

IMPROVED COMPOSITION-PROPERTY RELATIONS IN SILICATE GLASSES, PART I: VISCOSITY

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ABSTRACT

For the first time, several silicate glass property databases were analyzed *without using any a priori knowledge of the details of bonding and lumped as a single group*, as a function of the chemical composition. The viscosity of over 300 compositions including soda-lime glasses, borosilicates, glasses with high alkaline earth content, NIST glass viscosity standards, lead silicates, fluorosilicates, and phospho-silicates have been examined. Using multiple regression modeling, linear and multiplicative relations between the chemical composition and several properties, e.g. viscosity, thermal expansion, density, refractive index, electrical conductivity were developed. In this paper the modeling of the viscosity versus composition is discussed. The described relations have been found to link data of different authors and compositions into one global equation which (a) allows validation of glass property datasets, (b) quantifies the influences of glass components and component interactions, and (c) allows some conclusions regarding the nature of glass. The analysis so far makes it possible to estimate the viscosity isokoms at $\log(\eta/\text{Pa}\cdot\text{s}) = 12.0$ with an error of $\pm 7^\circ\text{C}$, at $\log(\eta/\text{Pa}\cdot\text{s}) = 6.6$ with an error of $\pm 9^\circ\text{C}$, and at $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$ with an error of $\pm 17^\circ\text{C}$. This research was partially funded by the US Department of Energy, Grant DE FG 07-96EE41262.

INTRODUCTION

This study was started within the framework of a larger project of the NSF Industry/University Center for Glass Research (CGR) to provide the glass industry a database and a method for calculating the properties of technical glasses within the composition and temperature limits of interest, as pioneered in the 19th century by Winkelmann and Schott [1] and summarized recently by Priven and Mazurin [2]. As part of it, the viscosities of 150 industrial glass variations (including float, container, low-expansion borosilicate, TV panel, wool, and textile fiber glasses) have been determined between $\log(\eta/\text{Pa}\cdot\text{s}) = 1-12$ by various groups. A statistical regression analysis of the results was extended to the data given by Lakatos [3], the NIST viscosity standards SRM 710A, 711, and 717A, as well as viscosity data of Owens-Illinois Glass Company [4], and Allison & Turner [5]. Common to all sources mentioned is the observation that industrial compositions were investigated systematically, in addition to providing a chemical analysis of the glasses.

EXPERIMENTAL DESIGN AND MEASUREMENT PROCEDURES

Member companies of the NSF Industry/University Center for Glass Research (CGR) selected six groups of industrial glasses for the study: float, container, low-expansion borosilicate, TV panel, wool, and textile fiber glasses. Starting from one base composition per glass

group, supplied by CGR member companies, twenty-four further composition variations per group were selected using a Plackett-Burman design based on weight percent. The concentration limits and all oxides of interest were given by CGR member representatives [6]. The glass preparation is described in [6, 7].

Viscosity measurements

The viscosity curve over $\log(\eta/\text{Pa}\cdot\text{s}) = 1-12$ was determined by three methods:

- 1) Beam bending, $\log(\eta/\text{Pa}\cdot\text{s}) = 10-12$, by J. E. Shelby, Alfred University, Alfred, NY
- 2) Parallel plate, $\log(\eta/\text{Pa}\cdot\text{s}) = 6-9$, by A. Fluegel and A. K. Varshneya, Alfred University
- 3) Cylinder rotation, $\log(\eta/\text{Pa}\cdot\text{s}) \sim 1-2$, by C. A. See et al., Pacific Northwest Laboratory (PNNL), Redland, WA [8]

The principles of the parallel-plate viscometry are described by Varshneya [9, 10], and details of this study are given in [7]. The beam bending and cylinder rotation measurement procedures, as well as all 150 analyzed glass compositions are summarized in [6]. The viscosity data are listed in Tables VI-VIII. Data at $\log(\eta/\text{Pa}\cdot\text{s}) = 6.6$ for two alkali-free borosilicates with ~ 20 mol% SiO_2 were included in this work at $\log(\eta/\text{Pa}\cdot\text{s}) = 6.6$ for testing the extension to wider glass composition areas in later studies.

STATISTICAL DATA ANALYSIS

All concentrations in the databases were converted to mol%, from the original numbers in wt% and molar fraction. The viscosity values were fitted for each investigator separately to the Vogel-Fulcher-Tammann equation (VFT), i.e., the three sources in [6] were *not* combined for enabling trend and offset analysis. The fits described the experimental data well. Following the VFT fits, for all glasses the temperatures of constant viscosities (isokom) were calculated for $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5, 6.6, \text{ and } 12.0$ ($\sim T_g$). The cylinder rotation measurements done by C. A. See et al. at PNNL [6] had to be analyzed with exceptional care, firstly because the original data vary significantly in the viscosity levels examined for $\log(\eta/\text{Pa}\cdot\text{s}) < 2.6$, and secondly because the number of datapoints was only 2-4 for each glass. If 3 or 4 datapoints were reported to cover the range around $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5 \pm 0.25$, a VFT fit was used, else a linear fit with 2 datapoints was employed. In $\sim 20\%$ of all cases however the reported viscosity levels were far off from $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$. Then, a datapoint from parallel plate measurements at $\log(\eta/\text{Pa}\cdot\text{s}) = 6.0$, obtained by Fluegel and Varshneya at Alfred University [6], was included in the VFT fit. As a result, the cylinder rotation measurements done at PNNL may appear less accurate than other data.

