Manifestation of the mixed alkali effect on some properties of water containing alkali borate glasses

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Measurements of viscosity, thermal expansion and stress relaxation of two alkali borate glasses containing lithium, sodium and potassium oxides with the total alkali oxide content of 15 mol% were made. Structural thermal expansion coefficients, glass transition temperatures, structural and stress relaxation parameters were determined. Analysis of water content was made by means of absorption spectroscopy in the near infrared region. No distinctive mixed alkali effect was found in the composition dependencies of thermal expansion coefficients and relaxation parameters. The glass transition temperatures and relaxation times showed negative deviations from the additivity and this behaviour reflected the behaviour of viscosity. The manifestation of mixed alkali effect in viscosity was connected with water content in these glasses.

It is known that on adding a second alkali oxide to an alkali containing glass the deviations of various properties can be observed. This effect is commonly referred to as the mixed alkali effect. In spite of the existence of many experimental facts and theoretical explanations of the mixed alkali effect in glasses, an adequate and generally applicable theory of this effect is still lacking.

The mixed alkali effect most clearly manifests itself in the transport properties associated with a change in the mobility of cations in the glass structure. The mixed alkali effect can also be observed for the properties that are not explicitly related to the motion of cations such as viscosity and thermal expansion.

It is considered that for the majority of glasses the mixed alkali effect manifests itself in the viscosity as a negative deviation from the additive behaviour. 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 the case of alkali borate glasses, the data obtained by different authors concerning the mixed alkali effect are rather contradictory.

Matusita *et al*[1] showed that no clearly defined minimum is observed in the viscosity isotherms of sodium potassium and lithium potassium glasses whose total alkali oxide contents are equal to 10 and 20 mol%. However, Kuppinger & Shelby[2,3] demonstrated that the isokoms (i.e. the temperatures at which equal viscosities are measured) of two alkali borate glasses with total alkali oxide contents of 30 and 20 mol% are characterised by a clear cut mixed alkali effect where the degree of deviation from additivity depends on the difference between the radii of alkali ions in the glasses under investigation.

Kuppinger & Shelby[2,3] attributed the disagreement between their own data and the results reported by Matusita *et al*[1] to the different forms of data presentation. Matusita *et al* used viscosity isotherms and hence could compare glasses with viscosities varying by several orders of magnitude within the same series. In the other authors' opinion[2] this approach was considered incorrect because the magnitude of the effect depends itself on the value of viscosity.

It should also be noted that Matusita *et al* used a more careful synthetic procedure. The glasses were synthesised at a temperature of 1000°C for 2–3 h in an electric furnace, after which the crucible with the glass melt was treated under a vacuum. As a result, glasses with minimal water content were obtained. In order to prevent the action of atmospheric moisture while measuring the viscosity, the dry gas was passed through the cell containing the sample. The glasses studied in Ref. 2 were prepared differently. The glass melts were heated at a temperature of 850–1000°C for 10–15 min. On melting, no special measures were employed to minimise water content in glasses. In our earlier works,[4,5] we also studied the viscosity and thermal expansion of single alkali borate glasses. It was shown that the preparation time affects the content of residual water in the glass. A comparison between the synthetic conditions shows that the water content in the glasses studied[2] was substantially higher than that in the glasses examined in Ref. 1. This fact enabled us to propose a probable link between the manifestation of the mixed alkali effect on viscosity and the residual water content in borate glasses.

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The main task of the present work is to study the manifestation of the mixed alkali effect in viscosity, thermal expansion, stress and structural relaxation parameters of mixed alkali borate glasses containing small amounts of residual water.

Experimental procedure

Three series of mixed alkali borate glasses were synthesised: $x R_2 O \cdot (15-x) R_2' O \cdot 85 B_2 O_3$ where R,R'=Li, Na, K; x=0, 3, 6, 7·5, 9, 12, 15. Reagent boric acid and alkali carbonates were used as raw materials. The mixture of batch components was melted in the electric furnace under air. The glasses were synthesised at 1150–1200°C for 2–2·5 h. Compositions of all the glasses studied were analysed by wet chemical analysis. The results of analysis showed that the difference in alkali oxide by batch composition and by analysis did not exceed 1 mol%. The glasses were stored in a desiccator to prevent water absorption. The samples were ground and polished using anhydrous suspensions.

