HIGH-TEMPERATURE VISCOSITY AND DENSITY
OF ALUMINO-BOROSILICATE GLASSES AS A MODEL SYSTEM
FOR COMMERCIAL E-GLASS

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High temperature viscosity and density of glass melts in the system MgO–CaO–B$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ with composition close to the E-glass were measured and interpreted with respect to the effect of oxides content on their physical properties. The Andrade model was applied for description of the temperature dependence of the glass viscosity within studied temperature range. The regression formulae describing the compositional dependence of the viscosity points $T_2 = T(\eta = 10^2 \, dPa.s)$, $T_3 = T(\eta = 10^3 \, dPa.s)$, $T_4 = T(\eta = 10^4 \, dPa.s)$ and molar volume of glass melts and glasses were proposed.

INTRODUCTION

Commercial E-glass melts must meet industry requirements (including ASTM specifications [1]), comply with environmental emission standards and have the lowest possible fiber forming temperature (or melt viscosity) that is consistent with a desired balance between material and energy costs. The melts also must be crystallization resistant as they pass through the furnace and bushings.

The melting behavior of glasses depends on their viscosity-temperature relationship [2]. Glassmelting furnace design and operation are largely determined by the temperature range within which melt viscosity allows successful melting, fining and conditioning of the glass. Therefore, the knowledge of the glass viscosity as a function of temperature and glass composition is crucial for efficient glassmaking.

Several papers have been published, dealing with viscosity temperature and glass composition relationships. It is worth to mention the work of P. Hrma [3], who published the Arrhenius models for glass viscosity vs. composition relationships of six types of commercially produced glasses; either local model (for composition range of given type of glass) or global model (includes composition ranges of all six glasses). More complex viscosity model for predicting the complete viscosity curve of glass, based on a global statistical approach and more than either 300 or 2000 composition-viscosity data, was reported by A. Fluegel et al. [4, 5]. The extensive work on physical properties of glass-es with composition which simulate the composition of commercially produced E-glass was reported by F. T. Wallenberger et al. [6-9].

The calcium aluminoborosilicate glasses with composition similar (or analogous) to commercial E-glass was studied by ^{17}O 3QMAS NMR, ^{11}B, ^{27}Al and ^{29}Si MAS NMR spectroscopy [10] and structural models for this type of glass were discussed in detail.

In the present study high-temperature viscosity and density of glasses and glass melts in the system MgO–CaO–B$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ with composition close to the E-glass were measured. The dependence of the measured glass properties on glass composition and temperature was analyzed by the multilinear regression analysis. The composition of the glasses studied (Table 1) varies around the average composition in such a way, that in each case the molar % of one oxide is either increased or decreased (reflecting the possible compositional change in glassworks) and the mutual molar ratios of other oxides in the system remain constant. In such manner the total of eleven glass compositions were studied and the change of physical properties with change of glass melt composition is discussed in details. The molar composition x_j (j = 1, …, 5) of particular oxide in the glass with the content of i-th oxide shifted by Δ_i mol % with respect to its average glass composition, x_i^{ave}, can be calculated using the data given in Table 1 by Equation (1).

$$x_i = \frac{x_i^{ave} \pm \Delta_i}{100 \pm \Delta_i} \, 100 \, \% \qquad x_{j \neq i} = \frac{x_j^{ave}}{100 \pm \Delta_i} \, 100 \, \% \qquad (1)$$

Table 1. The composition of studied glasses based on the average content of major oxides in the E-glass, the step Δ of change in the composition of each oxide, and the abbreviation of samples.

