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VISCOSITY OF COMMERCIAL GLASSES IN THE SOFTENING RANGE

Alexander Fluegel, Arun K. Varshneya, Thomas P. Seward, and David A. Earl
New York State College of Ceramics
Alfred University
2 Pine Street
Alfred, NY 14802

ABSTRACT

The medium range viscosity (log viscosity / Pa·s = 6 to 9) is of vital interest for forming and annealing in the glass industry. It is essential for the design of melting and annealing furnaces, as well as for the forming processes. In this work we determined the viscosity of 150 glass composition variations centered on the float, container, low-expansion borosilicate, TV panel, wool, and textile fiber glasses by parallel-plate viscometry. The composition-viscosity relationship was calculated through multiple regression.

INTRODUCTION

This study was part of a larger project of the NSF Industry/University Center for Glass Research (CGR) [1] to give the glass industry a database and a method for calculating the properties of technical glass melts within the composition and temperature limits of interest. 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 (η / Pa·s) = 1-12 by various groups. In this paper we concentrate on container, low-expansion borosilicate, textile fiber, and TV panel glasses within the range of log (η / Pa·s) = 6-9, as measured by parallel-plate viscometry.

EXPERIMENTAL DESIGN AND PROCEDURE

Experimental design

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. Twenty-five variations of a glass group with five independent variable components (converted to mol oxide / mol SiO_2) would allow for analysis using a full quadratic model, including all linear effects, 2-component interactions and squared terms. Even though each of the glass groups contained more than five variable components, not more than twenty-five variations per group were designed in order to keep the experimental work within reasonable limits. Therefore, full quadratic models could not be developed, and some of the 2-component interactions were partially aliased. Model coefficients were selected based on their individual significance levels using a stepwise regression procedure.

Glass preparation

Glass batches (1-2 kg) were prepared from analytical-grade chemicals: silica, alkali and alkali-earth carbonates, Al_2O_3, H_3BO_3, Na_2SO_4, Fe_2O_3, Co_2O_3, Cr_2O_3, TiO_2, ZrO_2, NaF, CeO_2, PbO, ZnO, Sb_2O_3, As_2O_3. The batches were ball-milled for two hours and melted for 4-5 hours in a platinum crucible at 1400-1600^{o}C. The melts were poured into a steel mold, cooled, crushed, re-melted for ~30 minutes, poured into a steel mold again, and annealed. All glasses were made either at Alfred University (container, float, and wool glasses) or at Corning Inc (TV panel, low-expansion borosilicate, and textile fiber glasses). Three of the low-expansion borosilicate glasses and two of the textile fiber glasses proved to be unsuitable for further analysis due to phase separation and/or crystallization.

All glasses were analyzed chemically by Corning Laboratory Services (Corning, NY) and Integrex Testing Systems (Granville, OH).

Following the chemical analysis, a linear correlation analysis (Pearson's matrix) [2] of the variable component levels showed no correlation between the linear coefficients and partial aliasing regarding 2-component interactions and squared terms.

Parallel-plate viscometer measurements

The principles of parallel-plate viscometry are described by Varshneya [3]. For this study, a Theta model "Rheotronic R" parallel-plate viscometer was used. The temperature reading and the LVDT displacement of the viscometer were calibrated first, using a thermocouple calibration multimeter, and samples of known height re-

spectively. A NIST viscosity standard 710A (soda-lime glass) was used for calibration. The standard deviation of all repeated 710A measurements over the 620-820°C range was 0.4°C. The calibration was confirmed by NIST standard 717A (borosilicate glass) from 600-780°C. During calibration with the NIST standards, no error trend was observed over temperature and time, assuming a constant temperature distribution within the furnace during all measurements. In addition, no temperature trend was observed over the cross-section of the vertical furnace chamber.

