# THE TEMPERATURE AND COMPOSITION DEPENDENCE OF CONTAINER GLASS VISCOSITY

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*The regression model of temperature and composition dependence of glass viscosity was developed by nonlinear regression analysis. A minimalisation of weighted sum of squared deviations included 753 viscosity points from 257 compositions of industrially produced container glasses. The temperature dependence of viscosity was described by Fulcher's equation with free volume theory term. The composition dependence of coefficients* $A, B, T_0$ *was expressed by linear polynomials of mole fractions of oxides MgO, CaO,* $Al_2O_3$*,* $Na_2O$ *and* $K_2O$*. The statistical methods were used to verify the reliability of the proposed model. Practical use of the regression model was shown by the calculation of glass composition with required values of viscosity curve.*

## INTRODUCTION

Because of enormous quantity of container glass products even though negligible change of chemical composition can result in the decrease of cost production. Therefore a considerable effort is aimed at the optimization of container glass composition.

When one is attempting to optimize container glass production, a detailed knowledge of the temperature and composition dependence of viscosity is of prime importance. The use of computers in the compositional optimization requires to express this dependence by mathematical function.

In the literature, numerous calculation methods can be found dealing with composition dependence of viscosity or composition and temperature dependence of viscosity of container glasses [1–5]. The use of these expressions in the calculation of viscosity values are often limited by possibility to calculate only main viscosity points or by narrow range of validity, respectively.

In presented work the proposed regression model of composition and temperature dependence of container glass viscosity can reduce these above mentioned disadvantages to minimum. This model has been developed by method [6] of nonlinear regression analysis, where all viscosity points for the widest range of industrially produced container glass compositions were calculated simultaneously.

## METHOD

Our previous experiences [7] showed that the temperature dependence of viscosity is satisfactory described by equation

$$\log \eta = 0.5 \log T + A + B/(T - T_0) \tag{1}$$

where $\eta$(dPa) is the viscosity, $T$(K) is temperature and $A, B, T_0$ are parameters dependent on composition. The dependence of these parameters on composition was expressed by mixed polynomials of type

$$y = \sum_{k}^{M} c_k x(\mathrm{MgO})^{e_{k,1}} x(\mathrm{CaO})^{e_{k,2}} x(\mathrm{Al_2O_3})^{e_{k,3}} \times \tag{2}$$
$$\times\, x(\mathrm{Na_2O})^{e_{k,4}} x(\mathrm{K_2O})^{e_{k,5}}$$

where $c_k$ are coefficients determined by regression analysis, $e_{k,i}$ are integral, nonnegative exponents, $x(\mathrm{MgO})$, $x(\mathrm{CaO})$, $x(\mathrm{Al_2O_3})$, $x(\mathrm{Na_2O})$, $x(\mathrm{K_2O})$ are the mole fractions of the respective oxides and $M$ is number of terms of mixed polynomial. The optimum form of polynomials was obtained by nonlinear regression analysis by minimalisation of the sum of squared deviations

$$U = \sum_{i,j} w_{ij} \left[ 0.5 \log T_{i,j} + A(\boldsymbol{x}_i) + \right. \tag{3}$$
$$\left. + \frac{B(\boldsymbol{x}_i)}{T_{i,j} - T_0(\boldsymbol{x}_i)} - \log \eta_{i,j}^{\mathrm{exp}} \right]^2$$

where $\boldsymbol{x}$ is the vector of mole fractions of the individual oxides in the $i$-th sample, $T_{ij}$ is the thermodynamic temperature for the $j$-th viscosity point of the $i$-th sample, $\eta_{ij}^{\mathrm{exp}}$ is the pertinent experimental value of the viscosity and $w_{ij}$ is weight coefficient of respective point.