Multiple regression model type and factors

A slack-variable model with variable intercept including multiplicative interactions and excluding silica was used (Eq. (1) [11]). The independent variables were the concentrations in mol% (single-component factors) and the multiplicative interactions (interaction factors); the dependent variables were the isokom temperatures in $^\circ\text{C}$ for $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5, 6.6, \text{ and } 12.0$. No squared terms were considered because of correlations with single-component factors.

$$T(\text{isokom}) = K_0 + \sum_{j=1}^n \left\{ K_{1j} \cdot C_j + \sum_{k=j+1}^n \left(K_{2k} \cdot C_j \cdot C_k + \sum_{m=j+k+1}^n K_{3m} \cdot C_j \cdot C_k \cdot C_m \right) \right\} \quad (1)$$

K0-K3 in the model equation Eq. (1) are the coefficients, with K0 being the intercept, K1 the single-component coefficients, K2 the coefficients of two-component interaction coefficients, and K3 the coefficients of three-component interactions. The variable n in Eq. (1) is the total number of glass components (excluding silica); j, k, and m are individual numbers of the glass components, and C are the concentrations in mol%.

The difference (observed – calculated) value is defined as residual.

The model type used in this study implies that all glasses are based on silica. In other words, all single-component and interaction coefficients in this work are in fact interaction coefficients with silica. Therefore silica-free glasses might not fit into this study.

Table I: Concentration limits in mol% and frequency of glass components used for the model at $\log(\eta/Pa \cdot s) = 6.6$; Minimum in each range is always zero except $C(SiO_2)_{min} = 20$ mol%; σ is the standard deviation of the concentration population. Outliers were not counted.

Component	Maximum in mol%	Average in mol%	σ in mol%	# with C > 0.5 mol%
SiO ₂	87.10	69.66	7.10	297
B ₂ O ₃	16.97	1.90	3.74	93
Al ₂ O ₃	9.99	1.62	2.31	167
MgO	16.90	3.96	3.24	230
CaO	28.05	8.52	5.51	271
SrO	7.03	0.29	1.30	22
BaO	30.30	0.52	2.69	40
Li ₂ O	11.81	0.25	1.22	27
Na ₂ O	18.32	11.21	4.22	285
K ₂ O	6.84	1.17	1.78	131
TiO ₂	0.82	0.10	0.22	23
ZrO ₂	1.76	0.07	0.33	14
PbO	18.90	0.09	1.11	10
ZnO	4.00	0.14	0.57	23
F	10.31	0.34	0.99	44
Fe ₂ O ₃	1.92	0.12	0.32	23
Y ₂ O ₃	2.00	0.01	0.16	2
CeO ₂	0.30	0.01	0.05	0
SO ₃	0.29	0.03	0.06	0
P ₂ O ₅	0.85	0.01	0.08	0
Se	0.02	0.00	0.00	0
Cr ₂ O ₃	0.16	0.01	0.03	0
Co ₃ O ₄	0.05	0.00	0.00	0
H ₂ O*	642*	281*	126*	/

The single-component factors in this work and the concentration limits for the model at $\log(\eta/Pa \cdot s) = 6.6$ are summarized in Table I. The models at $\log(\eta/Pa \cdot s) = 1.5$ and 12.0 have

* All water concentrations listed in Table I are in ppm weight, determined by J. E. Shelby using infrared spectroscopy. The values are valid only for the 150 glasses in reference [6]. The minimum water concentration measured was 80 ppm weight.

similar concentration limits [12]. Neglected were minor components with $C < 0.5$ mol%, because initial analyses proved their insignificance at these low levels: FeO, Cr₂O₃, Co₃O₄, CeO₂, Sb₂O₃, As₂O₃, Se, SO₃ and H₂O* (Table I). All two-component interactions of the following components were considered if the interaction occurred more than twenty five times: B₂O₃, Al₂O₃, MgO, CaO, SrO, BaO, Li₂O, Na₂O, K₂O, and F. In addition, all three-component interactions of the components B₂O₃, Al₂O₃, MgO, CaO, Na₂O, and K₂O were taken into account. The interaction limits, i.e. the quantitative limits of component combinations, are summarized in [12]. The interaction limits need to be considered before any calculation.

Dataset-specific correction factors

To the six datasets analyzed in this study (Shelby, Fluegel, See, Lakatos, Owens-Illinois, Allison), dataset specific correction factors were assigned:

Trend correction:

$$T(\text{isokom}), \text{observed} = T(\text{isokom}), \text{calculated} + K_{DT} \times T(\text{isokom}), \text{observed} \quad (2)$$

Offset correction:

$$T(\text{isokom}), \text{observed} = T(\text{isokom}), \text{calculated} + K_{DO} \quad (3)$$

All dataset-specific correction coefficients K_{DT} and K_{DO} were set to zero in the beginning. In case the data analysis described below resulted in significant trends or offsets of the residuals vs. the observed values, *either* K_{DT} *or* K_{DO} per dataset were allowed to vary. K_{DT} and K_{DO} were never varied simultaneously for one dataset because of strong correlation.

Modeling procedure

Before starting the multiple regression calculation, all single-component and interaction factors were checked for linear correlations (Pearson's matrix). Strongly correlated factors with absolute correlations > 0.8 were excluded from the model according to the hierarchy, the frequency of $C > 0.5$ mol%, and the factor average over all glasses. This procedure reduced the ~90 considered variables to ~55.

Multiple regression analysis was done in the programs MCA (Nextbridge Softwares, version 1999), as well as SPSS (Standard version for Windows, release 11.5.0, 6 Sept 2002, LEAD Technologies Inc).

Factors were excluded stepwise from the model if there was less than a ~95% confidence level in their significance (t-value < 2). After exclusion of all insignificant factors, the datasets were checked for trends (i.e. if the residual depended on the viscosity) and offsets (i.e. if the average of all residuals for one dataset was significantly different from zero). Trends and offsets in datasets were considered by corresponding dataset-specific correction factors according to Eq. (2) and Eq. (3), and summarized in Table II. Next, outlying data were analyzed. If the residual was larger than three times the model error, i.e. if the standardized residual was larger than three, the value was considered an outlier and deleted from the model. Finally, the complete modeling procedure was iterated, beginning from the correlation analysis until no further outlier could be found.