Viscosity measurements were made by the beam bending method at viscosities varying from 10^{10} up to 10^{13} dPas (where 1 dPas=1 Poise). The root mean square error of the logarithm of viscosity determined by this method was ±0·04.

The thermal expansion of the glasses was studied on the quartz dilatometer with a small measuring load. The dilatometer hysteresis curves of the glasses studied over a wide range of temperatures, including the glass transition range, were obtained. Glass transition temperatures T_g, thermal expansion coefficients in the range of temperatures below (α_g) and above (α_l) the glass transition and structural expansion coefficients α_s ($\alpha_s = \alpha_l - \alpha_g$) were determined. The instrumental error of thermal expansion coefficients determination was ±1×10^{-7} K^{-1}.

Measurements of stress relaxation were made on the relaxometer.[6] The relaxometer is designed to measure the time dependence of the stress in a glass sample at a constant strain. Coiled glass springs made from a glass fibre were used for these measurements.

Using the time dependencies of stress and the dilatometer curves, the relaxation parameters of the Tool–Narayanaswamy model were determined according to the ISC algorithm .[7] The constants b_s and the modulus K_s of structural relaxation and parameters b_σ and modulus K_s of stress relaxation were determined. The constant b_j (the subscript $j \equiv s$ in the case of structural relaxation and $j \equiv \sigma$ in the case of stress relaxation) characterises the width of the spectrum of the relaxation time τ_j, and describes the kinetics of change in the relaxation time by the equation

$$ M = \exp\left[-\left(\frac{t}{\tau_j} \right)^{b_j} \right] $$

where M is the relaxation function.

The modulus K_j is equal to the ratio of the viscosity to the relaxation time. These constants were calculated using the special optimising programmes developed in the laboratory for glass properties at the Institute of
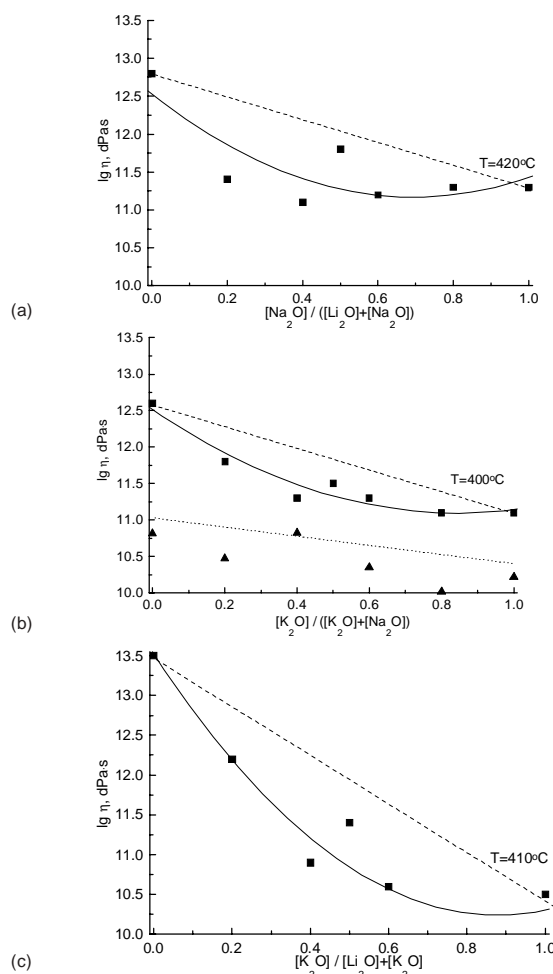
Figure 1. *Concentration dependencies of the viscosity isotherms for (a) $15 Li_2 O \cdot (15-x) Na_2 O \cdot 85 B_2 O_3$, (b) $15 Na_2 O \cdot (15-x) K_2 O \cdot 85 B_2 O_3$, (c) $15 Li_2 O \cdot (15-x) K_2 O \cdot 85 B_2 O_3$ glasses. Solid lines are best fits to the data, dashed lines are lines of the simple additivity of the viscosity logarithm. The error of the viscosity logarithm determination does not exceed the size of the symbols*
■ experimental points ▲ literature data[1]

Silicate Chemistry.[8] The errors in the determination K_j and b_j by these programs are ±0·1 and ±0·05, respectively.

