# Mixed Alkali Effect on Viscosity of Sodium Potassium Borate Glasses

Dr. Saad B. H. Farid

**Received on:**
**Accepted on:8/5/2008**

**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

**خلاصة**:

تمت دراسة تأثير محتوى الاكاسيد القلوية على لزوجة زجاج الصـوديوم-بوتاسـيوم-بورون. وقد وضع نموذج لتفسير انحراف قيم اللزوجة عن علاقة الاضافة الحسـابية البسـيطة لاستكشاف تأثير الاستبدال الجزئي لاحدى الاكاسيد القلوية بالآخر. تمت الاستفادة من قيم منشورة لدرجات الحرارة لقيم لزوجة زجاج ثابتة وكذلك لقيم طاقات التنشـيط لتركيبـات مـن زجـاج الصوديوم-بوتاسيوم-بورون واستخدمت حسابات القيمة الوسـطية التربيعيـة لغـرض تحليـل المعطيات.

وجدت علاقات خطية وغير خطية تحدد معـاملات اللزوجـة المرتبطـة بالمكونـات الكيميائية للزجاج تحت الدراسة. وقد تم حساب قيم اللزوجة حسب درجـة الحـرارة باسـتخدام النموذج المقترح وكذلك تم حساب حرارة الانصهار لهذا النوع من الزجاج. بالاضافة الى ذلـك، بين النموذج تأثيرات قلوية مختلطة من الدرجة الاولى والثانية على لزوجة الزجاج.

## 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

Dept of Materials Eng, Univ of Tech, Baghdad, Iraq

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$^{o}$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 μ with the temperature is expressed as [5]:

$$\mu = A\,T \exp(10^3 BT) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

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" Eμ of the viscous process [5]:

$$E\mu\,[J] = 10^3\,R\,B \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where R is the gas constant. Thus,

$$\mu = A\,T \exp(E\mu[J]/RT) = A\,T \exp(10^3\,E\mu[kJ]/RT) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Consequently, Eμ is regarded as function of glass composition similar to B.

$$E\mu = \sum_{i=1}^{i=n} Ci.Ni \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

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

The natural logarithm of equation (3) reads:

$$\ln\mu/T = \ln A + 10^3\,E\mu[kJ]/RT \quad \ldots\ldots\ldots \quad (5)$$

Accordingly, values of lnA can be calculated for a given set of viscosity μ

Dept of Materials Eng, Univ of Tech, Baghdad, Iraq

at certain temperature T and Eμ for a range of glass compositions.

The parameter B appears in equation (1) is approved to be linearly related to lnA [5]. Thus, Eμ 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 $R_1$, $R_2$ to establish better description of compositional effect on viscosity. Finally, the model equation for Eμ is expressed as:

$$E\mu = C_1.\text{mol\%}B_2O_3 + C_2.\text{mol\%}Na_2O + C_3.\text{mol\%}K_2O + C_4.R_1 + C_5.R_2 \quad \ldots\ldots (6)$$

where $R_1$ and $R_2$ represents first and second order mixed alkali effect:

$$R_1 = \frac{\text{mol\%}\,K_2O}{\text{mol\%}\,Na_2O + \text{mol\%}\,K_2O} \quad \ldots. (7)$$

$$R_2 = (R_1)^2 \quad \ldots\ldots (8)$$

The above equations calculate Eμ 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 $10^{10}$Pa.s and $10^{11}$Pa.s viscosity values and the associated activation energies Eμ [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 standard error of the measured Eμ is calculated by statistical method [6] and found to be equal to 23.52 kJ. I.e. a supposed model that calculates Eμ 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% $B_2O_3$ | Mol% $Na_2O$ | Mol% $K_2O$ | Temp. [$^oC$] at $10^{10}$Pa.s | Temp. [$^oC$] at $10^{11}$Pa.s | Eμ [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 |

$L^2$-regression technique [3, 7] is used to obtain calculated Eμ utilizing glass compositions and measured Eμ 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 Eμ is obtained. Several attempts were made to express Eμ as function of other terms such as the combinations of the mol% of oxide constituents. The standard error for calculated Eμ do not reduced until "mixed alkali effect" expressed by $R_1$

Dept of Materials Eng, Univ of Tech, Baghdad, Iraq

and $R_2$ terms is taken into account. The final standard error for Eμ 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 *Ci* that obtained by $L^2$-regression and correlates the sodium potassium borate glasses with activation energy of viscous flow Eμ.

