

Sodium/silver ion exchange between a non-bridging oxygen-free boroaluminosilicate glass and nitrate melts

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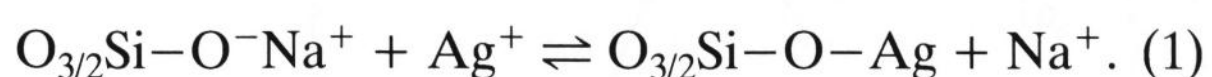
A sodium boroaluminosilicate glass, in which no non-bridging oxygen could be detected, is contacted with $\text{AgNO}_3\text{--NaNO}_3$ melts at 375 °C. A diffusion-controlled Na^+/Ag^+ exchange has been observed in the bulk of the glass up to a degree of exchange of 70 % (Fickian behaviour). For a higher degree of exchange network-structure relaxation processes appear as a result of the viscosity-lowering effect of silver, causing a change of the diffusion conditions during the ion exchange in the glass (non-Fickian behaviour). The time-independent equilibrium concentrations at the glass surface refer to a remarkable affinity of the glass for the highly polarisable Ag^+ cations (degree of exchange: 98 %). This result can be explained by coordinative binding of silver on the basic bridging oxygen of the $\text{AlO}_{4/2}$ tetrahedrons into the glass network.

Natrium/Silber-Ionenaustausch zwischen einem Boroalumosilicatglas ohne nichtbrückenbildenden Sauerstoff und Nitratschmelzen

An einem Natrium-Boroalumosilicatglas, in dem kein nichtbrückenbildender Sauerstoff nachgewiesen werden konnte, wird beim Kontakt mit $\text{AgNO}_3\text{--NaNO}_3$ -Schmelzen bei 375 °C im Glasvolumen ein diffusionsbestimmter Na^+/Ag^+ -Austausch bis zu Substitutionsgraden von 70 % beobachtet (Ficksches Verhalten). Bei höheren Austauschgraden treten zusätzlich infolge der viskositätssenkenden Wirkung des Silbers Netzwerk-Strukturrelaxationsprozesse auf, wodurch sich die Diffusionsbedingungen während des Ionenaustausches im Glas ändern (nicht-Ficksches Verhalten). Die zeitunabhängigen Gleichgewichtskonzentrationen an der Glasoberfläche weisen auf eine beachtliche Affinität des Glases ohne nichtbrückenbildenden Sauerstoff für die stark polarisierbaren Ag^+ -Kationen hin (Austauschgrad: 98 %). Dieser Befund wird durch eine koordinative Einbindung des Silbers am basischen Brückensauerstoff der $\text{AlO}_{4/2}$ -Tetraeder in das Glasnetzwerk erklärt.

1. Introduction

In context with the generation of refractive-index gradients in optical glasses by contact with appropriate salt melts, the equilibrium of sodium/silver ion distribution between such phases¹⁾ has been investigated frequently [1 to 3]. The exchange of these cations can be described by an equilibrium corresponding to equation (1):



The more covalent binding of silver on the glass network is an obligatory result of the distinctly smaller difference in Electro-Negativity (EN) for Ag–O bond ($\Delta\text{EN} = 1.6$; 53 % covalent portion, see also Ti–O bond [4]; for comparison: the Na–O bond with $\Delta\text{EN} = 2.6$; 18 % covalent portion). With regard to this aspect of covalency the Ag–O bond should be thoroughly comparable with the Si–O single binding ($\Delta\text{EN} = 1.7$; 49 %) of the silicate network. This obvious fact, which causes a drastical

change in the chemical binding for the mobile cations in the process of Na^+/Ag^+ exchange, is often disregarded in the interpretation of equilibrium data.

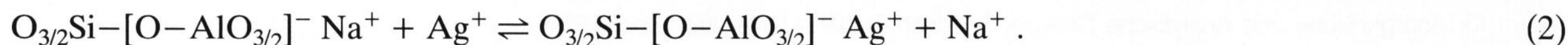
In all the studies on the Na^+/Ag^+ exchange equilibrium, silicate, borosilicate or soda-lime glasses show a significant high affinity for the Ag^+ ions [5 to 7], though these cations with a crystalline ionic radius of 126 pm are noticeably larger than the Na^+ ions with 96 pm. The preferred reception of the “ample” Ag^+ ions by the glass networks, whose “cavities” or M^+ cation sites are adapted to the smaller Na^+ ions in the process of freezing-in of the supercooled glass melt, can only be explained by the high electronic polarizability of Ag^+ ions ($\alpha_{\text{Ag}} = 2.10 \cdot 10^{-40} \text{ F m}^2$, compare: $\alpha_{\text{Na}} = 0.46 \cdot 10^{-40} \text{ F m}^2$ [8]) in double way. On the one hand, the pronounced ability for deformation of the Ag^+ electron shell (no rare-gas configuration: $\text{Kr } 4d^{10}$) renders the entering in the glass by a thermally activated diffusion process. In this way the Ag^+ ions demonstrate a “dynamic” radius which is smaller than the crystalline one [9 and 10]. On the other hand, the soft Ag^+ ions will be coordinated easily by soft Non-Bridging Oxygen (NBO) of the glass network in form of a (Lewis) acid-base complex $\text{O}_{3/2}\text{Si}-\overline{\text{O}} | \text{Ag}$, corresponding to a “soft-soft” interaction after Pearson [11] with an

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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 $\vartheta < T_g$.

energetic stabilization (generation of donor-acceptor complexes) [10].

