liquid will become richer in PbO. The reverse behavior is to be expected

TABLE 2. Change in composition and volatility on heating PbO-B₂O₃ melts

PbO			Volatilization loss
Calculated from batch	Found	After heating	
%	%	%	mg ¹
50.0	51.33	52.91	2 44
55.0	² 56.23	-----	67
60.0	60.98	-----	2 60
65.0	66.50	67.01	2 50
70.0	70.70	-----	2 64
75.0	75.54	76.48	2 28
80.0	79.94	80.40	2 16
82.0	82.08	81.21	2 13
84.0	² 84.12	83.64	2 13
86.0	² 85.97	-----	-----
88.0	² 88.04	87.92	-----
90.0	² 89.84	-----	2 33
92.0	² 91.91	91.63	2 126

¹ Glass sufficient to yield 0.3 ml was placed in standard 25 ml platinum crucibles and heated at approximately 900° C for 16 hr.

² Average of 2 determinations.

in that region where increasing PbO causes the surface tension to fall. From 84 percent upward there is more PbO in the surface than in the body of the liquid. Therefore, relatively more PbO is lost and the liquid becomes poorer in that oxide.

The last column of table 2 is a record of some volatilization experiments. Although the results are somewhat scattered, there is evidence of minimum volatility at about 82 percent of PbO. If the surface tension is considered as arising from an internal attraction of the molecules, it is obvious why a composition having a high surface tension should also have a low volatility. However, caution must be exercised in applying these conclusions to other liquids, because the relation between the surface and the interior of such liquids may vary greatly from that of the compositions under consideration.

(d) Temperature Coefficient of Surface Tension and Expansivity

The temperature coefficient of surface tension is related to the mean coefficient of cubical expansion [7]. It has been deduced from theoretical considerations that the ratio of the coefficient of surface tension to the coefficient of cubical expansion should be equal to 2.33. For many substances, the ratio is approximately constant, and the average is about 2.3. Data on the volume expansion of lead borates at 900° C were not available and, therefore, the expansion coefficients

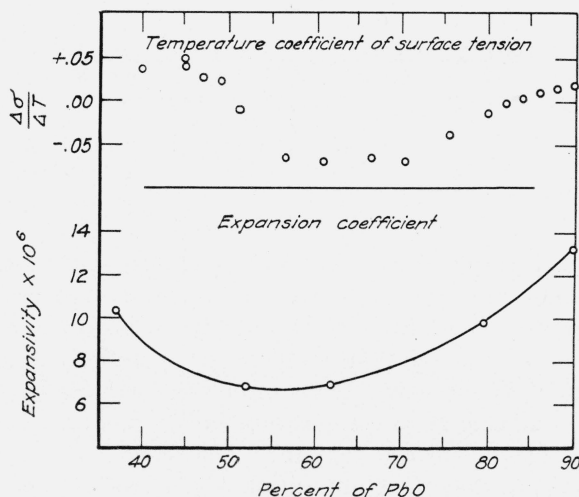


FIGURE 4. Comparison of the temperature coefficient of surface tension with expansivity [3].

Surface tensions of compositions in the system PbO-B₂O₃ at 900° C. Expansivity determined between room temperature and 250° C.

from room temperature to 250° C [3] have been plotted in figure 4. One sees that the two curves are similar.

2. The System PbO-SiO₂

(a) Surface Tension Data

Table 3 presents the data obtained on compositions ranging from 0 to 35 percent of SiO₂. Melts containing more than 35 percent of SiO₂ were difficult to obtain with the apparatus available. Figure 5 shows a plot of the surface tension at 1,000° C versus percentage of SiO₂. The upper