Oxide	Average composition (mol.%) Sample "Average"	Δ (mol.%)	Sample abbreviation
MgO	4.97	± 4.97	MgO$^+$/MgO$^-$
CaO	25.80	± 3.00	CaO$^+$/CaO$^-$
B$_2$O$_3$	4.47	± 2.00	B$_2$O$_3$$^+$/B$_2O_3$$^-$
Al$_2$O$_3$	8.73	± 3.00	Al$_2$O$_3$$^+$/Al$_2O_3$$^-$
SiO$_2$	56.03	± 4.00	SiO$_2$$^+$/SiO$_2$$^-$

EXPERIMENTAL

Glass batches have been prepared using fine powdered analytical grade purity Al$_2$O$_3$, CaCO$_3$, MgO, H$_3$BO$_3$, and SiO$_2$. Batches to produce 400 g of glass were weighed into plastic bottles using a three decimal place balance and mixed thoroughly in a homogenizer for 24 h. The prepared batches were added to a Pt-10%Rh crucible which was placed in the superkanthal furnace at 1500°C. Any batch was filled in the crucible in a stepwise manner. After 1 h to allow material to become batch free, a motorized Pt-10%Rh stirrer was lowered into crucible and switched on. Melts were stirred at ~ 30 rpm for a further 4 h in ambient atmosphere. The stirrer was then removed and molten glasses were poured into preheated stainless steel mould, allowed to cool slightly, and the glass blocks were then placed in an electric muffle furnace and annealed at temperature of approximately 500°C. Samples were held at this temperature for 1 h to relieve internal stress, and were then slowly cooled down to room temperature at ~ 1°C/min.

The high-temperature viscosity and density of melts in the given temperature range (1150 - 1500°C) were measured by falling sphere method. Experimental equipment was calibrated using NIST Standard Reference Material 710a. Densities of the glasses at RT have been measured by the Archimedes method using distilled water as the suspension medium.

RESULTS AND DISCUSSION

The measured temperature dependence of viscosity for the studied glass melts is shown on Figure 1. As clearly seen, the trends in the viscosity-temperature relationship with change of composition, for the glass melts are the following: (1) increasing amount of glass modifier oxides, either MgO or CaO, decreases the melt viscosity over the measured temperature range and *vice versa*, (2) increasing amount of glass network former SiO$_2$ quite significantly increases the glass melt viscosity, but decreasing amount of SiO$_2$ only slightly affects the melt viscosity in the given temperature range when

compared to the glass melt denoted as "Average", (3) decreasing amount of glass network former B$_2$O$_3$ quite significantly increases the glass melt viscosity, but increasing amount of B$_2$O$_3$ only slightly affects the melt viscosity in the given temperature range when compared to glass melt denoted as "Average", (4) the change in the amount of Al$_2$O$_3$ slightly affects the glass melt viscosity in the measured temperature range (an increase in amount of Al$_2$O$_3$ increases glass melt viscosity and *vice versa*).

The measured temperature dependence of glass melt density for the studied glasses is shown on Figure 2. The trends in the glass melt density with change of composition of glass melts can be summarized as follows: (1) increasing amount of glass modifier oxides, either MgO or CaO, increases the melt density over the measured temperature range and *vice versa*, (2) increasing amount of glass former SiO$_2$ significantly decreases the glass melt density, but decreasing amount of SiO$_2$ does not affect the melt density in the given temperature range when compared to glass melt denoted as "Average", (3) increased/decreased amount of glass former B$_2$O$_3$ decreases/increases the melt density in the given temperature range when compared to glass melt denoted as "Average", (4) either increase or decrease of amount of Al$_2$O$_3$ decreases the melt density in the given temperature range when compared to glass melt denoted as "Average".

The viscosity-temperature relationship of studied glass melts in measured temperature range was sufficiently well described by the Andrade equation [11]:

$$\log(\eta / \mathrm{dPas}) = A + \frac{B}{T} = \log(\eta_0 / \mathrm{dPas}) + \frac{E_a}{2{,}303R}\frac{1}{T} \qquad (2)$$

where A and B parameters, which are functions of the glass composition, are routinely determined by regression analysis of experimental data, and T is thermodynamic temperature. The temperature independent viscous flow activation energy, E_a, was calculated from the slope of $\log(\eta/\mathrm{dPas}) = f(1/T)$ according to Equation (3). All relevant data are summarized in Table 2.

$$E_a = \left(\partial \ln \eta / \partial (1/T)\right)_P = \ln(10)RB = 2.303RB \qquad (3)$$

where R is the molar gas constant.