Comparing the differences of temperature at high and low values of viscosity curve, we can see, that difference of viscosity $10^{0.1}$ dPas at viscosity point $10^{13.1}$ dPas represents the difference of temperature about 2 K, while the same difference of viscosity at viscosity point $10^{2.0}$ dPas corresponds to the temperature difference higher than 30 K. Therefore the sum of squares of relative deviations was minimalised in the optimization to ensure tha balance between high and low viscosity experimental points. Thus the weight coefficients are expressed as

$$w_{ij} = \left[\log\left(\eta_{ij}^{\mathrm{exp}}/\mathrm{dPas}\right)\right]^{-2} \tag{4}$$

The regression model was proved by the Fischer F statistics, which is defined by the ratio between the variance of the experimental values $s^2(\log\eta)$, and the residual variance, ${s_{res}}^2$,

$$s^2(\log\eta) = \sum_{i,j}\left[\log\eta_{ij}^{exp} - E(\log\eta^{exp})\right]^2 / (N-1) \quad (5)$$

$$s_{res}^2 = \sum_{i,j}\left[\log\eta_{ij}^{clc} - \log\eta_{ij}^{exp}\right]^2 / \nu \quad (6)$$

$$F = s^2(\log\eta) / s_{res}^2 \quad (7)$$

where $N$ is total number of experimental values, $\nu$ is the number of degrees of freedom, i.e. $\nu = N - p$, where $p$ is the number of coefficients in polynomials (8–10), $\eta^{clc}$ is calculated value of viscosity from the regression model and $E(\log\eta^{exp})$ is average value of viscosity from experimental values $\log\eta^{exp}$.

The Student t-test was used to test the statistical significance of $c_k$ coefficients of the regression polynomials. All these coefficients should be statistically significant at minimum level of 99% [8].

## RESULTS AND DISCUSSION

The values of main viscosity points $10^{2.0}$, $10^{4.0}$, $10^{7.65}$, $10^{13.1}$ dPas of 257 samples of industrially produced container glasses were used in the calculation of regression dependence of viscosity on temperature and composition. The composition of these glasses ranged between the following values of respective oxides (wt. %): 0.0–4.7% MgO, 5.2–11.7% CaO, 0.1–6.7% $Al_2O_3$, 10.3–17.5% $Na_2O$, 0.0–3.8% $K_2O$ and 65.8–74.7% $SiO_2$. The extreme values were eliminated by statistic test of extreme values.

The optimum form of approximation polynomials $A(x)$, $B(x)$, and $T_0(x)$ is expressed by equations (8–10):

$$A = -1.448 - 6.594x(MgO) - 7.990x(CaO) - 23.839x(Al_2O_3) - 6.453x(Na_2O)\ [-] \quad (8)$$

$$B = 4782.1 + 3689.5x(MgO) + 31591.2x(Al_2O_3)\ [K] \quad (9)$$

$$T_0 = 500.5 + 492.6x(CaO) - 1366.1x(Al_2O_3) - 535.2x(Na_2O) - 367.7x(K_2O)\ [K] \quad (10)$$

where $x(MgO)$, $x(CaO)$, $x(Al_2O_3)$, $x(Na_2O)$ and $x(K_2O)$ are mole fractions of respective oxides.

The sum of squares of relative deviations, 0.272, corresponds to the standard relative deviation 1.9% of the value of logarithm viscosity at 740 degrees of freedom. The value of F-statistic calculated from (5–7) F = 536 is highly statistically significant. The distribution of deviatons between experimental and calculated values of viscosity is represented in Fig. 1.

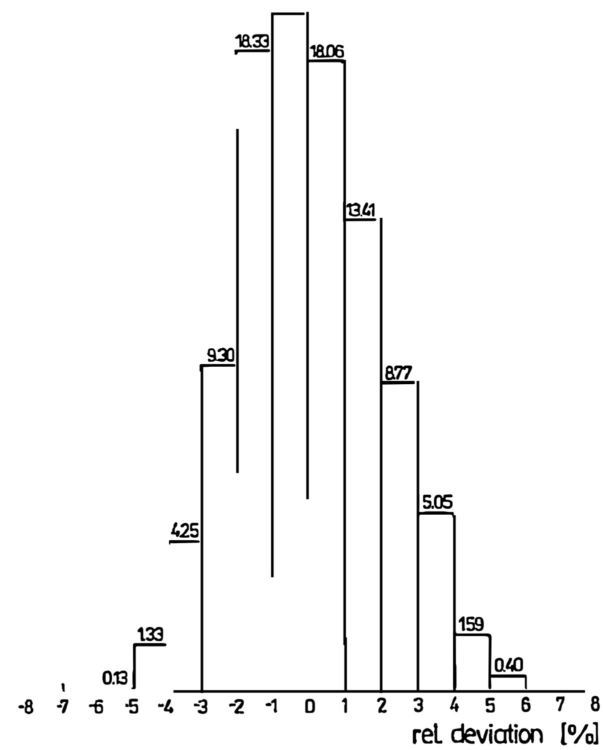


*Fig. 1. Histogram of distribution of the relative deviations between experimental and calculated values* $\log\eta$ *for 753 viscosity points included into regression analysis (Numbers above particular columns represent percentual portion of points with the relative deviations in range marked on x-axis).*