RESULTS

Table II shows the dataset properties, e. g. the total number of glasses and viscosity levels investigated, trends, offsets, etc. In addition, Table II presents the standard deviation σ of all

* Even though H₂O is reported to strongly influence the viscosity [23], it was insignificant in this study.

residuals per dataset, which is related to the dataset consistency within itself, i.e., its precision. The dataset specific correction factors, combined with the percentage of outliers per dataset, and the standard deviation of all residuals per dataset give an estimate of the comparability of a dataset in relation to other datasets, i.e. the total dataset quality.

Tables III, IV, and V list all significant coefficients, as well as their standard errors, t-values, and excluded strong correlations > 0.8. Insignificant factors and their correlations are not mentioned. The t-values reveal the factor significance; the standard errors reflect the coefficient accuracy. The excluded strong correlated factors might be significant in reality, but the mentioned interferences make it impossible to detect them based on the used composition matrix. Therefore any correlated factor coefficient is the sum of all correlated influences, whereby the most important one is stated as the factor name.

The coefficients in Tables III, IV, and V are valid only within the concentration and interaction limits stated in Table I and [12]. The models in this paper are valid for homogeneous, clear or colored glasses with insignificant crystal content and phase separation. The best viscosity isokom predictions are possible if all factors are within $\pm 2 \sigma$ (standard deviation) of the considered factor.

Table II: Dataset properties (Fl = Fluegel, Sh = Shelby)

Data source	# of data	Viscosity level in log(η /Pa·s)	Offset in °C	Trend	σ of residuals	# of outliers
[3]	30	1.5	0	0	5.1	0
[3]	30	6.6	0	0	3.9	0
[3]	30	12.0	0	0	3.5	0
[5]	28	1.5	-50.0	0	13.2	0
[5]	28	6.6	-14.2	0	5.7	0
[5]	28	12.0	-9.5	0	4.3	0
[4]	102	1.5	0	0	16.3	8
[4]	102	6.6	0	0.0063	7.2	8
[6, 8]-See	147*	1.5	0	0	18.1	21
[6]-Fl	146	6.6	0	0	10.4	6
[6]-Sh	136	12.0	0	0.0119	7.9	9

Viscosity prediction; a calculation example

Since Eq. (1) and the large number of coefficients in Tables III, IV, and V may appear very complicated at first sight, the viscosity prediction for the Standard Reference Material 710A is illustrated here as example (Certificate from: National Institute of Standards & Technology (NIST), Gaithersburg, MD, 20899, USA; March 20, 1991):

- 1) The standard 710A is known to be a homogeneous, clear glass, which is a condition for applying the models in this paper.
- 2) Next, the glass composition in mol% is obtained from the certificate. The mol% composition is: 71.37 SiO₂, 1.31 Al₂O₃, 9.62 CaO, 8.25 Na₂O, 6.27 K₂O, 2.81 ZnO, 0.32 TiO₂, 0.04 Sb₂O₃, 0.02 As₂O₃. These lie within the acceptable ranges [12].

* 24 of 147 values were extrapolated (s. appendix, Table VI).

Table III: Significant model coefficients, $\log(\eta/Pa \cdot s) = 1.5$

Factor	Coefficient	St. error	t	# > 0.5	Excluded correlations
Single-component coefficients (K1)					
B ₂ O ₃	-13.49	0.97	-13.90	76	/
Al ₂ O ₃	4.35	1.76	2.47	155	Al ₂ O ₃ *CaO
MgO	-5.99	0.80	-7.53	225	MgO*Na ₂ O
CaO	-18.00	0.71	-25.29	259	Al ₂ O ₃ *CaO
SrO	-20.09	1.05	-19.08	24	Al ₂ O ₃ *SrO, SrO*BaO, SrO*Na ₂ O, SrO*K ₂ O
BaO	-22.26	1.19	-18.63	37	Al ₂ O ₃ *BaO, BaO*Na ₂ O, BaO*K ₂ O
Li ₂ O	-29.14	0.90	-32.38	28	MgO*Li ₂ O, CaO*Li ₂ O, Li ₂ O*Na ₂ O
Na ₂ O	-25.10	0.79	-31.79	271	Na ₂ O*F
K ₂ O	-19.21	1.12	-17.20	124	Na ₂ O*K ₂ O
PbO	-23.22	1.00	-23.25	12	/
ZnO	-9.42	1.92	-4.91	22	/
F	-14.73	1.82	-8.11	45	MgO*F
Fe _x O _y	-15.33	3.24	-4.74	23	/
Two-component interaction coefficients (K2)					
B ₂ O ₃ *CaO	-0.225	0.050	-4.48	75	B ₂ O ₃ *Al ₂ O ₃ , B ₂ O ₃ *Al ₂ O ₃ *CaO
B ₂ O ₃ *Na ₂ O	-0.536	0.078	-6.86	76	/
Al ₂ O ₃ *MgO	-0.526	0.151	-3.49	180	Al ₂ O ₃ *MgO*CaO
Al ₂ O ₃ *Na ₂ O	0.761	0.152	5.00	258	Al ₂ O ₃ *CaO*Na ₂ O
MgO*K ₂ O	0.788	0.248	3.18	109	MgO*Na ₂ O*K ₂ O
CaO*Na ₂ O	0.215	0.071	3.02	257	/
CaO*F	1.017	0.222	4.58	40	/
Three-component interaction coefficients (K3)					
MgO*CaO*Na ₂ O	-0.0211	0.0072	-2.94	232	/
Dataset-specific correction coefficients for datasets with trends or offsets					
Offset for ref. [5]	-50.01	3.77	-13.25	28	/

Intercept (K0) = $(1816.4 \pm 11.4)^\circ\text{C}$; Standard model error = 16.71°C ; $R^2 = 0.961$

Adequate precision = signal/noise ratio = $(\text{max. prediction} - \text{min. prediction}) / (\text{number of coefficients} \times (\text{model error})^2 / \text{number of glasses in model})^{0.5} = 123.4$