The selected physical properties of glass melts and glasses are summarized in Table 3. As it is clearly seen from Table 3, the temperatures corresponding to the significant glass viscosity fixpoints, melting point - T_2 = $T(\eta = 100\ \mathrm{dPa.s})$ and $T_4 = T(\eta = 10000\ \mathrm{dPas})$ - working point, as well as the fiber forming temperature - $T_3 = T(\eta = 1000\ \mathrm{dPas})$ decrease with increasing amount of RO oxides (CaO and MgO) in glass melts or with decreasing SiO$_2$/RO ratio; the ratio of B$_2$O$_3$/Al$_2$O$_3$ oxides is constant in this case. On the other hand, those temperatures increase with increasing amount of SiO$_2$

a)

b)

c)

d)

e)
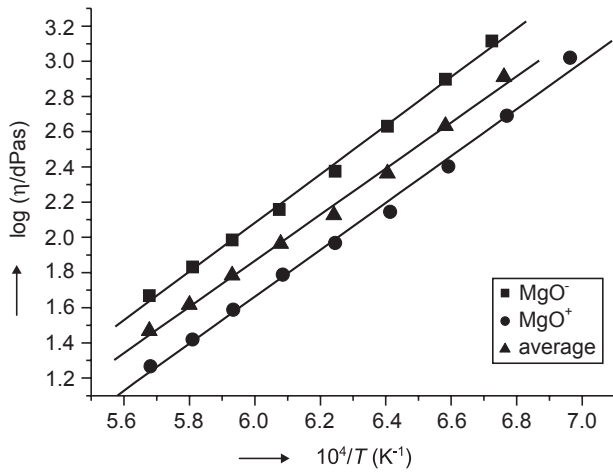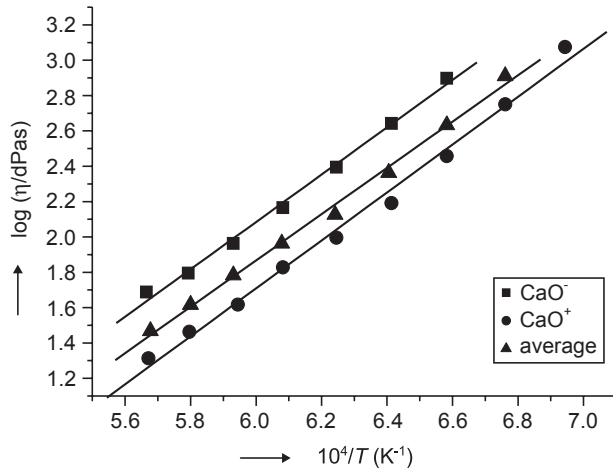
or with increasing SiO_2/RO ratio. In other words, increasing amount of modifiers (CaO and MgO) decreases viscosity of glass melts, however, the glass former SiO_2 increases the viscosity with its increasing amount in melt. These results are in accordance with previous studies [6-9, 13]. In the case of B_2O_3 and Al_2O_3 oxides, the increasing amount of B_2O_3 slightly decreases and Al_2O_3 slightly increases viscosity of glass melt when compared to viscosity of the melt denoted as "Average".
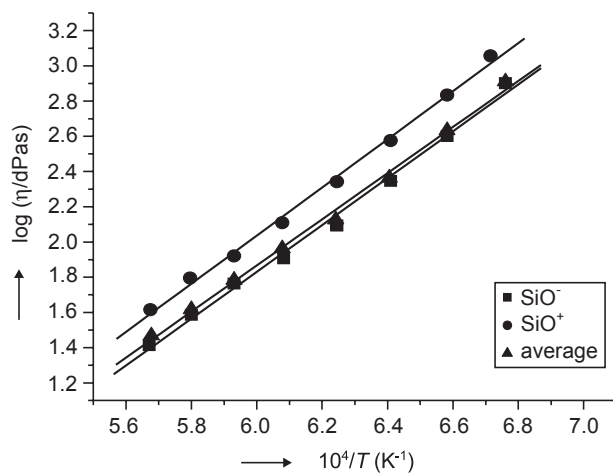
Fluegel et al. [12], reported first-order model for temperature-composition relationship for given viscosity fixpoint, corresponding to the equation
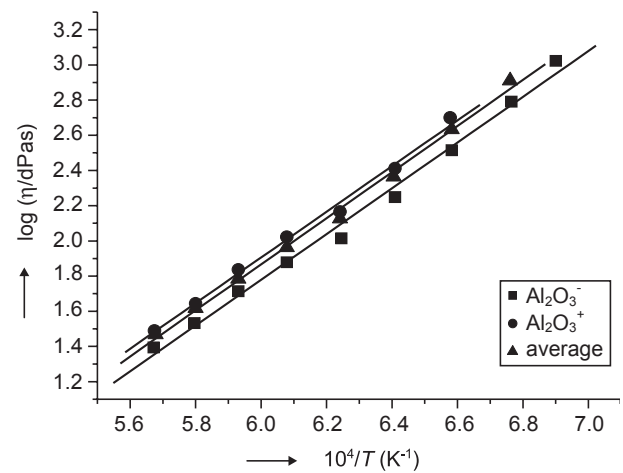
$$T_\eta = T_0 + \sum_{i=1}^{S} b_i x_i \qquad (4)$$

