

## Mixed Alkali Effect on Viscosity of Sodium Potassium Borate Glasses

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### Abstract:

The effect of the alkali oxide content on viscosity has been studied for sodium-potassium borate glasses. The deviation of viscosity values from additivity has been modeled to investigate the effect of partial substitution of one alkali oxide for another. Published data on isokom temperatures and activation energies for sodium-potassium borate glass compositions has been utilized along with  $L^2$ -regression optimization technique for analysis.

It is found that both linear and nonlinear relations determine the viscosity coefficients associated with chemical components of the glasses under study. This model allows the calculation of viscosity for a given temperature and accordingly, the fusion temperature of these glasses. Furthermore, the established model relations show first and second order mixed alkali effect on viscosity.

**Keywords:** Simulation, Viscosity model, sodium-potassium borate glass

### Introduction:

A specialist on glass science and technology is generally interested in a simulation tools that helps in prediction of glass properties due to lack of

comprehensive information on glass and melt properties in literature. The simulation methods are based on experimental property data and calculate glass properties including glasses that have not been studied so

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far. The changes in the composition areas of glass often lead to the changes of simulation models. The reliability of the simulation model is examined by comparing the results with experimental data for glasses belonging to a system of interest. Due to its obvious importance, simulation of glass properties is continued to be an active field in glass science and technology [1].

Alkali oxide borate glasses are of interest as sealing glasses for electrochemical, electrical, electronic and optical applications. The fusion temperatures (at which the viscosity value is 20 Pa.s [2]) of these glasses are around 600°C. The viscosity of alkali oxide borate glass melt is very sensitive to the temperature and to the composition. Thus, calculating the viscosity at given temperature noticeably save time and cost. Also, these calculations comprise a valuable tool to the glass designer. The variation of alkali oxide borate glass viscosity at a given temperature with alkali content is not linear. Therefore, a model to describe the alkali effect on viscosity is necessary [3].

The nonlinear behavior of viscosity with sodium potassium content for the glass type under study is shown by Kuppinger and Shelby [4]. The authors show that the isokom temperature (temperature at which different glass members shows the same viscosity) is not linear with sodium and potassium content. Their data shows a "mixed alkali effect", that is, the isokom temperature is decreased as sodium is replaced by potassium until it reaches a minimum and begins to increase. This deviation from linearity is increases as the total sodium and potassium content increases. What really matters is that this behavior

means that the viscosity is not linear with the alkali oxide content at constant temperature. The goal of a simulation model is to reproduce the viscosity for a given sodium potassium borate glass. The viscosity simulation can be accomplished by explaining the effective composition related terms that describing the viscosity.

**Composition-Viscosity Model:**

The variation of viscosity  $\mu$  with the temperature is expressed as [5]:

$$\mu = A T \exp(10^3 BT) \dots\dots\dots (1)$$

where A and B are constants and T is the absolute temperature.

The parameter B is believed to be a function of glass composition; in addition, the parameter B can be replaced by the "energy of activation"  $E_\mu$  of the viscous process [5]:

$$E_\mu [J] = 10^3 R B \dots\dots\dots (2)$$

where R is the gas constant. Thus,  
 $\mu = A T \exp(E_\mu [J] /RT) = A T \exp(10^3 E_\mu [kJ] /RT) \dots\dots\dots (3)$

Consequently,  $E_\mu$  is regarded as function of glass composition similar to B.

$$E_\mu = \sum_{i=1}^{i=n} C_i . N_i \dots\dots\dots (4)$$

where  $N_i$  is the molar percentages mol% of the  $i$ th component composing the glass and  $C_i$  is the coefficient associated with that glass component. The terms  $(C_i . N_i)$  can also include nonlinear combination of more than one glass component. Thus,  $n$  represents the total number of terms used to calculate  $E_\mu$ .

The natural logarithm of equation (3) reads:

$$\ln\mu/T = \ln A + 10^3 E_\mu [kJ]/RT \dots\dots\dots (5)$$

Accordingly, values of  $\ln A$  can be calculated for a given set of viscosity  $\mu$

at certain temperature T and E<sub>μ</sub> for a range of glass compositions.

The parameter B appears in equation (1) is approved to be linearly related to lnA [5]. Thus, E<sub>μ</sub> and lnA are linked linearly according to equation (2).