- 3) For the viscosity level $\log(\eta/Pa \cdot s) = 1.5$, the coefficients from Table III are: K0 = 1816.4, K1(Al₂O₃) = 4.35, K1(CaO) = -18.00, K1(Na₂O) = -25.10, K1(K₂O) = -19.21, K1(ZnO) = -9.42, K2(Al₂O₃*Na₂O) = 0.761, K2(CaO*Na₂O) = 0.215. All remaining coefficients in Table III do not apply for 710A. Since no coefficients are mentioned in Table III for TiO₂, Sb₂O₃, and As₂O₃, those minor components must be neglected for the isokom calculation at the viscosity level $\log(\eta/Pa \cdot s) = 1.5$. The same procedure has to be repeated with the coefficients from Tables IV and V. It should be noted that in

Table IV: Significant model coefficients, $\log(\eta/Pa \cdot s) = 6.6$

Factor	Coefficient	St. error	t	# > 0.5	Excluded correlations
Single-component coefficients (K1)					
B ₂ O ₃	-3.16	0.55	-5.77	93	/
Al ₂ O ₃	15.48	1.09	14.17	167	Al ₂ O ₃ *CaO
MgO	4.02	1.00	4.03	230	/
CaO	-2.77	0.38	-7.37	271	Al ₂ O ₃ *CaO
SrO	-3.01	0.61	-4.91	22	Al ₂ O ₃ *SrO, SrO*BaO, SrO*Na ₂ O, SrO*K ₂ O
BaO	-4.16	0.50	-8.31	40	Y ₂ O ₃ , B ₂ O ₃ *BaO, MgO*BaO, CaO*BaO
Li ₂ O	-16.81	0.46	-36.16	27	MgO*Li ₂ O, CaO*Li ₂ O, Li ₂ O*Na ₂ O
Na ₂ O	-11.27	0.53	-21.39	285	/
K ₂ O	-11.90	0.85	-14.02	131	Na ₂ O*K ₂ O
ZrO ₂	9.51	2.26	4.22	14	/
PbO	-8.62	0.57	-16.02	10	/
ZnO	-1.67	1.03	-1.61*	23	/
F	-6.14	0.62	-9.94	44	MgO*F, Na ₂ O*F
Fe _x O _y	-6.79	1.73	-3.93	23	/
Two-component interaction coefficients (K2)					
B ₂ O ₃ *Al ₂ O ₃	-0.625	0.091	-6.87	62	B ₂ O ₃ *Al ₂ O ₃ *CaO
B ₂ O ₃ *CaO	-0.117	0.032	-3.61	86	B ₂ O ₃ *Al ₂ O ₃ *CaO
B ₂ O ₃ *Na ₂ O	0.156	0.042	3.74	91	/
Al ₂ O ₃ *MgO	-0.911	0.144	-6.34	181	Al ₂ O ₃ *MgO*CaO
Al ₂ O ₃ *Na ₂ O	-0.686	0.104	-6.60	270	Al ₂ O ₃ *CaO*Na ₂ O
Mg*Na ₂ O	-0.174	0.081	-2.14	234	s. footnote ^a
CaO*Na ₂ O	0.207	0.038	5.45	266	/
CaO*K ₂ O	0.334	0.091	3.66	146	CaO*Na ₂ O*K ₂ O
K ₂ O*F	-0.565	0.279	-2.03	29	/
Three-component interaction coefficients (K3)					
Al ₂ O ₃ * MgO*Na ₂ O	0.0732	0.0188	3.89	221	/
MgO*CaO* Na ₂ O	-0.0282	0.0043	-6.56	236	/
Dataset-specific correction coefficients for datasets with trends or offsets					
Offset, [5]	-14.15	2.09	-6.77	28	/
Trend, [4]	0.0063	0.0027	2.34	94	/

Intercept (K0) = (876.7 ± 6.6)°C; Standard model error = 8.94°C; R² = 0.974

T(isokom, average) = 727.1°C; σ of all T(isokom) values = 53.4°C; signal/noise ratio = 136.4

* ZnO factor not excluded despite $t < 2$, since it may be needed for glasses with increased ZnO concentrations.

^a The MgO*Na₂O interaction is correlated with MgO. The correlation coefficient is 0.83. The MgO*Na₂O interaction was not excluded from the model because of its high frequency (234).

Table V: Significant model coefficients, $\log(\eta/\text{Pa}\cdot\text{s}) = 12.0$

Factor	Coefficient	St. error	t	# > 0.5	Excluded correlations
Single-component coefficients (K1)					
B ₂ O ₃	-3.10	0.85	-3.67	62	/
Al ₂ O ₃	11.24	0.74	15.28	153	Al ₂ O ₃ *CaO
MgO	-1.54	0.27	-5.73	127	MgO*CaO
CaO	1.05	0.28	3.80	167	Al ₂ O ₃ *CaO
SrO	2.25	0.48	4.67	23	Al ₂ O ₃ *SrO
Li ₂ O	-21.06	1.13	-18.70	25	Al ₂ O ₃ *Li ₂ O, CaO*Li ₂ O, Li ₂ O*Na ₂ O
Na ₂ O	-7.30	0.47	-15.48	179	/
K ₂ O	-11.94	0.86	-13.93	112	Na ₂ O*K ₂ O
ZrO ₂	9.03	1.86	4.87	12	/
PbO	-4.61	0.46	-10.11	11	/
F	-9.33	0.86	-10.82	34	Na ₂ O*F
Two-component interaction coefficients (K2)					
B ₂ O ₃ *Al ₂ O ₃	-0.626	0.112	-5.60	51	B ₂ O ₃ *Al ₂ O ₃ *CaO
B ₂ O ₃ *Na ₂ O	0.573	0.084	6.78	63	/
B ₂ O ₃ *K ₂ O	0.585	0.119	4.93	36	B ₂ O ₃ *Al ₂ O ₃ *K ₂ O
CaO*Na ₂ O	0.157	0.039	4.08	164	/
CaO*K ₂ O	0.468	0.088	5.33	127	CaO*Na ₂ O*K ₂ O
Three-component interaction coefficients (K3)					
B ₂ O ₃ *Al ₂ O ₃ *Na ₂ O	-0.0449	0.0131	-3.43	54	/
B ₂ O ₃ *CaO*Na ₂ O	-0.0111	0.0054	-2.07	54	/
Al ₂ O ₃ *CaO*Na ₂ O	-0.0285	0.0063	-4.50	154	/
Dataset-specific correction coefficients for datasets with trends or offsets					
Offset for ref. [5]	-9.48	2.52	-3.76	28	/
Trend for ref. [6]	0.0119	0.0041	2.90	127	/

