

Specific Features of Changes in the Properties of One- and Two-Alkali Borate Glasses Containing Water: II. Viscosity of Mixed Alkali Borate Glasses

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Abstract—The temperature dependences of the viscosity for mixed alkali borate glasses containing lithium, sodium, and potassium oxides with a total alkali oxide content of 15 mol % are measured by the central rod bending method in the temperature range corresponding to a change in the viscosity from 10^{10} to 10^{13} dPa s. Analysis of the results obtained and the data available in the literature demonstrates that the content of residual structural water affects the manifestation of the mixed alkali effect in the viscosity of borate glasses. No significant change in the degree of fragility is found upon replacement of one alkali oxide by another alkali oxide in the studied glasses.

INTRODUCTION

The dependences of many glass properties deviate to a greater or lesser extent from a simple additive behavior upon replacement of one component by another component in the glass composition. When an alkali oxide in the glass composition is replaced by another oxide, the composition dependences of the property under consideration exhibit pronounced extrema [1, 2]. Although this phenomenon, termed the mixed alkali effect, has been known for more than half a century, a unified theory that could describe the available experimental data on different properties of glasses with various compositions in the framework of this effect is as yet absent.

The mixed alkali effect most clearly manifests itself in the transport properties (such as the electrical conductivity, dielectric losses, and diffusion) associated with a change in the mobility of cations in the glass structure (for these properties, the mixed alkali effect in [3] was referred to as the neutralization effect). Moreover, the mixed alkali effect is observed for other properties that are not explicitly related to the motion of cations (for example, thermal expansion). The change in these properties is attributed to an increase in the mobility of the anionic glass network. For properties such as the density and refractive index, the mixed alkali effect virtually does not exceed the experimental error.

Among the physical properties of glass-forming melts, the viscosity is of special interest. Upon cooling of glass-forming melts, the structural transformations associated with the motion of constituent particles (including more mobile modifier cations and glass-forming network) become so slow that they cannot be observed experimentally. The melt structure is frozen,

and the glass is formed. It is reasonable to assume that, in the presence of several structural units differing in mobility, the freezing can occur at different temperatures. Although the viscosity of glass-forming melts does not depend directly on the mobility of alkali cations, the concentration dependences of the viscosity for the majority of glasses are also characterized by the mixed alkali effect when one alkali oxide in the glass-forming melt is replaced by another alkali oxide. According to the data of different researchers (see, for example, [4–7]), the mixed alkali effect in the viscosity manifests itself as a negative deviation from the additive behavior and, in some cases, the viscosity of mixed alkali glasses appears to be even considerably less than the viscosities of the relevant one-alkali glasses. The isocomes (lines of equal viscosity) constructed for mixed alkali glasses, as a rule, exhibit temperature minima at certain ratios between alkali oxides in the glass composition depending on the type of alkali ions. In the majority of cases, the composition corresponding to the minimum viscosity depends on the ratio between the sizes of alkali cations, their total content, and the viscosity chosen for constructing the isocom. Izard [1] and Kappinger and Shelby [7] assumed that the manifestation of the mixed alkali effect in the viscosity decreases with a decrease in the concentration of alkali oxides and an increase in the temperature.

However, there is some evidence that the manifestation of the mixed alkali effect in the viscosity is not a property common to all mixed alkali glasses.

In particular, Nemilov [6] studied the viscosity of alkali silicate glasses and observed a negative deviation from additivity for sodium potassium silicate glasses with a total alkali oxide content of 20 mol %. However, this deviation was less pronounced for lithium potas-

sium silicate glasses with a similar composition. Matusita *et al.* [8] made the inference that negative deviations from additivity in the viscosity isotherms can be observed only for series of mixed alkali glasses that are characterized by relatively close viscosities of the corresponding one-alkali glasses.

It should be noted that the data available in the literature on the manifestation of the mixed alkali effect in the viscosity are rather contradictory. Matusita *et al.* [9] showed that, despite the close values of the viscosity of the binary one-alkali glasses, no clearly defined minimum is observed in the viscosity isotherms of sodium potassium and lithium potassium glasses whose total alkali oxide content is equal to 10 mol %. The viscosities of sodium potassium borate glasses with an alkali oxide content of 20 mol % also almost monotonically change upon replacement of potassium oxide by sodium oxide. However, Kappinger and Shelby [7, 10] demonstrated that the isocoms of two-alkali borate glasses containing lithium, sodium, potassium, rubidium, and cesium oxides with total alkali oxide contents of 30 and 20 mol % are characterized by a clear-cut mixed alkali effect and that the degree of deviation from additivity depends on the difference between the radii of alkali ions entering into the composition of the glasses under consideration.