Cylindrical samples (diameter 8.5-9 mm, height 4-6 mm) were prepared through core drilling and grinding off both ends until they were parallel to ± 10 µm. The accuracy of the sample dimensions was sufficient, as demonstrated by the repeated 710A calibration runs mentioned above. The samples were placed into the viscometer between two thin electronic-grade alumina substrates. The applied load was 500 g, and the heating rate was 1 K/min. A data logger recorded the temperature and the sample height every 20 seconds, where the expansion of the silica push rod was compensated automatically through a reference rod directly adjacent to it. Additionally, the expansion of the alumina substrates was compensated. Next, the viscosity was calculated within the range of circa $dh/dt < 10^{-5}$ cm/s, assuming no-slip conditions to the contacting alumina substrates, as established by Varshneya [4]:

$$\eta = \frac{2 \cdot \pi \cdot M \cdot g \cdot h^5}{3 \cdot V \cdot dh/dt \cdot (2 \cdot \pi \cdot h^3 + V)} \qquad (1)$$

where η = viscosity in Pa·s; M = applied load; g = gravity acceleration; h = sample height; V = sample volume; dh/dt = deformation or sag rate. Next, the isokom temperatures for log (η / Pa·s) = 6, 7, 8, and 9 were calculated, after fitting the experimental data to the Vogel-Fulcher-Tammann equation. The standard deviation of the temperature errors during repeated viscosity measurements of different sections of the same glasses due to inhomogeneities in the glasses and due to other experimental irregularities was 2°C. This means that the standard error of the viscosity models must be > 2°C, otherwise the model error would be unrealistically low due to "over-fitting."

Multiple regression analysis

Multiple regression analysis was done in the programs "Design Expert" and "Multiple Correlation Analysis" with the analyzed concentrations in mol / mol SiO_2, as independent variables, and the four isokom temperatures in °C as dependent variables. All data sets proved to be suitable for the analysis. Initially, linear fits including all glass components were performed for each isokom temperature. No outliers were found within all data sets analyzed. Then, a component was excluded from the model if there was less than a 90% confidence level in its significance ("Student-t" test parameter << 2), which resulted in a reduction of the model standard error. Finally,

all 2-component interactions and non-linear influences were analyzed stepwise based on the model:

$$T_{isokom} = F0 + \sum_{j=1}^{n} \left(F1_j \cdot C_j + F2j \cdot C_j^2 + \sum_{k=j+1}^{n} (F3_k \cdot C_j \cdot C_k) \right) \quad (2)$$

where F0-F3 are the model coefficients, with F0 being the intercept, F1 the linear coefficients, F2 the squared terms of the same component, and F3 the coefficients for 2-component interactions. All F2 and F3 were set to zero for the linear models. The n in Eg. (2) is the total number of glass components (excluding silica), j and k are individual numbers of the glass components, and C are the analyzed concentrations in mol / mol SiO_2. In cases where 2-component interactions were partially aliased, the most significant interaction was selected for the model, resulting in the lowest model error.

RESULTS

Table I. Compositions of the investigated glasses in mol%, as analyzed

LO	**SiO_2**	**B_2O_3**	**Al_2O_3**	**CaO**	**Na_2O**	**K_2O**	**BaO**				
Avg:	77.30	11.33	2.84	1.06	6.08	0.96	0.43				
Min:	66.89	8.01	1.25	0.00	3.07	0.00	0.00				
Max:	86.21	14.28	4.67	2.43	8.95	2.19	0.89				
Co	**SiO_2**	**Al_2O_3**	**MgO**	**CaO**	**Li_2O**	**Na_2O**	**K_2O**	**Fe_2O_3**	**Cr_2O_3**	**TiO_2**	**SO_3**
Avg:	72.17	1.24	2.24	10.14	0.87	12.25	0.66	0.08	0.06	0.19	0.10
Min:	62.90	0.60	0.02	7.18	0.00	9.76	0.01	0.01	0.00	0.01	0.01
Max:	81.27	1.94	5.03	13.25	2.13	14.79	1.37	0.18	0.13	0.41	0.22
E	**SiO_2**	**B_2O_3**	**Al_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**Fe_2O_3**	**TiO_2**	**F^-**	
Avg:	58.88	4.07	8.22	4.00	22.32	1.02	0.16	0.16	0.39	0.78	
Min:	42.62	0.00	5.77	0.69	15.17	0.00	0.00	0.00	0.00	0.00	
Max:	73.60	8.45	9.99	8.79	28.05	2.27	0.37	0.33	0.81	1.93	
TV	**SiO_2**	**Al_2O_3**	**MgO**	**CaO**	**SrO**	**BaO**	**Li_2O**	**Na_2O**	**K_2O**	**TiO_2**	**CeO_2**
Avg:	70.04	1.63	1.16	1.93	3.74	3.43	0.55	8.36	5.42	0.26	0.14
Min:	62.16	0.76	0.00	0.00	0.61	0.80	0.00	5.83	4.08	0.06	0.00
Max:	87.10	2.62	2.68	4.26	7.03	6.31	1.29	11.34	6.84	0.46	0.30
	ZrO_2	**PbO**	**ZnO**	**As_2O_3**	**Sb_2O_3**	**F^-**					
Avg:	0.82	0.44	0.65	0.05	0.10	1.27					
Min:	0.00	0.00	0.00	0.00	0.04	0.00					
Max:	1.76	0.96	1.65	0.11	0.17	3.01					