The "mixed alkali effect" suggested by Kuppinger and Shelby [4] is taken into account. The only difference is that our model includes first and second order mixed alkali effect R<sub>1</sub>, R<sub>2</sub> to establish better description of compositional effect on viscosity. Finally, the model equation for E<sub>μ</sub> is expressed as:

$$E_{\mu} = C_1.mol\%B_2O_3 + C_2.mol\%Na_2O + C_3.mol\%K_2O + C_4.R_1 + C_5.R_2 \dots\dots\dots (6)$$

where R<sub>1</sub> and R<sub>2</sub> represents first and second order mixed alkali effect:

$$R_1 = \frac{mol\% K_2O}{mol\% Na_2O + mol\% K_2O} \dots\dots (7)$$

$$R_2 = (R_1)^2 \dots\dots\dots (8)$$

The above equations calculate E<sub>μ</sub> as function of the glass compositions. These equations, together with equation (5) represent composition-viscosity model for sodium potassium borate glasses.

**Simulation Technique:**

Published data by Kuppinger and Shelby [4] has been used to carry out necessary calculation. The data includes table of mol% of the glass composition along with its isokom temperature at 10<sup>10</sup>Pa.s and 10<sup>11</sup>Pa.s viscosity values and the associated activation energies E<sub>μ</sub> [kJ]. These data are shown in the following table.

Calculated lnA has been obtained from table (1) utilizing equation (5). ....which shows linear relation connecting them. The figure also shows the equation of the least squares line passing through the data points. The Dept of Materials Eng, Univ of Tech, Baghdad, Iraq

standard error of the measured E<sub>μ</sub> is calculated by statistical method [6] and found to be equal to 23.52 kJ. I.e. a supposed model that calculates E<sub>μ</sub> cannot attain standard error less than that found no matter what successful it is.

Table (1): The composition and viscous flow properties of reference glasses

No	Mol% B <sub>2</sub> O <sub>3</sub>	Mol% Na <sub>2</sub> O	Mol% K <sub>2</sub> O	Temp. [°C] at 10 <sup>10</sup> Pa.s	Temp. [°C] at 10 <sup>11</sup> Pa.s	E <sub>μ</sub> [kJ]
1	100	0	0	281	265	356
2	70	30	0	489	478	996
3	70	27	3	474	462	875
4	70	24	6	463	451	850
5	70	21	9	453	442	904
6	70	18	12	447	435	812
7	70	15	15	442	430	804
8	70	12	18	439	427	795
9	70	9	21	437	426	862
10	70	6	24	439	427	795
11	70	3	27	443	432	879
12	70	0	30	458	447	917
13	80	20	0	474	459	699
14	80	16	4	455	440	663
15	80	12	8	446	431	646
16	80	10	10	440	424	594
17	80	8	12	440	425	636
18	80	4	16	429	415	661
19	80	0	20	437	423	674
20	95	2.5	2.5	326	307	352
21	90	5	5	371	353	427
22	85	7.5	7.5	414	396	490
23	75	12.5	12.5	447	433	695
24	65	17.5	17.5	423	412	829

L<sup>2</sup>-regression technique [3, 7] is used to obtain calculated E<sub>μ</sub> utilizing glass compositions and measured E<sub>μ</sub> shown in table (1). When the non-additive behavior is not taken into account (only the first three terms of equation 6 is counted up), high standard error for E<sub>μ</sub> is obtained. Several attempts were made to express E<sub>μ</sub> as function of other terms such as the combinations of the mol% of oxide constituents. The standard error for calculated E<sub>μ</sub> do not reduced until "mixed alkali effect" expressed by R<sub>1</sub>

and  $R_2$  terms is taken into account. The final standard error for  $E_\mu$  using our model is 36.29 kJ which is only 0.5 times larger than the standard error of the raw data. Table (2) shows the final coefficients  $C_i$  that obtained by  $L^2$ -regression and correlates the sodium potassium borate glasses with activation energy of viscous flow  $E_\mu$ .

Table (2): Coefficients  $C_i$  associated with the glass composition.

Coefficient	Value
$C_1$	3.498
$C_2$	23.37
$C_3$	21.41
$C_4$	-457
$C_5$	463

Fig.(1) has been used to obtain calculated  $\ln A$ 's from calculated  $E_\mu$ . Table (3) shows the values of  $R_1$ ,  $R_2$  terms used to model  $E_\mu$  that associated with glass compositions listed in table (1). The table also shows calculated  $E_\mu$  and  $\ln A$ .

