RELATING THE TEMPERATURE DEPENDENCE OF VISCOSITY TO THE CHEMICAL COMPOSITION OF CONTAINER GLASS

MARTIN MÍKA, GREGORY F. PIEPEL

Battelle, Pacific Northwest Laboratories
P.O. Box 999, Richland, Washington 99352, U.S.A.

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A new approach is developed for modeling the temperature and composition dependence of glass viscosity in the system Na_2O-CaO-MgO-Al_2O_3-SiO_2. The temperature dependence is described using the equation $\log(\log \eta) = A + B \log T$. The dependence of the coefficients A and B on chemical composition of the glass is expressed using reduced full-cubic mixture polynomials. The new approach is much simpler to develop and use than the previous approach, and it has the potential to yield better property-composition models. The new approach yields an improved model for the dependence of viscosity on composition in the Na_2O-CaO-MgO-Al_2O_3-SiO_2 glass system studied.

INTRODUCTION

Measured viscosity data for a test matrix of 16 container glass compositions in the system Na_2O-CaO-MgO-Al_2O_3-SiO_2 were reported in a previous paper [1]. The contents of Na_2O, CaO, and MgO were varied, while the content of SiO_2 was kept constant. Al_2O_3 was an impurity present in silica sand used as a SiO_2 source, and hence also was constant. The test ranges of the components were:

$$\begin{aligned} &0 \le MgO \le 6 \text{ wt.\%} \\ &4 \le CaO \le 14 \text{ wt.\%} \\ &12 \le Na_2O \le 16 \text{ wt.\%} \\ &SiO_2 (+Al_2O_3) = 74 \text{ wt.\%} \end{aligned} \qquad (1)$$

Thus, MgO + CaO + Na_2O = 26 wt.% for the 16 test glasses. Table 1 lists the test glass compositions in wt.%. The rest of the entries in table 1 are discussed later in the paper.

In the previous paper [1], the dependence of viscosity on glass composition was modeled by splitting the composition region into two subregions, transforming each triangular subregion to a regular simplex region, and fitting separate models for each subregion. Although this "split region" approach worked quite well for the glass system studied, it was also quite complicated. This led to applying a less complicated and more flexible "single region" approach. The new approach keeps the composition region undivided, and develops a single model using least squares regression and statistical methods for model reduction.

The old (split region) approach is described in the next section, and the new (single region) approach is described in the section following that. Then, the results of the two approaches are compared. The paper ends with some conclusions and recommendations.

SPLIT-REGION APPROACH

In the previous paper [1], the temperature dependence of the viscosity data for each glass was fitted via the equation:

$$\log(\log \eta) = A + B \log T \qquad (2)$$

where η is viscosity in dPa s, T is temperature in K, and A and B are composition-dependent coefficients determined from the data. The parallelogram compositional region represented by the 16 test glasses was divided into two triangular subregions (see figure 1). The dependence of equation (2) coefficients A and B on composition was modeled separately in each subregion by a special-cubic mixture polynomial [2]

$$y = b_1z_1 + b_2z_2 + b_3z_3 + b_{12}z_1z_2 + b_{13}z_1z_3 + b_{23}z_2z_3 + b_{123}z_1z_2z_3 \qquad (3)$$

where y denotes either A or B; b_1, b_2, and b_3 are linear blending coefficients; b_{12}, b_{13}, and b_{23} are quadratic blending coefficients; b_{123} is a special-cubic blending coefficient; and z_1, z_2, and z_3 are mass fractions of pseudocomponents ($z_1 + z_2 + z_3 = 1$). The pseudocomponents are defined separately for each of the two subregions, corresponding to the three vertices of each of the subregions. For subregion I, $z_1 = (-10X_1 + 3X_2 + 3X_3)/78$, $z_2 = (2X_1 - 24X_2 + 15X_3)/156$, and $z_3 = (8X_1 + 8X_2 - 5X_3)/52$. For subregion II, $z_1 = (-6X_1 - 6X_2 + 7X_3)/52$, $z_2 = (-2X_1 + 24X_2 - 15X_3)/156$, and $z_3 = X_1/6$. For both subregions, X_1, X_2, and X_3 denote the wt.% values of MgO, CaO, and Na_2O, respectively. The z_1, z_2, and z_3 values for the 16 glasses are given in table 1 next to their X_1, X_2, and X_3 values. Note that the b coefficients in equation (3) represent blending properties of the pseudocomponents z_1, z_2, and z_3, not the blending pro-

Table 1. Component wt.% (X_i) and pseudocomponent mass fractions (z_i) in test glasses and the measured and calculated values of *A* and *B* coefficients.

