Original Paper

Thermodynamic behaviour of the non-bridging oxygen-free glass system $X Ag_2O \cdot (2-X) Na_2O \cdot 2 Al_2O_3 \cdot 3 SiO_2 \cdot B_2O_3$ in contact with nitrate melts

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Equilibrium data for the Na^+/Ag^+ ion exchange at 375 °C between the glass $2 Na_2O \cdot 2 Al_2O_3 \cdot 3 SiO_2 \cdot B_2O_3$ ($T_g = 560$ °C), which is free of non-bridging oxygen, and $AgNO_3-NaNO_3$ salt melts are analyzed in two different ways (I and II). With the description of the glass as a regular solution (I) as well as with that as a mixed phase with a $\bar{n}$-type behaviour (II), the high selectivity of the glass system for the Ag^+ ions, having the larger crystalline ionic radius as compared to the Na^+ ions, is reflected by model-owned parameters. However, the existence of mechanical compressive stress and its partial reduction by structure relaxation in consequence of the viscosity-lowering effect of a high silver content are considerably differently in the two models.

Thermodynamisches Verhalten des Glassystems $X Ag_2O \cdot (2-X) Na_2O \cdot 2 Al_2O_3 \cdot 3 SiO_2 \cdot B_2O_3$ ohne nichtbrückenbildenden Sauerstoff in Kontakt mit Nitratschmelzen

Gleichgewichtsdaten des Na^+/Ag^+-Ionenaustausches bei 375 °C zwischen dem Glas $2 Na_2O \cdot 2 Al_2O_3 \cdot 3 SiO_2 \cdot B_2O_3$($T_g = 560$ °C), das frei von nichtbrückenbildendem Sauerstoff ist, und $AgNO_3-NaNO_3$-Salzschmelzen werden auf zwei verschiedenen Wegen (I und II) ausgewertet. Sowohl bei der Beschreibung des Glases als reguläre Lösung (I) als auch bei der als Mischphase mit $\bar{n}$-Typverhalten (II) wird die hohe Selektivität des Glassystems für Ag^+-Ionen, die im Vergleich zu Na^+-Ionen den größeren kristallchemischen Ionenradius aufweisen, durch modelleigene Parameter widergespiegelt. Das Auftreten von mechanischen Druckspannungen und deren partieller Abbau durch Strukturrelaxation infolge der viskositätserniedrigenden Wirkung der hohen Silbergehalte werden dagegen von beiden Modellen merklich unterschiedlich reflektiert.

1. Introduction

Sodium/silver ion-exchange investigations on the Na_2O-rich boroaluminosilicate glass of composition $(Na_2O)_{0.25}(Al_2O_3)_{0.25}(SiO_2)_{0.375}(B_2O_3)_{0.125}$ (denotation: NAB-25) at 375 °C ($\vartheta < T_g$; $T_{g,\,NAB\text{-}25} = 560$ °C) have shown a pronounced selectivity for the larger Ag^+ ions [1]. With X-ray Photoelectron Spectroscopy (XPS) measurements it could be demonstrated that this glass is free of non-bridging oxygen (NBO) within the limits of detection (sensitivity: $c_{NBO} \approx 5 \cdot 10^{20}$ cm^{-3}). Therefore, the network should dominantly consist of $SiO_{4/2}$, $AlO_{4/2}$ and $BO_{3/2}$ polyhedrons [2]. Consequently, only bridging oxygen (BO) is possible for oxocoordination of the mobile cations Na^+ and Ag^+, respectively, after the Na^+/Ag^+ exchange at $\vartheta < T_g$. The high covalency of the Ag–O bond (covalent portion 49 %), which is in contrast to the Na–O bond with about 18 %, permits the assumption of a linear coordination of the Ag^+ ion between two bridging oxygens of the glass network (| O–Ag–O |). Such a conception is supported by recent Electron Spin Resonance (ESR) investigations. Thus, the Na^+/Ag^+-exchanged glass NAB-25 shows an ESR signal with a g factor of 2.063, also known from such complexes like $[Ag(pyr)_4]^{2+}$ or $[Ag(o\text{-}phen)_2]^{2+}$ with a L–Ag–L coordination [3]. Moreover, the glass NAB-25 with the notably high Na^+ concentration of $c_{Na} = 0.986 \cdot 10^{22}$ cm^{-3} = = 16.4 mol l^{-1} is interesting because of the possibility of realizing such a remarkable Ag^+ concentration by way of Na^+/Ag^+ exchange at $\vartheta < T_g$ without a change in the network structure.

The Na^+/Ag^+-exchange isotherm at 375 °C ($\vartheta < T_g$) between the glass NAB-25 and corresponding nitrate melts as well as assumptions of the oxocoordination of Na^+ and Ag^+ ions are represented in figure 1. Both the aspect of the changing oxocoordination (place and type) for the mobile cations (Na^+, Ag^+) during the ion-exchange process and also the lack of knowledge of the Na^+/Ag^+-exchange behaviour of high Na_2O- and likewise high Al_2O_3-containing glasses (in each case 25 mol%) gave rise to a thorough analysis of the thermodynamic behaviour of the NBO-free glass system

$$X\,Ag_2O \cdot (2-X)\,Na_2O \cdot 2\,Al_2O_3 \cdot 3\,SiO_2 \cdot B_2O_3$$

at $\vartheta < T_g$.