Water related infrared spectra of studied glasses were recorded on the SF-2-LSS spectrometer.[9] The recording of infrared spectra was recorded at room temperature at the range of wavelengths 2·5–4 μm. The spectra obtained included two bands that characterise different types of structural insertion of hydroxyl groups into the glass network with the maximum absorption at about 2·8 and 3·5 μm (so-called 'free' and 'bonded' hydroxyl groups[10]). Unfortunately, the problem concerning the determination of the water content in alkali borate glasses still remains unsolved. For this reason the data obtained by means of infrared spectroscopy enabled us only to judge the form of the water in the glass structure.

Results

Figure 1 shows the concentration dependencies of viscosity for three series of studied glasses at constant temperatures. The temperatures for each series was cho-
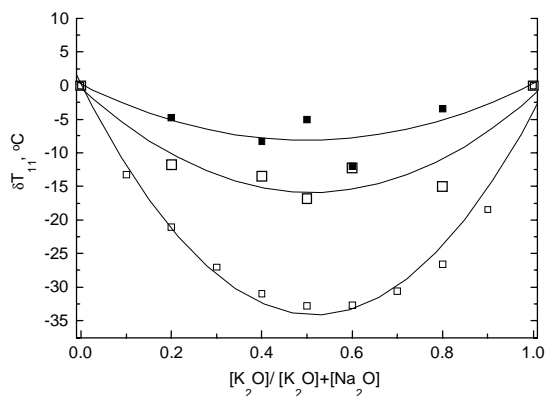
Figure 2. *Deviations of temperatures from the additive values for sodium potassium glasses at viscosity* $\eta = 10^{11}$ *(dPa s)*
■ results of the present work
□, ◻ data taken from Ref. 2 for glasses with total alkali oxide content of 20 and 30 mol% respectively

sen so that the measured values fell in the range corresponding to the ordinate axis represented in this figure. It is seen that negative deviations from the additivity are observed for all three series. In Figure 1(b) the data taken from Ref. 1 for sodium potassium borate glasses, with a total alkali content of 10 mol%, are also displayed. As can be seen from Figure 1, despite using the same type of data representation in the form of viscosity isotherms, our data on the viscosity of studied glasses indicate the manifestation of the mixed alkali effect which was absent according to the data obtained in Ref. 1.

In Figure 2 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 Ref. 2 for similar glasses with total alkali oxide contents of 30 and 20 mol% are compared. This comparison demonstrates that our results are in good agreement with the data obtained in Ref. 2 and confirm the conclusion that the magnitude of the mixed alkali effect depends on the total alkali oxide content in the glass composition.

In Figure 3 the concentration dependencies of glass transition temperatures and structural thermal expansion coefficients (STEC) of the three series of glasses being studied are displayed. The lines in the figures are the results of best fitting to the experimental data. It is seen that the glass transition temperatures show negative deviations from the additive values. This behaviour correlates with the composition dependencies of viscosity. The values of STEC increase on replacement of a smaller alkali cation by a larger one and this increase is the largest in the case of the lithium potassium glass series. Deviations from the additivity in the composition dependencies of STEC are not observed.

