

Impact of boron complexation by Tris buffer on the initial dissolution rate of borosilicate glasses

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ABSTRACT

Tris(hydroxymethyl)aminomethane is a commonly used buffer for leaching studies on glasses. In this work, we demonstrate that it plays a role on the alteration kinetics of borosilicate glasses. Comparative dissolution experiments on a soda-lime silicate glass and a sodium borosilicate glass, in several solutions with or without Tris at neutral pH, are carried out in order to assess the specific effects of the ionic strength and of the Tris molecules on the initial dissolution kinetics. Tris has no effect on the dissolution of the soda-lime silicate glass, while it significantly enhances the dissolution of the borosilicate glass, by increasing the B, Na, and Si release rates. This specific effect on the borosilicate glass is attributed to the Tris–boron complexation and discussed. The bidentate complexation of boron by Tris(hydroxymethyl)aminomethane (Tris) with a 1:1 stoichiometry is directly demonstrated by infrared and NMR spectroscopies. Complexation constants are determined for the Tris–borate complex and its protonated form Tris–boric, from the ¹¹B and ¹H NMR spectra. This complexation should be taken into account when using the Tris/HCl buffer in alteration experiments of borosilicate glasses.

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1. Introduction

The chemical durability of silicate glasses, especially against aqueous corrosion, is a key property in most of their applications and notably for their use in toxic waste immobilization. In particular, high-level nuclear wastes are immobilized in borosilicate matrices whose excellent chemical durability must be demonstrated on the very long term. The chemical durability is generally assessed by measuring the glass dissolution kinetics in leaching experiments where the surface to volume ratio (*S/V*), the temperature, the composition, and the pH of the solution are controlled. Among the various factors that influence the glass corrosion kinetics, it is well known that one of them is the leaching solution chemistry, such as its complexation properties toward the components of the glass, in solution or at the glass surface. However, this knowledge is mainly inspired by experiments on the dissolution of simple oxides or hydroxides [1], and experimental studies of such effects on multicomponent glasses are scarce. The enhancement of the glass dissolution by organic acids has been put in evidence in several studies [2–6] and attributed to protonation of the glass surface and chelation of the metallic surface sites by the anion associated with the acid. Both processes promote the

detachment of the metallic cations out of the glass and accelerate the dissolution, although contradictory results, showing inhibition of the dissolution, are also found in the literature [7]. On the other hand, similar effects of other molecules than organic acids are not clearly mentioned in the literature.

Tris(hydroxymethyl)aminomethane (*pK_a* = 8.1 at 25 °C), with formula C₄O₃NH₁₁ and referred to as Tris, is widely used as a buffer in the slightly basic 7–9 pH range. It was first proposed by Gomori [8]; then, it was used, for example, in biological research [9] because it is stable over time and inert with other constituents of the solution. Particularly, bioactivity of materials was studied using simulated body fluid (SBF) buffered with Tris [10,11]. Few years later, a significant effect of Tris on bioactive glass–ceramic dissolution was demonstrated [12,13]. The glass ceramics used in these studies are composed of apatite–wollastonite type and residual glass phases. The Tris/HCl buffer considerably increased the dissolution rate of the crystalline phases, compared to a solution containing no Tris, this effect being attributed to the possible formation of a soluble Ca–Tris complex. A similar enhancing effect of Tris on the dissolution of Ca-containing bioactive glasses has been reported [14,15].

Tris/HCl is also used as a buffer in dissolution studies of borosilicate glasses in the framework of research on nuclear waste containment glasses [16–18]. To our knowledge, the effect of Tris on the borosilicate glass dissolution has not been specifically studied, although complexing properties of Tris toward boron are

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suspected. Several complex compounds of boron with polyols are known, such as complexes formed with sorbitol, mannitol, fructose, glycerol, and ethylene glycol [19]. Polyols and Tris have two hydroxyl groups as a common point, potentially acting as ligands for boron coordination. Moreover, in biochemistry field, Michov [20] demonstrates the existence of a “Tris–boric” complex, through acid titration method and IR spectra, not shown in the publication.

The aim of this study is thus to characterize the effect of Tris on the dissolution kinetics of a sodium borosilicate glass. Other effects such as ionic strength and the presence of chloride anions in the solution will also be evaluated, in order to discriminate the specific effect of Tris from other possible factors. The paper is divided into two parts. First, the existence, stoichiometry and formation constant of the Tris–boron complex are elucidated by ^{11}B and ^1H NMR and IR-ATR spectroscopies. Then, the role of the Tris–boron complex on the glass dissolution kinetics is put in evidence by comparing dissolution experiments on two glasses, a sodium borosilicate glass and a boron-free soda-lime silicate glass, in different leaching solutions.