Intercept (K0) = $(618.4 \pm 6.5)^\circ\text{C}$; Standard model error = 7.24°C ; $R^2 = 0.983$

T(isokom, average) = 561.7°C ; σ of all T(isokom) values = 52.2°C ; signal/noise ratio = 123.8

Table V one three-component coefficient needs to be considered: $K3(\text{Al}_2\text{O}_3*\text{CaO}*\text{Na}_2\text{O}) = -0.0285$.

- 4) Next, all single-components coefficients must be multiplied with the applicable concentrations, the obtained products have to be added, as well as the intercept. For glass 710A at $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$, the single-component contribution is:
 $1816.4 + 4.35 \times 1.31 - 18.00 \times 9.62 - 25.10 \times 8.25 - 19.21 \times 6.27 - 9.42 \times 2.81 = 1294.95$
- 5) Next, add the applicable 2, and/or 3- interaction coefficients from Table III multiplied by the corresponding mol% composition. The result is:
 $1294.95 + 0.761 \times 1.31 \times 8.25 + 0.215 \times 9.62 \times 8.25 = 1320$, which is the temperature in $^\circ\text{C}$ at which the viscosity of the glass 710A is predicted to be $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$.
- 6) Similarly for $\log(\eta/\text{Pa}\cdot\text{s}) = 6.6$ we obtain 727°C using the coefficients in Table IV, and for $\log(\eta/\text{Pa}\cdot\text{s}) = 12.0$ we obtain 546°C using the coefficients in Table V.

- 7) By fitting the three temperature-viscosity points from step 6) to the VFT equation, we attain the complete viscosity curve: $\log(\eta/\text{Pa}\cdot\text{s}) = -2.753 + 4625 / (T \text{ in } ^\circ\text{C} - 232.5)$. Those findings are the same as the data in the original NIST certificate within the range of the model errors established in this work.

Compared to viscosity data of investigators not included in this study [16-19], the models in this work result in the same findings approximately within the error ranges stated in Tables III-V.

DISCUSSION

The principle of the viscosity models presented in this study is proposed as a basis for the systematization of glass property data in the literature. To the authors' knowledge, the models in this paper are based on more data than in any previous work, *without* having any a priori knowledge of the details of bonding, e.g. as in [13, 14]. The models presented are mathematical in principle, and as a result they are able to incorporate various glass structures. For technical glasses the models in this study are superior to previous works [3, 7, 11, 15, 16] by maintaining or improving the prediction accuracy, and/or by extending the composition area covered, and through an advanced data analysis technique.

Multiple regression on mol% basis allows separating various influences: The interaction coefficients in combination with those for single components confirm that glass is neither an ideal random mixture of its components, nor a perfectly stoichiometric chemical compound, but an intermediate of both. Preferred short-range and intermediate-range structures exist, in addition to having the influences of single components.

The NIST viscosity standards 711, 710A, and 717A fit well into the models with residuals less than 4°C. The only exception occurs for 717A at $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$ where the residual is -9.5°C. The standards 711 and 717A are the only glasses that have a significantly higher influence (leverage) on the model results at $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$ and 6.6 respectively than all other glasses; the Cook distances [20, 21] are higher than one. A model extension to additional borosilicate glasses and lead silicates, as well as an exact chemical analysis of 711 and 717A may reduce the leverage.

Viscosity values of investigators in the literature that fall into the composition and interaction ranges of this work, but with viscosity isokom residuals larger than three times the model errors in Tables III, IV, and V may be questionable and should be analyzed further.

The large offsets in the data from Allison & Turner [5], determined in the models presented in this work (Tables III, IV, V), need further examination despite appearing to be thorough. Little is said regarding the calibration of the Pt/Pt-Rh thermocouple data acquisition system and pyrometer used. Also, no viscosity standard had been established yet by the time the paper [5] was published. The two trend coefficients in Table II are just on the limit to be significant, and it is hardly possible to distinguish them from offset corrections of ~5°C. Consideration of additional viscosity-composition data could result in further improvements. The combination of trend and offset to a linear correction may be advisable in future studies.

The single-component coefficients in this model have the unit K/mol%; they correspond to the temperature change (+/-) needed by an increase of 1 mol% oxide in exchange for 1 mol% SiO₂ to maintain the same viscosity. E.g. if at the glass softening point ($\log(\eta/\text{Pa}\cdot\text{s}) = 6.6$) 1 mol% MgO is introduced into a silicate glass in exchange for 1 mol% SiO₂, the temperature may be increased 4°C for maintaining the same viscosity due to MgO, plus further variations due to MgO interactions.

The model intercepts K_0 are supposed to represent the viscosity isokom temperatures of the residual comprising mainly SiO_2 , and traces of minor components not considered here, such as H_2O , fining agents, transition element oxides etc. Glasses with silica concentrations above ~ 85 mol% do not fit into this study (Table I).

Lakatos [3] was one of the first to estimate single-component influences over wide temperature ranges through a solely mathematical model with remarkable success. By including 2-, and 3-component interactions, our model is a step forward in expanding the compositional range over which glass properties may be estimated.