2. Experimental conditions and analyzing procedure

The Na^+/Ag^+ ion exchange was carried out on plane glass samples ((15 × 15 × 10) mm^3) by contact with

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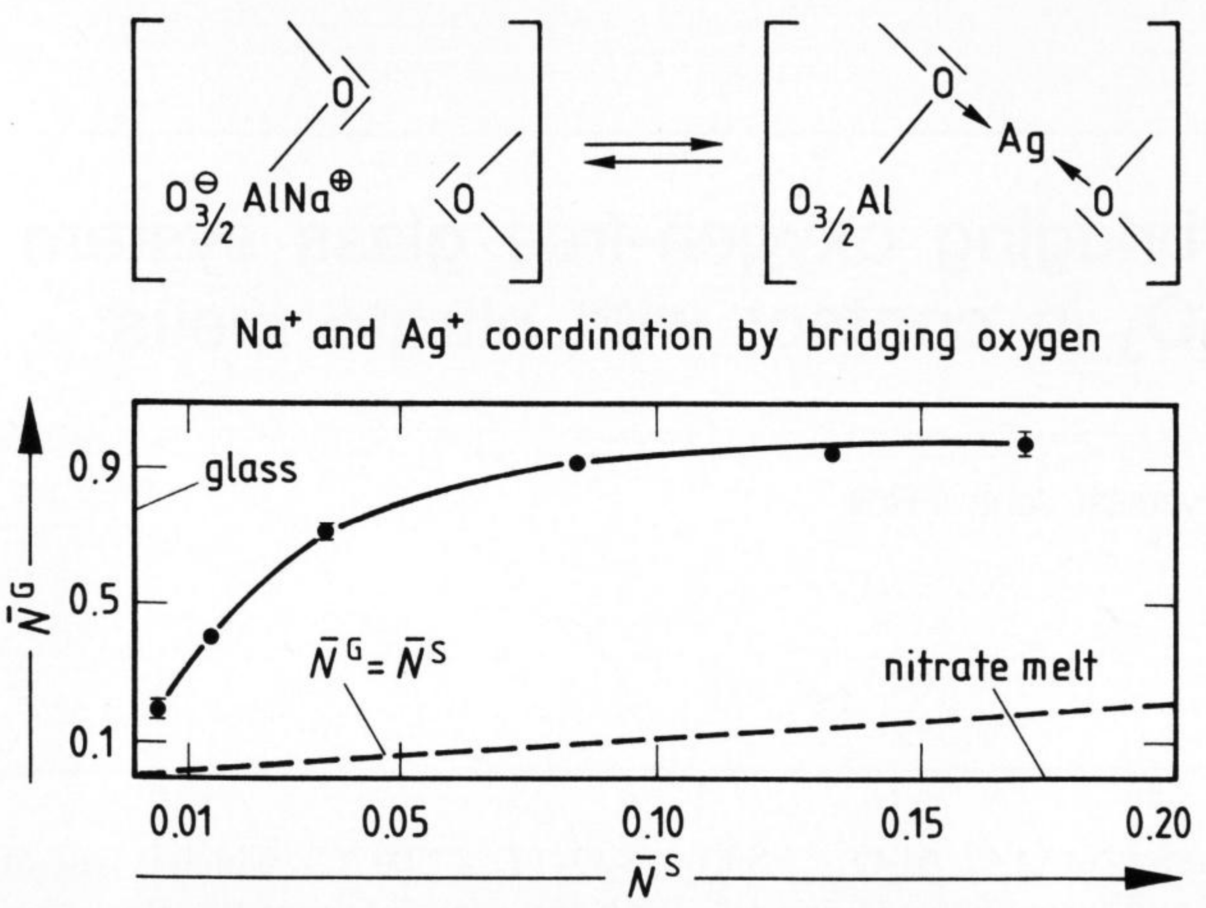

Figure 1. Isotherm of the Na^+/Ag^+ ion exchange between the glass NAB-25 and $NaNO_3$ – $AgNO_3$ melts at $\vartheta = (375 \pm 2)$ °C: oxocoordination of Na^+ and Ag^+ cations.

$(NaNO_3)_{1-s}$ $(AgNO_3)_s$ melts $(0.01 \leq s \leq 0.20)$ at a temperature of (375 ± 2) °C. The silver-concentration gradients, caused by the ion-exchange kinetics in the bulk glass, could be estimated by a "step-by-step"-etching process with the help of half-concentrated HNO_3 at (35 ± 1) °C and following titration of the solution [1].