The disagreement between their own data and the results reported by Matusita *et al.* [9] was attributed by Kappinger and Shelby [10] to the different forms of representation of the results obtained. Matusita *et al.* [9] used viscosity isotherms, which led them to compare glasses with viscosities varying by several orders of magnitude within the same series. In the authors' opinion [10], this approach to consideration of the mixed alkali effect is incorrect because the magnitude of the effect depends on the viscosity. Furthermore, within this approach, it is impossible to observe small deviations from additivity (up to 5 K), which are characteristic of glasses with a low alkali oxide content (less than 10 mol %).

It should be noted that Matusita *et al.* [9] used a more careful procedure of glass synthesis. The glasses were synthesized at a temperature of 1100°C for 2–3 h in an electric furnace, after which the crucible with the glass melt was treated under vacuum. As a result of this additional treatment, the synthesized glasses had a minimum content of residual water. When measuring the viscosity, the dry gas was passed through a cell with the sample in order to prevent the action of atmospheric moisture on the sample. The glasses studied in [10] were prepared in quite a different way, namely, the glass melts were heat treated at a temperature of 850–1000°C for 10–15 min. In our earlier works [11–13], we synthesized one-alkali borate glasses and investigated their viscosity, thermal expansion, and structural relaxation parameters. It was shown that the synthesis time affects the content of residual structural water in the glass. A comparison between the synthesis condi-

tions of the glasses in [9] and [10] enabled us to assume that the water content in the glasses studied in [10] was substantially higher than that in the glasses examined in [9]. As a consequence, in these works, the results were obtained for glasses of different compositions.

In the present work, we investigated the viscosity of mixed alkali borate glasses containing lithium, sodium, and potassium oxides with a total alkali oxide content of 15 mol %. Unfortunately, the problem concerning the determination of the water or bound hydroxyl content in mixed alkali borate glasses still remains unsolved. For this reason, the analysis of the results obtained in this work and the inferences are based on the investigations of one-alkali glasses and are hypothetical in character.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Ternary borate glasses with alkali cations of two types were synthesized in a platinum crucible with a volume of 200 ml in a Globar-heater electric furnace. Boric acid and carbonates of the corresponding alkali metals (chemically pure) were used as the initial components for the preparation of the batch.

We synthesized three series of mixed alkali borate glasses with the following pairs of alkali oxides: Li₂O–Na₂O, Na₂O–K₂O, and Li₂O–K₂O. The total alkali oxide content was equal to 15 mol %. The alkali oxide composition varied with a step of 3 mol %. Therefore, each series involved five glasses (see table).

The glasses were synthesized at a temperature of 1150–1200°C for 1.5 h. The actual residence time of glass melts in the furnace was somewhat longer, because, simultaneously with preparation of samples for this work, we coiled springs from a fiber drawn from the melt of the studied glass for the investigation into the mechanical relaxation of mixed alkali borate glasses. The results of this investigation will be published in a separate work. In the course of producing the springs, the glass melt was removed several times and again placed in the furnace heated to the melting temperature. The total residence time of melts of all the glasses in the furnace was nearly identical, and, hence, the studied glasses should have approximately the same content of residual water.

The viscosity of the studied glass samples was measured on a viscometer by the central rod bending method in the temperature range corresponding to a change in the viscosity from 10¹⁰ to 10¹³ dPa s. Polished rectangular samples 32 × 4 × 2 mm in size were used for measurements. The method and the setup used were described in detail in [13, 14]. The root-mean-square error $\delta(\log \eta)$ of measurements using this method did not exceed $\pm 0.04 \log \eta$.

Designations, compositions (mol %), and parameters of the Vogel–Fulcher–Tammann equation describing the temperature dependences of the viscosity of the studied glasses

