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ABSTRACT

Viscosity and electrical conductivity of 79 simulated borosilicate glasses in the expected range of compositions to be produced in the Hanford Waste Vitrification Plant were measured within the temperature span from 950 to 1250°C. The nine major oxide components were SiO_2, B_2O_3, Li_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, and ZrO_2. The test compositions were generated statistically. The data were fitted by Fulcher and Arrhenius equations with temperature coefficients being multilinear functions of the mass fractions of the oxide components. Mixture models were also developed for the natural logarithm of viscosity and that of electrical conductivity at 1150°C. Least squares regression was used to obtain component coefficients for all the models.

INTRODUCTION

Numerous attempts have been made to predict viscosity as a function of glass composition. The modelling approaches fall into three categories: (1) analytical functions with empirical coefficients [1-9], (2) "structural" approaches combined with empirical fitting [10-12], and (3) graphical methods [13-14]. Electrical conductivity models are less common than those for viscosity. The model by Jantzen [11] belongs to the "structural" category. The "structural" or "first principle" approaches use formulas that involve atomic radii, valencies, or number of non-bridging oxygens.

The empirical modeling approach has been adopted for the region of Hanford waste glasses. First- or second-order polynomials fit experimental data and allow interpolation with acceptable accuracy if the concentration ranges of major components are sufficiently narrow so that viscosity and electrical conductivity are relatively simple functions of composition within the region of interest. Extrapolation of the

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empirical model functions over a wider region is not recommended because properties of molten glasses are generally nonlinear functions of composition [7,15-17].

COMPOSITION AND PROPERTY RANGES

Nine major components [estimated to be the major components of glasses that will be produced in the Hanford Waste Vitrification Plant (HWVP)] were varied in a suite of 79 test glasses (including replicates). These components and their mass fraction ranges are shown in Table 1. The remaining waste components were treated as a tenth component, "others." For most of the test glasses, "others" composition was constant and—in the order of mass fractions—consisted of Nd_2O_3, CdO, La_2O_3, NiO, MoO_3, F, SO_3, CeO_2, Cs_2O, CuO, MnO_2, RuO_2, Cr_2O_3, BaO, Pr_6O_{11}, SrO, P_2O_5, PdO, Rb_2O, Rh_2O_3, Sm_2O_3, and Y_2O_3. In four glasses, "others" were composed of a smaller number of components mixed in varying proportions. Varying the "others" composition did not have any significant effect on glass viscosity and electrical conductivity. Although the glass viscosity values of the test glasses at 1150°C ranged from 0.4 to 84 Pa·s, most of the glasses had viscosity within the desired range opf 2 to 10 Pa·s. The electrical conductivity values at 1150°C ranged from 7 to 66 S/m.

EXPERIMENTAL

Compositions of glasses were statistically selected using the MIXSOFT™ [18] and ACED [19] software packages. Glasses were batched, melted, crushed, and remelted under a lid. The viscosity was measured within the temperature range from 950 to 1250°C in 50°C increments using a rotating spindle viscometer (Brookfield Digital Viscometer, Model LVTD). The Pt-20% Rh spindle (1.4 cm in diameter) was submerged in molten glass in a Pt crucible (5 cm in diameter). Electrical conductivity was determined in the same temperature range as viscosity in 100°C increments using a Pt-20% Rh probe with 0.7 × 3.8 cm blades set 0.9 cm apart, 1 kHz frequency ac current, and HP4262A LCR meter. A National Institute of Standards and Technology glass No. 711 was used to calibrate both instruments. To detect the time-dependent viscosity of some glasses due to crystallization, viscosity at 1150°C was measured three times: at the beginning, in the middle, and at the end of the experimental run. Small scattered spinel crystals had no measurable effect on viscosity. Larger crystals affected the viscosity of three glasses. These data points were deleted from model analysis.

EMPIRICAL MODELS

Viscosity (η) and electrical conductivity (ε) data were modeled as functions of absolute temperature (T) and composition by expressing the coefficients in the Fulcher equation [15], $\ln \eta = A + B/(T-T_0)$, and Arrhenius equation [15], $\ln \eta = C + D/T$ and $\ln \varepsilon = E + F/T$, as first-order mixture models:

$$\ln \eta = \sum_{i=1}^{10} A_i g_i + \sum_{i=1}^{10} B_i g_i / (T - \sum_{i=1}^{10} T_{0i} g_i) \qquad (1)$$

$$\ln \eta = \sum_{i=1}^{10} C_i g_i + \sum_{i=1}^{10} D_i g_i / T \qquad (2)$$

$$\ln \varepsilon = \sum_{i=1}^{10} E_i g_i + \sum_{i=1}^{10} F_i g_i / T \qquad (3)$$

where g_i is the mass fraction of i-th component and A_i, B_i, T_{0i}, C_i, D_i, E_i, and F_i are empirical coefficients obtained by fitting the models to the data using least squares regression. The fitted values of these coefficients are given in Table 1. Statistical analysis showed that Fulcher equation provides a significantly better fit to viscosity data than Arrhenius equation. The difference is practically significant only at temperatures close to or outside the range of our study (950°C to 1250°C). The R^2 values are 0.98 for each of the viscosity models and 0.96 for the electrical conductivity model.