Table (2): Coefficients *Ci* 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 lnA's from calculated Eμ. Table (3) shows the values of $R_1$, $R_2$ terms used to model Eμ that associated with glass compositions listed in table (1). The table also shows calculated Eμ and lnA.

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 $R_1$, $R_2$, Eμ, lnA and fusion temperatures.

Table (3): List of $R_1$, $R_2$, Eμ and lnA calculated for glass compositions in table (1).

| No | $R_1$ | $R_2$ | calculated Eμ [kJ] | calculated lnA |
|---|---|---|---|---|
| 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 |
| Eμ [kJ] | 709.5 | 737.9 | 763.8 |
| lnA | -101.3 | -105.4 | -109.2 |
| Calculated fusion temperature. | 602 °C | 600 °C | 598 °C |

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

**Discussion:**

Dept of Materials Eng, Univ of Tech, Baghdad, Iraq

Fig. (2) shows the scattering of the raw data (solid symbols) around the trend line. This scattering explains the standard error predicted for Eμ. Obviously, the standard error can take smaller value for larger number of raw data. The large values of Eμ shown in table (1) together with equation (3) demonstrates that The viscosity μ and the activation energy Eμ is very sensitive to minor errors in measuring the temperature T. Thus, minimizing the scattering in measuring Eμ 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 Eμ is shown by fig.(2). Eμ increases as the total alkali oxide content is increases. However, as sodium oxide is replaced by potassium oxide or vice versa, Eμ 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 Eμ 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 Eμ 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.

**References**:

1. Mazurin O.V. (2005), "History, perspectives, and problems of measurement and calculation of glass properties", Third Balkan Conference on Glass Science and Technology. Varna, p.p.1-8.
2. Taylor J. R. and Bull A. C. (1986), "Ceramics Glaze Technology", Pergamon Press Inc. New York, USA, p.p. 192-193.
3. Fluegel A., Varshneya A. K., Earl D. A., Seward T. P., Oksoy D. (2004), "Improved Composition-Property Relations in Silicate Glasses, Part I: Viscosity", Proceedings of the 106th Annual Meeting of the American Ceramic Society, Ceramic Transactions, 170, p.p. 129-143.
4. Kuppinger C. M. and Shelby J. E. (1985), "Viscosity and Thermal Expansion of Mixed Alkali Sodium Potassium Borate Glasses", J. Amer. Ceram. Soc., 68, p.p. 463-467.
5. N'dala I., Cambier F., Anseau M. R. and Urbain G. (1984), "Viscosity of Liquid Feldspars Part I: Viscosity Measurements", Br. Ceram. Trans. J. 83, p.p. 105-107.
6. Motulsky H.J. (2003), "*Prism* 4 Statistics Guide-Statistical analyses for laboratory and clinical researchers", GraphPad Software Inc., San Diego CA, p.p. 30-31.

Dept of Materials Eng, Univ of Tech, Baghdad, Iraq

7. Vanderbei R. J. (2001), "Linear Programming: Foundations and Extensions", Princeton University, Princeton, USA, p.p. 193-196.