	X_i (wt.%)			z_i (mass fractions)			measured*		calculated**	
glass	MgO	CaO	Na_2O	MgO	CaO	Na_2O	A	B	A	B
1	0.0	10.00	16.00	1.0	0.0	0.0	7.53825	-2.22705	7.53430	-2.22625
2	6.0	4.00	16.00	0.0	1.0	0.0	7.38098	-2.16776	7.38223	-2.16868
3	6.0	8.00	12.00	0.0	0.0	1.0	7.83251	-2.30365	7.82972	-2.30318
4	3.0	7.00	16.00	0.5	0.5	0.0	7.44671	-2.19449	7.45071	-2.19547
5	6.0	6.00	14.00	0.0	0.5	0.5	7.51956	-2.21077	7.52625	-2.21202
6	3.0	9.00	14.00	0.5	0.0	0.5	7.59091	-2.23620	7.59833	-2.23941
7	4.0	7.33	14.67	0.3333	0.3333	0.3333	7.48493	-2.20357	7.47931	-2.20233
8	4.8	7.60	13.60	0.2	0.2	0.6	7.53064	-2.21601	7.52538	-2.21485
9	2.4	8.40	15.20	0.6	0.2	0.2	7.55896	-2.22873	7.56784	-2.23112
10	0.0	14.00	12.00	0.0	1.0	0.0	7.89267	-2.33386	7.89084	-2.33363
11	0.0	12.00	14.00	0.5	0.5	0.0	7.78905	-2.30443	7.79685	-2.30584
12	3.0	11.00	12.00	0.0	0.5	0.5	7.74407	-2.28352	7.74141	-2.28136
13	2.0	10.67	13.33	0.3333	0.3333	0.3333	7.76105	-2.28961	7.72582	-2.27909
14	3.0	10.20	12.80	0.2	0.3	0.5	7.65192	-2.25481	7.67626	-2.26251
15	1.2	12.40	12.40	0.1	0.7	0.2	7.82715	-2.31026	7.83235	-2.31231
16	4.8	5.72	15.48	0.2	0.6667	0.1333	7.40078	-2.17832	7.39253	-2.17498

* Coefficients from equation (2) estimated by least squares from measured viscosity data for individual glasses.

** Coefficients from equation (2) calculated using coefficients from table 2 substituted in equation (5).

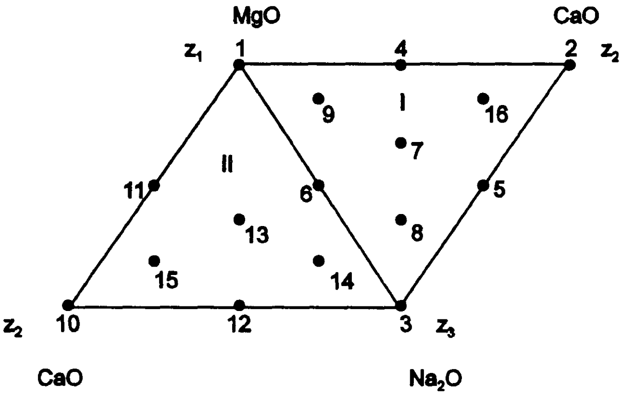

Figure 1. Glass composition region, subregions, and experimental glasses.

perties of the components X_1, X_2, and X_3. The *b* coefficients are determined separately for *A* and *B*, and for subregions I and II.

The special-cubic models in equation (3) were exactly fitted to the *A* and *B* data from glasses 1-7 for subregion I, and glasses 1, 3, 6, 10, 11, 12, 13 for subregion II [1]. Because glasses 1, 3, and 6 were used to fit the *A* and *B* models for both subregions, only 11 out of the 16 glasses were used. The two models (corresponding to the two subregions) for each of *A* or *B* have a total of 14 coefficients. However, the linear and quadratic blending coefficients for MgO and Na_2O are the same for the models corresponding to subregions I and II [1]. Hence, the two models (corresponding to the two subregions) together effectively have 11 coefficients.