There are some interesting single-component influences observed in Table V. For instance, in the glass transformation range, BaO should not influence the viscosity whereas SrO should. This is supported by re-plotting experimental data of twenty-five TV panel glasses, all containing SrO and/or BaO within limited composition ranges, taken from Ref [6]. Linear relations applicable for $\log(\eta/\text{Pa}\cdot\text{s}) = 6, 7, 8, 9, 10, 11,$ and 12 from these data were constructed and the viscosity isokom coefficients calculated. The results, shown in Figure 1, support the premise that BaO and SrO influence viscosity less and less at lower temperatures; SrO substituting for SiO_2 may even increase the viscosity around T_g .

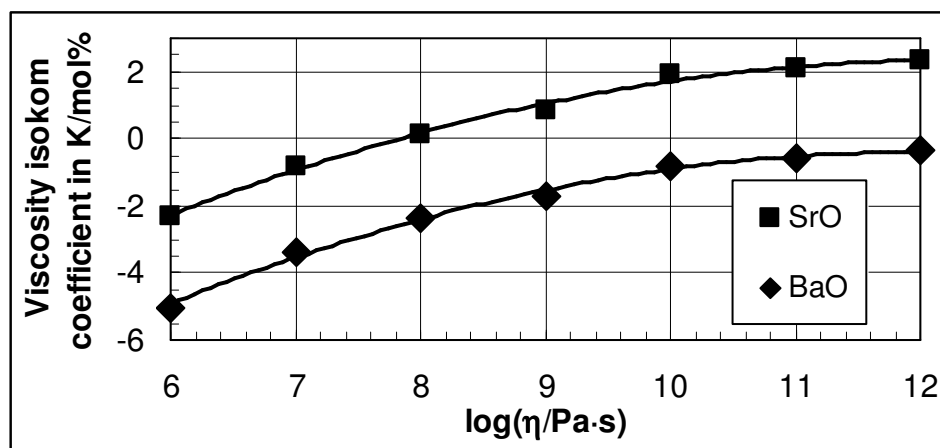


Fig. 1: Linear viscosity isokom coefficients of SrO and BaO in TV panel glasses

The fact that CaO increases the viscosity around T_g , but MgO decreases it, is supported by Lakatos [3]. One may wonder why substitutions by ZrO_2 have an insignificant influence at $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$ but significant, on the other hand, at higher viscosities. The ZrO_2 concentrations in this study may be too low for a detailed analysis of the ZrO_2 influence.

For direct comparisons of single-component coefficients with interaction coefficients it is necessary to calculate the square root for two-component interactions, and the cube root for three-component interactions respectively. Because many interactions had to be excluded in this work due to correlations, a model extension to additional glass composition-viscosity data is advisable.

The well-known boric oxide anomaly is represented in the models through the $\text{B}_2\text{O}_3*\text{Na}_2\text{O}$ and $\text{B}_2\text{O}_3*\text{K}_2\text{O}$ interactions. It is known, for instance see Akimov [22], that the increase in viscosity due to alkali additions around 13 mol% (a characteristic of "the boric oxide anomaly") decreases with increasing temperature. This gradual disappearance of boric oxide anomaly at higher temperatures is clearly substantiated by examining the $\text{B}_2\text{O}_3*\text{Na}_2\text{O}$ interactions listed in Tables III, IV and V which, actually, become negative around $\log(\eta/\text{Pa}\cdot\text{s}) = 1.5$. Besides boric

oxide, Al_2O_3 also shows strong interactions, even though the Al_2O_3 concentrations are mostly low (Table I). Additional research is required. The well-known "mixed alkali effect" could not be analyzed so far because the influence of K_2O and the $\text{Na}_2\text{O}*\text{K}_2\text{O}$ interaction could not be isolated within the composition matrices used here. The influence of Fe_xO_y could not be separated into the component contributions of the various oxidation states because of limited data.

The successful incorporation of two alkali-free borosilicate glasses mentioned in the introduction with $\text{C}(\text{SiO}_2) \sim 20$ mol% into the model at $\log(\eta/\text{Pa}\cdot\text{s}) = 6.6$, may demonstrate further potential of the technique established here. The influence of the two glasses on the model result was insignificant (Cook distance < 0.02). Even though the chemical compositions were very uncommon, it was still possible to relate them directly to "ordinary" industrial soda-lime glasses and borosilicates through the modeling procedure. To the authors' knowledge, this was not done before without structural assumptions.

It is possible that the models presented in this study could be refined by including even those glass property data where only the batched composition is known. In particular, a large volume of T_g data could be incorporated. According to Priven [13], traditionally reported T_g for glasses may be approximated to $\log(\eta/\text{Pa}\cdot\text{s}) \sim 12.3$ and the current model could be shifted from $\log(\eta/\text{Pa}\cdot\text{s}) = 12.0$ to 12.3 for use in the industry.

Future extensions may also include changing to a canonical model* to describe all existing glasses, including non-oxide glasses.

CONCLUSIONS

This study is proposed to be a first step to modeling of glass properties on a global basis. In this paper, the viscosity of a large number of silicate glasses with widely varying compositions have been modeled in terms of single component influence and mutual interactions. Some important glass components are not included as yet. A number of interactions are correlated too strongly for analysis within the composition ranges covered. Notwithstanding these shortcomings, success is demonstrated in the estimation of viscosity from chemical composition.

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REFERENCES

¹A. Winkelmann, O. Schott: "Über die Elastizität und über die Druckfestigkeit verschiedener neuer Gläser in ihrer Abhängigkeit von der chemischen Zusammensetzung"; Ann. Physik Chemie, vol. 51, 1894, p 697; and "Über thermische Widerstandskoeffizienten verschiedener Gläser in ihrer Abhängigkeit von der chemischen Zusammensetzung ", vol. 51, 1894, p 730; and "Über die spezifischen Wärmen verschieden zusammengesetzter Gläser", vol. 49, 1893, p 401

²A. I. Priven, O. V. Mazurin: "Comparison of methods used for the calculation of density, refractive index and thermal expansion of oxide glasses"; Glass Technol., 44 (4), 2003, p 156-166

* A canonical model would be very similar to Eq. (1). It would include silica and all silica interactions, the intercept K_0 would be zero, and no squared terms would be allowed. Eq. (1) does not contain squared terms already because of strong correlations with single-component factors.