LO - low-expansion borosilicate, Co - container, E - textile fiber, TV - TV panel

Table I shows the average, minimum, and maximum concentrations in mol% of the investigated glasses, as analyzed chemically. "LO" symbolizes the low-expansion borosilicate glasses, "Co" the container glasses, "E" textile fiber glasses, and "TV" the TV panel glasses. The concentration ranges (max-min) of the individual components in mol / mol SiO_2 (SiO_2 average), multiplied by the corresponding linear model coefficients shown below give approximations concerning the relative influences of the components, and the significance/error ratio can be calculated from the standard deviations in Tables II-IV.

Table II. Model coefficients for the low-expansion borosilicate glasses

LO	$F1_{B2O3}$	$F1_{Al2O3}$	$F1_{CaO}$	$F1_{Na2O}$	$F1_{K2O}$	$F1_{BaO}$	F0	$F3_{AlB}$	$F3_{AlNa}$	$F3_{KNa}$	σ
6	-405.1	766.9	-140.2	-1044	-934.3	-400.2	955.2	0	0	0	**13.9**
7	-374.0	523.5	7.9	-753.3	-693.6	-15.5	863.5	0	0	0	**10.9**
8	-355.6	356.4	131.2	-537.9	-527.6	151.9	796.8	0	0	0	**9.0**
9	-344.5	234.1	233.9	-371.2	-405.1	212.7	746.2	0	0	0	**8.1**
6	-425.1	743.2	0	-1074	-984.4	0	958.3	0	0	0	**13.4**
7	-374.6	524.5	0	-753.5	-694.0	0	863.6	0	0	0	**10.2**
8	-346.9	376.5	0	-520.5	-500.1	0	795.5	0	0	0	**8.7**
9	-331.4	269.4	0	-343.3	-361.1	0	744.2	0	0	0	**8.6**
6	-207.9	2376	0	-1142	-3208	0	934.0	-6026	-8438	26104	**9.2**
7	-272.7	1663	0	-710.5	-2232	0	846.4	-3017	-7988	18144	**7.0**
8	-312.7	1205	0	-399.3	-1527	0	781.3	-1219	-7553	12214	**6.6**
9	-339.2	890.4	0	-164.5	-986.8	0	731.1	-81.11	-7127	7569	**7.4**

In Tables II-IV the model coefficient data are presented in three sets of four rows. The first column shows the viscosity levels (log (η / Pa·s) = 6, 7, 8, 9) the coefficients are valid for. The first set of four rows corresponds to the linear model including all components, the second set of four rows excludes insignificant components from the linear model, and the last set includes significant components plus interactions and non-linearities. Beginning with the second column, the linear coefficients F1 for each component and the intercept F0 are displayed. Then follow the coefficients for the non-linear models: $F3_{AlB}$-(Al_2O_3)*(B_2O_3), $F3_{AlNa}$-(Al_2O_3)*(Na_2O), $F3_{KNa}$-(K_2O)*(Na_2O), $F2_{Na}$-$(Na_2O)^2$, $F3_{AlCa}$-(Al_2O_3)*(CaO), $F3_{LiNa}$-(Li_2O)*(Na_2O), $F2_B$-$(B_2O_3)^2$. Finally, the last column gives the model standard error σ for each viscosity level in °C.