Extrapolations of the silver content from the silver-concentration gradients on the glass surface permitted the estimation of values for the ion-exchange equilibrium between the glass and the salt melt. These surface silver contents were checked in respect of temporal invariancy for controlling a time-independent equilibrium. By the ion exchange at $\vartheta < T_g$ it was possible to realize partially Na^+/Ag^+-exchanged equilibrium compositions of the glass system[1])

$$X\, Ag_2O \cdot (2-X)\, Na_2O \cdot 2\, Al_2O_3 \cdot 3\, SiO_2 \cdot B_2O_3$$

(range of X: $0.384 \leq X \leq 1.96$) in the glass surface. The chemical analysis of the starting glass NAB-25 yielded a molar composition

$$(Na_2O)_{0.243}(Al_2O_3)_{0.255}(SiO_2)_{0.378}(B_2O_3)_{0.124}\,.$$

All data from ion exchange refer to this analyzed composition and are converted into the nominal composition of the glass NAB-25. The $AgNO_3$ content of the nitrate melt, corresponding to the equilibrium at the glass surface, was estimated from the starting salt mixture taking into account the part of silver, which migrated into the glass.

The equilibrium, described by equation (1), between a glass G and a salt melt S is characterized by an equilibrium constant $\tilde{K}$ (at a given temperature and pressure) after equation (2). This equilibrium constant $\tilde{K}$ is related to the selectivity coefficient (or rational equilibrium constant [4]) K'_N by equations (3 and 4) using the molar fractions N and activity coefficients f.

$$[Na^+]_G + [Ag^+]_S \overset{\tilde{K}}{\rightleftharpoons} [Ag^+]_G + [Na^+]_S\,, \tag{1}$$

$$\tilde{K} = \frac{a^G_{Ag} \cdot a^S_{Na}}{a^G_{Na} \cdot a^S_{Ag}} \tag{2}$$

with a_i = thermodynamic activity of the ion i and $a_i = f_i \cdot N_i$,

$$\tilde{K} = \frac{\bar{N}^G \cdot f^G_{Ag} \cdot (1 - \bar{N}^S) \cdot f^S_{Na}}{(1 - \bar{N}^G) \cdot f^G_{Na} \cdot \bar{N}^S \cdot f^S_{Ag}} \tag{3}$$

where $\bar{N}^G = N^G_{Ag}/(N^G_{Ag} + N^G_{Na})$ and

$$1 - \bar{N}^G = N^G_{Na}/(N^G_{Ag} + N^G_{Na})\,,$$

$$\tilde{K} = K'_N \frac{f^G_{Ag} \cdot f^S_{Na}}{f^G_{Na} \cdot f^S_{Ag}}\,. \tag{4}$$

K'_N varies with the glass composition, where the glasses containing only Ag_2O or Na_2O (compositions with $X = 0$ and $X = 2$; see section 1.) are defined as standards with $f^G = 1$ for $\bar{N}^G \to 0$ and $\bar{N}^G \to 1$, respectively.

Because of diverse assumptions the thermodynamic behaviour of the glass system was analyzed in two different ways (I and II) with the help of equations (2 and 4).

2.1. Glass as a regular solution (way I)

Due to small changes in composition, the activity coefficients f^S of the salt melt are approximately constant (equation (5)). The glass is regarded as a regular solution, where the ratio of the activity coefficients f^G for the glass corresponds to equation (6) [5 and 6].

$$\frac{f^S_{Na}}{f^S_{Ag}} = \text{const}\,, \tag{5}$$

$$\frac{f^G_{Ag}}{f^G_{Na}} = \frac{a^G_{Ag}}{\bar{N}^G} \Big/ \frac{a^G_{Na}}{1 - \bar{N}^G} = \exp \frac{\tilde{E}^G_{mix}}{R\,T} (1 - 2\,\bar{N}^G)\,. \tag{6}$$

From equations (4 to 6), relation (7) results:

$$\lg K'_N = \left(\lg \tilde{K} - \frac{\tilde{E}^G_{mix}}{R\,T \cdot 2.303} + \text{const}'\right) + + \frac{2\,\tilde{E}^G_{mix}}{R\,T \cdot 2.303} \cdot \bar{N}^G. \tag{7}$$

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[1]) In a strict sense glass does not represent an equilibrium phase. The exchangeable alkali ions (mobile "sublattice") are exclusively able to realize a thermodynamic balance with a contacted salt melt at $\vartheta < T_g$.

The graphic representation of lg K'_N in dependence on $\bar{N}^G$ reveals the estimation of the energy $\tilde{E}^G_{mix}$ from the slope of the curve $(2\,\tilde{E}^G_{mix}/(R\,T\cdot 2.303))$.