2. Experiments and techniques

2.1. Characterization of the Tris–boron complex and speciation calculations

Several solutions were prepared in order to characterize and quantify the Tris–boron complex by Attenuated Total reflectance (ATR)-IR spectroscopy and ^1H , ^{11}B NMR, all with pure water (milliQ system, resistivity 18.2 M Ω). First of all, a Tris solution at 0.1 M and pH = 7.5 was prepared from Tris powder (VWR Prolabo Normapur) and about 0.08 M HCl (VWR Prolabo AnalAR Normapur) to adjust the pH. Afterward, a second solution of H_3BO_3 (Merck Prolabo Rectapur) at 0.1 M and pH 7.5 was prepared with pure water and NaOH 2 M. The Tris and $\text{B}(\text{OH})_3$ solutions at pH 7.5 were mixed together in equal volume (1/1 for Tris/boron ratio); then, the boric acid solution was diluted 2 and 4 times and mixed with one volume of the Tris solution, to prepare mixtures with 2/1 and 4/1 Tris/boron ratio. Three other solutions at pH = 10 and 1/1, 2/1, and 4/1 for the $\text{Tris}/\text{B}(\text{OH})_4^-$ ratio were prepared from the three previous solutions, by adding concentrated NaOH to increase the pH. A last solution with 1/1 $\text{Tris}/\text{B}(\text{OH})_4^-$ ratio, and pH = 8.3 was also prepared.

ATR-IR analyses were performed with a Nicolet 6700 ThermoFisher Scientific instrument in order to put in highlight the presence of the complex Tris–boron at pH = 7.5.

Measurements were performed in a liquid cell clamped onto an attenuated total reflection accessory. The ATR crystal is a horizontal ZnSe crystal ($A = 3.14 \text{ mm}^2$) covered by a diamond layer with one internal reflection on the upper surface and an angle of incidence of 45° . A flow cell with a constant velocity of 0.2 mL/min maintained by a peristaltic pump (Ismatec S.A.) was used with the background solution (water) then with the analyzed solution [21,22]. Spectra were recorded at a resolution of 4 cm^{-1} with 256 co-added scans using OMNIC software.

NMR spectra were recorded on a Bruker Avance 400 spectrometer equipped with a 5-mm z-gradient broadband inverse probe head and operating at 400.1 and 128.4 MHz for ^1H and ^{11}B , respectively. Spectra were acquired in standard conditions, and chemical shifts were referred to external Et_2O , BF_3 (0 ppm) for ^{11}B and TMS for ^1H spectra.

The complexation constants for Tris–boron complexes have been obtained using FITEQL software [23]. For each experimental point, the input consisted of the total concentrations of Tris and boron, the concentration of complexed boron and the pH. Formation constants of protonated Tris, borate ion and triborate ion from

boric acid, proton and Tris species, have also been entered. Formation constants of Tris–boric and Tris–borate have been simultaneously fitted, starting from initial values by Michov [20]. Then, these values have been added in the thermodynamic database of MEDUSA software [24] to calculate speciation diagrams.

2.2. Dissolution kinetics

Two glasses have been synthesized in the laboratory. The first is a sodium borosilicate glass with 18 mol% of B_2O_3 and 18 mol% of Na_2O , referred to as NSB18. The second is a soda-lime silicate glass with 14 mol% of CaO and 18 mol% of Na_2O , referred to as NSC14. In both glasses, 1 mol% Eu_2O_3 has been added in order to provide a local structural probe, not used in the present paper. Table 1 gives the molar compositions as measured by ICP-AES analysis of the glasses.

The glass pieces were crushed in an agate mortar and sieved to obtain the 125–250 μm size fraction. The powder was then cleaned ultrasonically in acetone several times to remove the fine glass particles. Specific surface (about $300 \text{ cm}^2/\text{g}$) was measured by BET method from Kr adsorption isotherms, using a BELSorp Max instrument, and is given for each glass in Table 2.