The inverse problem to find the temperature at certain viscosity can be solved by any numerical technique such as the "finite step method". Thus, the fusion temperature can be found by setting viscosity to 20 Pa.s. Table (4) shows supposed sodium potassium borate glass compositions with calculated  $R_1$ ,  $R_2$ ,  $E_\mu$ ,  $\ln A$  and fusion temperatures.

Table (3): List of  $R_1$ ,  $R_2$ ,  $E_\mu$  and  $\ln A$  calculated for glass compositions in table (1).

No	$R_1$	$R_2$	calculated $E_\mu$ [kJ]	calculated $\ln A$
1	0	0	349.8	-49.0
2	0.00	0.00	945.9	-135.7
3	0.10	0.01	898.9	-128.8
4	0.20	0.04	861.2	-123.3
5	0.30	0.09	832.7	-119.2

6	0.40	0.16	813.5	-116.4
7	0.50	0.25	803.6	-115.0
8	0.60	0.36	802.9	-114.9
9	0.70	0.49	811.5	-116.1
10	0.80	0.64	829.4	-118.7
11	0.90	0.81	856.5	-122.7
12	1.00	1.00	892.9	-127.9
13	0.00	0.00	747.2	-106.8
14	0.20	0.04	666.4	-95.0
15	0.40	0.16	622.7	-88.7
16	0.50	0.25	614.7	-87.5
17	0.60	0.36	616.0	-87.7
18	0.80	0.64	646.4	-92.1
19	1.00	1.00	713.8	-101.9
20	0.50	0.25	331.4	-46.4
21	0.50	0.25	425.9	-60.1
22	0.50	0.25	520.3	-73.8
23	0.50	0.25	709.2	-101.3
24	0.50	0.25	898.1	-128.7

Table (4): Simulation parameters, energy of activation and fusion temperature shown for hypothetical glass compositions.

No.	1	2	3
Mol% $B_2O_3$	75	75	75
Mol% $Na_2O$	10	5	20
Mol% $K_2O$	15	20	5
$R_1$	0.600	0.800	0.200
$R_2$	0.360	0.640	0.040
$E_\mu$ [kJ]	709.5	737.9	763.8
$\ln A$	-101.3	-105.4	-109.2
Calculated fusion temperature.	602 °C	600 °C	598 °C

Finally, Fig (2) shows how  $E_\mu$  varies with total alkali content and with replacement of potassium by sodium. Both raw and calculated values of  $E_\mu$  are presented.

**Discussion:**

Fig. (2) shows the scattering of the raw data (solid symbols) around the trend line. This scattering explains the standard error predicted for  $E_{\mu}$ . Obviously, the standard error can take smaller value for larger number of raw data. The large values of  $E_{\mu}$  shown in table (1) together with equation (3) demonstrates that The viscosity  $\mu$  and the activation energy  $E_{\mu}$  is very sensitive to minor errors in measuring the temperature  $T$ . Thus, minimizing the scattering in measuring  $E_{\mu}$  is expected to be a hard experimental task. This is an additional reason, together with time and cost, which pushes the designer of glass to use simulation models.

The alkali oxide effect on activation energy  $E_{\mu}$  is shown by fig.(2).  $E_{\mu}$  increases as the total alkali oxide content is increases. However, as sodium oxide is replaced by potassium oxide or vice versa,  $E_{\mu}$  values decreases to a minimum and start to increase again. Thus, fig. (2) fully illustrates the "mixed alkali effect" on viscosity of sodium potassium borate glasses.

Furthermore, fig. (2) shows that the calculated  $E_{\mu}$  value (hollow symbols) and the trend line connecting them reasonably represents the raw data. This supports the insertion of  $R_1$  and  $R_2$  terms, that reflecting the "mixed alkali effect", in expressing  $E_{\mu}$  shown in the model equation (6). The terms  $R_1$  and  $R_2$  are function of alkali oxide contents only, accordingly, the quantitative simulation presented in this study, supports the suggestion by Kuppinger and Shelby [4] that a mixed alkali effect initiated due to short range interaction between the alkali ions.

### Conclusions:

1. A model for simulation of viscosity as function of sodium potassium glass compositions has been obtained. The model and the simulation technique can be utilized in the field of glass science and technology.
2. The suggestion that mixed alkali effect originates from short range interaction between alkali ions has been supported by the presented model.