where b_i is the significant component coefficient, S is the number of significant components and T_0 comprises
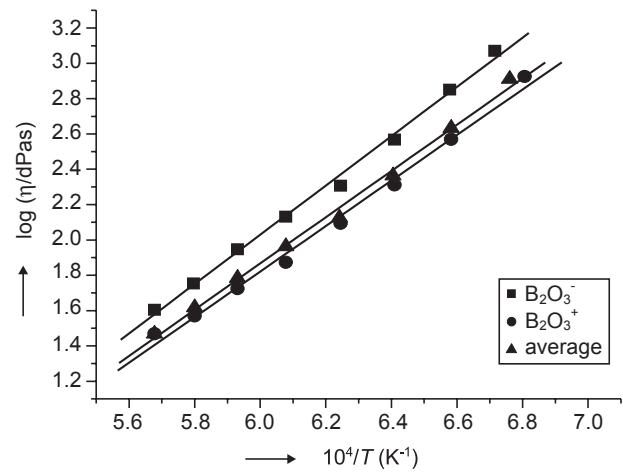
Figure 1. Andrade plot of viscosity-temperature dependence for the glass melt with average composition and glass melts: MgO^+/MgO^-, CaO^+/CaO^-, SiO_2^+/SiO_2^-, $B_2O_3^+/B_2O_3^-$, $Al_2O_3^+/Al_2O_3^-$.

one component other than significant components. This Equation (4) can be rearranged into the form

$$T_\eta = \sum_{i=1}^{N} a_i x_i \qquad (5)$$

where $a_i = b_i + T_0$ $(i = 1, \ldots, S)$, $N = S + 1$, and $a_n = T_0$, $x_n = 1 - \sum_{i=1}^{S} x_i$

In above mentioned case, the number of significant components S differs by unity from the total number of components N. However, in general case, when the difference is greater than 1, $N - S > 1$, the corresponding equations for ai and T_0 are more complicated. Following the above scheme, one can obtain the Equations (6) and (7) for general case.

$$b_i = a_i - \sum_{i=1,2\ldots S}^{N} a_j \qquad (6)$$

$$T_0 = \sum_{j=S+1}^{N} a_j \left[1 - \sum_{\substack{k=S+1 \\ k \neq j}}^{N} \bar{x}_k \right] \qquad (7)$$

where $\bar{x}_k$ denotes the average molar composition of component other than significant components.

In order to obtain the statistically significant parameters for compositional relationship of glass melt properties, using either Equations (4) or (5), the multilinear regression analysis was applied using the experimental data for all 11 studied glass melts. The results of the multilinear regression analysis are summarized in Table 4, and for selected properties are also shown on Figure 3.