Leaching solutions were prepared from pure water (MilliQ system, 18.2 M Ω at 25°C). Three solutions did not contain Tris and consisted of pure water alone, pure water with potassium chloride ($4 \times 10^{-2} \text{ M}$), and pure water with potassium nitrate ($4 \times 10^{-2} \text{ M}$). Two other solutions contained Tris and were Tris/HCl buffer at pH 7.5 ($5 \times 10^{-2} \text{ M}$ of Tris(hydroxymethyl)aminomethane and $4 \times 10^{-2} \text{ M}$ of HCl) and Tris/ HNO_3 at pH 7.5 (same concentrations with HNO_3 instead of HCl). The alteration experiments were carried out at 80°C in an oil bath, by adding 0.5 g (NSB18) or 1 g (NSC14) of glass powder to 500 mL of leaching solution at 80°C , giving a S/V ratio of about 0.2 cm^{-1} and 0.6 cm^{-1} , respectively. Aliquots of solution (10 mL) are taken every 15 min, then 30 min, over the first three hours of the alteration. These aliquots were compensated by an equal volume of fresh solution to keep the alteration volume constant. All aliquots were filtered at $0.45 \mu\text{m}$, checked for pH at room temperature, and then analyzed by ICP-AES.

ICP-AES measurements were performed using an iCAP6000 ThermoFisher Scientific instrument. All samples were acidified with 2 vol% HNO_3 (67–70%, SCP Science) and measured in triplicate. Standard single element solutions (1000 mg/L, SCP Science) were used for the preparation of the calibration solutions (highest concentration standard and dilution by 2, 5, and 10). The blank solution was pure water acidified with 2 vol% HNO_3 . The element concentrations of the highest concentration standard were

Table 1
Fractions of complexed boron and free boron obtained by integration of ^{11}B NMR spectra (at pH 10 and pH 7) and of ^1H NMR spectra (at pH 10).

	Tris/B	1/1	2/1	4/1
pH 10 RMN ^{11}B	Complexed B (%)	50	65	70
	Free B (%)	50	35	30
	RMN $^1\text{H}^a$			
	Complexed B (%)	51	68	72
Calculation ^b	Free B (%)	49	32	28
	Complexed B (%)	54	64	64
	Free B (%)	46	36	36
pH 7 RMN ^{11}B	Complexed B (%)	18	27	35
	Free B (%)	82	73	65
	Calculation ^b			
	Complexed B (%)	20	24	32
	Free B (%)	80	76	68

^a Assuming bidentate coordination by Tris and 1:1 Tris–boron stoichiometry.

^b Fractions of complexed boron and free boron obtained by calculation using formation constants $\text{pK1} = 1.78$ and $\text{pK2} = -7.55$.

Table 2

Molar composition of the two glasses as measured by ICP-AES, glass density (Archimède method with water) and specific area by BET analysis of Kr adsorption isotherms.

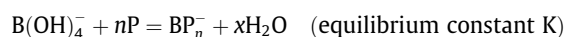
Glass	SiO ₂	Na ₂ O	CaO	B ₂ O ₃	Eu ₂ O ₃	Density (g/cm ³)	Specific area (m ² /g)
NSC14	65.3	18.9	14.7	/	1.1	2.7 ± 0.10	3.0.10 ⁻² ± 0.2
NSB18	62.6	18.2	/	18.2	1	2.6 ± 0.03	2.0.10 ⁻² ± 0.2

adjusted following the expected concentration values for the dissolution experiments. For every quantified element, the limit of quantification was determined by multiplying by ten the standard deviation of the background fluctuations measured over ten analyses of the blank. These limits were 22 ppb for B, 55 ppb for Ca, 70 ppb for Na, and 12 ppb for Si. Moreover, the standard deviation as computed from the triplicate analysis is typically 5% for every element.

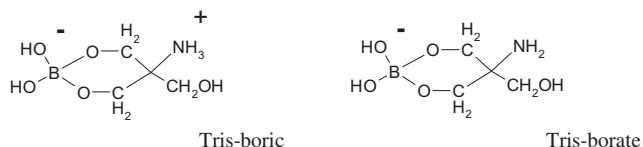
3. Results

3.1. Identification of the Tris–boron complexation in solution

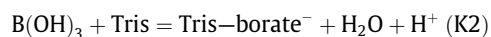
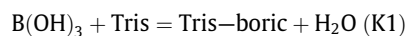
Association numbers for polyol:borate stoichiometry with value of $n = 1$ (ethylene glycol) to $n = 2.6$ (sorbitol) have been found by acid–base titration [19]. For complexation reactions as



apparent (i.e., neglecting ionic strength effect on activity) pK values from 8.6 for ethylene–glycol to 3.6 for sorbitol were found [19]. Concerning Tris which bears three alcohol groups, Michov [20] suggested a 1:1 Tris–boron complex, with a deprotonated form (the acid–base property being carried by the amine group):