Glass no.	Glass designation	Glass composition, mol %				Parameters of the Vogel–Fulcher–Tammann equation		
		B ₂ O ₃	Li ₂ O	Na ₂ O	K ₂ O	A	B, K	T ₀ , K
		as-analyzed (as-batched)	as-analyzed (as-batched)	as-analyzed (as-batched)	as-analyzed (as-batched)			
1	L15B	84.7(85)	15.3(15)	–	–	–5.75	4943.8	426.0
2	N15B	84.5(85)	–	15.5(15)	–	–18.4	14900	191.2
3	K15B	86.0(85)	–	–	13.4(15)	–15.7	12084	222.8
4	L12N3	85(85)	11.9(12)	2.9(3)	–	–6.30	5624.3	375.7
5	L9N6	85(85)	8.7(9)	6.2(6)	–	–1.81	3319.4	435.7
6	LN7.5	84.6(85)	7.7(7.5)	7.7(7.5)	–	–4.82	4572.2	417.3
7	L6N9	85.2(85)	5.8(6)	9(9)	–	–1.74	2873.3	471.5
8	L3N12	84.8(85)	3(3)	12.2(12)	–	0.47	1996.2	509.2
9	N12K3	84.7(85)	–	12.5(12)	2.8(3)	–11.2	9902.2	243.6
10	N9K6	84.7(85)	–	8.8(9)	5.9(6)	–1.55	2900.6	446.6
11	NK7.5	85.5(85)	–	7.3(7.5)	7.3(7.5)	–3.0	3632.7	421.0
12	N6K9	85.2(85)	–	6.0(6)	8.9(9)	–3.62	3921.3	409.6
13	N3K12	85.4(85)	–	2.9(3)	11.7(12)	–5.79	5106.5	371.9
14	L12K3	84.8(85)	12.4(12)	–	2.8(3)	–3.12	3550.1	450.8
15	L9K6	85.8(85)	8.5(9)	–	5.8(6)	–17.0	13683.0	192.2
16	LK7.5	85.4(85)	7.3(7.5)	–	7.3(7.5)	–6.1	5200.6	385.5
17	L6K9	85.5(85)	5.8(6)	–	8.8(9)	1.83	1602.3	499.3
18	L3K12	85.9(85)	2.3(3)	–	11.3(12)	–6.41	5200.6	385.5

The experimental viscosities obtained were approximated by the Vogel–Fulcher–Tammann equation

$$\log \eta = A + \frac{B}{T - T_0},$$

where A , B , and T_0 are the parameters of the equation and T is the absolute temperature (K).

The parameters of the equation were calculated using the special program developed at the Laboratory of Glass Properties, Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences. The as-batched and as-analyzed compositions of the synthesized glasses and the parameters of the Vogel–Fulcher–Tammann equation, which describes the temperature dependences of the viscosity for the studied glasses with an approximation error of no more than the experimental error $\delta(\log \eta)$, are presented in the table.

RESULTS

Figure 1 shows the concentration dependences of the viscosity for three studied series of glasses at constant temperatures chosen for each series so that the measured values fall in the range corresponding to the ordinate axis represented in this figure. It is seen from

Fig. 1 that the negative deviations from additivity are observed for all three series.

In addition to our results, the data taken from [9] for sodium potassium borate glasses with a total alkali oxide content of 10 mol % are displayed in Fig. 1b. As can be seen from this figure, despite the same type of data representation in the form of viscosity isotherms, our data on the viscosity of the studied glasses indicate the manifestation of the mixed alkali effect, which is absent according to the data obtained in [9].

The deviations of the temperatures from the additive values at the viscosity $\eta = 10^{11}$ dPa s for our sodium potassium glasses and the data taken from [10] for similar glasses with total oxide contents of 30 and 20 mol % are compared in Fig. 2. A comparison demonstrates that our results are in good agreement with the data obtained in [10] and confirms the conclusion that the magnitude of the mixed alkali effect depends on the total alkali oxide content in the glass composition.

It is expedient to consider the results obtained in the present work, together with the results for one-alkali borate glasses [13], in the framework of the fragility concept, which has gained wide acceptance in recent years. The notion of strong and fragile glasses was introduced by Angell [15–17] for the classification of glasses according to the behavior of their structure-sen-