Figure 4 presents the concentration dependencies of structural and stress relaxation parameters b_s and b_σ respectively. In addition the relaxation times τ_s and τ_s, calculated from the ratio $K_j = \eta / \tau_j$, where K_j is modulus determined on treatment of structural relaxation ($j \equiv s$) or stress relaxation ($j \equiv \sigma$) data are shown. As seen from this figure the behaviour of concentration dependencies of relaxation times correlates with the behav-
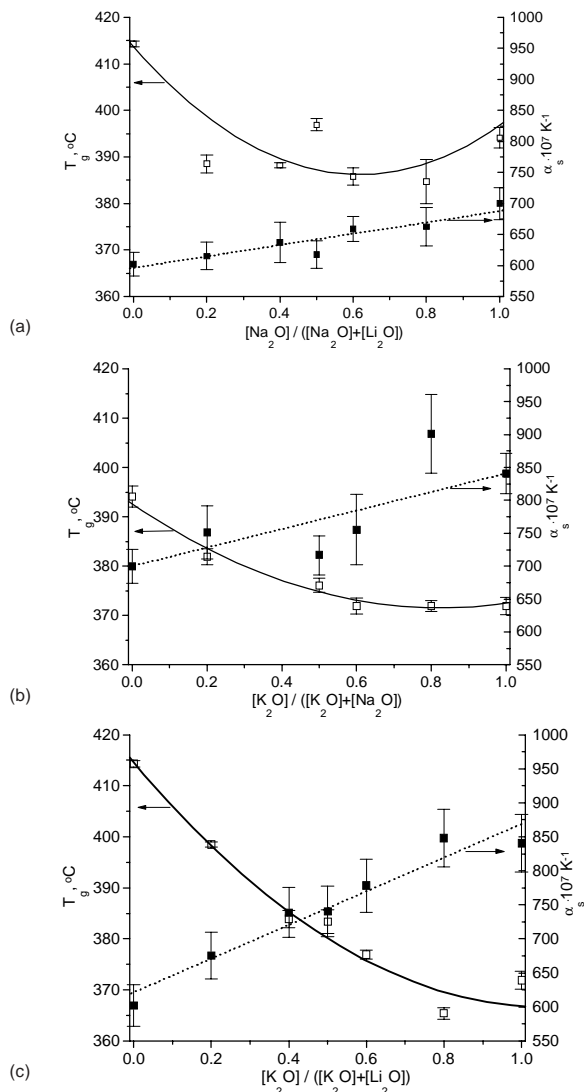

Figure 3. *Changes of properties with composition for (a)* $15Li_2O.(15-x)Na_2O.85B_2O_3$, *(b)* $15Na_2O.(15-x)K_2O.85B_2O_3$, *(c)* $15Li_2O.(15-x)K_2O.85B_2O_3$ *glasses. Lines drawn are best fits to the data*
■ structural thermal expansion coefficients α_s
□ glass transition temperatures T_g

iour of concentration dependencies of viscosity. Values of the parameter b_s increase on replacement of one alkali oxide by another. However, the deviations from additivity in the concentration dependencies of structural relaxation parameters are not observed. Values of the parameters b_s are constant within the error of their determination.