From pH measurements of mixtures of boric acid with Tris, these authors calculated formation constants for Tris–boric species of -2.53 and for Tris–borate species of 6.97 according to the following equilibria ($n = 1$):



Thus, K2/K1 is the acidity constant of Tris–boric acid, with pK_a value = 9.5 . The effect of ionic strength has been taken into account using Guntelberg's approximation of extended Debye–Hückel [25]. The comparison with polyol–borate complexes can be made, showing a complexation constant (7 with $n = 1$) in the range of values found for polyols. This publication brings an indirect evidence of the complexation of boron by Tris based on pH measurements. To support this phenomenon, we have used in situ spectroscopies to identify this complex, ATR-IR and NMR.

3.1.1. ATR-IR spectroscopy

Spectra of boric acid B(OH)_3 (0.1 M at pH 7.5), borate anion B(OH)_4^- (0.1 M at pH 10), Tris/HCl (0.1 M at pH 7.5), and the mix $1:1$ of boric acid and Tris/HCl (0.05 M at pH 7.5) solutions have been recorded by ATR-IR spectroscopy as shown in Fig. 1. The trigonal planar boric acid has been clearly identified by a broad asymmetric B–O stretching (3) band at 1409 cm⁻¹ and the in-plane

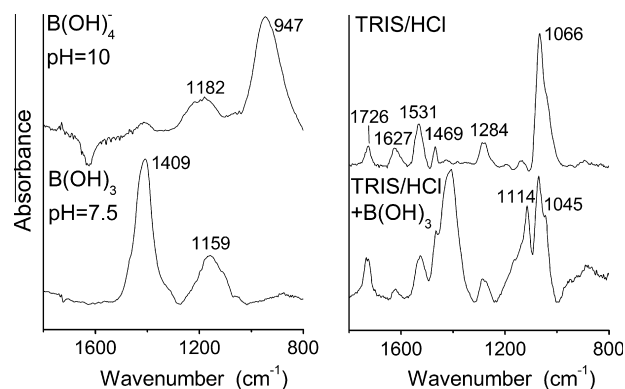


Fig. 1. ATR-IR spectra of solutions (0.1 M) with pH adjusted at 7.5 except B(OH)_4^- solution adjusted at pH 10 .

B–O–H bending at 1159 cm⁻¹. For borate, the B–O stretching band occurs at 950 cm⁻¹ and the B–O–H bendings at 1182 cm⁻¹ [26]. The buffer Tris/HCl is characterized by a strong peak at 1066 cm⁻¹ attributed to the C–O stretching mode. Concerning the equimolar solution of Tris/HCl and B(OH)_3 , a new peak appears at 1114 cm⁻¹ which is attributed to the complex Tris–boron.

3.1.2. NMR spectroscopy

¹¹B and ¹H NMR spectra of the Tris/ B(OH)_4^- mixture at 0.1 M were sufficiently resolved and quantifiable to allow the determination of the stoichiometry and structure of the complex.

3.1.2.1. ¹¹B NMR. Fig. 2 reports the ¹¹B NMR spectra of boric acid, borate anion, and $1/1$ Tris/ B(OH)_3 mixtures at pH 7.5 , 8.3 and 10 . First, ¹¹B NMR spectra of B(OH)_3 at pH 7.5 and B(OH)_4^- at pH 10.0 were recorded, and their respective chemical shifts are 22.2 and 6.3 ppm. At pH 7.5 , spectra of Tris/boron at different ratio ($1/1$; $2/1$ and $4/1$) show two species: B(OH)_3 at 22.2 ppm and one peak at 4.2 ppm corresponding to the Tris–boron complex. Boron complexation (obtained by peak integration) increases with the ratio: 18% to 35% (5%) for $1/1$ to $4/1$ Tris/boron mixtures (Table 2). At pH 10 , the NMR spectra show two peaks, B(OH)_4^- at 6.3 ppm and the chemical shift of complexed boron at 4.0 ppm, that is consistent with fourfold coordinated boron. Similarly, boron complexation increases with the Tris/boron ratio: $50\text{--}70\%$ (5%) (Table 2).