Data for the remaining 5 out of 16 glasses (# 8, 9, 14, 15, and 16) were used in the original paper [1] to validate the two models. The two models predicted the temperature dependence of viscosity for these five glasses with a maximum deviation of 11°C within the viscosity range studied. Specifically, for each glass: (I) temperatures corresponding to viscosities of 10^2, 10^3, and 10^4 dPa s were interpolated from the measured data using equation (2), and (ii) temperatures corresponding to viscosities of $10^{7.6}$, 10^{13}, and $10^{14.5}$ dPa s were extrapolated using equation (2). Temperatures corresponding to these viscosities were calculated for each of the five glasses by substituting the *A* and *B* models (from subregion I or II, depending on the glass) from equation (3) into equation (2). These temperatures were then compared to the temperatures interpolated or extrapolated from measured data. As noted above, the maximum measured - calculated temperature deviation was 11 °C. The average measured - calculated temperature deviations for glasses # 8, 9, 14, 15, and 16 were -6.5, 5.7, -8.8, 7.0, and -6.7 °C, respectively. While this performance is quite good, the approach of splitting the composition region into subregions, performing separate composition transformations for each subregion, and developing and applying separate models for each subregion is quite complicated. Fitting saturated models (using the same number of data points as coefficients to be estimated from the data) for each subregion is also a negative aspect of the approach, since it does not provide for detecting bad data points or inadequate models as part of the fitting process.

SINGLE-REGION APPROACH

As in the previous paper [1], equation (2) was used to fit the temperature dependence of viscosity for each glass. The resulting A and B values (denoted "measured" in table 1) for each glass were then modeled using the full-cubic mixture model

$$y = c_1x_1 + c_2x_2 + c_3x_3 + c_{12}x_1x_2 + c_{13}x_1x_3 + c_{23}x_2x_3 + c_{123}x_1x_2x_3 + d_{12}x_1x_2(x_1 - x_2) + d_{13}x_1x_3(x_1 - x_3) + d_{23}x_2x_3(x_2 - x_3) \quad (4)$$

where y denotes either A or B; c_1, c_2, and c_3 are linear blending coefficients; c_{12}, c_{13}, and c_{23} are quadratic blending coefficients; c_{123} is a special-cubic blending coefficient; d_{12}, d_{13}, and d_{23} are cubic blending coefficients; and x_1, x_2, and x_3 are mass fractions (wt.%/100) of MgO, CaO, and Na_2O, respectively. The blending coefficients quantify the blending properties of the components expressed as mass fractions.

The full-cubic mixture model (4) was fitted separately to the A and B data, but in each case the special-cubic term ($MgO \times CaO \times Na_2O$) was found to be statistically insignificant. This term was deleted, and a reduced full-cubic model

$$y = c_1x_1 + c_2x_2 + c_3x_3 + c_{12}x_1x_2 + c_{13}x_1x_3 + c_{23}x_2x_3 + d_{12}x_1x_2(x_1 - x_2) + d_{13}x_1x_3(x_1 - x_3) + d_{23}x_2x_3(x_2 - x_3) \quad (5)$$

was then separately fitted to the A and B data using the least squares regression capabilities in Minitab [3]. The resulting coefficients and coefficient standard errors are listed in table 2. Also listed in table 2 are s, R^2, and $R^2_{\text{Predicted}}$ statistics that summarize how well the model (5) fits the A and B data. Interpretations of these statistics are given in the footnotes to table 2.

For both A and B, the coefficients for the $CaO \times Na_2O$ and $CaO \times Na_2O \times (CaO-Na_2O)$ terms are only about 1.7 to 2.0 times larger than their standard errors (see table 2). The statistical significance levels for these coefficients range from 0.08 to 0.13 (which are the probabilities of incorrectly declaring the coefficients to be different from zero). This suggests that the $CaO \times Na_2O \times (CaO-Na_2O)$ cubic blending term may not be needed in the models, so the A and B data were refitted to model (5) without that term. The refitted models experienced only slight decreases in R^2, but moderate decreases in $R^2_{\text{Prediction}}$. Hence, it was decided to use the models for A and B containing the $CaO \times Na_2O \times (CaO-Na_2O)$ cubic blending term, as given in equation (5).