³T. Lakatos, L.-G. Johansson and B. Simmingsköld, "Viscosity temperature relations in the glass system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-CaO-MgO}$ in the composition range of technical glasses"; *Glass Technology* Vol. 13 No. 3, June 1972, p 88-95

⁴Owens-Illinois Glass Company, General Research Laboratory: "Effect of Barium Oxide and Zinc Oxide on the Properties of Soda-Dolomite Lime-Silica Glass" *J. Am. Ceram. Soc.*, vol. 25, no. 3 (1942), p 61-69; "Effect of Iron Oxide on the Properties of Soda-Dolomite Lime-Silica Glass" *J. Am. Ceram. Soc.*, vol. 25, no. 14 (1942), p 401-408; "Effect of Substituting MgO for CaO on Properties of typical Soda-Lime Glasses" *J. Am. Ceram. Soc.*, vol. 27, no. 8 (1944), p 221-225; "Effect of Fluorine and Phosphorus Pentoxide on Properties of Soda-Dolomite Lime-Silica Glass" *J. Am. Ceram. Soc.*, vol. 27, no. 12 (1944), p 369-372; "Effect of Boric Oxide on Properties of Soda-Dolomite Lime-Silica Glass" *J. Am. Ceram. Soc.*, vol. 31, no. 1 (1948), p 8-14; "Effect of K_2O and Li_2O on Properties of Soda-Dolomite Lime-Silica Glasses" *J. Am. Ceram. Soc.*, vol. 33, June (1950), p 181-186

⁵R. S. Allison, W. E. S. Turner; "Further Investigations upon the Influence of Boric Oxide on the Rate of Melting of the Batch, and on the Rate of Refining and of Setting of Commercial Glasses of the Soda-Lime-Silica Type"; *J. Soc. Glass Technol.*, 1954, vol. 38, No. 182, p 297

⁶<http://www.osti.gov/servlets/purl/809193-hMV00M/native/> (full publication in preparation)

⁷A. Fluegel, A. K. Varshneya, T. P. Seward, D. A. Earl "Viscosity of commercial glasses in the softening range"; in: *Proceedings 7th International Conference, Advances in Fusion and Processing of Glass III* (Ceramic Transactions, Volume 141; Eds.: J. R. Varner, T. P. Seward, H. Schaeffer), Rochester, New York, USA, July 27-31, 2003

⁸C. A. See, O. P. Lam, K. B. C. Minister, P. R. Hrma, "Viscosity of Commercial Glasses – Data Package", prepared for the U.S. Department of Energy under Contract DE-AC06-76RL01830, Pacific Northwest National Laboratories, March 2003

⁹A. K. Varshneya, "Fundamentals of Inorganic Glasses", Academic Press, Boston 1993

¹⁰A. K. Varshneya, N. H. Burlingame and W. H. Schultze, "Parallel Plate Viscometry to Study Deformation-Induced Viscosity Changes in Glass"; *Glastechn. Ber.* 63K (1990), 447-459

¹¹M. B. Volf; "Mathematical Approach to Glass"; *Glass Science and Technology*, vol. 9, Elsevier, 1988

¹²<http://cgr.alfred.edu/meltprops/meltprops.html> & <http://glassproperties.com>

¹³A. I. Priven, "Calculation of the Viscosity of Glass-Forming Melts: VI. The $\text{R}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ and $\text{RO-B}_2\text{O}_3\text{-SiO}_2$ Ternary Borosilicate Systems"; *Glass Physics and Chemistry*, vol. 27, no. 4, 2001, p 360-370

¹⁴A. I. Priven, "Calculation of the Viscosity of Glass-Forming Melts: IV. A Unified Method for Calculating the Viscosity of Silicate and Aluminate Melts"; *Glass Physics and Chemistry*, vol. 24, no. 1, 1998, p 31-40

¹⁵K. C. Lyon, "Prediction of the Viscosities of Soda-Lime Silica Glasses"; *J. Res. Nat. Bur. Standards A, Physics and Chemistry*, vol. 78A, no. 4, July-Aug 1974, p 497-504

¹⁶D. Öksoy, D. L. Pye, E. N. Boulos; "Statistical analysis of viscosity-composition data in glassmaking" *Glastechn. Ber. Glass Sci. Technol.* 67 (1994), no. 7, p 189-195

¹⁷H. A. Robinson, C. A. Peterson, "Viscosity of recent container glass"; *J. Am. Ceram. Soc.*, vol. 27, no. 5, 1944, p 129

¹⁸A. Napolitano, E. G. Hawkins, "Viscosity of a standard soda-lime-silica glass"; *J. Res. Nat. Bur. Stand.*, vol. 68A, no. 5, 1964, p 439

¹⁹O. G. Burch, C. L. Babcock, "Effect of glass color on sintering rates in manufacture of glass bottles"; *J. Am. Ceram. Soc.*, vol. 21, no. 10, 1938, p 345

²⁰D. G. Montgomery, "Design and Analysis of Experiments", John Wiley & Sons, 2001

²¹S. Dowdy and S. Wearden, "Statistics for Research", John Wiley & Sons, 1983

²²V. V. Akimov, "Viscosity of sodium borosilicate glasses in the glass transition range", The Soviet Journal of Glass Physics and Chemistry, Fizika i Khimiya Stekla, 1991, vol. 17, no. 4, p 348; and No. 5, p 425

²³C. J. R. Gonzalez-Oliver, P. S. Johnson, P. F. James, "Influence of water content on the rates of crystal nucleation and growth in Lithia-silica and soda-lime-silica glasses"; J. Mater. Sci., vol. 14, no. 5, 1979, p. 1159

APPENDIX

Table VI: Isokom temperatures in °C at $\log(\eta / Pa \cdot s) = 1.5$ from ref. [6]; values in parentheses are extrapolated/questionable; 00 - base glasses, TV - TV panel glasses, E - E-type textile fiber glasses, LE - Low expansion borosilicate glasses, Co - Container glasses, FL - Float glasses, Wo - Wool fiber glasses