All coefficients are valid only within the concentration range stated in Table I. When divided by 100, the coefficients equal the temperature change (+/-) needed by an increase of 0.01 mol oxide (or interaction) / mol SiO_2 in the base glass to maintain the same viscosity.

Table III. Model coefficients for the container (Co) and textile fiber (E) glasses

Co	$F1_{Al2O3}$	$F1_{MgO}$	$F1_{CaO}$	$F1_{Li2O}$	$F1_{Na2O}$	$F1_{K2O}$	$F1_{Fe2O3}$	$F1_{Cr2O3}$	$F1_{TiO2}$	$F1_{SO3}$	F0	$F2_{Na}$	$F3_{AlCa}$	$F3_{AlNa}$	$F3_{LiNa}$	σ
6	823.2	-32.9	74.5	-1858	-764.5	-756.5	427.3	2390	-239.8	1405	885.5	0	0	0	0	**8.6**
7	781.3	-11.2	147.2	-1811	-670.1	-714.9	781.8	3214	-115.1	1671	800.2	0	0	0	0	**7.5**
8	698.8	-8.4	185.6	-1767	-613.8	-723.0	924.4	2921	-75.5	1510	744.9	0	0	0	0	**7.3**
9	611.7	-12.4	207.9	-1728	-576.8	-745.5	964.0	2243	-67.3	1208	706.1	0	0	0	0	**7.8**
6	840.5	0	78.0	-1861	-755.0	-745.7	0	0	0	0	885.6	0	0	0	0	**8.1**
7	810.5	0	152.8	-1803	-652.1	-696.3	0	0	0	0	800.6	0	0	0	0	**7.5**
8	728.1	0	191.1	-1756	-596.5	-706.1	0	0	0	0	745.3	0	0	0	0	**7.2**
9	636.6	0	212.3	-1717	-563.4	-733.6	0	0	0	0	706.4	0	0	0	0	**7.3**
6	2544	0	111.0	-3942	-2762	-705.5	0	0	0	0	1052	5709	-4674	-6249	11894	**3.9**
7	2921	0	204.7	-3852	-2237	-640.8	0	0	0	0	925.7	4581	-5374	-7946	11731	**3.5**
8	2615	0	238.8	-3715	-2357	-660.1	0	0	0	0	887.1	5049	-5246	-6793	11205	**2.9**
9	2098	0	248.9	-3569	-2673	-704.8	0	0	0	0	881.6	5972	-4860	-4714	10572	**2.7**

E	$F1_{B2O3}$	$F1_{Al2O3}$	$F1_{MgO}$	$F1_{CaO}$	$F1_{Na2O}$	$F1_{K2O}$	$F1_{Fe2O3}$	$F1_{TiO2}$	$F1_{F-}$	F0	$F2_{B}$	σ
6	-575.5	486.8	-149.6	-192.7	-628.7	482.7	550.0	252.9	-205.8	963.1	0	**14.4**
7	-538.5	427.5	-130.9	-141.2	-653.1	481.8	456.9	227.6	-275.4	901.9	0	**12.9**
8	-513.5	378.4	-119.8	-104.6	-651.4	459.9	434.2	201.7	-328.8	855.4	0	**11.9**
9	-496.2	337.2	-113.3	-77.6	-636.8	427.2	446.5	177.0	-371.6	818.9	0	**11.3**
6	-572.5	480.6	-144.2	-191.8	-640.6	0	0	0	0	965.2	0	**13.3**
7	-533.1	411.8	-123.0	-142.1	-671.8	0	0	0	0	904.4	0	**12.3**
8	-506.5	355.3	-109.8	-106.8	-675.1	0	0	0	0	858.3	0	**11.8**
9	-487.9	308.3	-101.6	-80.8	-664.2	0	0	0	0	822.1	0	**11.6**
6	-1157	303.2	-140.6	-220.6	-806.4	0	0	0	0	1004	4143	**11.8**
7	-1052	254.4	-119.9	-167.6	-818.9	0	0	0	0	938.5	3675	**11.1**
8	-977.0	212.7	-107.0	-129.9	-808.5	0	0	0	0	889.2	3332	**10.8**
9	-921.0	177.0	-99.0	-102.1	-787.0	0	0	0	0	850.6	3067	**10.7**

All coefficients not shown in Tables II and III are insignificant.

