

SURFACE TENSION OF BOROSILICATE MELTS WITH THE COMPOSITION CLOSE TO THE E-GLASS

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The composition of the commercially produced E-glass was approximated by the five component system MgO-CaO-B₂O₃-Al₂O₃-SiO₂. Ten additional glass compositions were derived from the mean composition by two-level scheme consisting in shifting the content of each particular oxide of definite positive and negative value preserving the mutual molar ratio of remaining oxides. The surface tension was measured by the sessile drop method using the melt density value obtained by independent experiment. The profile of sessile drop was analyzed by nonlinear regression using the numerical integration of Laplace's equation. The results were compared with the approximate formula proposed by Dorsey for large drops. The Dorsey's formula results were about 6% higher than the results of the drop full profile analysis. The additive linear model was proposed describing the compositional dependence of the surface tension with the standard deviation of approximation of 10 mN/m.

INTRODUCTION

The surface tension of E-glass melt represents a key factor in the production of E-glass fibers. In connection with the contemporary glass melting technology utilizing the oxygen gas burning accompanied with relatively high water vapor partial pressure in the melting furnace atmosphere the melt surface tension significantly influences the foam formation and its stability [1, 2, 3]. On the other hand, the surface tension influences the process of glass filaments drawing. Therefore the aim of the present work resides in estimation of the dependence of the surface tension on the E-glass melt composition.

EXPERIMENTAL

The average E-glass composition was represented by the five component oxide system (Table 1, glass Center). Then ten additional glass compositions were derived from the central composition by two-level scheme consisting in shifting the content of each particular oxide of definite positive and negative value with preserving the mutual molar ratio of remaining oxides. The glass batches were prepared from analytical grade purity oxides and carbonates and melted in a superkanthal furnace in platinum crucibles at 1600°C for two hours. The homogeneity was ensured by continuous stirring by the platinum stirrer. The glass melt density was determined by the Archimedes method by weighting

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Table 1. Analyzed glass composition in mol.%.

Glass	SiO ₂	CaO	Al ₂ O ₃	B ₂ O ₃	MgO
Center	56.92	24.89	8.80	4.55	4.85
MgO-	58.83	26.82	9.45	4.89	0.00
MgO+	53.96	23.54	8.72	4.40	9.38
CaO-	57.62	23.45	9.15	4.67	5.11
CaO+	55.48	26.85	8.50	4.35	4.83
B ₂ O ₃ -	57.21	26.20	8.89	2.62	5.09
B ₂ O ₃ +	56.19	24.28	8.70	5.98	4.85
Al ₂ O ₃ -	57.82	26.61	5.92	4.22	5.43
Al ₂ O ₃ +	55.89	24.82	11.10	3.23	4.97
SiO ₂ -	56.06	25.44	9.14	4.25	5.12
SiO ₂ +	58.10	23.97	8.95	4.22	4.77

a Pt-Ir sphere immersed in the melt (Table 2) [4, 5, 6]. Sessile drops were prepared from the glass cubes of approximate (3×3×3) mm³ dimensions on glassy carbon plate in the atmosphere of pure nitrogen. The drop profile was recorded by the CCD camera and digitized (Figure 1) using the Lucia[®] software (LIM, a.s. Prague). The temperature at which the symmetric drop shape was reached during the sample heating with the heating rate of 5°C/min. was chosen for recording of the drop profile.

RESULTS AND DISCUSSION

The values of surface tension, γ^{exp} , were obtained by the least squares method by minimization of the sum of squares of deviations between the experimental and calculated drop profile. The calculated drop profile was obtained by the numerical integration of the Laplace

Table 2. Experimental values of the density (ρ) and surface tension obtained by drop profile analysis (γ^{exp}) and by Dorsey's approximate method (γ^{apr}).

Glass	T (°C)	ρ (g/cm ³)	γ^{exp} (mN/m)	γ^{apr} (mN/m)
Center	1050	2.5525	259.6 ± 2.2	279.5
MgO-	1110	2.5104	276.0 ± 2.8	287.5
MgO+	1180	2.5552	281.7 ± 2.6	299.0
CaO-	1150	2.4996	255.5 ± 2.9	276.6
CaO+	1050	2.5872	270.0 ± 1.8	298.2
B ₂ O ₃ -	1180	2.5489	305.5 ± 2.8	308.2
B ₂ O ₃ +	1050	2.5143	270.7 ± 3.1	267.4
Al ₂ O ₃ -	1080	2.5224	275.5 ± 3.2	310.0
Al ₂ O ₃ +	1230	2.5104	294.3 ± 2.6	306.2
SiO ₂ -	1060	2.5515	283.2 ± 1.8	302.8
SiO ₂ +	1100	2.5230	260.8 ± 1.9	279.9

equation [7, 8] using the experimental density values (Table 2). For comparison the approximate surface tension values, γ^{apr} , were calculated by the commonly used formula proposed by Dorsey [9, 10]:

$$\gamma^{apr} = g\rho r^2 (0.052 / f - 0.12268 + 0.0481f) \quad (1)$$

$$f = (r_{45^\circ} - h_{45^\circ}) / r - 0.04142 \quad (2)$$

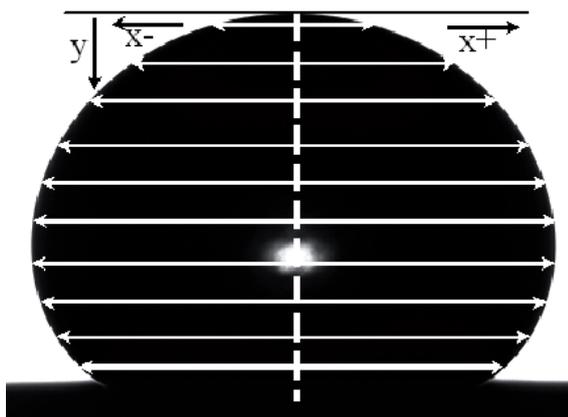


Figure 1. Coordinate system for the drop profile digitization.

where g is the gravity acceleration, ρ - density, r the drop equatorial radius, and r_{45} and h_{45} are the drop radius and height from the level of 45 degree tangent (see Figure 2).