For the temperatures corresponding to given viscosity points, $T_2 = T(\eta = 10^2 \text{ dPas})$, $T_3 = T(\eta = 10^3 \text{ dPas})$ and $T_4 = T(\eta = 10^4 \text{ dPas})$, the regression analysis of the experimental data showed that statistically significant coefficients could be obtained only in the case when 3 oxides, namely MgO, CaO and B_2O_3, were chosen as significant components; the oxides Al_2O_3 and SiO_2 are considered as other components than significant. In this case, the statistically significant coeficients can be discussed in the terms of either substitution of fictive mixture of Al_2O_3 and SiO_2 of a given average composition by significant components (MgO, CaO and B_2O_3) or mutual substitution of significant components. As can be seen from Table 4, the substitution of Al_2O_3 and SiO_2 by any of oxides MgO, CaO or B_2O_3

Table 2. Coefficients of the Andrade equation, viscous flow activation energies, their standard deviations and standard deviation of the log η approximation s_{apr}.

Sample	A	B	E_a (kJ/mol)	s_{apr} (log(η/dPas))
Average	-5.99 ± 0.22	13097 ± 348	251 ± 7	0.035
MgO$^+$	-6.33 ± 0.23	13319 ± 363	255 ± 7	0.045
MgO$^-$	-6.21 ± 0.19	13812 ± 299	264 ± 6	0.030
CaO$^+$	-6.43 ± 0.28	13557 ± 446	260 ± 9	0.055
CaO$^-$	-5.95 ± 0.26	13391 ± 425	256 ± 8	0.035
$B_2O_3^+$	-5.92 ± 0.29	12896 ± 462	247 ± 9	0.048
$B_2O_3^-$	-6.34 ± 0.23	13952 ± 377	267 ± 7	0.037
SiO_2^+	-6.16 ± 0.21	13664 ± 335	262 ± 6	0.033
SiO_2^-	-6.15 ± 0.26	13301 ± 422	255 ± 8	0.043
$Al_2O_3^+$	-5.88 ± 0.27	12974 ± 439	248 ± 8	0.035
$Al_2O_3^-$	-6.02 ± 0.27	12996 ± 435	249 ± 8	0.053

Table 3. Selected physical properties of studied glasses (molar volume of glass melt, V_m^{melt}, volume thermal expansion coefficient of glass melt β, density of glass at 20°C, ρ^{20}, and corresponding molar volume V_m^{glass}).

Sample	T_2 (K)	T_3 (K)	T_4 (K)[#]	V_m^{melt} (cm³/mol)[§]	$10^5 \beta$(K^{-1})[$]	ρ^{20} (g/cm³)	V_m^{glass} (cm³/mol)
Average	1639	1457	1311	24.77	3.92	2.664	23.32
MgO$^+$	1599	1428	1290	24.10	3.93	2.694	22.69
MgO$^-$	1683	1500	1353	25.47	3.92	2.632	24.05
CaO$^+$	1609	1438	1300	24.54	4.06	2.700	22.95
CaO$^-$	1684	1496	1346	25.15	3.86	2.629	23.71
$B_2O_3^+$	1629	1446	1300	25.08	3.85	2.645	23.55
$B_2O_3^-$	1672	1463	1349	24.50	3.85	2.694	23.02
SiO_2^+	1673	1491	1345	24.73	3.54	2.644	23.37
SiO_2^-	1632	1454	1310	24.69	3.99	2.678	23.24
$Al_2O_3^+$	1646	1461	1313	25.16	3.78	2.678	23.63
$Al_2O_3^-$	1620	1433	1286	24.44	3.92	2.679	22.75

[#] Temperatures correspond to the given viscosity point $T_2 = T(\eta = 10^2 \text{ dPas})$, $T_3 = T(\eta = 10^3 \text{ dPas})$ and $T_4 = T(\eta = 10^4 \text{ dPas})$
[§] Molar volume of glass melt at temperature $T = 1645$ K, corresponding to the centre of measured temperature range of density.
[$] Thermal expansion coefficient of glass melt, $\beta = (1/V)(\partial V/\partial T)_P$.

decreases the values of T_2, T_3, and T_4, and consequently decreases the viscosity of the glass melt which is in accordance with the experimental findings. The effect of MgO on the temperatures at given viscosity is less pronounced than that of oxides CaO and B_2O_3. These results are in agreement with the study of P. Hrma [3] on E-glasses.