2.2. Glass as a mixed phase with $\tilde{n}$-type behaviour (way II)

If the activity coefficients f^S of the salt melt show no sufficient constancy, the behaviour of the melt can also be described as a regular solution. Therefore, equation (8) yields the ratio of the activities a^S in analogy to equation (6).

$$\frac{a^S_{Ag}}{a^S_{Na}} = \left(\frac{\bar{N}^S}{1-\bar{N}^S}\right) \exp \frac{\tilde{E}^S_{mix}}{R\,T}(1-2\,\bar{N}^S)\,. \tag{8}$$

The $\tilde{n}$-type behaviour of mixed phases is known from polycrystalline ion exchangers [7 and 8]. Accordingly the ratio of activities a^G for the glass can be expressed by equation (9):

$$\frac{a^G_{Ag}}{a^G_{Na}} = \left(\frac{\bar{N}^G}{1-\bar{N}^G}\right)^{\tilde{n}}. \tag{9}$$

For an ion-exchange equilibrium the linear relation (10) between $A(\bar{N}^S)$ and $B(\bar{N}^G)$ follows from equations (2, 8 and 9). Equation (10) is convenient for estimating the equilibrium constant $\tilde{K}$ as well as the thermodynamic factor (or non-ideality factor) $\tilde{n}$ in case the excess-interaction energy $\tilde{E}^S_{mix}$ of the salt melt is given.

$$\underbrace{\lg\left(\frac{\bar{N}^S}{1-\bar{N}^S}\right) + \frac{\tilde{E}^S_{mix}}{R\,T\cdot 2.303}(1-2\,\bar{N}^S)}_{A(\bar{N}^S)} = \tilde{n}\,\underbrace{\lg\left(\frac{\bar{N}^G}{1-\bar{N}^G}\right)}_{B(\bar{N}^G)} - \lg\tilde{K}\,. \tag{10}$$

3. Results and discussion

3.1. Glass as a regular solution (way I)

Figure 2 shows the selectivity coefficients $K'_N \equiv \equiv \bar{N}^G\cdot(1-\bar{N}^S)/\bar{N}^S\cdot(1-\bar{N}^G)$ of the investigated glass system (symbol: ●) corresponding to equation (7) in form of lg K'_N as a function of $\bar{N}^G$. The values $K'_N \gg 1$ demonstrate a high selectivity for the larger Ag^+ ions of the analyzed boroaluminosilicate glass in Na^+/Ag^+ ion-exchange equilibrium.

However, it is well-known that at a Na^+/K^+ ion exchange Na_2O-containing glasses usually prefer the smaller Na^+ to the K^+ ions [9 and 10]. Such a selective behaviour of glasses is easily understandable on the basis of the crystalline radius ($r_{Na} = 95$ pm; $r_K = 133$ pm), because these alkali ions are hard cations, characterized by rare-gas electron configurations.

The remarkable affinity of many Na_2O-containing glasses for Ag^+ ions (a non-alkali ion with $r_{Ag} = 126$ pm) is not yet explicable by the "crystalline largeness" of the ions. On the contrary, including the pronounced electronic polarizability of silver ions (possibility of deformation as a consequence of the non rare-gas electron configuration [Kr] $4d^{10}$) the high covalency of the Ag–O bond and also the formation of stable (Lewis) acid-base complexes ($O_{3/2}Si-\bar{O}\,|\,Ag$) with strong interactions between "soft" non-bridging oxygen (NBO) and "soft" Ag^+ ions should commonly be taken into consideration [1]. However, because the investigated boroaluminosilicate glass NAB-25 contains no NBO, it should be noted that an oxocoordination of Ag^+ cations is only possible by bridging oxygen (BO) of the $AlO_{4/2}$ units of the glass network. Doubtless, the observed preference of the glass NAB-25 for silver ions indicates a remarkable thermodynamic stability of silver configurations with BO, pointed out in figure 1. The bridging oxocoordination of silver (| O–Ag–O |) implies a certain function of a network former, although the binding strength is weak,