Table IV. Model coefficients for the TV panel glasses

TV	$F1_{Al2O3}$	$F1_{MgO}$	$F1_{CaO}$	$F1_{SrO}$	$F1_{BaO}$	$F1_{Li2O}$	$F1_{Na2O}$	$F1_{K2O}$	$F1_{TiO2}$	All linear coefficients not shown in this Table are zero. Non-linear coefficients were not analyzed.
6	906.0	70.1	390.4	-29.5	-197.3	-1492	-813.0	-389.4	-3277	
7	801.3	88.2	465.4	52.3	-111.3	-1406	-740.5	-351.9	-2551	
8	757.1	99.6	504.3	104.0	-61.3	-1366	-680.6	-325.5	2011	
9	744.3	106.4	523.7	138.1	-31.6	-1351	-630.1	-305.9	-1594	

	$F1_{CeO2}$	$F1_{ZrO2}$	$F1_{PbO}$	$F1_{ZnO}$	$F1_{As2O3}$	$F1_{Sb2O3}$	$F1_{F-}$	**F0**	σ
6	-1512	818.1	-1237	-424.4	5417	-5274	-802.0	884.9	**16.0**
7	-954.5	849.0	-1153	-378.4	5998	-3292	-801.9	794.7	**14.3**
8	-635.0	841.0	-1109	-350.2	6561	-2443	-788.0	728.0	**13.1**
9	-442.6	815.5	-1089	-334.2	7112	-2171	-768.8	676.6	**12.2**

TV	$F1_{Al2O3}$	$F1_{CaO}$	$F1_{SrO}$	$F1_{BaO}$	$F1_{Li2O}$	$F1_{Na2O}$	$F1_{K2O}$	$F1_{TiO2}$	$F1_{ZrO2}$	$F1_{PbO}$	$F1_{F-}$	**F0**	σ
6	961.0	391.6	-31.4	-213.5	-1438	-828.8	-410.4	-3370	860.0	-1198	-777.2	876.9	**15.7**
7	837.4	469.0	50.3	-124.8	-1354	-751.8	-360.3	-2673	880.4	-1103	-772.0	790.7	**13.8**
8	784.6	508.9	101.9	-73.9	-1314	-690.5	-327.0	-2153	868.1	-1050	-754.0	726.1	**12.9**
9	768.7	528.4	135.8	-44.1	-1297	-640.0	-303.7	-1750	841.4	-1022	-731.4	675.9	**12.6**

For refinement of the non-linear models in the Tables II and III, and for establishing a non-linear model for the TV panel glasses, further glass compositions need to be analyzed.

DISCUSSION

The above coefficients can be used to calculate the isokom temperatures in ^{o}C (Table V), e.g., for a typical container glass with the composition 74 SiO_2, 1 Al_2O_3, 0.5 MgO, 11 CaO, 13 Na_2O, 0.5 K_2O (mol%) and compared with an earlier model by Lakatos et al. [5]:

Table V. Model comparison, isokom temperatures and σ in ^{o}C

η	LAK	FL, all lin.	FL, sign. lin.	FL, sign. non-lin.
6	765.32	768.06	770.88	764.86
7	713.34	710.01	715.00	710.00
8	671.30	669.16	673.98	668.56
9	636.60	638.82	642.63	635.96
σ of diff.		3.06	2.14	1.46

The second column shows the isokom temperatures in ^{o}C calculated by Lakatos' linear model (LAK), next column using our linear model for container glasses including all components (see Table III), the fourth column using our linear model including the significant components only, and finally the last column using our non-linear model. The last row in Table V displays for each model comparison the standard deviation of the differences (LAK-FL). One should bear in mind that the accuracy of viscosity models tends to decrease with increasing variable components and phase separation/crystallization tendency. Further models over extended viscosity ranges and all six glass groups are available at the Center for Glass Research at Alfred University.

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