In the case of molar volumes of glass melts and glasses, all oxides were considered as significant components. The significant component coefficients are all positive, but the values for the oxides Al_2O_3 SiO_2 and B_2O_3 are significantly higher than the values for the glass modifier oxides MgO and CaO. The substitution of any of oxides Al_2O_3, SiO_2 or B_2O_3 by oxides MgO or CaO leads to the decrease of molar volume and consequently to the increase of glass melt density or density of glass. On the other hand, increasing amount of oxides Al_2O_3, SiO_2 or B_2O_3 in glass melt increases the value of molar volume, so that decreases the glass melt density.
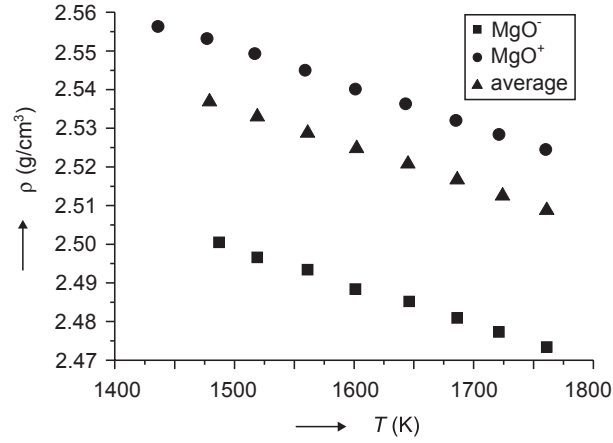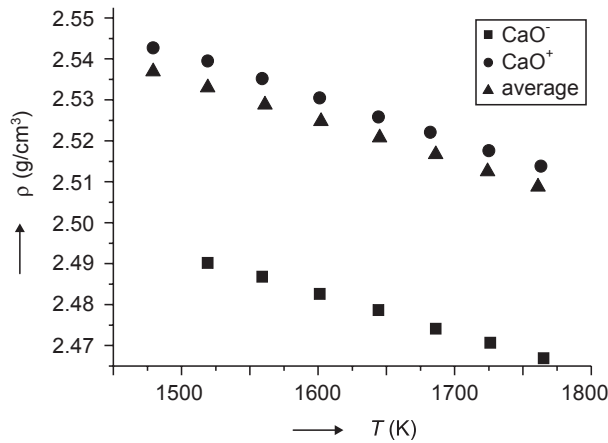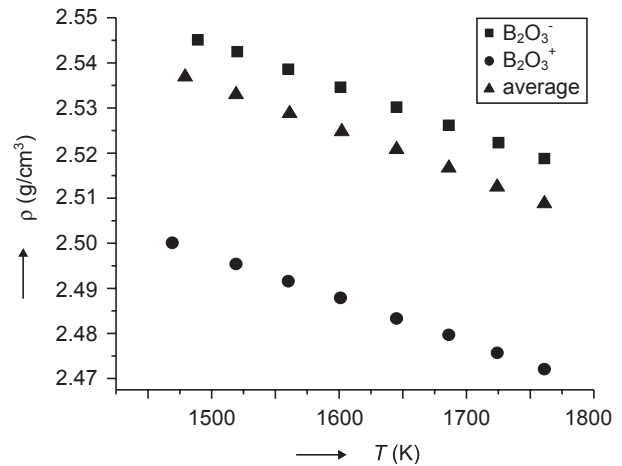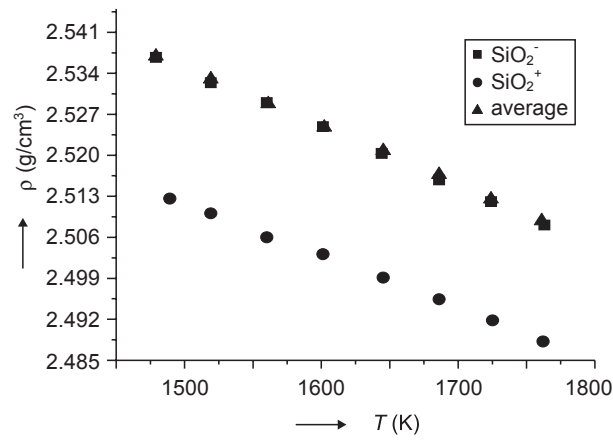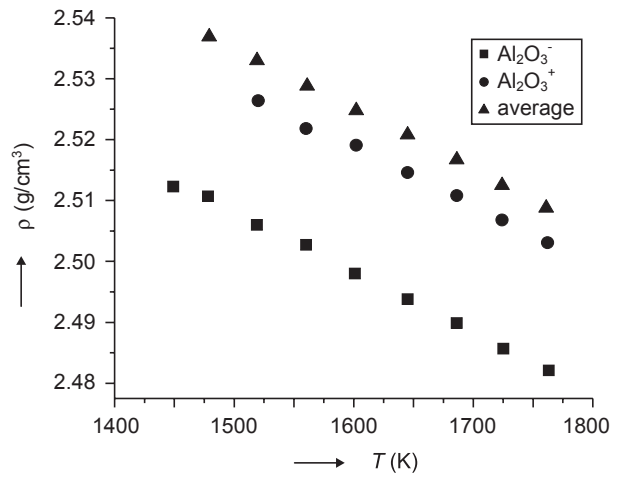