The coefficients of approximation polynomials (8–10) with their standard deviations and values of Student t-criterion are presented in Tables I–III. From these values we can conclude (critical value $t_{krit} = 2.58$ on a 99% level of significance), that proposed regression model describes the temperature and composition dependence of container glass viscosity appropriately.

This regression model can be successfuly used, for instance, in the optimalization of glass composition to obtain the composition for required values of the viscosity curve.

Let's suppose, that we have $N$ points $(\eta_i, T_i)$, $i = 1, 2 \ldots N$ and our task is to find such glass composition $x$, which comply with the condition

$$\eta_i = f(x, T_i) \quad i = 1, 2 \ldots N \quad (11)$$

where $f(x,T) = \eta$ is known regression model of temperature and composition dependence of viscosity. This problem is possible to solve by minimalisation of the function

$$U(x) = \sum_i^N \left[f(x, T_i) - \eta_i\right]^2 \quad (12)$$

*Table I*

Exponents $e_{k,i}$ and coefficients $c_k$ of the approximation polynomial (12) for the dependence of the parameter $A = A(x)$ together with standard deviations $s(c_k)$ and Student t-statistics $t_k$

| $k$ | $e_{k,1}$ | $e_{k,2}$ | $e_{k,3}$ | $e_{k,4}$ | $e_{k,5}$ | $c_k$ | $s(c_k)$ | $t_k$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | -1.4476 | 0.14 | 10.3 |
| 2 | 1 | 0 | 0 | 0 | 0 | -6.5940 | 0.71 | 9.3 |
| 3 | 0 | 1 | 0 | 0 | 0 | -7.9897 | 0.46 | 17.4 |
| 4 | 0 | 0 | 1 | 0 | 0 | -23.8389 | 4.05 | 5.9 |
| 5 | 0 | 0 | 0 | 1 | 0 | -6.4529 | 0.53 | 12.2 |

*Table II*

Exponents $e_{k,i}$ and coefficients $c_k$ of the approximation polynomial (12) for the dependence of the parameter $B = B(x)$ together with standard deviations $s(c_k)$ and Student t-statistics $t_k$

| $k$ | $e_{k,1}$ | $e_{k,2}$ | $e_{k,3}$ | $e_{k,4}$ | $e_{k,5}$ | $c_k$ | $s(c_k)$ | $t_k$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 4782.1 | 76.1 | 62.8 |
| 2 | 1 | 0 | 0 | 0 | 0 | 3689.5 | 625.2 | 5.9 |
| 3 | 0 | 0 | 1 | 0 | 0 | 31591 | 6265 | 5.0 |

*Table III*

Exponents $e_{k,i}$ and coefficients $c_k$ of the approximation polynomial (12) for the dependence of the parameter $T_0 = T_0(x)$ together with standard deviations $s(c_k)$ and Student t-statistics $t_k$

| $k$ | $e_{k,1}$ | $e_{k,2}$ | $e_{k,3}$ | $e_{k,4}$ | $e_{k,5}$ | $c_k$ | $s(c_k)$ | $t_k$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 500.53 | 10.9 | 45.9 |
| 2 | 0 | 1 | 0 | 0 | 0 | 492.57 | 42.5 | 11.6 |
| 3 | 0 | 0 | 1 | 0 | 0 | -1366.1 | 377.8 | 3.6 |
| 4 | 0 | 0 | 0 | 1 | 0 | -535.19 | 51.8 | 10.3 |
| 5 | 0 | 0 | 0 | 0 | 1 | -367.69 | 139.1 | 2.6 |

In the case that viscosity points $(\eta, T_i)$ lie in the parts of viscosity curve with significantly different slope the following function should be minimalised

$$U(x) = \sum_{i}^{N} \left\{ [f(x, T_i) - \eta_i]^2 + \right. \tag{13}$$

$$\left. + [f^{-1}(x, \eta_i) - T_i]^2 \right\}$$

where $f^{-1}(x, \eta) = T$ is inverse function to the function $f(x, T)$.