Table 2. Reduced full-cubic model coefficients and standard errors for A and B.

component	A coef.	A standard error	B coef.	B standard error
MgO	495.61	60.7	-145.45	18.6
CaO	47.40	15.9	-13.21	4.9
Na_2O	-3.61	8.0	0.82	2.5
MgO×CaO	-1891.25	322.7	548.94	99.2
MgO×Na_2O	-3042.59	366.7	897.53	112.7
CaO×Na_2O	128.00	74.7	-42.19	23.0
MgO×CaO×(MgO-CaO)	-2313.58	518.2	651.60	159.2
MgO×Na_2O×(MgO-Na_2O)	-8654.45	1130.0	2552.22	347.1
CaO×Na_2O×(CaO-Na_2O)	-1378.19	680.0	376.06	208.9
s *	0.01804		0.005544	
R^2 **	0.994		0.995	
$R^2_{\text{Prediction}}$ ***	0.952		0.974	

* s is the root mean square of differences between measured and calculated values of the response variable (A or B). If s is significantly larger than the measurement uncertainty in the response variable, then the model may have a significant lack-of-fit.

** R^2 is the proportion of variation in the response variable (A or B) accounted for by the fitted model, and hence must be between 0 and 1. The closer R^2 is to 1, the better the fit of the model to the data.

*** $R^2_{\text{Prediction}}$ is the proportion of variation in the response variable (A or B) accounted for by the model, where each data point is in turn left out of the model when assessing the predictive performance of the model for that point. $R^2_{\text{Prediciton}}$ is sometimes referred to as $R^2_{\text{Crossvalidation}}$ or R^2_{PRESS}.

The A and B models listed in table 2 are valid in the composition region denoted by equation (1). Calculated values of A and B were obtained by applying the model coefficients in table 2 to the glass mass fractions (z_i) in table 1, and are listed in the final columns of table 1. Plots of calculated versus measured values of A and B are shown in figure 2. These plots demonstrate that the models in table 2 capture the effect of composition on viscosity with no bias and excellent precision. The 45° lines in figure 2 represent perfection, which occurs when calculated values exactly equal measured values.

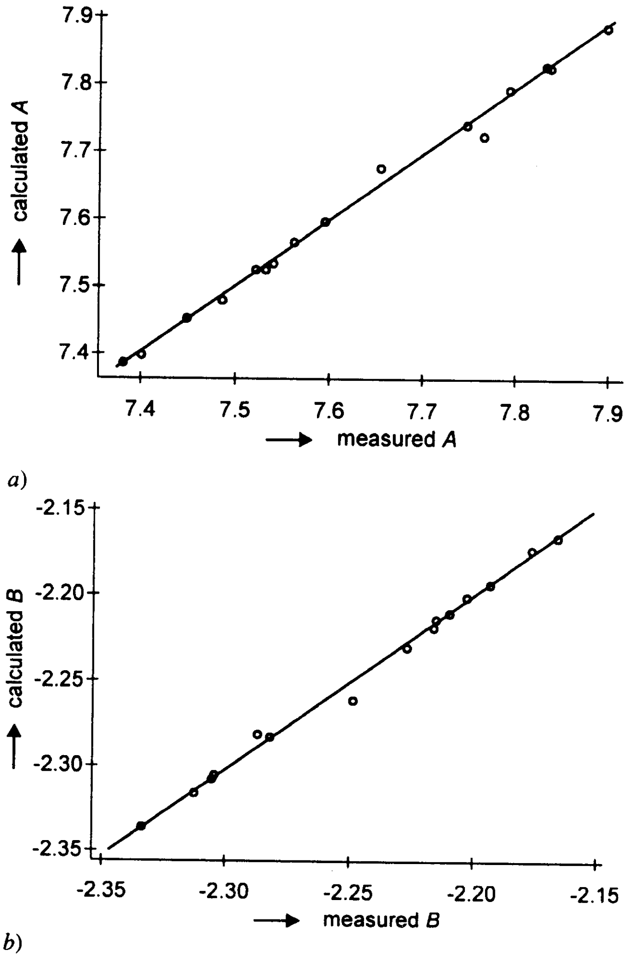

Figure 2. Calculated (from table 2 models) versus measured plots of: *a*) A and *b*) B.