First-order Scheffe mixture model [20]

$$\ln \xi = \sum_{i=1}^{10} a_i g_i \qquad (4)$$

was also fitted to viscosity at 1150°C ($\xi = \eta_{1150}$) and electrical conductivity at 1150°C ($\xi = \varepsilon_{1150}$) values, where a_i and b_i are the linear blending coefficients for the i-th component. The 1150°C values were obtained from individual $\eta(T)$ and $\varepsilon(T)$ fits. The R^2 values for η_{1150} and ε_{1150} were 0.96 and 0.92, respectively. The fitted first-order coefficients for $\ln \eta_{1150}$ and $\ln \varepsilon_{1150}$ are listed in Table 1. The results of fitting second-order models to $\ln \eta_{1150}$ with only a small number of second-order terms selected by stepwise regression methods were presented elsewhere [21].

COMPONENT EFFECTS

The linear coefficients, such as D_i, F_i, or a_i, approximate the partial specific variables common in classical thermodynamics [22]. The linear coefficients and partial specific variables become identical if at least one of the following conditions is met: (1) the composition range approaches zero or (2) the mixture is linear in the sense that its properties are represented exactly by first-order models on the composition range in question. The partial specific variables express the effects of component mass fractions on mixture properties: if an i-th component replaces an n-th component, the property change is proportional to the difference between the related linear coefficients, e.g., $\partial \ln \xi / \partial g_i = a_i - a_n$ [23].

No simple relationship between a component effect and the linear coefficients exists if the i-th component is simply added to or removed from the mixture (instead of replacing another component). The effect of component addition was analyzed by Piepel [24] and can be expressed by the formula [25,26]

Table 1. First-order coefficients for Arrhenius constants, Fulcher constants, and 1150°C values of viscosity (in Pa·s) and electrical conductivity (in S/m).

		Viscosity						Electrical Conductivity		
		Fulcher Model			Arrhenius Model		Scheffe 1150°C	Arrhenius Model		Sheffe 1150°C
Glass Oxide	Mass Fraction Range	A	B 10^3 K	T_o °C	C	D 10^3 K	ln η	E	F 10^3 K	ln ε
SiO_2	0.42-0.57	-4.86	10.21	524	-10.74	28.01	8.79	8.39	-10.87	0.71
B_2O_3	0.05-0.20	-7.26	-1.18	411	-17.23	15.86	-6.28	12.73	-15.00	2.26
Na_2O	0.05-0.20	-6.81	-0.07	-221	-12.34	2.49	-10.72	4.88	9.80	11.89
Li_2O	0.01-0.07	-13.56	4.93	-2561	-7.49	-39.15	-34.61	6.15	28.01	26.13
CaO	0.00-0.10	-19.47	16.85	-334	-20.70	19.59	-6.25	15.65	-21.65	0.56
MgO	0.00-0.08	-16.12	17.05	-227	-21.94	27.55	-1.89	12.38	-17.16	0.19
Fe_2O_3	0.02-0.15	-17.60	3.04	-1167	-7.67	10.98	0.06	10.18	-11.32	2.38
Al_2O_3	0.00-0.15	0.23	7.48	436	0.37	14.90	11.05	7.01	-8.53	0.83
ZrO_2	0.00-0.13	-18.98	16.60	1066	-28.42	50.73	7.81	8.94	-11.84	0.59
Others	0.01-0.10	-12.83	18.28	-598	-12.30	15.56	-0.82	18.38	-21.18	3.29

$$(\partial p/\partial g_i)_{add} = (p_i - p)/(1 - g_i) \quad (i=1,..,10) \qquad (5)$$

where p is the (predicted) mixture property at a selected point in the composition space, p_i is the linear coefficient, and the subscript "add" denotes component addition. The component effects defined by Equation (5) depend on composition even if the mixture is linear. Adding an i-th component increases the value of the transformed property $[(\partial p/\partial g_i)_{add} > 0]$ if $p_i > p$ and decreases it if $p_i < p$. The values of $(\partial p/\partial g_i)_{add}$ for some properties ($\ln \eta_{1150}$, $\ln \varepsilon_{1150}$, D, and F) of HW39-4 glass are shown in Table 2.

EFFECT OF COMPOSITION ON η AND ε

Ordering the components according to their effects on melt properties at 1150°C (Table 2), we obtain the following series for increasing viscosity:

$$Li_2O \ll Na_2O \ll B_2O_3 \approx CaO \ll MgO < Others < Fe_2O_3 \ll ZrO_2 < Al_2O_3 \ll SiO_2$$

and for decreasing electrical conductivity:

$$Li_2O \gg Na_2O \gg Others > Fe_2O_3 \approx B_2O_3 > Al_2O_3 \approx ZrO_2 \approx CaO \approx MgO > SiO_2$$

Generally, viscosity of a typical HWVP glass, such as HW39-4, is decreased by adding Li_2O, Na_2O, B_2O_3, or CaO and increased by adding SiO_2, Al_2O_3, or ZrO_2; "others," Fe_2O_3, and MgO exhibit a mild decreasing tendency. Electrical conductivity of a typical glass is strongly increased by adding alkali oxides (Li_2O and Na_2O) and mildly decreased by all other oxides. These results show that electrical conductivity

Table 2. Component effects for viscosity (in Pa·s) and electrical conductivity (in S/m) at 1150°C and Arrhenius coefficients D (in 10^3 K) and F (in 10^3 K) related to HW39-4 glass ($\ln \eta = 2.0$, $\ln \varepsilon = 3.4$, $D = 20 \times 10^3$ K, and $F = -8.3 \times 10^3$ K).