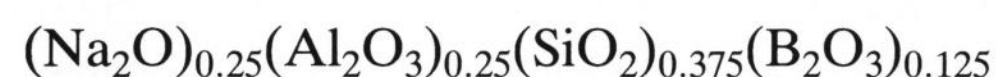
The question is what Na^+/Ag^+ exchange behaviour oxide glasses show, in which – despite a large Na^+ content – no NBO is detectable on the glass network. It is known that in sodium-rich aluminosilicate glasses with a sodium/aluminium molar ratio near to 1/1 the positive charge of the Na^+ ion is compensated by a negative charge distributed on the NBO-free $\text{AlO}_{4/2}$ structural unit. In such glasses the equilibrium of Na^+/Ag^+ exchange can be described according to equation (2):



The aim of the paper is the study of the formation of the Na^+/Ag^+ exchange equilibrium in a Na_2O -rich (25 mol%) and at the same time NBO-free glass by contact with appropriate nitrate melts.

2. Preparation and characterization of the glass

For the investigation a borosilicate glass with the chemical composition



(denotation: NAB-25) was used, from which a minimum NBO content could be expected after measured values of optical basicity and ^{11}B NMR data [12]. The addition of B_2O_3 to the sodium aluminosilicate glass melt was necessary for a melting with a sufficient glass quality.

The glass was melted in a platinum crucible with a capacity of 1 l at temperatures near to 1520 °C using Na_2CO_3 , $\text{Al}(\text{OH})_3$, SiO_2 and H_3BO_3 as raw materials. After cooling with a rate of 10 K/h the glass NAB-25 shows a transition temperature T_g of 560 °C and a mass density of 2.438 g cm^{-3} . A chemical analysis of the glass yields values indicated in table 1 which result in a molar glass composition of



corresponding to a Na^+ concentration of $c_{\text{Na}} = 16.4 \text{ mol l}^{-1}$ and $0.986 \cdot 10^{22} \text{ cm}^{-3}$, respectively.

The absence of NBO in the glass network of NAB-25 was proved by XPS (X-ray Photoelectron Spectroscopy) measurements [13]. Figures 1a and b demonstrate the O 1s spectrum of the glass NAB-25 (figure a) in comparison with that of the binary sodium silicate glass N-21 (figure b). The composition of the glass N-21 was chosen in such a manner that in the two glasses the same Na^+ concentration ($c_{\text{Na}} \equiv \text{Na}^+/\text{volume} \approx 1 \cdot 10^{22} \text{ cm}^{-3}$) is realized. However, in the binary sodium silicate glass N-21 every Na^+ cation involves a NBO anion ($\text{O}_{3/2}\text{Si}-\text{O}^-$) in the network by necessary. The high-symmetric energy distribution in the spectrum of the glass NAB-25, represented in figure 1a, verifies the absence of NBO in the limits of detection (relative sensitivity: 5 %, relating to $c_{\text{NBO}} \approx 5 \cdot 10^{20} \text{ cm}^{-3}$).

silicate glasses with a sodium/aluminium molar ratio near to 1/1 the positive charge of the Na^+ ion is compensated by a negative charge distributed on the NBO-free $\text{AlO}_{4/2}$ structural unit. In such glasses the equilibrium of Na^+/Ag^+ exchange can be described according to equation (2):

In detail, the O 1s spectra in figures 1a and b demonstrate that the two glasses consist above all of bridging oxygen (BO; for instance: $\text{O}_{3/2}\text{Si}-\text{O}-\text{SiO}_{3/2}$, $\text{O}_{3/2}\text{Si}-\text{O}-\text{AlO}_{3/2}$) corresponding to a binding energy for O 1s electrons of about $(532.2 \pm 0.3) \text{ eV}$. The spectrum of the glass N-21 indicates a second band at a lower binding energy of about 530.6 eV, which proves the positive detection of the additional NBO content in the network of this glass [14].