COMPARING THE SINGLE-REGION AND SPLIT-REGION APPROACHES

Models (4) and (5) used in the single-region approach have two advantages over model (3) used in the split-region approach. First, models (4) and (5) can capture full-cubic blending behavior of components, whereas model (3) can capture only special-cubic blending behavior. Second, models (4) and (5) are expressed in terms of mass fractions of the three components of interest (MgO, CaO, and Na_2O), whereas model (3) is expressed in terms of pseudocomponents that are linear combinations of these three components. Working directly in the mass fractions of the components of interest rather than in two different sets of pseudocomponents (one for each of the two subregions of the split composition region) makes the single-region approach much easier to develop and apply than the split-region approach.

Table 3 lists temperatures calculated using equation (2). The "measured" (meas.) temperature values are actually calculations using the A and B values from table 1 (which were obtained from measured viscosity and temperature data for each glass using the least squares method) in equation (2). The calculated (calc.) temperature values were obtained using the reduced full-cubic model representations of A and B (from table 2) in equation (2). Temperatures were compared at constant viscosities $\eta = 10^2, 10^3, 10^4, 10^{7.6}, 10^{13}$ and $10^{14.5}$ dPa s. The maximum measured - calculated temperature deviation was 8 °C. The average measured - calculated temperature deviations for glasses # 8, 9, 14, 15, and 16 (which were not exactly fitted by the split-region approach) were 2.0, -1.7, -0.8, 1.5, and -2.7 °C, respectively.

The 8 °C maximum deviation for the single-region approach is somewhat better than the maximum deviation of 11 °C for the split-region approach. Also, the average temperature deviations for glasses # 8, 9, 14, 15, and 16 obtained using the single-region approach are from 4 to 8 °C smaller than those obtained using the split-region approach. These comparisons are somewhat misleading for two reasons. First, 11 of the 16 data points were fitted exactly by the split-region approach, and thus any errors in the data are undetectable. The single-region approach would be less affected by errors in one or more data points, and the resulting measured - calculated deviations could help detect problems undetectable with the split-region approach. Second, glasses # 8, 9, 14, 15, and 16 were not used to develop models with the split-region approach, but they were used to develop models with the single-region approach. Hence, the measured - calculated deviations for these points might be smaller for the single-region approach.

To assess how much using glasses # 8, 9, 14, 15, and 16 to develop the single-region models contributed to reducing the average measured - calculated temperature deviations, these five glasses (along with the other eleven) were used in a modified version of the split-region approach. Specifically, separate special-cubic mixture models were fit to all of the subregion I data (glasses # 1-9, 16) and all of the subregion II data (glasses # 1, 3, 6, 10-15). The maximum measured - cal-

Table 3. Temperatures (°C) obtained from measured data (meas.) using equation (2) and calculated data (calc.) using the reduced full-cubic model of equation (5). Viscosity η is in dPa s.

	temperature at log η = 2			temperature at log η = 3			temperature at log η = 4		
glass	meas.	calc.	diff.	meas.	calc.	diff.	meas.	calc.	diff.
1	1504	1501	3	1208	1206	2	1029	1027	2
2	1572	1569	3	1257	1254	3	1067	1065	2
3	1586	1584	2	1286	1284	2	1103	1101	2
4	1531	1532	-1	1226	1228	-2	1042	1043	-1
5	1568	1573	-5	1260	1264	-4	1073	1077	-4
6	1546	1541	5	1245	1240	5	1061	1058	3
7	1547	1544	3	1241	1238	3	1056	1053	3
8	1557	1554	3	1251	1248	3	1065	1063	2
9	1532	1534	-2	1232	1234	-2	1050	1051	-1
10	1517	1515	2	1231	1230	1	1057	1055	2
11	1503	1508	-5	1216	1221	-5	1041	1046	-5
12	1544	1552	-8	1249	1255	-6	1068	1074	-6
13	1539	1537	2	1245	1242	3	1066	1063	3
14	1547	1546	1	1247	1247	0	1065	1066	-1
15	1537	1534	3	1246	1244	2	1068	1066	2
16	1544	1549	-5	1235	1239	-4	1048	1051	-3