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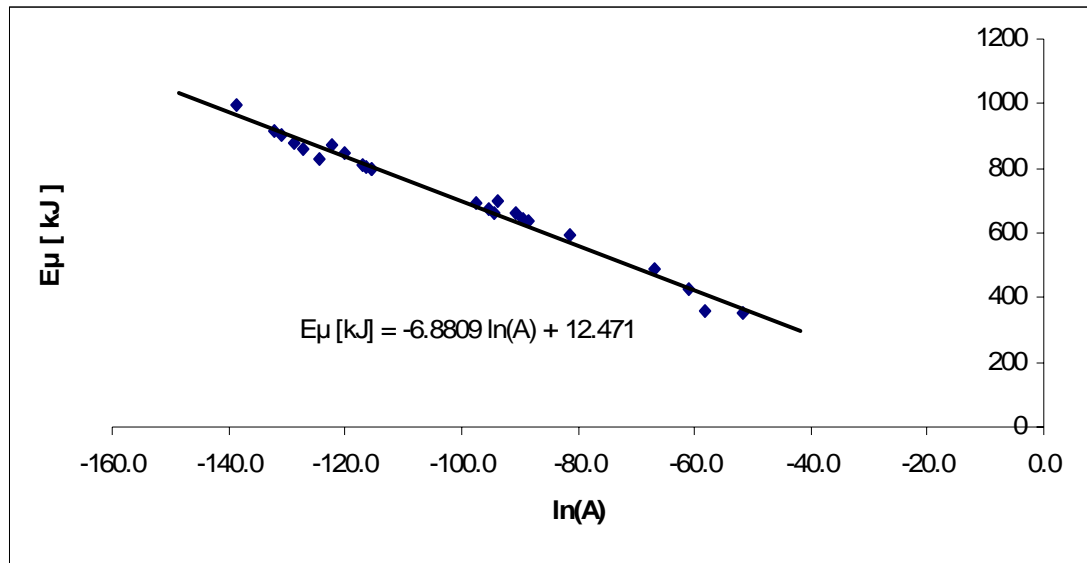


Fig. (1): Activation energy versus lnA. The equation of least squares line representing the data is also shown.

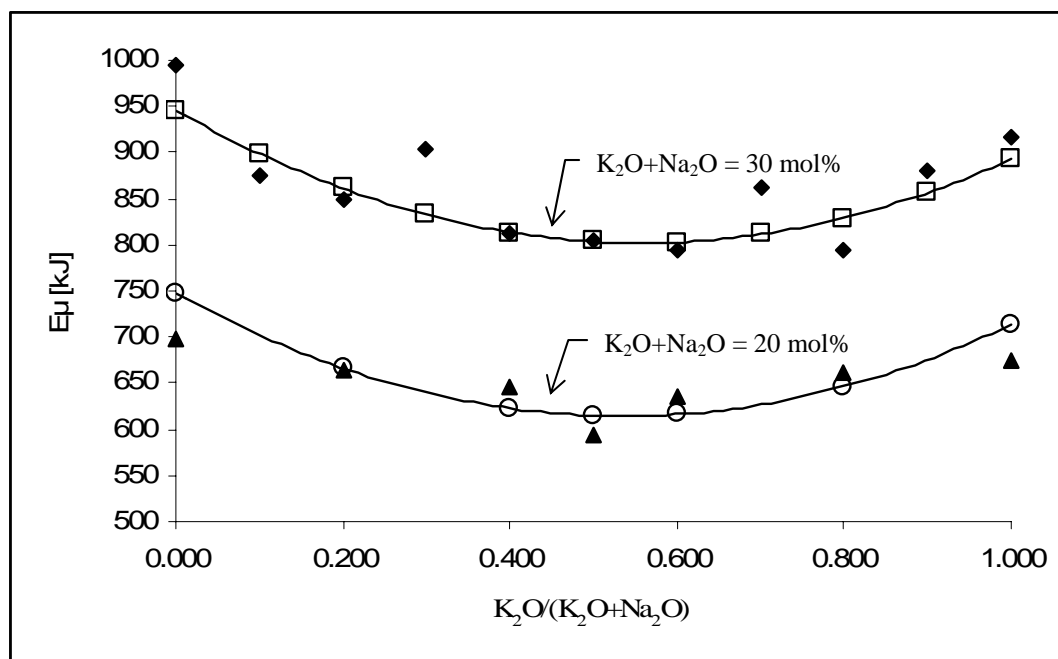


Fig (2): The variation of  $E_{\mu}$  with alkali content. The solid symbols represent raw data, while the hollow symbols represent the calculated  $E_{\mu}$ . The total alkali oxide contents are indicated in the figure.