Figure 5 shows the comparison between infrared absorption spectra of the mixed alkali borate glasses with equal amounts of both alkali oxide and spectra of the relevant single alkali glasses. The spectra are shown in the form of $K(\lambda)$ (K is the absorption coefficient, cm^{-1}, λ the wavenumber, μm). As seen from Figure 5, the intensities of bands with the maximum absorption at 2·8–2·9 μm are similar for the glasses within one series. The intensities of absorption bands of the so called 'bonded' hydroxyl groups with the absorption maximum at 3·5 μm for mixed alkali glasses, are lower than that for the single alkali borate glasses. According to Ref. 10 this band characterises water in
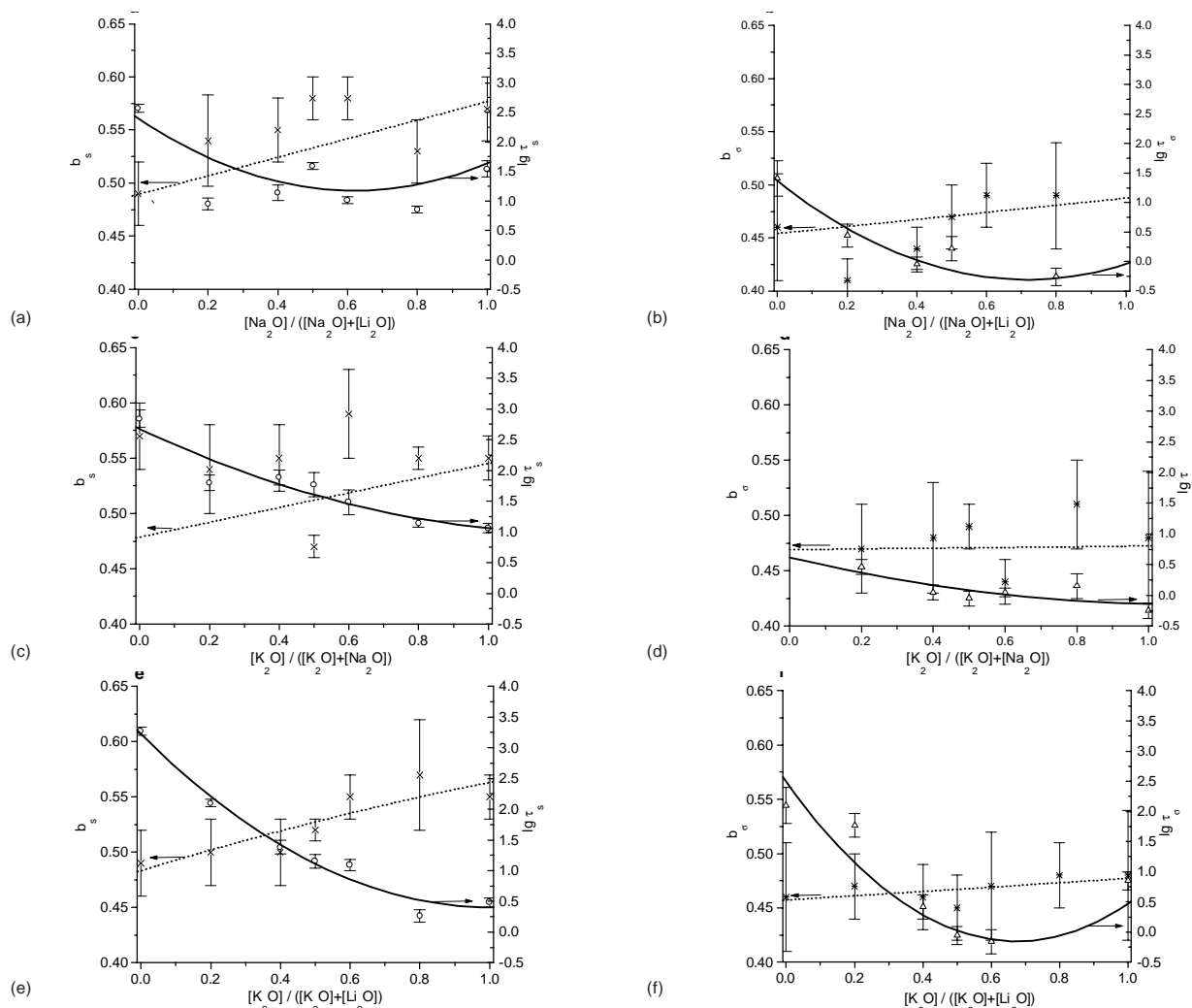
Figure 4. *Changes of relaxation parameters* c *with composition for (a,b) 15Li$_2$O.(15–x)Na$_2$O.85B$_2$O$_3$, (c,d) 15Na$_2$O.(15–x)K$_2$O.85B$_2$O$_3$, (e,f) 15Li$_2$O.(15–x)K$_2$O.85B$_2$O$_3$ glasses*
× b_s ○ τ_s * b_σ △ τ_s

the glass structure in the form of hydroxyl groups forming hydrogen bonds with neighbouring nonbridging oxygen atoms. The decrease in the absorption intensity implies a decrease in hydrogen bonding in glasses with mixed alkali oxides.

Discussion

The changes in the coordinated state of boron atoms in mixed alkali glasses were earlier studied by NMR