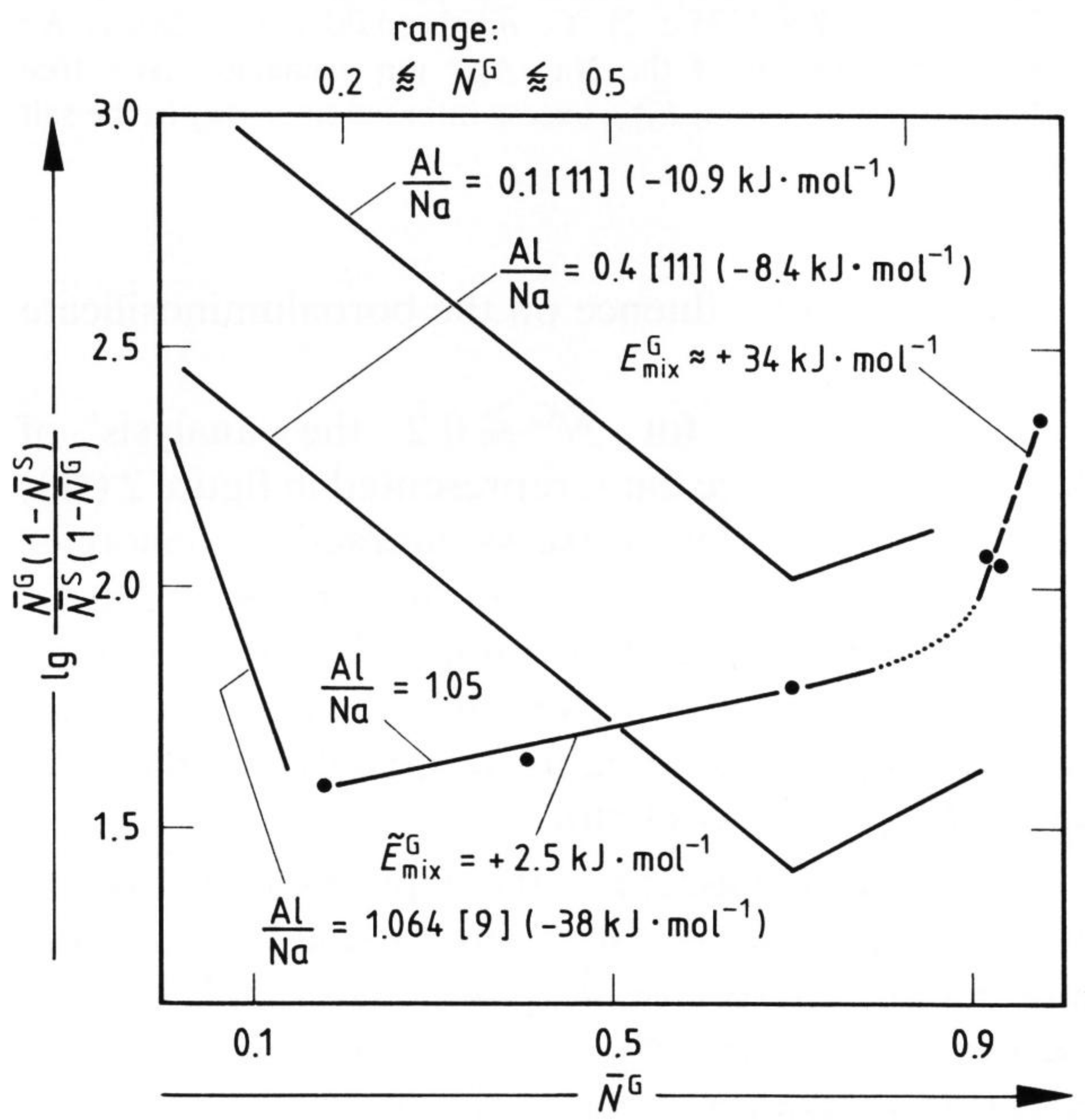

Figure 2. Logarithm of the selectivity coefficient $K'_N = \bar{N}^G(1-\bar{N}^S)/(\bar{N}^S(1-\bar{N}^G))$ as a function of the molar fraction of silver $\bar{N}^G$ in different aluminosilicate glasses after the model of regular solutions according to equation (7). ●: investigated glass system $X\,Ag_2O\cdot(2-X)\,Na_2O\cdot 2\,Al_2O_3\cdot 3\,SiO_2\cdot\cdot B_2O_3$, $\tilde{E}^G_{mix}$: excess-interaction energy in the glass ($\tilde{E}^G_{mix} < 0$: exothermic reaction, $\tilde{E}^G_{mix} > 0$: endothermic reaction).