In practice the inverse function $f^{-1}$ can not be usually expressed analytically and so its numerical solution leads to the long time of minimalisation of function U. When one or two parameters are optimalized, the graphical methods may be used, too [9].

In the case, when less required viscosity points than

*Table IV*

The comparison of measured ($\eta^{exp}$) and calculated ($\eta^{clc}$) values of viscosity curve of industrially produced container glass France'78

| $t/°C$ | $\log\{\eta^{exp}/dPas\}$ | $\log\{\eta^{clc}/dPas\}$ |
|---|---|---|
| 1502 | 2.0 | 1.98 |
| 1054 | 4.0 | 4.03 |
| 732 | 7.65 | 7.69 |
| 543 | 13.1 | 13.09 |

*Table V*

The calculated values of viscosity curve for the optimalized glass composition, which are practically identical with that of France'78 glass

| $t/°C$ | $\log\{\eta^{clc}/dPas\}$ |
|---|---|
| 1502 | 1.99 |
| 1054 | 4.01 |
| 732 | 7.64 |
| 543 | 13.10 |

the number of independent variables (oxides concentrations) are prescribed in the optimalization of glass composition, more solutions (different glass compositions) with equivalent viscosity curve can be found. This fact is shown in Tables IV–V. Table IV gives measured and calculated values of viscosity curve for industrially produced container glass France'78, with the following composition in wt. %: 2.55% MgO, 10.67% CaO, 1.68% $Al_2O_3$, 13.25% $Na_2O$, 0.19% $K_2O$, 0.14% $Fe_2O_3$, 0.08% $SO_3$, 71.06% $SiO_2$. Table V contains calculated values of viscosity curve for the glass composition (wt. %): 1.44% MgO, 11.57% CaO, 1.02% $Al_2O_3$, 13.19% $Na_2O$, 0.61% $K_2O$ and 72.15% $SiO_2$. This glass composition we have found from the proposed regression model by minimalisation of equation (12) for the values of viscosity curve given in Table IV.

## CONCLUSION

It can be concluded that, the temperature and composition range of 257 samples of industrially produced container glasses, can be adequately described by Fulcher's equation (1). It is sufficient to describe the coefficients $A, B, T_0$ by linear polynomial of their dependence on chemical composition corresponding to molar fractions of respective oxides. The results of statistical analysis indicate that it is possible to disregard variable contents of some minorit species ($SO_3$, $Fe_2O_3$) within studied composition interval (of industrially produced container glasses). The proposed regression model yields simple solution of the task of calculation of the chemical composition corresponding to prescribed course of viscosity curve.

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## ZÁVISLOSŤ VISKOZITY OBALOVÉHO SKLA OD TEPLOTY A ZLOŽENIA

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Aplikáciou nelineárnej regresnej analýzy sa navrhlo analytické zloženie závislosti viskozity od teploty a chemického zloženia obalového skla. Do minimalizácie váženej sumy štvorcov odchýliek bolo zahrnutých 753 viskozitných bodov z 257 zložení priemyselne vyrábaných obalových skiel. Získaná regresná funkcia je založená na Fulcherovej rovnici s voľhoobjemovým členom. Koeficienty $A, B, T_0$ sú pritom vyjadrené ako lineárne funkcie chemického zloženia reprezentované mólovými zlomkami oxidov MgO, CaO, $Al_2O_3$, $Na_2O$ a $K_2O$. Platnosť navrhnutého modelu sa overila štatistickými metódami. Praktické využitie navrhnutého regresného modelu sa ilustrovalo na výpočte chemického zloženia skla s požadovanými hodnotami viskozitnej krivky.

*Obr. 1. Histogram rozdelenia relatívnych odchýliek medzi experimentálnymi a vypočítanými hodnotami* $\log\eta$ *pre 753 viskozitných bodov zahrnutých do regresnej analýzy. Čísla nad jednotlivými stĺpcami udávajú percentuálne zastúpenie bodov s relatívnou odchýlkou v rozmedzí vyznačenom na x-ovej osi.*