Glass Oxide	g_i	$\partial \ln \eta/\partial g_i$	$\partial \ln \varepsilon/\partial g_i$	$\partial D/\partial g_i$	$\partial F/\partial g_i$
SiO_2	0.5353	17.4	-6.9	17.5	-5.6
B_2O_3	0.1053	-7.8	-1.8	-4.5	-7.5
Na_2O	0.1125	-12.8	9.0	-19.6	20.4
Li_2O	0.0375	-36.7	23.1	-61.3	37.7
CaO	0.0083	-7.0	-3.4	-0.3	-13.5
MgO	0.0084	-2.6	-3.7	7.7	-9.0
Fe_2O_3	0.0719	-0.7	-1.6	-9.6	-3.3
Al_2O_3	0.0231	10.6	-3.1	-5.1	-0.2
ZrO_2	0.0385	7.4	-3.4	32.1	-3.7
Others	0.0592	-1.6	-0.6	-4.6	-13.7

of molten glass is affected primarily by alkali oxides, whereas momentum transfer (flow) is affected by most of the components. Both viscosity and electrical conductivity are affected by Li_2O considerably more than by Na_2O. Because Na_2O and Li_2O have comparable effects on durability [26], Li_2O is a better choice for adjusting transport properties (η and ε) of glass than Na_2O.

COMBINED EFFECT OF COMPOSITION AND TEMPERATURE ON η AND ε

Arrhenius coefficients D and F represent the effect of temperature on mixture viscosity and electrical conductivity. Glasses that change viscosity only mildly with temperature (have a low value of D) are called "long" (a glass blower could handle such a glass for a longer time compared to "short" glasses with a rapid change of viscosity with temperature). According to Table 2, the "length" of a typical Hanford waste glass, such as the HW39-4 glass, increases (D decreases) in the order of component additions:

$$ZrO_2 >> SiO_2 >> MgO >> CaO > B_2O_3 \approx \text{Others} \approx Al_2O_3 > Fe_2O_3 >> Na_2O >> Li_2O$$

Hence, ZrO_2, SiO_2, and MgO make glass "shorter" (the effect of ZrO_2 is almost twice as strong as that of SiO_2 and four times as strong as that of MgO), whereas Li_2O, Na_2O, and Fe_2O_3 make glass "longer"; Al_2O_3, "others," and B_2O_3 exhibit a mild "lengthening" effect, whereas CaO has virtually no effect at all. The effect of Li_2O is three times as strong as that of Na_2O. Inspecting Fulcher component coefficients (Table 1) reveals that the effects of ZrO_2 and Li_2O are due to their T_{0i} values rather than their effects on the (Fulcher) activation energy, represented by B.

Analogous to "length," the effect of temperature on electrical conductivity is expressed by the F coefficient. The activation energy for electrical conductivity ($E_\varepsilon = -RF$, where R is the gas constant) of a typical glass decreases (F increases) in the order of component additions:

$$\text{Others} \approx CaO < MgO \approx B_2O_3 < SiO_2 < ZrO_2 \approx Fe_2O_3 \approx Al_2O_3 << Na_2O << Li_2O$$

Thus alkali oxides make the electrical conductivity dependence on temperature less steep, whereas "others," alkali earth oxides, and B_2O_3 make this dependence sharper.

OTHER MODELS

Second-order models for viscosity at T=1150°C were presented by Redgate et al. [21]. The models consist of the full set of first-order terms and several second-order terms. Three different second-order models for viscosity exhibit $B_2O_3 \times B_2O_3$ nonlinearity, share $B_2O_3 \times Fe_2O_3$ interaction, and show no evidence of mixed-alkali effect. The $B_2O_3 \times B_2O_3$ nonlinearity is characteristic also for electrical conductivity, but alkali oxides are present in several interactive terms, indicating the mixed-alkali effect.

First- and second-order models based on mole fractions, x_i, and component-to-silica molar ratio, $y_i = x_i/x_s$, where x_s is the mole fraction of SiO_2 in the glass, were also fitted to the data. Neither these nor the mass fraction based second-order models showed a significant improvement over the mass fraction based first-order models.

CONCLUSIONS

First-order mixture models for viscosity and electrical conductivity of borosilicate glasses for Hanford nuclear waste immobilization within the temperature span from 950 to 1250°C fit the experimental data fairly well, accounting for roughly 98 and 96% of the variability in the data, respectively. The models show no evidence of biased predictions.

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