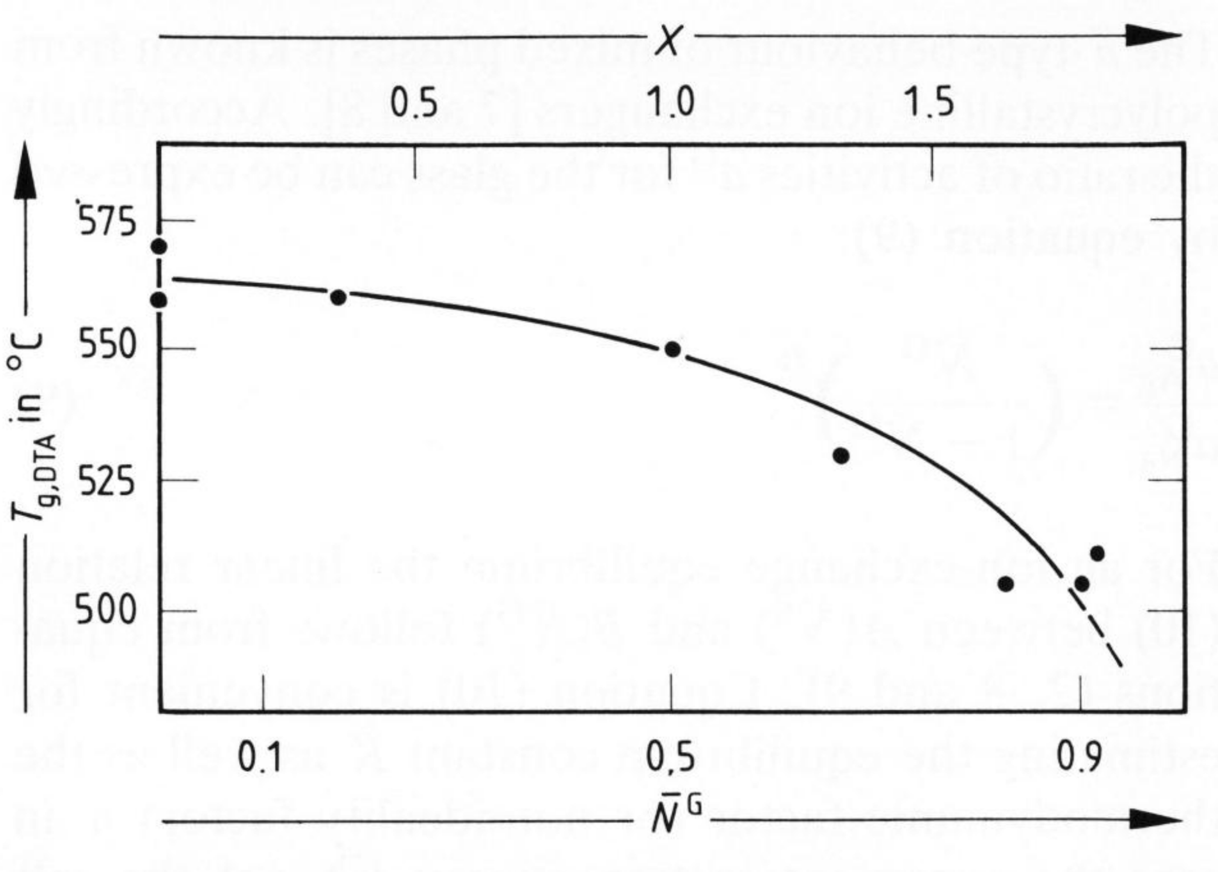

Figure 3. Glass transition temperature T_g as a function of the silver content of the glass system $X\,Ag_2O \cdot (2-X)\,Na_2O \cdot 2\,Al_2O_3 \cdot 3\,SiO_2 \cdot B_2O_3$. $\bar{N}^G$: molar fraction of silver in the glass NAB-25, X: Ag_2O content of the investigated glass system.

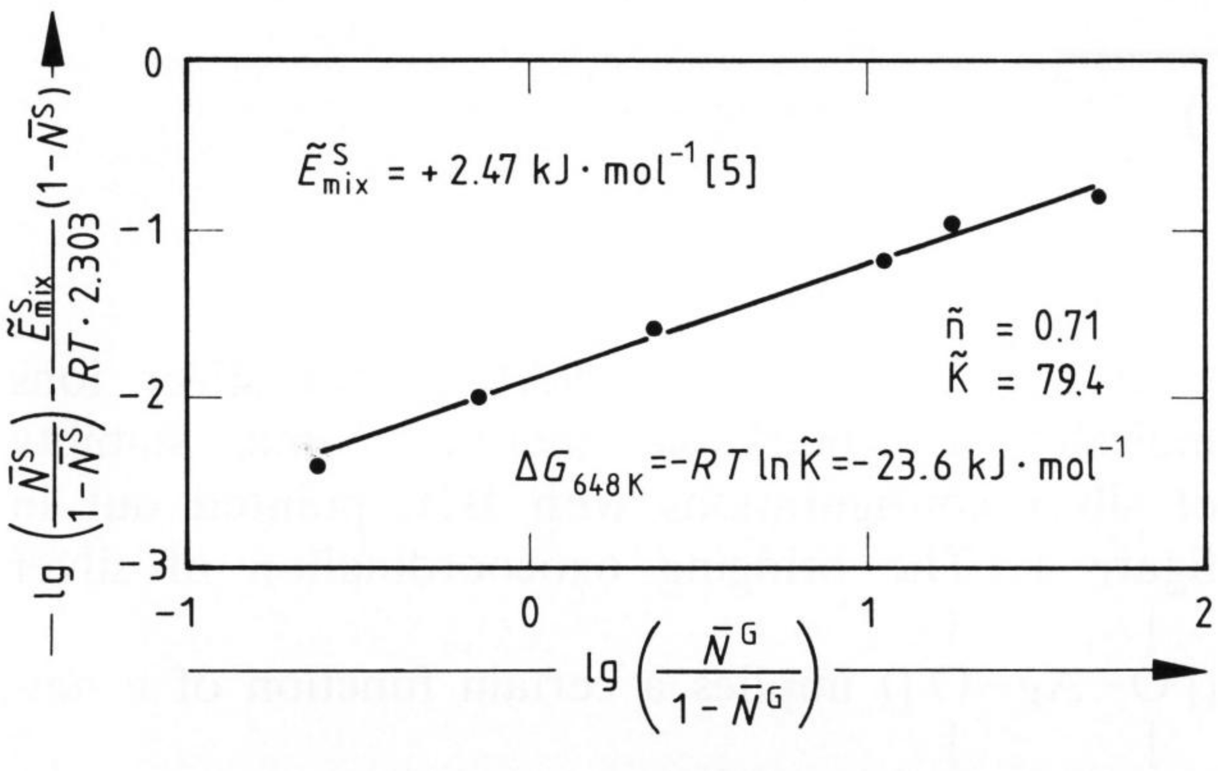

Figure 4. Test of the $\tilde{n}$-type behaviour for the glass system $X\,Ag_2O \cdot (2-X)\,Na_2O \cdot 2\,Al_2O_3 \cdot 3\,SiO_2 \cdot B_2O_3$ with $0.384 \le X \le 1.96$ at $\vartheta = (375 \pm 2)$ °C. $\tilde{n}$: thermodynamic factor. $\tilde{K}$: equilibrium constant of the Na^+/Ag^+ ion exchange, ΔG: free enthalpy of the reaction, $\tilde{E}^S_{mix}$: excess-interaction energy in the salt melt.

but not without influence on the boroaluminosilicate network.