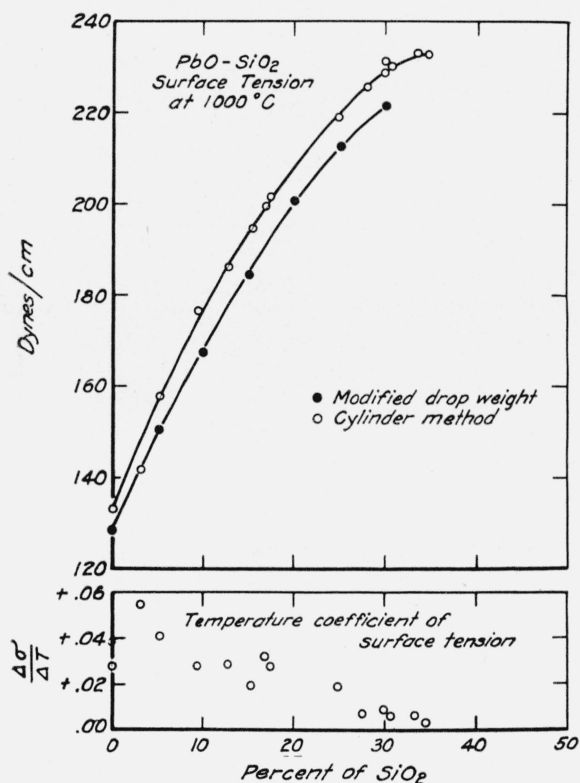


FIGURE 5. Surface tension and temperature coefficient of surface tension of compositions in the system PbO-SiO₂ at 1,000° C.

curve shows the data obtained by using the maximum-pull method, and the lower curve shows the data obtained by Appen [8], who used a modified drop-weight method. Although Appen's results are distinctly lower, the difference being ascribed to the different methods, both curves show a rapid increase in surface tension with increasing amounts of silica.

Surface Tension of PbO-B₂O₃ and PbO-SiO₂

TABLE 3. Surface tension of compositions in the system PbO-SiO₂

SiO ₂	Number of tests	Surface tension (in dynes/cm) at—							
		700° C	800° C	900° C	1,000° C	1,100° C	1,200° C	1,300° C	1,400° C
Percent									
3.20	1	-----	-----	134.4	142.0	145.4	154.2	158.0	161.3
5.17	1	-----	-----	147.8	157.7	152.1	158.0	164.1	162.7
9.36	1	-----	-----	173.6	176.5	179.2	182.0	183.3	-----
13.18	2	-----	-----	183.7	186.5	189.6	193.9	197.3	-----
15.30	2	-----	187.3	192.4	194.6	196.1	-----	-----	-----
16.76	3	-----	-----	-----	199.4	202.2	205.7	210.2	-----
17.50	2	193.2	196.8	199.1	201.6	204.4	208.2	209.4	-----
24.30	3	-----	-----	217.1	219.1	221.0	222.6	223.4	-----
27.12	3	-----	-----	224.5	225.6	225.7	226.5	227.2	-----
28.31	3	-----	-----	-----	227.8	228.4	227.5	228.5	-----
30.08	3	-----	-----	-----	231.3	232.0	232.7	230.5	229.1
30.16	2	-----	-----	-----	230.0	230.8	230.8	231.7	232.2
32.74	3	-----	-----	-----	233.7	235.0	235.6	234.5	235.1
34.91	2	-----	-----	-----	233.0	233.7	234.0	235.0	235.7

(b) Surface Tension and Volatility

Inasmuch as the surface tension rises as the percentage of silica is increased, it is to be expected that the volatility will decrease. This was found to be the case by Preston and Turner [9] in their important work on the volatility of various systems.

(c) Temperature Coefficient of Surface Tension and Expansivity

The lower part of figure 5 is a plot of the temperature coefficient of surface tension versus composition. The temperature coefficients are all positive, become smaller as the percentage of silica increases, and approach zero at about 35 percent of SiO₂. From the parallelism that was shown to exist between the expansion coefficient and the temperature coefficient of surface tension, the expansion coefficient should decrease with increasing silica. Expansion values were available only in the range from room temperature to a few hundred degrees. As the following data [6] show, these values decrease as the silica increases.

SiO ₂	Coefficient of expansion from 200° 300° C
Percent	
12	13.1 × 10 ⁻⁶
21	10.4
34	7.9

IV. Summary

The surface tensions of a series of molten lead borates and lead silicates have been measured; the changes in composition on heating and the volatility of the compositions have been related to their surface tensions; and the similarity of the composition-expansivity curve to the composition-temperature coefficient of surface tension curve has been pointed out.

V. References

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