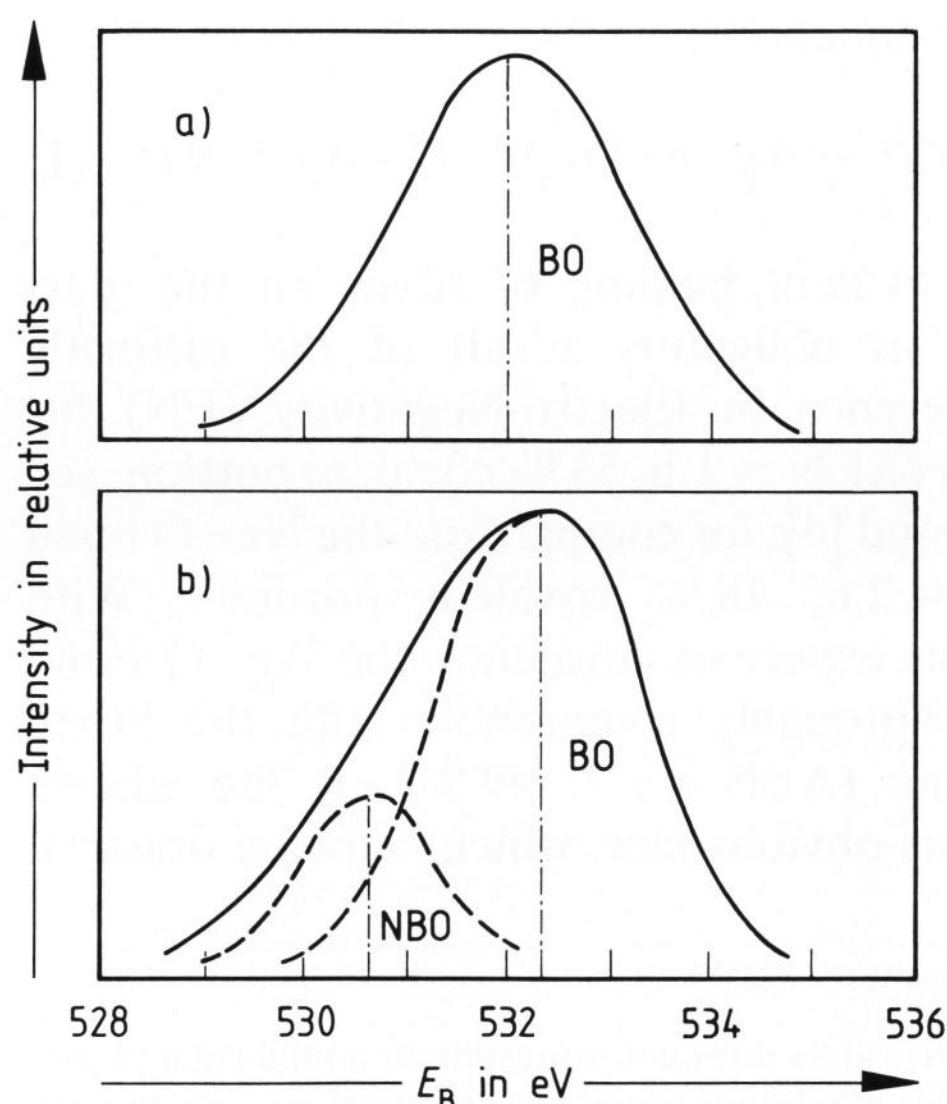
3. Experimental conditions

3.1. Na/Ag ion exchange

For the investigation of the Na^+/Ag^+ exchange the glass NAB-25 was used in form of plane bulk samples ($(15 \times 15 \times 10) \text{ mm}^3$) and contacted with melts of different salt mixtures $(\text{NaNO}_3)_{1-s}(\text{AgNO}_3)_s$ containing molar AgNO_3 contents of $s = 0.01, 0.03, 0.05, 0.10, 0.15$ and 0.20 ($s = \text{molar fraction of AgNO}_3$).

Table 1. Composition (in wt%) of the glass NAB-25

	Na_2O	Al_2O_3	SiO_2	B_2O_3
synthesis	21.46	35.30	31.20	12.04
analysis	20.73	35.76	31.61	11.90



Figures 1a and b. O 1s spectra from XPS measurements on the glasses NAB-25 (figure a) and N-21 (figure b).

The Na^+/Ag^+ exchange was carried out in a furnace with a zone of constant temperature ($\Delta T \approx 1 \text{ K}$) at $(375 \pm 2)^\circ\text{C}$. The exchange time was $(40.0 \pm 0.5) \text{ h}$. In a vessel of silica glass, the samples of NAB-25 were completely covered by the salt melt (15 g). For the purpose of homogenization the components of the salt melt were mixed, melted and mortared before application. After the ion exchange the bulk glass samples could be released from the melted salt by resolution of the nitrates with hot distilled water.

3.2. Determination of the silver content in glass samples and salt melts

For analyzing the absolute amount of Ag^+ cations in the glass and its distribution over the depth into the bulk (concentration gradient), the ion-exchanged NAB-25 samples were etched step by step, followed in each case by a titration of the solution. After every step of etching the mass and geometrical dimensions were estimated.

For etching the glass samples were treated with 150 ml of half-concentrated HNO_3 (stirring with 90 min^{-1}) at $(35 \pm 1)^\circ\text{C}$. In order to realize in all cases an optimum of about 20 mg silver in the solution, the duration of an etching step was increased systematically with the actual depth on a glass sample. The time for an etching step ranged from 10 to 160 min.

The silver amount of the solutions was estimated by a (precipitation) titration against a NaCl standard solution with a potentiometric indication of terminus. For analyzing of 20 mg in one etching step, an optimum concentration of 50 mmol l^{-1} could be ascertained for the NaCl standard solution. Determinations with a 10 ml burette (0.02 ml graduation) resulted in average values of $(98.0 \pm 2.5) \%$. Before the titration, the solutions were evaporated to the dryness for the flocculation of silicic acid and resolved with 50 ml distilled water.

The corresponding equilibrium value of the Ag^+ content of the salt melt was estimated from the initial composition of the $\text{AgNO}_3\text{-NaNO}_3$ mixture, considering the amount of silver which has migrated into the glass sample.