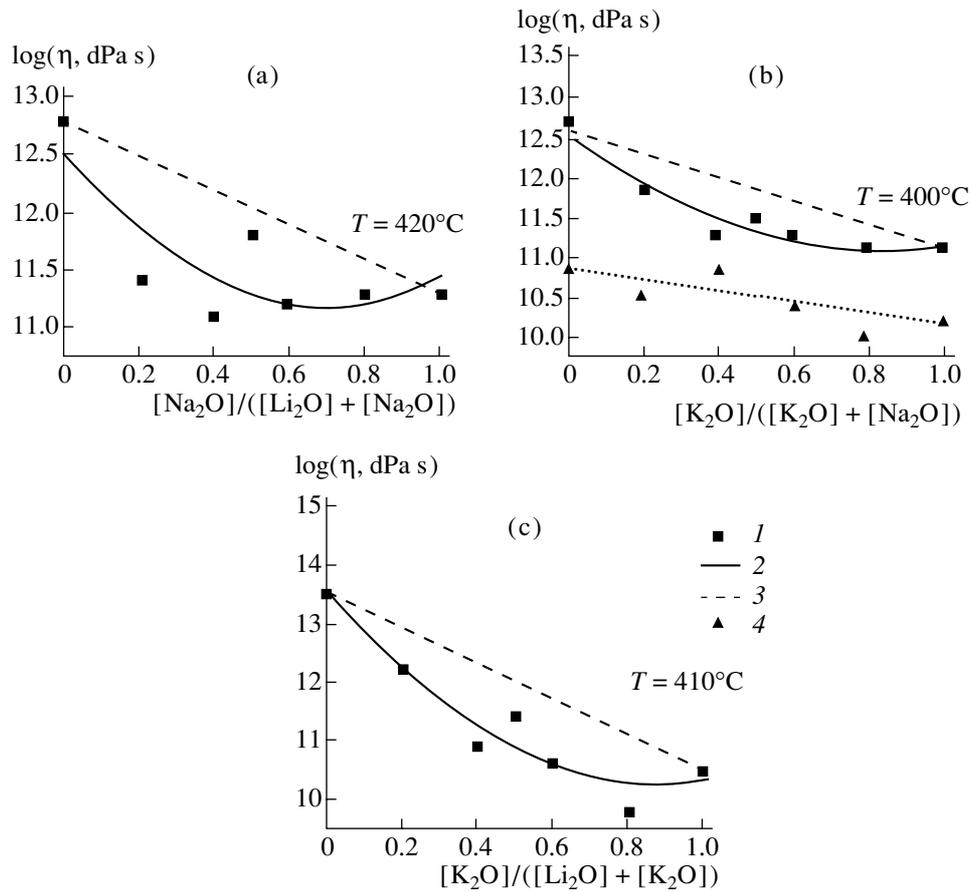


Fig. 1. Concentration dependences of the viscosity isotherms for (a) lithium sodium, (b) sodium potassium, and (c) lithium potassium glasses: (1) the experimental data, (2) the results of the best fitting to the experimental data, (3) the additivity line of the viscosity logarithm, and (4) the data taken from [9] for sodium potassium borate glasses with a total alkali oxide content of 10 mol %.

sitive and transport properties. The classification is based on the type of the dependence of the viscosity on the reciprocal of the temperature with respect to the temperature corresponding to the logarithm $\log(\eta, \text{dPa s}) = 13$, i.e., on the type of the plot in the $\log \eta - T_{13}/T$ coordinates. According to this classification, strong liquids exhibit an Arrhenius dependence over a wide range of temperatures, whereas fragile liquids are characterized by a pronounced deviation from linearity. The degree of fragility of glasses is an important parameter, because it characterizes the valence structure of the glass and is associated with the nature of internal structural transformations observed in the liquid [13, 18].

As an example, the curve plotted in the $\log \eta - T_{13}/T$ coordinates for the studied sodium potassium glasses is depicted in Fig. 3.

In [13, 19], the degree of fragility is characterized by the parameter S defined as

$$S = \lim_{\frac{T_{13}}{T} \rightarrow 1} \frac{d \log \eta}{d(T_{13}/T)}.$$

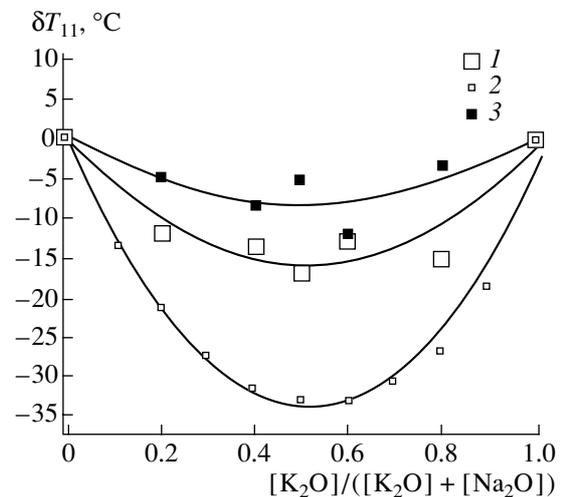


Fig. 2. Deviations of the temperatures from the additive values for sodium potassium glasses at the viscosity $\eta = 10^{11}$ dPa s: (1) the results of the present work and the data taken from [10] for glasses with total oxide contents of (2) 30 and (3) 20 mol %.