It can be seen, that the Dorsey's approximate surface tension values are of about 6 % higher than correct values obtained from the drop profile analysis. As far as the Dorsey's formula was derived for large drops, this difference can be attributed to the smaller drop size.

The multilinear regression analysis of experimental surface tension values obtained by the drop full profile analysis resulted in the regression equations:

$$\gamma^{exp} \text{ (mN/m)} = (399 \pm 141)x(\text{MgO}) + (886 \pm 98)x(\text{CaO}) - (539 \pm 338)x(\text{B}_2\text{O}_3) + (639 \pm 226)x(\text{Al}_2\text{O}_3) \quad (3)$$

that reproduces the experimental data with the standard deviation of approximation of 10 mN/m and the Fisher's statistics $F = 2086$ (Figure 3).

Analogously the Dorsey's approximate surface tension values posses the regression equation:

$$\gamma^{apr} \text{ (mN/m)} = (501 \pm 102)x(\text{MgO}) + (1065 \pm 71)x(\text{CaO}) - (603 \pm 244)x(\text{B}_2\text{O}_3) + (288 \pm 163)x(\text{Al}_2\text{O}_3) \quad (4)$$

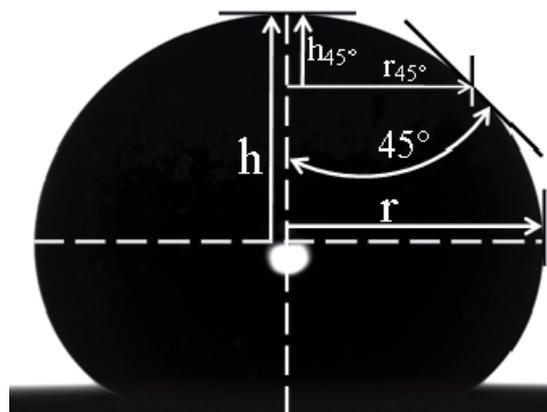


Figure 2. Coordinates used for the Dorsey's approximate method (Equations (1, 2)).

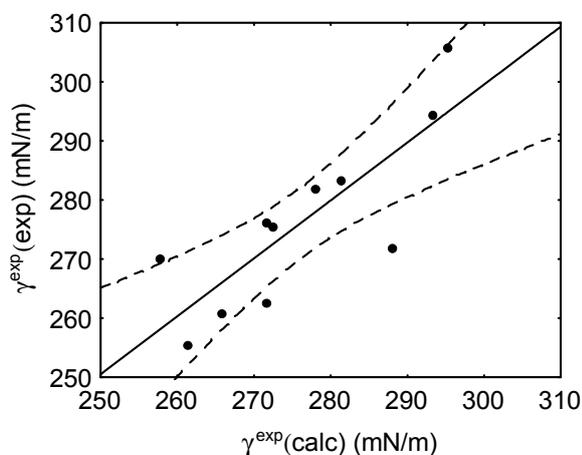


Figure 3. Comparison of experimental (exp) and calculated (calc) values of surface tension (points) obtained from drop profile analysis. Dashed lines correspond to 95% significance limit of the regression equation.

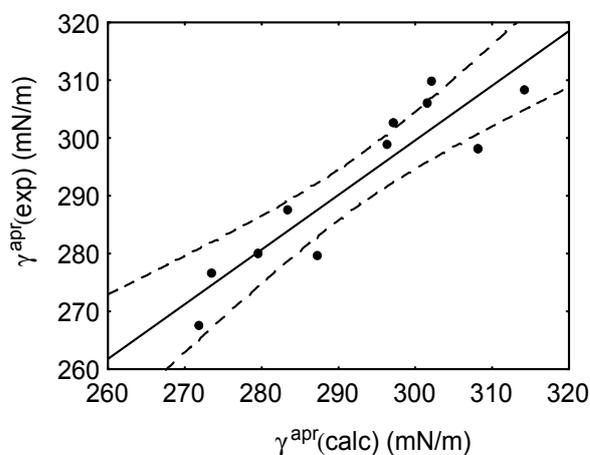


Figure 3. Comparison of experimental (exp) and calculated (calc) values of surface tension (points) obtained from Dorsey approximate method. Dashed lines correspond to 95% significance limit of the regression equation.

with the standard deviation of approximation of 7.2 mN/m and the Fisher's statistics $F = 4498$ (Figure 3).

It is worth noting that the influence of SiO_2 content on the surface tension is not explicitly included because only the statistically significant terms were retained in the regression Equations (3, 4). Glass surface tension generally decreases with increasing concentration of acidic oxides indicating that the anionic groups are surface active [11-13]. Thus the negative sign of the B_2O_3 coefficient is in harmony with this assumption. The highly positive values of the MgO and CaO coefficients can be rationalized due to decrease of the surface tension by increasing the SiO_2 content. The positive but statistically not very significant value of the alumina coefficient may be, at least principally, explained by its amphoteric character.

CONCLUSION

The surface tension of eleven glasses from the system MgO-CaO- B_2O_3 - Al_2O_3 - SiO_2 was measured by the sessile drop method. The multilinear regression analysis was applied to find out the relationship between the surface tension and molar fraction of oxides and coefficients of this relationship were obtained. It was found, that glass surface tension generally decreases with increasing concentration of acidic oxides.

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