4. Results and discussion

4.1. Kinetics of the Na/Ag ion exchange

Figure 2 represents the silver concentration profiles over the glass sample depth, x^3 , after Na^+/Ag^+ exchange at 375°C (40 h) with salt melts of different AgNO_3 contents, s . The value $c_{\text{Ag}} = c_{\text{max}} = 16.4 \text{ mol l}^{-1}$ corresponds to a complete Na/Ag exchange (100%). In the case of nitrate melts from the lower AgNO_3 range ($0.01 \leq s \leq 0.05$) the form of

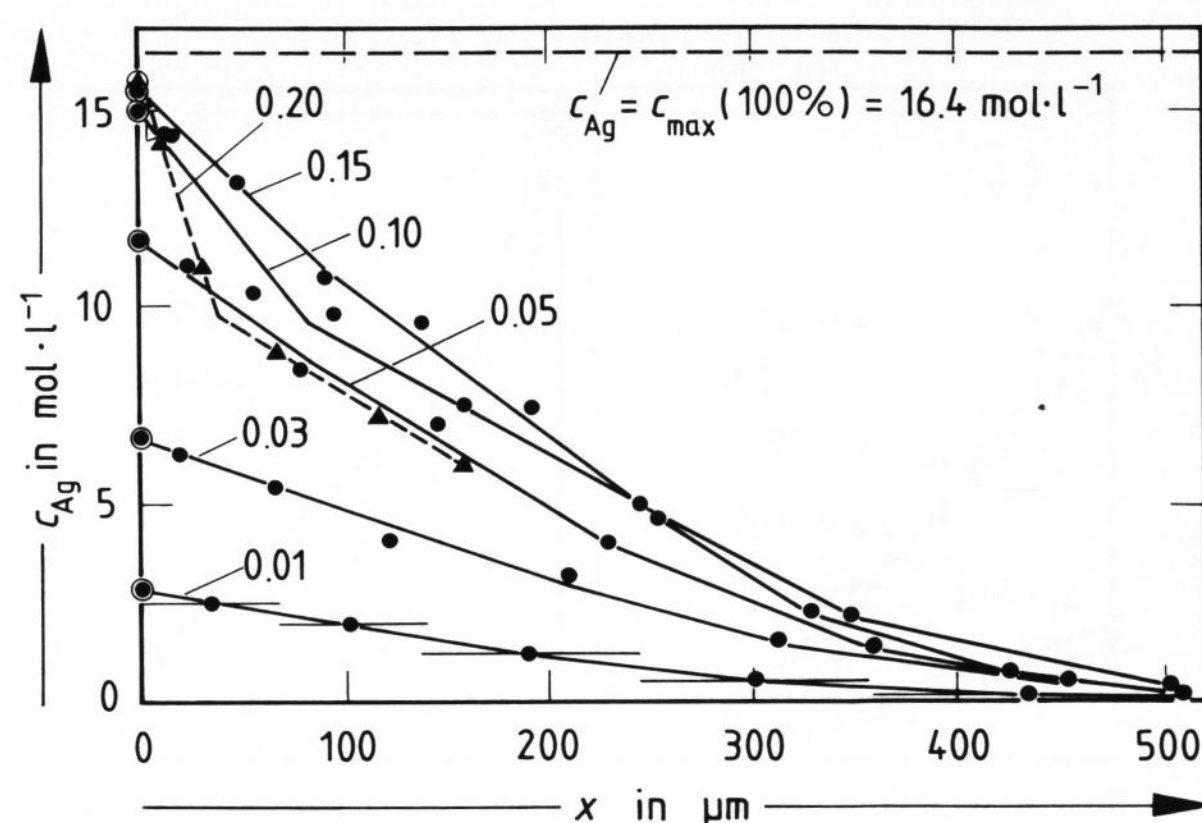


Figure 2. Silver concentration profiles in the glass NAB-25 after a Na^+/Ag^+ exchange at $\vartheta = (375 \pm 2)^\circ\text{C}$ and $t = (40 \pm 0.5) \text{ h}$ by contact with $(\text{NaNO}_3)_{1-s}(\text{AgNO}_3)_s$ melts.

the silver concentration profiles refers to concentration-independent Na^+/Ag^+ exchange kinetics in the glass NAB-25 (chemical diffusion coefficient $\tilde{D}_{\text{Na}/\text{Ag}} \neq f(c_{\text{Ag}})$; see $(\text{erf} - 1)$ profiles with error function erf [15]). An analysis of the silver concentration profiles in this range demonstrates also that the diffusion coefficients $\tilde{D}_{\text{Na}/\text{Ag}}$ are independent of the silver content of the glass in the limits of this rough evaluation:

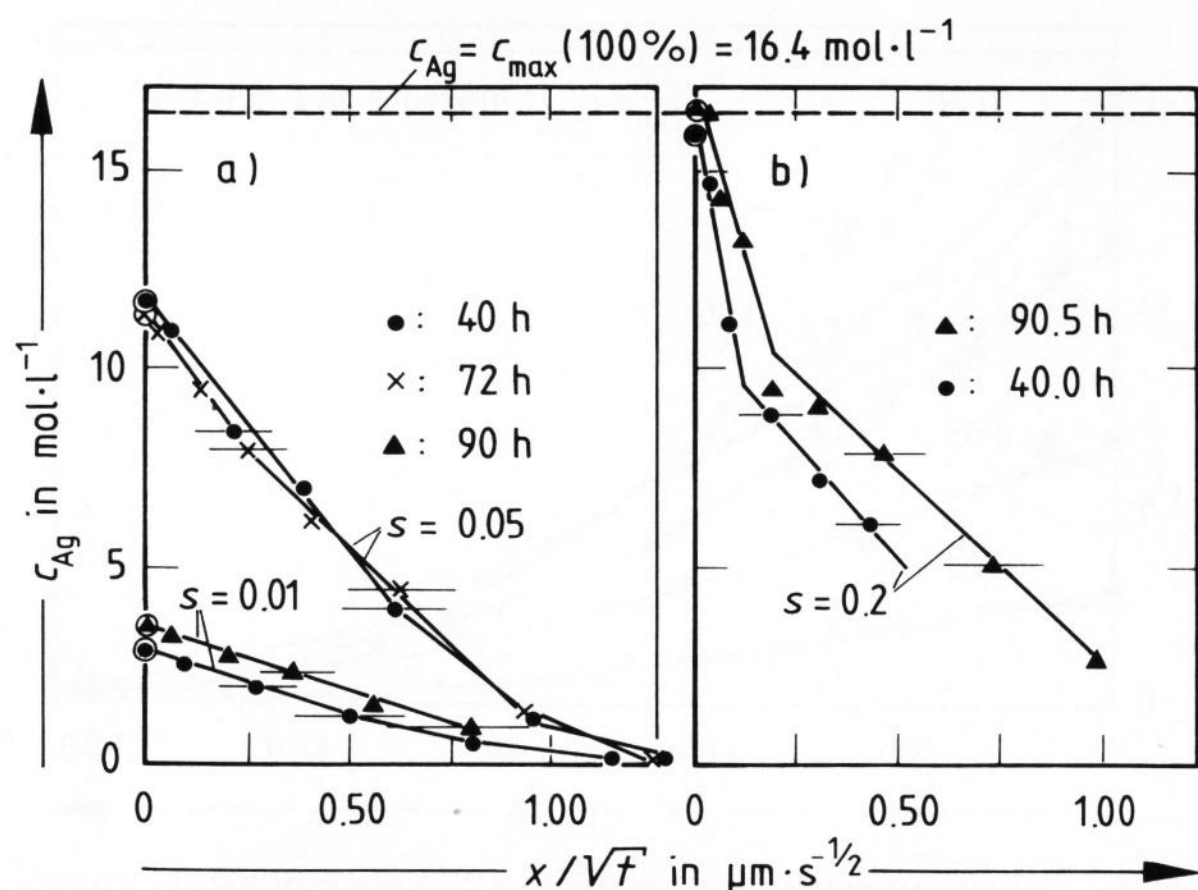
$$\begin{aligned} \tilde{D}_{\text{Na}/\text{Ag}} &= (2.12 \pm 0.34) \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ for } s = 0.01; \\ &= (2.41 \pm 0.25) \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ for } s = 0.03; \\ &= (2.01 \pm 0.17) \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ for } s = 0.05. \end{aligned}$$

The average value $\tilde{D}_{\text{Na}/\text{Ag}} = (2.18 \pm 0.25) \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ corresponds with that of $\tilde{D}_{\text{Na}/\text{Ag}} = 3 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, derived from refractive-index profiles after an Na^+/Ag^+ exchange in the glass NAB-25 ($4 \lesssim c_{\text{Ag}}/\text{mol l}^{-1} \lesssim 10$) [12]. In accordance with expectation the average value $\tilde{D}_{\text{Na}/\text{Ag}}$ estimated from the curves of figure 2 is somewhat higher than the silver tracer-diffusion coefficient $D_{\text{Ag}}^* \approx 6.3 \cdot 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ (375°C) of the glass NAB-25 [12] and a little smaller than the chemical diffusion coefficient $\tilde{D}_{\text{Na}/\text{Ag}} \approx 1 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 375°C in an aluminosilicate glass with a distinctly enlarged Na_2O content of 31.8 mol% ($(\text{Na}_2\text{O})_{0.318}(\text{Al}_2\text{O}_3)_{0.058}(\text{SiO}_2)_{0.624}$) [16].

However, there is no blinking the fact that after exchange experiments with melts of higher AgNO_3 contents ($s \leq 0.10$) an additional increase of silver concentration near the glass surface (in depths up to $100 \mu\text{m}$) exists. This result hints at a remarkably modified Na^+/Ag^+ exchange rate in that region compared to the bulk of the glass or to areas with a distinctly lower silver content.

²⁾ Interval of confidence with $P = 95 \%$ after eight analyses.

³⁾ The extension of the single steps of etching are marked for instance in the curve with $s = 0.01$ by finite lines. For clearness the experimental points of the profile with $s = 0.20$ are indicated differently by triangles.



