

Effect of composition on viscosity of many-component molten glasses

P. HRMA^{1*}, M. H. NELSON² AND A. A. KRUGER³

¹Pacific Northwest National Laboratory, Richland, WA 99352, USA (*correspondence: pavel.hrma@pnnl.gov)

²Uppsala University, Box 256, 751 05 Uppsala, Sweden (mary.h.nelson@ricealumni.net)

³U.S. Department of Energy, Office of River Protection, Richland, WA 99352, USA (Albert_A_Kruger@orp.doe.gov)

Both geological and nuclear waste glasses contain large numbers of viscosity-affecting components. The Vogel-Fulcher-Tammann (VFT) equation, $\ln(\eta) = C + D/(T - T_0)$, where η is the viscosity, T is the temperature, and C , D , and T_0 are coefficients, fits viscosity versus temperature data over several orders of magnitude. However, VFT equation fails at high temperatures at which the melt is depolymerized and behaves more like an ordinary liquid. For such melts, with viscosity typically $<10^2$ - 10^3 Pa s, the adequate model is the Arrhenius relationship, $\ln(\eta) = A + B/T$, where A and B are coefficients. In addition, coefficient A is independent of composition for sufficiently large families of glasses, such as nuclear waste glasses [1,2].

To check these assertions, three models with different numbers of composition-dependent coefficients were fitted to a viscosity dataset: in Arrhenius Model A1, only B coefficient changed with composition; in Arrhenius Model A2, both A and B coefficients were functions of composition; and in Model VFT, all three coefficients, C , D , and T_0 , varied with composition. The dataset consisted of 399 η values of high-level waste borosilicate glasses with 15 major components (plus one with all minor components added) and η ranging from 4 to 2400 Pa s. Another dataset [2] with 326 η values and 15 major components was used for validation. Composition regions of the original and validation datasets had 12 common major components.

Table 1 lists correlation coefficients, R^2 , and the number of parameters, p , in parentheses.

Model	R^2 (p)	
	Original	Validation
A1	0.985 (17)	0.788 (14)
A2	0.989 (32)	0.760 (26)
VFT	0.994 (48)	0.652 (39)

Table 1: Correlation coefficients, R^2 , and numbers of parameters, p (in parentheses), for three viscosity models fitted to original dataset and applied to validation dataset.

The R^2 of the original dataset (to which the models were fitted) increased as the number of parameters increased, but was high enough for only B composition-dependent; doubling and tripling the number of parameters brought little improvement. For the validation dataset, to which the models were applied, the R^2 decreased as the number of parameters increased. This clearly shows that the Arrhenius equation with constant A adequately represents the response of η to temperature and composition. The additional coefficients in the other two models only compensate for measurement errors in the original dataset and thus are counterproductive for applications.

[1] Hrma (2008) *J. Non-Cryst. Solids* **354**, 3389-3399. [2] Hrma et al. (2009) *J. Non-Cryst. Solids* **355**, 891-902.