spectroscopy.[11] Negative deviations from the additive values of the fraction of fourfold coordinated boron for two alkali oxide glasses with a total alkali oxide content of 40 mol% were found. The structure sensitive properties studied in the present work, thermal expansion, structural and stress relaxation parameters for glasses with total alkali oxide of 15 mol%, did not reflect this structural transformation. However, the manifestation of the mixed alkali effect in the viscosity of studied glasses was found. It seems likely that
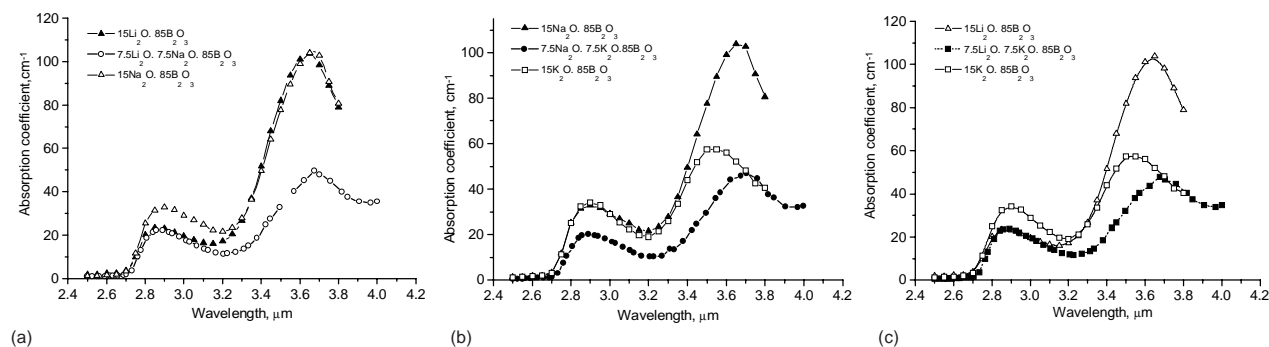

Figure 5. *Infrared absorption spectra for (a) 15Li$_2$O.(15–x)Na$_2$O.85B$_2$O$_3$, (b) 15Na$_2$O.(15–x)K$_2$O.85B$_2$O$_3$, (c) 15Li$_2$O.(15–x)K$_2$O.85B$_2$O$_3$ glasses*

the mixed alkali effect manifests itself in the viscosity of mixed alkali borate glasses only in the case when the glasses contain water. This inference agrees with the results obtained in Refs 2 and 3 and correlates with the data of infrared spectroscopy, Figure 5. The decrease in hydrogen bonding in glasses with two alkali oxides relieves the viscous flow and leads to the deviations from the additivity in the composition dependencies of viscosity.

Summary

The mixed alkali effect in composition dependencies of thermal expansion coefficients, structural and stress relaxation parameters for two alkali borate glasses containing lithium, sodium and potassium oxides with total alkali content of 15 mol% was not found. The glass transition temperatures and relaxation times did however show negative deviations from the additivity and this behaviour is reflected in the viscosity behaviour.

The water content in alkali borate glasses affects the manifestation of the mixed alkali effect in the viscosity of these glasses. This is in agreement with the available literature data and with the results of the recording of water related infrared spectra of studied glasses.

References

1. Matusita, K., Watanabe, T., Kamiya, K, Sakka, S. *Phys. Chem. Glasses*, 1980, **21** (2), 78.
2. Kuppinger, K. M. & Shelby, J. E. *J. Am. Ceram. Soc*, 1985, **68** (9), 463.
3. Kuppinger, K. M. & Shelby, J. E. *J. Am. Ceram. Soc*, 1986, **69** (12), 292.
4. Golubeva, O. Yu. & Startsev, Yu. K. *Phys. Chem. Glasses*, 2002, **43C**, 471.
5. Startsev, Yu. K. & Golubeva, O. Yu. *Glass Phys. Chem.*, 2002, **28** (3), 159.
6. Rekhson, S. M. & Mazurin, O. V. *Glass Technol.*, 1977, **18** (1), 7.
7. Mazurin, O. V., Khodakovskaya, R. Ya. & Startsev, Yu. K. *The relaxation theory of glass annealing and calculation of annealing regimes on its basis.* 1986. Leningrad. Nauka, 160P. (In Russian.)
8. Priven', A. I. & Startsev, Yu. K. *Glass Phys. Chem.,* 1993, **19** (2), 157.
9. Prokhorenko, O. A., Mazurin, O. V., Chistokolova, M. V., Tarakanov, S. V., Reznik, Yu. E. & Anfimova, I. N. *Glass Phys. Chem.*, 2000, **26** (2), 187.
10. Scholze, H. *Glastech. Ber.*, 1959, **32**, 81–8, 278–81, 314–20, 381–6.
11. Zhong, J. &, Bray, P. J. *J. Non-Cryst. Solids*, 1989, **111** (1)**,** 67.