Figures 3a and b. Silver concentration profiles with normalization on x/\sqrt{t} after a Na^+/Ag^+ exchange in the glass NAB-25 at $\vartheta = (375 \pm 2)^\circ\text{C}$ and different contact times t with $(\text{NaNO}_3)_{1-s}(\text{AgNO}_3)_s$ melts in the range $0.01 \leq s \leq 0.05$ (figure a) and $s = 0.20$ (figure b).

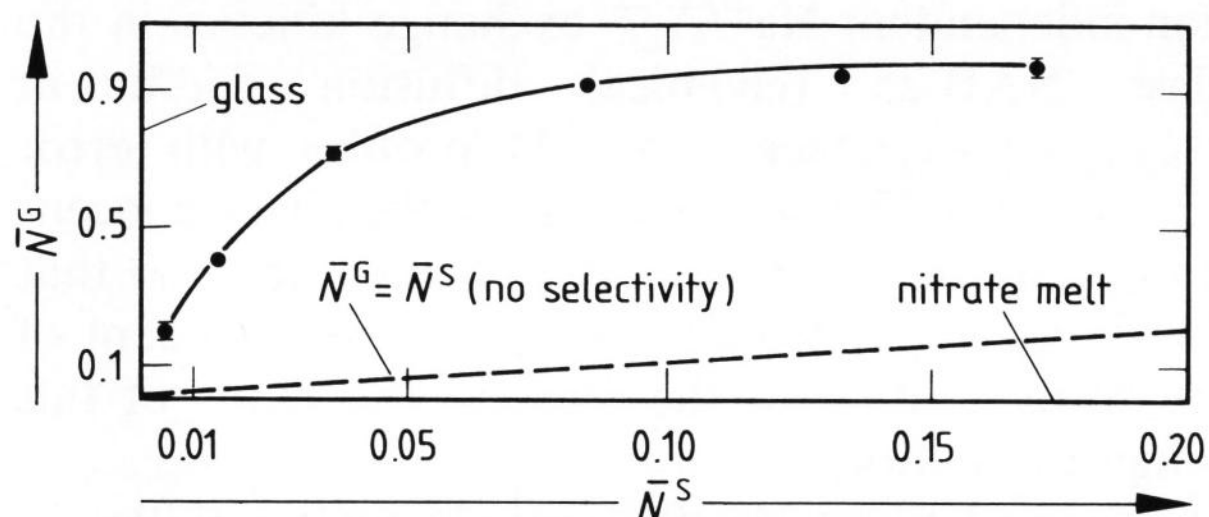


Figure 4. Na^+/Ag^+ exchange isotherm between the glass NAB-25 and $(\text{NaNO}_3)_{1-s}(\text{AgNO}_3)_s$ melts at $\vartheta = (375 \pm 2)^\circ\text{C}$.

In figures 3a and b a normalization test of the silver concentration profiles ($c_{\text{Ag}} = f(x/\sqrt{t})$) is presented for discussion of the real influence of time on ion-exchange kinetics. Exchange experiments with doubled contact times between glass sample and nitrate melts at AgNO_3 contents of $s = 0.01, 0.05$ and 0.20 verify first of all that the silver concentrations at the surface, estimated already after an exchange time of 40 h, can be reproduced. These values correspond to time-independent equilibrium concentrations of the glass for different nitrate melt compositions.

Whereas for the range $0.01 \leq s \leq 0.05$ (figure 3a) a consistence of the silver profiles is proved, a notable divergence between the profiles after 40.0 and 90.5 h has to be observed for higher AgNO_3 contents $s = 0.20$ (figure 3b)⁴⁾. The consistence indicates a

strong diffusion-controlled Na^+/Ag^+ exchange process with a time-independent diffusion coefficient $\tilde{D}_{\text{Na}/\text{Ag}}$ (figure 3a, Fickian behaviour). Compared to it, the observed divergence between the profiles (figure 3b, non-Fickian behaviour) is to be discussed in connection with the additional enhancement of the Na^+/Ag^+ exchange rate at the glass surface. The actual diffusion conditions are changing in this glass region during an exchange run. This alteration is caused by a permanent decrease of the glass viscosity or by an acceleration of structure-relaxation processes as a consequence of the remarkable insertion of silver. Controlling this effect of silver on the glass viscosity, a thermoanalytical measurement on Na^+/Ag^+ -exchanged NAB-25 glass (375°C ; 40 h; $s = 0.15$) with an average silver content of about 9 mol Ag l^{-1} showed a glass transition temperature of $T_g = 520^\circ\text{C}$ (for comparison: T_g (NAB-25 glass) = 560°C).

4.2. Equilibrium of the Na/Ag ion exchange

Table 2 contains the silver equilibrium concentration, c_{Ag} , deduced from the silver profiles at the glass surface, and corresponding average values of the molar fraction for silver in the glass $\bar{N}^G = N_{\text{Ag}}^G / (N_{\text{Ag}}^G + N_{\text{Na}}^G)$, calculated under the precondition of a stoichiometric Na^+/Ag^+ exchange (1 : 1). The molar fraction for silver of the salt melt \bar{N}^S results from the AgNO_3 content s of the used nitrate mixture, corrected by the silver amount changing into the glass in the process of equilibration.