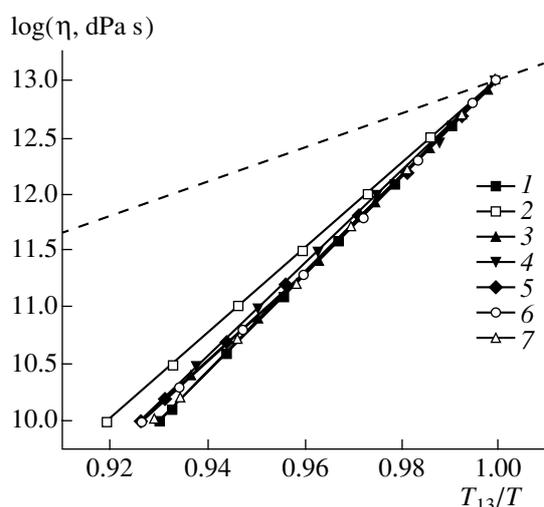


Fig. 3. Dependences of the viscosity logarithm $\log \eta$ on the reciprocal of the temperature T_{13}/T for different glasses: (1) N15B, (2) N12K3, (3) N9K6, (4) NK7.5, (5) N6K9, (6) N3K12, and (7) K15B (according to the designations given in the table).

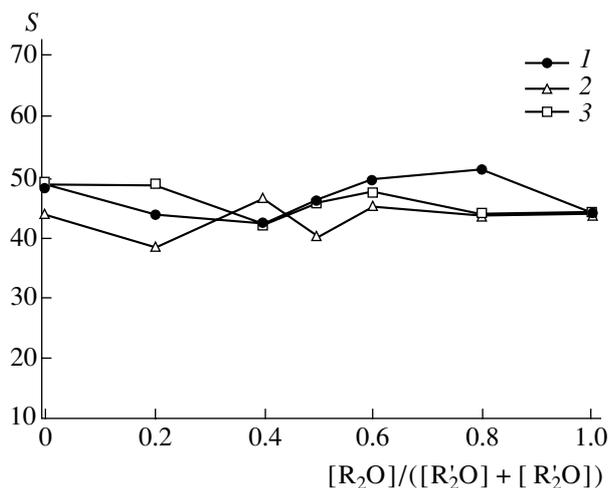


Fig. 4. Composition dependences of the fragility parameter S for (1) lithium sodium, (2) sodium potassium, and (3) lithium potassium borate glasses.

The least parameters S are observed for the strong glasses, which are characterized by a network formed by tetrahedra linked together through four vertices by bridging bonds. The glasses built up of chains or molecules have a more developed structure (due to the appearance of additional degrees of freedom that facilitate the motion of glass network units in the course of viscous flow) and, correspondingly, a larger fragility.

Using binary lithium and sodium borate glasses as an example, Chryssikos *et al.* [19] showed that the S parameter increases with an increase in the alkali oxide content in the composition of borate glass.

The composition dependences of the S parameter for the three series of mixed alkali borate glasses studied in the present work are plotted in Fig. 4. It can be seen from this figure that the replacement of one oxide by another oxide at the given total content of alkali oxides in the glass composition does not affect the degree of fragility of the glass.

DISCUSSION

The aforementioned temperature dependences of the viscosity for alkali borate glasses with a total alkali oxide content of 15 mol % permit us to assume that the mixed alkali effect manifesting itself as a negative deviation from additivity can take place; however, this deviation is most likely associated with the presence of residual water in the glass structure. This assumption is based on analysis of the results obtained in our work and the data taken from [9, 10].

As is known [20], boron in alkali borate glasses can occur in the threefold-coordinated and fourfold-coordinated states. This is responsible for the so-called "boron anomaly," which manifests itself in the appearance of pronounced extrema in the concentration dependence of the structure-sensitive properties of binary alkali borate glasses with an increase in the alkali oxide content, in particular, in the appearance of a minimum in the isocoms. This effect is explained by the fact that the fraction of threefold-coordinated or fourfold-coordinated boron atoms depends on the alkali oxide content in the glass composition. The NMR investigation of one-alkali borate glasses showed that, with an increase in the alkali oxide content, the number of fourfold-coordinated boron atoms increases and passes through a maximum in the range of 30–40 mol % R_2O [21].