Figure 2. Density-temperature plot for the glass melt with average composition and glass melts: MgO^+/MgO^-, CaO^+/CaO^-, SiO_2^+/SiO_2^-, $B_2O_3^+/B_2O_3^-$, $Al_2O_3^+/Al_2O_3^-$.

Table 4. Component coefficients of multi-linear regression analysis (see Equations (4) and (5)) of selected physical properties of studied glasses with statistical parameters (standard deviation of coefficients, standard deviation of approximation - s_{apr}, correlation coefficient - R, and Fischer´s F-statistics - F)

	T_2 (K)[#]	T_3 (K)[#]	T_4 (K)[#]	V_m^{melt} (cm³/mol)[§]	V_m^{glass} (cm³/mol)
T_0	2252	1967	1745	-	-
$s(T_0)$	79	81	84	-	-
$b(MgO)$	-1440	-1226	-1065	11.11	9.62
$s(b(MgO))$	162	166	172	0.66	1.05
$b(CaO)$	-1786	-1420	-1156	14.92	10.78
$s(b(CaO))$	269	276	286	0.97	1.54
$b(B_2O_3)$	-1694	-1696	-1664	39.89	37.07
$s(b(B_2O_3))$	366	376	389	1.67	2.65
$b(Al_2O_3)$	-	-	-	37.43	38.42
$s(b(Al_2O_3))$	-	-	-	1.09	1.74
$b(SiO_2)$	-	-	-	27.38	26.83
$s(b(SiO_2))$	-	-	-	0.47	0.74
F	31	22	16	628700	219500
R	0.964	0.951	0.935	0.999	0.999
s_{apr}	9.5	9.8	10.1	0.046	0.074

[#] Temperatures correspond to the given viscosity point $T_2 = T(\eta = 10^2$ dPas), $T_3 = T(\eta = 10^3$ dPas) and $T_4 = T(\eta = 10^4$ dPas)
[§] Molar volume of glass melt at temperature $T = 1645$ K, corresponding to the centre of measured temperature range of density.