In figure 4 the molar fractions \bar{N}^G and \bar{N}^S of the Na^+/Ag^+ exchange equilibrium between the glass NAB-25 and $\text{NaNO}_3\text{-AgNO}_3$ melts are presented in kind of an exchange isotherm⁵⁾ for 375°C . First of all it is clearly discernible that the NBO-free glass NAB-25 shows a noticeable affinity for the larger

⁴⁾ Two steps of etching are presented for every profile as examples.

⁵⁾ The marked strips (◆) characterise the scattering range of \bar{N}^G from the experimental variation of contact time. The scattering of \bar{N}^S is smaller than the largeness of the circle symbol.

Table 2. Derived values of the Na^+/Ag^+ exchange equilibrium

molar fraction s of AgNO_3 in the used salt melts	Na^+/Ag^+ exchange at constant contact time			Na^+/Ag^+ exchange at different contact times			\bar{N}^G (glass)	\bar{N}^S (salt melt)
	c_{Ag} in mol l^{-1}	N^G	exchange time in h	c_{Ag} in mol l^{-1}	N^G	exchange time in h		
0.01	2.9	0.177	40	3.3	0.207	90	0.192	0.0060
0.03	6.7	0.409	40	—	—	—	0.409	0.0155
0.05	11.7	0.713	40	11.4	0.695	72	0.704	0.0370
0.10	15.0	0.915	40	—	—	—	0.915	0.0860
0.15	15.5	0.945	40	—	—	—	0.945	0.1330
0.20	15.6	0.951	40	16.5	1.006	90.5	0.979	0.1720

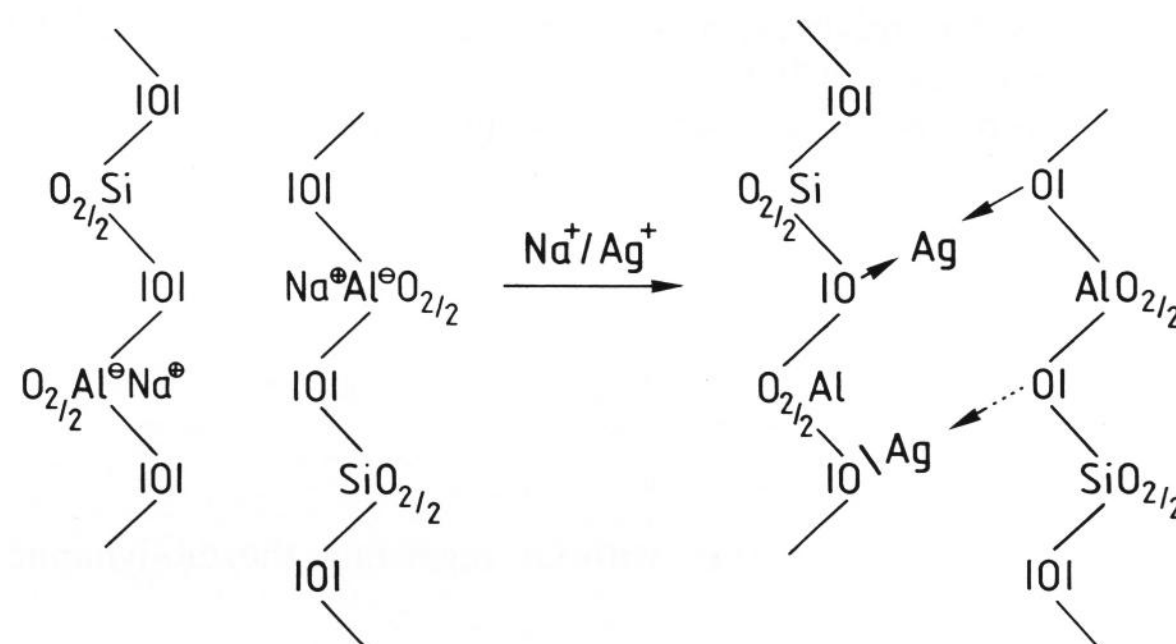
Table 3. Coefficients of selectivity K'_N from Na^+/Ag^+ and Na^+/K^+ exchange in NBO-containing and NBO-free glasses

glass no.	glass type	exchange temperature in °C	\bar{N}^S	\bar{N}^G	K'_N	references
Na⁺/Ag⁺ exchange						
1	NAB-25	375	0.006–0.17	0.19–0.98	40–225	
2	$(\text{Na}_2\text{O})_{0.2}(\text{SiO}_2)_{0.8}$	350	0.03–0.28	0.70–0.99	75–40	[18]
3	$(\text{Na}_2\text{O})_{0.207}(\text{Al}_2\text{O}_3)_{0.22}(\text{SiO}_2)_{0.572}$	378	–	0.01–0.135	450–38	[19]
4	$(\text{Na}_2\text{O})_{0.2}(\text{Ga}_2\text{O}_3)_{0.2}(\text{SiO}_2)_{0.6}$	350	0.05–0.47	0.60–0.95	29–21	[20]
Na⁺/K⁺ exchange						
2	$(\text{Na}_2\text{O})_{0.2}(\text{SiO}_2)_{0.8}$	350	0.21–0.07	0.03–0.50	0.12–0.03	[18]
3	$(\text{Na}_2\text{O})_{0.207}(\text{Al}_2\text{O}_3)_{0.22}(\text{SiO}_2)_{0.572}$	378	–	0.50–0.90	0.03–0.02	[19]

Ag^+ cations. The distribution coefficient $\beta = \bar{N}^G/\bar{N}^S$ of silver amounts to the range $32 \geq \beta \geq 5.7$ for $0.06 \leq \bar{N}^S \leq 0.17$. This means that despite of the absence of NBO the investigated boroaluminosilicate glass network prefers the larger Ag^+ ions against the Na^+ ions up to the 32fold of the relative silver content of the adequate nitrate melt. The thermodynamic equilibrium can also be characterised by a balance between a glass, in which 98 % of the Na^+ content is substituted by Ag^+ ions, and a nitrate melt with only 17 % AgNO_3 .