Table 3. Continued.

	temperature at log η = 7.6			temperature at log η = 13			temperature at log η = 14.5		
glass	meas.	calc.	diff.	meas.	calc.	diff.	meas.	calc.	diff.
1	703	701	2	494	492	2	457	456	1
2	724	722	2	505	504	1	467	466	1
3	768	767	1	552	551	1	514	513	1
4	709	710	-1	496	496	0	458	459	-1
5	734	737	-3	517	519	-2	478	481	-3
6	728	726	2	515	513	2	477	476	1
7	720	718	2	505	504	1	468	466	2
8	729	727	2	513	512	1	475	474	1
9	719	720	-1	506	508	-2	469	471	-2
10	737	736	1	529	529	0	493	492	1
11	722	725	-3	515	518	-3	479	481	-2
12	740	744	-4	528	530	-2	490	493	-3
13	738	735	3	527	523	4	490	486	4
14	734	735	-1	520	522	-2	483	485	-2
15	742	742	0	532	531	1	495	494	1
16	711	713	-2	496	497	-1	459	460	-1

culated temperature deviation over all glasses and viscosities was 8 °C, and the average temperature deviations for glasses # 8, 9, 14, 15, and 16 were -4.8, 5.8, -6.5, 6.5, and -5.0 °C, respectively. Thus, in spite of using glasses 8, 9, 14, 15, and 16 to fit the models in the revised split-region approach, the resulting average differences are still larger than those obtained with the single-region approach. Hence, it appears that the advantage of the single-region approach is due mainly to the presence of full-cubic terms in the model.

The total number of coefficients in the single-region, reduced full-cubic model (5) is 9, compared to 14 coefficients (effectively 11, as noted earlier) in the split-region, special-cubic models [1]. Hence, the single-region approach also has the advantage of yielding a smaller, and (as seen above) a better-fitting model for characterizing the effect of composition on viscosity.

CONCLUSIONS AND RECOMMENDATIONS

The reduced full-cubic model fits the experimental viscosity-composition data very well for the Na_2O-CaO-MgO-Al_2O_3-SiO_2 container glass system studied. The reduced full-cubic mixture model has two fewer coefficients and fits the data slightly better than the two special-cubic mixture models developed previously [1]. The greatest advantage of the new (single region) approach, however, is that it is much simpler to develop and apply than the previous (split region) approach.

In general, the choice of an approach for developing a property-composition relationship will depend on the nature of the problem. If the relationship can be adequately represented over the whole composition space of interest by a single model, then that is the best approach to take. In other cases where the property-composition relationship changes in a fashion not easily captured by a single model, splitting the composition region into two or more subregions and developing separate models for each subregion may be a better approach. When separate models for each subregion are to be obtained empirically or semi-empirically, we recommend that the number of data points taken for each subregion should exceed the number of model coefficients to be determined. In that way, the adequacy of the separate models can be assessed, and any outlying data points can be detected as part of the fitting process. In such split-region cases, it is also recommended that the separate models for each subregion be fit in a single fitting step, so that consistent model predictions are obtained along subregion boundaries. Regression software capable of fitting piecewise models (e.g., SAS [4]) is required to do this.

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Submitted in English by the authors.

VZTAH MEZI TEPLOTNÍ ZÁVISLOSTÍ VISKOZITY A CHEMICKÝM SLOŽENÍM OBALOVÉHO SKLA

MARTIN MÍKA, GREGORY F. PIEPEL

Battelle, Pacific Northwest Laboratories
P.O. Box 999, Richland, Washington 99352, U.S.A.

Byl vypracován nový přístup k modelování závislosti viskozity skla na teplotě a chemickém složení v soustavě Na_2O-CaO-MgO-Al_2O_3-SiO_2. Teplotní závislost je popsána rovnicí $\log(\log \eta) = A + B \log T$. Závislost koeficientů A a B na chemickém složení skla je vyjádřena redukovanými úplnými kubickými polynomy. Nový přístup je mnohem jednodušší co do výpočtu i použití a umožňuje získat přesnější modely závislosti vlastností na chemickém složení.