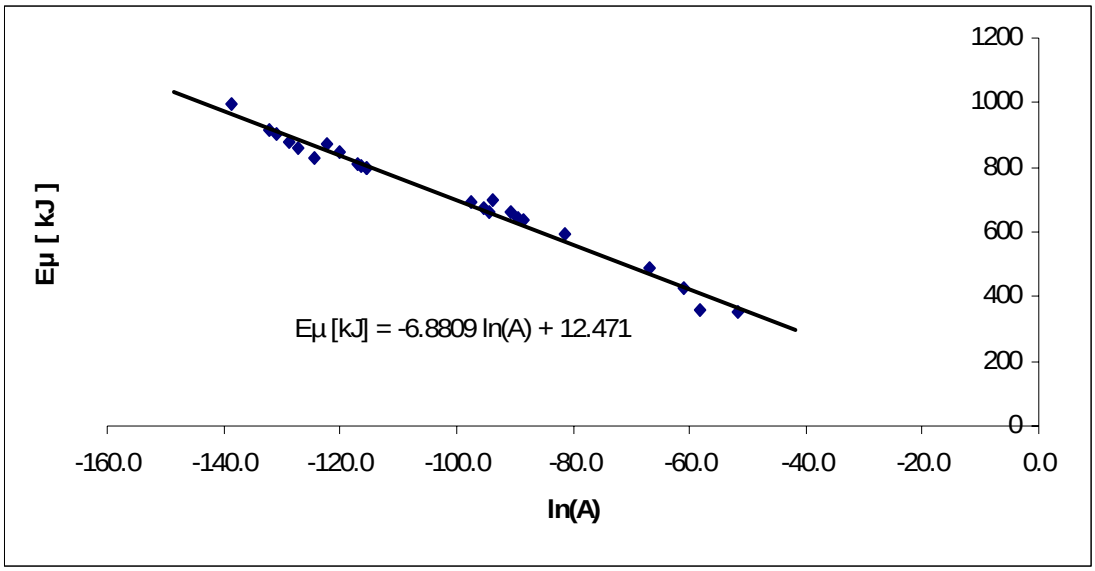


Fig. (1): Activation energy versus lnA. The equation of least squares line representing the data is also shown.

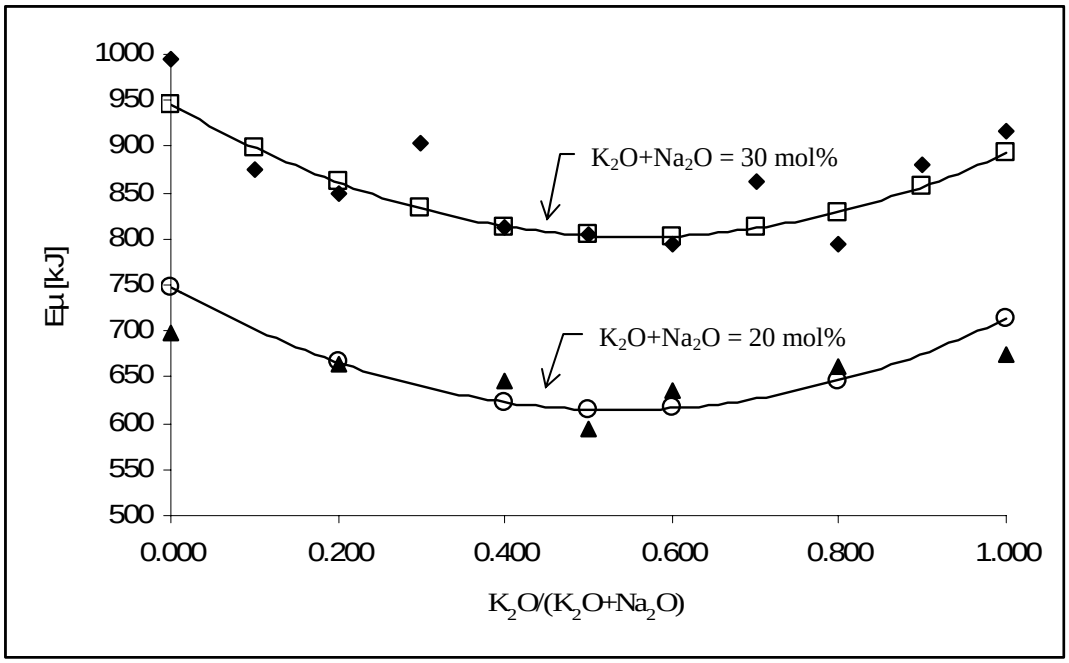


Fig (2): The variation of Eμ with alkali content. The solid symbols represent raw data, while the hollow symbols represent the calculated Eμ. The total alkali oxide contents are indicated in the figure.