#	TV	E	LE	Co	FL	Wo
00	1301.4	1273.7	(1690.0)*	1323.1	1299.1	1163.0
01	1351.8	(1612.6)*	(1724.6)*	1458.0	1395.9	(1359.2)
02	1456.8	1491.8	(1624.2)*	1350.4	1259.5	1309.1
03	1437.7	1269.3	1365.7	1205.7	(1316.0)	(1125.0)
04	1488.6	1491.8	(1934.8)*	1306.4	1245.8	1281.6
05	1398.2	1295.2	1446.2	1244.3	1247.5	(1167.3)
06	1168.8	1299.7	1480.1*	1218.3	1225.7	(1129.5)
07	1168.7	(1353.6)	1467.5	1317.5	1295.0	1086.5
08	1195.0*	1206.1	1342.3	1373.8	1250.4	(1054.1)
09	1150.1	(1163.8)	1242.6*	1220.4	1332.7	(1061.8)*
10	1171.7	1207.3	1503.2*	1345.9	1250.1	(1095.9)
11	1251.6	1249.3	1564.2*	1225.3	1236.0	(1100.0)
12	1195.0	1294.9	(1749.3)*	1352.6	1306.0	1226.1
13	1241.5	1321.2	(1137.3)*	1304.8	1300.1	1163.0
14	1122.2	1359.3	1472.2	1375.7	1291.5	1269.6
15	1298.2	1424.8	1506.5	1244.7	1272.8*	1175.9
16	1315.9	1506.8	/	1392.6	1293.9	1368.6
17	1158.7	1406.3	(1703.2)*	1225.3	1313.4	1251.7
18	1237.2	1293.2	(1547.6)*	1258.3	1282.0	/
19	1308.6	1367.7	(1220.5)*	1354.2	1349.7	1104.4
20	1342.8	/	1578.0*	1394.6	1265.9	1210.1
21	1236.5	1186.1	1321.9	1300.5	1327.7	1221.4*
22	1276.1	1381.6	(1799.0)*	1400.5	1323.2	1173.9*
23	1359.1	1174.7	1333.9	1294.4	1345.5	1058.3
24	(1551.8)	(1088.0)	1270.6	1158.6	1367.9	963.2

* Marked data had to be excluded during the regression analysis, because they were designated as outliers at one step.

Table VII: Isokom temperatures in °C at $\log(\eta/Pa \cdot s) = 6.6$ from ref. [6]; values in parentheses are extrapolated/questionable; 00 - base glasses, TV - TV panel glasses, E - E-type textile fiber glasses, LE - Low expansion borosilicate glasses, Co - Container glasses, FL - Float glasses, Wo - Wool fiber glasses

#	TV	E	LE	Co	FL	Wo
00	700.7	846.2	806.7	730.8	721.0	677.8
01	700.9	(999.6)*	831.6	765.4	746.8	724.4
02	700.4	928.0	/	762.5	705.8	692.8
03	684.2*	861.1	758.8	681.3	690.3	657.6
04	775.7	921.4	832.9	712.2	694.0	695.6
05	787.4	901.3	763.7	655.9	688.9	679.4
06	696.5	870.4	769.5	686.1	690.9	682.4
07	686.7	819.7	767.6	710.3	729.8	671.4
08	690.5*	829.7	752.7	714.9	707.4	681.8
09	621.7	778.3	733.6	683.0	734.1	663.4
10	629.9	827.2	749.1	720.8	702.9	676.2
11	667.8	822.4	769.1	705.0	689.8	649.4
12	671.2	856.7	829.9*	776.8	727.8	718.2
13	709.2	872.6	763.4	685.9	735.0	654.8
14	646.6	914.2	785.6	710.0	708.9	729.2
15	703.7	907.1	792.4	706.9	699.9	672.7
16	700.3	958.7	/	751.9	719.5	713.8
17	648.5	896.2	824.0	713.7	735.5	700.6
18	702.2	910.2	779.5	704.6	708.9	709.0
19	650.8*	844.0	763.7	728.3	731.8	687.9
20	703.0	/	/	789.2	711.8	696.3
21	664.3	823.1	741.1	711.9	723.0	706.0
22	688.2	873.4	822.2*	754.7	742.6	705.8
23	687.9	810.6	733.5	683.8	737.5	661.3
24	765.9	779.5	720.8	662.4	735.5	627.5

* Marked data had to be excluded during the regression analysis, because they were designated as outliers at one step.

Table VIII: Isokom temperatures in °C at $\log(\eta/Pa \cdot s) = 12.0$ from ref. [6]; 00 - base glasses, TV - TV panel glasses, E - E-type textile fiber glasses, LE - Low expansion borosilicate glasses, Co - Container glasses, FL - Float glasses, Wo - Wool fiber glasses

#	TV	E	LE	Co	FL	Wo
00	521	663	554*	564	551	543
01	507	/	594	573	561	556
02	483	742*	/	589	520	/
03	487*	698	591	531	521	529
04	558	709	579	540	538	/
05	591	699*	587	496	529	548
06	532	705	595	530	542	555
07	520	645	566	/	555	549
08	529	/	581	532	543	556
09	474	632	576	538	559	/
10	474	665	558	538	546	558
11	496	654	570	552	528	/
12	498	677	583*	604	559	563
13	538	699	594*	524	562	522
14	496*	725	600	524	538	566
15	507	705	600	557	552	518
16	515	740	/	560	546	/
17	489	707	591	559	566	551
18	532	737	592	543	542	564
19	473	658	553*	559	550	548
20	506	656	/	611	551	/
21	491	661	582	548	550	569
22	522	681	560*	569	571	564
23	502	652	566	523	552	/
24	520	630	571	517	554	/

* Marked data had to be excluded during the regression analysis, because they were designated as outliers at one step.