Nevertheless, for $\bar{N}^G \gtrsim 0.2$ the analysis of Na^+/Ag^+-exchange data, represented in figure 2 (●), yields endothermic excess-interaction energies ($\tilde{E}^G_{mix} > 0$) under the preconditions corresponding to equation (7) (way I). In the range $0.2 \lesssim \bar{N}^G \lesssim 0.8$ the glass system shows approximately the behaviour of a regular solution (a straight line), characterized by a value $\tilde{E}^G_{mix} = +\,2.5\ kJ\ mol^{-1}$.

The drastical ascent of the experimental curve at $\bar{N}^G \gtrsim 0.9$ corresponds to a remarkable endothermic interaction energy of $\tilde{E}^G_{mix} \approx +\,34\ kJ\ mol^{-1}$. This increase is caused by a notable change in the structure-relaxation state of the glass network. The viscosity-lowering effect of the silver cations, which migrated into the glass, renders a relaxation of the boroaluminosilicate network (see [1]; compare footnote [1]) and also [11]), the actual network remarkably differing from that of the inserted glass NAB-25. It is provable that the glass transition temperature (T_g) for glasses of this composition range ($\bar{N}^G \gtrsim 0.9$) is decreased from 560 down to 500 °C at least. Figure 3 demonstrates the viscosity-lowering effect of the silver content by means of experimental T_g values. The glass transition temperature was measured by differential thermoanalysis ($5\ K\ min^{-1}$) on NAB-25 glass powder (grain size: 160 to 315 μm) after Na^+/Ag^+ ion exchange (415 °C; 41 h) with different $AgNO_3-NaNO_3$ melts. Both the silver molar fraction $\bar{N}^G$ and the Ag_2O content X of the glass system $X\,Ag_2O \cdot (2-X)\,Na_2O \cdot 2\,Al_2O_3 \cdot 3\,SiO_2 \cdot B_2O_3$ are deduced from a chemical analysis of the integral silver content of the glass powder after the Na^+/Ag^+ exchange.

Obviously, in the process of the Na^+/Ag^+ exchange at $\bar{N}^G \gtrsim 0.9$ an additional energy is necessary for working against the progressively plastically deformable glass network, causing the value $\tilde{E}^G_{mix}$ to increase (figure 2). As demonstrated in [1], these changes of the glass state at $\bar{N}^G \gtrsim 0.9$ have also a notable influence on the kinetics of Na^+/Ag^+ ion exchange in this boroaluminosilicate glass.

Regarding the reference data for the Na^+/Ag^+-exchange equilibrium in other aluminosilicate glasses [9 and 12], figure 2 shows decreasing selectivity coefficients K'_N for an increasing Al_2O_3 content in the range $0.2 \lesssim \bar{N}^G \lesssim 0.5$ (rising Al/Na ratio, where the Na_2O content is approximately constant; $20 \le Na_2O\ (mol\%) \le 25$). Moreover, the excess-interaction energy $\tilde{E}^G_{mix}$ changes from -109 to $+2.5\ kJ\ mol^{-1}$ indicating a transition from an exothermic to a slow endothermic reaction. Figure 2 shows that also for high silver contents ($\bar{N}^G > 0.8$) from [9 and 12] that the selectively for Ag^+ ions is again increasing as already stated.

3.2. Glass as a mixed phase with $\tilde{n}$-type behaviour (way II)

Figure 4 presents the data of the relation corresponding to equation (10). It turns out that under the assumption of $\tilde{n}$-type behaviour for the glass and of a regular solution for the salt melt the Na^+/Ag^+-exchange equilibrium can be described in the whole composition range ($0.384 \le X \le 1.96$ or $0.19 \le \bar{N}^G \le 0.98$) by one and the same parameter set ($\tilde{K}$, $\tilde{n}$). From the straight line in figure 4 an equilibrium constant of $\tilde{K} = 79.4$ and a thermodynamic factor of $\tilde{n} = 0.71$ are derivable for the Na^+/Ag^+ ion exchange. The analyzed value $\tilde{K}$ matches a free enthalpy of reaction at 375 °C of $\Delta G = -23.6\ kJ\ mol^{-1}$. The high equilibrium constant $\tilde{K} \gg 1$ corresponds with the elevated selectivity coefficient K'_N (way I) and reflects again the large affinity of the boroaluminosilicate system for the considerably covalent-bonded silver cations. The value of the thermodynamic factor $\tilde{n}$, which is doubtlessly estimated as $\tilde{n} < 1$, represents a positive deviation from the ideal behaviour of the glass system. All $\tilde{n}$ values, known from investigations of the Na^+/Ag^+ ion exchange in different glasses, are larger than one, reflecting a negative deviation of the ideal behaviour (Na_2O-containing silicate, aluminosilicate (Al/Na < 1) and galliumsilicate glasses [10]; borosilicate glasses [12]; soda-lime glasses and commercial multicomponent glasses [13]).