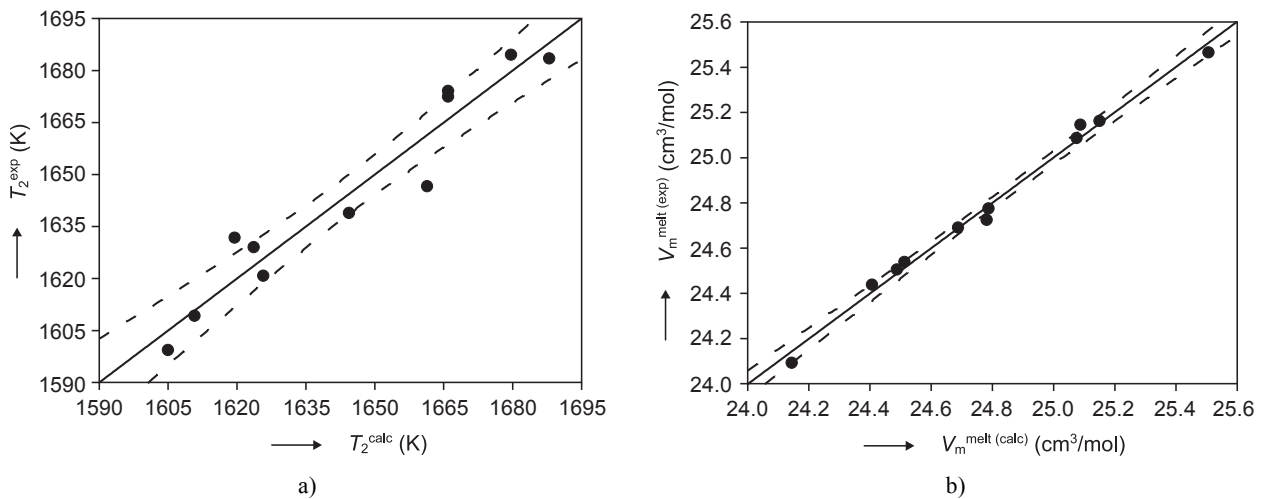a)   b)

Figure 3. Comparison of experimental (exp) and calculated (calc) values of T_2 and V_m^{melt}. The dotted line corresponds to 95 % confidence interval.

CONCLUSION

For the measured temperature range of glass melt viscosity, the Andrade equation represents the viscosity-temperature relationship reasonably well. Using parameters of Andrade equation, the temperatures corresponding to the significant glass viscosity fixpoints, $T_2 = T(\eta = 100$ dPas) - melting point, $T_4 = T(\eta = 10000$ dPas) - working point, as well as the fiber forming temperature - $T_3 = T(\eta = 1000$ dPa.s), were calculated. From the temperature dependence of glass melt density, molar volumes of glass melts were calculated at temperature $T = 1645$ K, corresponding to the centre of measured temperature range of density. Multilinear regression analysis was used to describe the compositional relations of selected physical properties of glass melts and glasses. This allowed us to discuss the effect of substitution of particular oxides on the physical properties of glasses in terms of significant component coefficients. It was found, that the substitution of Al_2O_3 and SiO_2 by any of oxides MgO, CaO or B_2O_3 decreases the values of T_2, T_3, and T_4, and consequently decreases the viscosity of the glass melt. The substitution of any of oxides Al_2O_3, SiO_2 or B_2O_3 by oxides MgO or CaO decreases the molar volume and consequently increases the glass melt density or density of glass.

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VYSOKOTEPLOTNÁ VISKOZITA A HUSTOTA BORITANO-HLINITANOKREMIČITANOVÝCH SKIEL AKO MODELOVÉHO SYSTÉMU PRIEMYSELNE VYRÁBANÉHO E-SKLA

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Pre sklotvorné taveniny v sústave $MgO–CaO–B_2O_3–Al_2O_3–SiO_2$, so zložením blízkym zloženiu E-skla, bola nameraná teplotná závislosť ich viskozity a hustoty. Andradeho model bol použitý na vyjadrenie teplotnej závislosti viskozity sklotvornej taveniny pre študovaný teplotný interval. Navrhnuté boli regresné rovnice opisujúce závislosť vybraných teplôt pri danej viskozite $T_2 = T(\eta = 10^2 \text{ dPa.s})$, $T_3 = T(\eta = 10^3 \text{ dPa.s})$, $T_4 = T(\eta = 10^4 \text{ dPa.s})$ a molárneho objemu sklotvorných tavenín a skiel od zloženia. Uvedené závislosti umožňujú diskutovať vplyv substitúcie jednotlivých oxidov na fyzikálne vlastnosti študovaných sklotvorných tavenín a skiel.