Zhong and Bray [22] studied the change in the coordination state of boron atoms in mixed alkali borate glasses by NMR spectroscopy. Figure 5 shows the composition dependence of the fraction N_4 of fourfold-coordinated boron (contribution from groupings involving boron in this state) for one-alkali and two-alkali borate glasses containing identical concentrations of alkali oxides at a total alkali oxide content of 40 mol %. The dashed lines represent the N_4 fractions calculated by using the simple additivity of the corresponding fractions, that is,

$$N_4 = 0.5N_4(R'_4O) + 0.5N_4(R''_4O).$$

As can be seen from Fig. 5, the experimental values of N_4 are not only smaller than the calculated N_4 values but, in most cases, are smaller than the N_4 values for the corresponding one-alkali glasses.

These structural transformations should be reflected in the viscosity as a structure-sensitive property. This is confirmed by the results of our work and the data obtained in [10]. It should be noted that the water-containing glasses studied in our work were also studied by

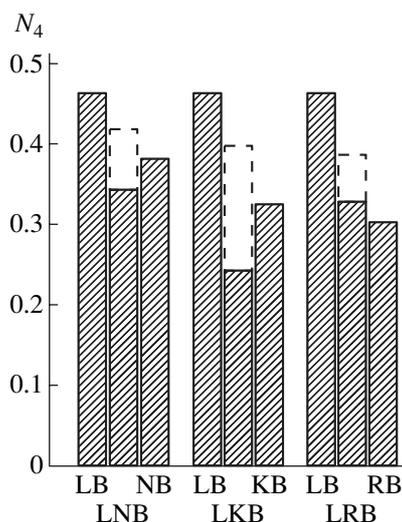


Fig. 5. Composition dependence of the fraction N_4 of fourfold-coordinated boron (contribution from groupings involving boron in this state) for one-alkali and two-alkali borate glasses containing identical concentrations of alkali oxides at a total alkali oxide content of 40 mol % (according to the data taken from [22]). Alkali borate glasses containing Li_2O , Na_2O , K_2O , and Rb_2O oxides are designated as LB, NB, KB, and RB, respectively. Lithium sodium, lithium potassium, and lithium rubidium mixed alkali borate glasses with identical concentrations of alkali oxides are denoted as LNB, LKB, and LRB. Dashed lines represent the N_4 fractions calculated reasoning from the simple additivity of the corresponding fractions.

Kappinger and Shelby [10] and Zhong and Bray [22], who investigated mixed alkali borate glasses by NMR spectroscopy. This inference is drawn reasoning from analysis of the synthesis condition of the glasses explored in [9, 10]. In [9], the authors prepared almost completely anhydrous alkali borate glasses by treating the glasses under vacuum and passing the dry gas during high-temperature measurements of the melt viscosity in the range 10^9 – 10^7 Pa s. It should be emphasized that no quantitative characteristics providing a means of estimating the water concentration were reported in the above works.

It seems likely that the mixed alkali effect can manifest itself in the viscosity of mixed alkali borate glasses only in the case when the glasses contain water in one form or another. No mixed alkali effect was observed for anhydrous glasses [9].

This inference agrees with the results obtained in [22]. In this work, the authors investigated glasses that were not subjected to additional heat treatments with the aim of removing water and the found minimum of the fraction of fourfold-coordinated boron in mixed alkali glasses could be associated with the presence of water in the glass structure.

Chryssikos *et al.* [19] demonstrated that the fragility parameters S for lithium borate glasses are somewhat larger than those for sodium borate glasses. This was

attributed to the fact that the fraction of fourfold-coordinated boron in lithium borate glass is higher than that in sodium borate glass of the corresponding composition. Our experimental results for mixed alkali borate glasses demonstrated that the S parameter remains constant for the studied series of glasses, even though according to the NMR data, the fraction of the fourfold-coordinated boron should change. This could indicate that the degree of fragility is not sufficiently sensitive to such structural transformations that occur in glasses with a similar composition and is an appropriate parameter only for characterizing materials whose structure and (or) bond types differ significantly.

CONCLUSIONS

The results of the above investigation into the temperature and concentration dependences of the viscosity for mixed alkali borate glasses containing lithium, sodium, and potassium oxides with a total alkali oxide content of 15 mol % allowed us to make the following inferences.

(1) The water content in alkali borate glasses affects the manifestation of the mixed alkali effect in the viscosity of these glasses: negative deviation from the additive behavior is observed for the composition dependence of the viscosity for water-containing glasses in each of the three series of the mixed alkali glasses under investigation. This is in agreement with the available NMR data.

(2) The degree of fragility remains unchanged upon replacement of one alkali oxide by another alkali oxide in the composition of mixed alkali borate glasses.

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