However, it can be demonstrated that the analysis of the investigated NBO-free boroaluminosilicate glass system yields a thermodynamic factor $\tilde{n}$ smaller than one, also in way I. Using the relation $\tilde{n} = 1 - \tilde{E}^{G}_{mix}/2\,R\,T$ (range of validity after [14]: $0.2 \lessapprox \tilde{N}^G \lessapprox 0.8$), which likewise corresponds to the theory of regular solutions [15], a value $\tilde{n} = 0.77$ is estimated, indicating also an endothermic (attractive) interaction between Na^+ and Ag^+ ions. Such positive deviations from the ideal behaviour have been observed hitherto exclusively in the ion exchange of small alkali ions by larger ones (for instance Na^+/K^+ exchange) at temperatures $\vartheta < T_g$ [16]. Under these conditions the difference in ionic radius governs the generation of mechanical compressive stress, because no structure relaxation of the network is possible. In fact, a compressive stress up to −380 MPa was measured in the surface of the glass NAB-25 after an Na^+/Ag^+ ion exchange (416 °C; 41.5 h; $(NaNO_3)_{0.9}(AgNO_3)_{0.1}$) [17].

4. Conclusions

It can be stated that with both methods of analysis (ways I and II) the NBO-free boroaluminosilicate glass system $X\,Ag_2O \cdot (2-X)\,Na_2O \cdot 2\,Al_2O_3 \cdot 3\,SiO_2 \cdot B_2O_3$ reflects, independently of the individual assumptions in the models, the strong selectivity for the larger Ag^+ ions by model-owned parameters. Furthermore, a mechanical compressive stress, generated in the glass during the Na^+/Ag^+ exchange at $\vartheta < T_g$, gives rise to an endothermic (attractive) interaction between Na^+ and Ag^+ ions or a positive deviation from the ideal behaviour (way I: $\tilde{E}^{G}_{mix} > 0$ (or $\tilde{n} < 1$) and way II: $\tilde{n} < 1$). Although the Ag^+ cation with an electronic polarizability of $\alpha = 2.67 \cdot 10^{-40}$ F m² [18] can be regarded as a soft ion, the difference of crystalline radii $\Delta r = r_{Ag} - r_{Na} = 31$ pm is sufficient for a generation of compressive stress in the rigid boroaluminosilicate network, exclusively containing bridging oxygen (Young's modulus of elasticity of the glass NAB-25: 64 GPa [19]), at low degrees of Na^+/Ag^+ exchange ($\tilde{N}^G < 0.9$).

In case that the equilibration process of Na^+/Ag^+ exchange produces higher degrees of exchange ($\tilde{N}^G > 0.9$) the drastically enlarged Ag_2O content enables a partial reduction of the mechanical stress via viscosity-lowering effect of silver. This structure-relaxation process of the glass network at highest Ag_2O contents ($X > 1.8$ or $Ag_2O > 22.5$ mol%) is mirrored by the analysis of the thermodynamic behaviour in ways I and II considerably differently in the two models.

5. Nomenclature

5.1. Symbols

$A(\bar{N}^S)$	A is a mathematical function of $\bar{N}^S$
a_i	(thermodynamic) activity of the ion i in mol l^{-1}
$B(\bar{N}^G)$	B is a mathematical function of $\bar{N}^G$
c_i	concentration of the ion i in the glass in mol l^{-1} or cm^{-3}
$\tilde{E}_{mix}$	excess-interaction energy in the glass in kJ mol^{-1}
f_i	activity coefficient of the ion i
ΔG	free enthalpy of exchange reaction in kJ mol^{-1}
g	g factor (Lande factor) of the Electron Spin Resonance (ESR)
$\tilde{K}$	thermodynamic equilibrium constant
K'_N	coefficient of selectivity or rational equilibrium constant, defined on the basis of molar fractions N
$\tilde{N}$	molar fraction of silver under defined equilibrium conditions, related to the Na^+/Ag^+ exchange
N_i	molar fraction of the ion i, related to the total glass composition
$\tilde{n}$	thermodynamic factor or non-ideality factor
R	universal gas constant in kJ mol^{-1} K^{-1}
s	composition of the used salt melt, molar fraction of $AgNO_3$
T_g	glass transition temperature in °C
X	variable of the composition in the investigated glass system
ϑ	exchange temperature in °C

5.2. Superscripts

G	glass
S	salt melt
~	characterization of the thermodynamic equilibrium conditions
–	average value
′	efficient value, i.e. without regarding thermodynamic activities

5.3. Subscripts

i	ion
mix	mixture
N	molar fraction

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