The Na^+/Ag^+ exchange isotherm presented in figure 4 corresponds to coefficients of selectivity (rational equilibrium coefficients, [17] $K'_N = \bar{N}^G/(1 - \bar{N}^S)/\bar{N}^S(1 - \bar{N}^G)$) from 40 up to 225. These values are compared with references for the Na^+/Ag^+ or Na^+/K^+ exchange in other or similar glass types with a constant Na^+ concentration of $c_{\text{Na}} \approx 1.0 \cdot 10^{22} \text{ cm}^{-3}$ in table 3. The coefficients K'_N of the Na^+/Ag^+ exchange prove for all regarded glasses – independently of the NBO content – with values $K'_N \gg 1$ a distinct affinity for the Ag^+ cations. Contrary to that, the coefficients $K'_N \ll 1$ of Na^+/K^+ exchange demonstrate missing tendencies for K^+ insertion into the glass networks.

The geometric-electrostatic concept of Eisenmann [21] is a useful tool for interpretation of selectivity sequences of monovalent cations in zeolites. After this model the ample $\text{AlO}_{4/2}$ structural unit with an effective anionic radius of $r_a \approx 200 \text{ pm}$ realizes sites for larger cations in comparison with the compact $\text{O}_{3/2}\text{SiO}$ unit ($r_a \approx 90 \text{ pm}$) [22]. Accordingly, a selectivity for larger monovalent cations (in addition to Ag^+ also for K^+ ions) should be expected in aluminosilicate glasses. Such a behaviour can not be observed, however, on the regarded glasses (no. 3 in table 3 and no. 1, presented in [23]⁶). This experi-

Figure 5. Imagination for coordinative insertion of Ag^+ cations into the network of the glass NAB-25.

mental fact speaks against an Ag^+ insertion caused dominantly by geometric-electrostatic conditions.

For an explanation of the preferred insertion of the Ag^+ ion into the network of the glass NAB-25, the high polarisability of Ag^+ cations or the covalent saturation of the silver valencies on the basic bridging oxygen of the $\text{AlO}_{4/2}$ tetrahedrons remains necessary. With respect to the tendency of silver for a linear double coordination ($\text{L}-\text{Ag}-\text{L}$), finding in stable manifold complexes with chelate ligands [24] and also discussed in the case of dative binding of AgO_n polyhedrons ($2 \leq n \leq 6$) in NBO-containing glasses [25], some structural arrangements are imaginable. These are outlined in figure 5. For an insertion of silver into the NBO-free network of the glass NAB-25 in the described manner, also the high optical transparency [26] of the Na^+/Ag^+ -exchanged glass argues.

5. Nomenclature

5.1. Symbols

c_i	concentration of the ion i in the glass in mol l^{-1} or cm^{-3}
$\tilde{D}_{\text{Na/Ag}}$	interdiffusion coefficient for the counterdiffusion of Na^+ and Ag^+ ions in the glass in $\text{cm}^2 \text{ s}^{-1}$
ΔEN	difference of electronegativities
erf	error function
$f(c)$	(general) function of the concentration

⁶ The comparability of the oxygen densities (concentrations) in the glasses NAB-25 ($c_{\text{O}} = 4.33 \cdot 10^{22} \text{ cm}^{-3}$) and N-21 ($c_{\text{O}} = 4.27 \cdot 10^{22} \text{ cm}^{-3}$; see section 2.) contradicts also an assumption of a larger occupied volume for $\text{AlO}_{4/2}$ tetrahedrons.

K'_N	coefficient of selectivity or rational equilibrium constant, defined on the basis of molar fractions N
L	ligand in a coordinative compound
\bar{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
n	coordination number in the case of oxocoordination
P	interval of confidence in %
r_i	crystalline ionic radius of the ion i after Pauling [24] in pm
s	composition of the used salt melt, molar fraction of AgNO_3
ΔT	difference of the temperature in K
T_g	glass transition temperature in $^\circ\text{C}$
t	contact time in h
x	diffusion depth in the glass sample in μm
α_i	electronic polarizability of the ion i in F m^2
β	distribution coefficient of silver between the glass and the salt melt = \bar{N}^G/\bar{N}^S
ϑ	exchange or diffusion temperature in $^\circ\text{C}$

5.2. Superscripts

G	glass
S	salt melt
—	average value
'	efficient value, i.e. without regarding thermodynamic activities

5.3. Subscripts

a	anionic
i	ion
max	maximum
N	molar fraction

6. References

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