3.1.2.2. ¹H NMR. At pH 7.5 , the ¹H NMR spectrum of the Tris/boron mixture shows a single peak at 3.57 ppm corresponding to Tris-methylene chemical shift, suggesting fast exchange between free and complexed Tris. Moreover, ¹¹B spectrum indicates a low proportion of complex at this pH. At pH 10 , spectrum of the $1/1$ mixture is shown in Fig. 3. The two doublets at $\delta = 3.57$ and 3.36 ppm with a coupling constant $^2J = 11$ Hz correspond to diastereotopic methylene protons proving the coordination of this hydroxymethyl group to the boron center. The singlet at 3.41 ppm corresponds to uncoordinated hydroxymethyl group protons of the Tris–boron complex and to free Tris-methylene protons which have the same chemical shift.

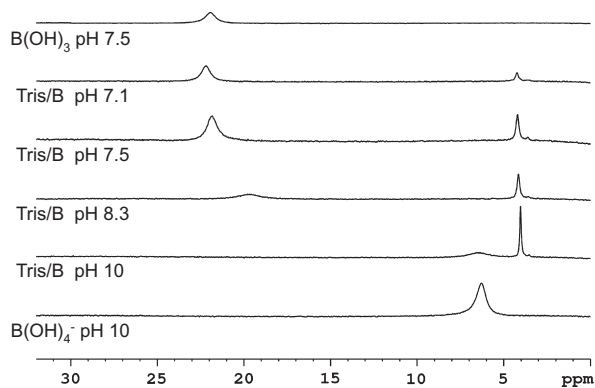


Fig. 2. ^{11}B NMR of Tris/boron 1/1 solutions as a function of their pH.

Then, several hypotheses have been attempted concerning the number of hydroxymethyl groups coordinated to the boron center (monodentate versus bidentate hypotheses) and concerning the stoichiometry of the Tris–boron complex. Only the bidentate hypothesis with 1:1 stoichiometry, as proposed by Michov, could achieve mutual agreement of the ^1H and ^{11}B NMR spectra at $\text{pH} = 10$, for all mixtures with varying Tris/boron ratio (at $\text{pH} = 7.5$, integration of the ^1H spectra was not possible because the Tris–boron complex was not resolved). The excellent agreement between the fractions of complexed boron, from integration of the ^{11}B NMR spectra and from that of the ^1H NMR spectra assuming bidentate coordination and 1:1 stoichiometry, is shown in Table 2.

3.1.3. Complexation constants

The fractions obtained by ^{11}B NMR have been used to determine the complexation constants of Tris–boric and Tris–borate species. Using a fitting software, their values have been obtained based on the analysis of seven mixtures: 1/1; 2/1 and 4/1 Tris/boron ratio at $\text{pH} 10$ and $\text{pH} 7.5$ and 1/1 Tris/boron ratio at $\text{pH} 8$. Apparent pK_1 and pK_2 of -1.78 and 7.55 , respectively, have been obtained (thus, pK_a for Tris–boric acid is 9.33). A try using only Tris–borate species (as polyols–boron system) resulted in a very bad fitting of experimental values, supporting the existence of two Tris–boron complexes as suggested by Michov. The speciation diagram obtained with these complexation constants is shown in Fig. 4. The fractions of complexed boron, as calculated from the pK_1 and pK_2 values, are reported in Table 2.

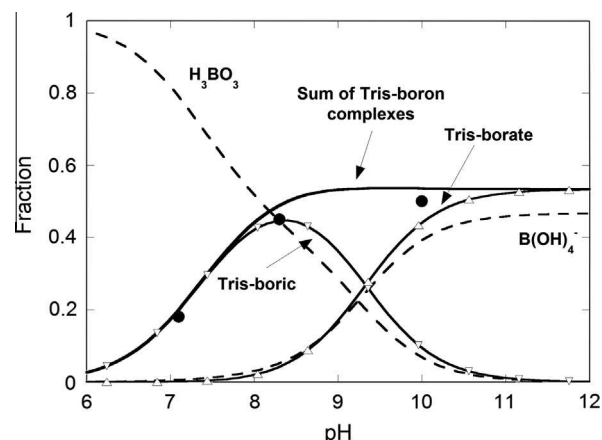


Fig. 4. Speciation diagram of Tris (0.05 M) and $\text{B}(\text{OH})_3$ (0.05 M) (Meduza software) calculated using the complexation constants determined in this study ($\text{pK}_1 = 1.78$ and $\text{pK}_2 = 7.55$).

3.2. Dissolution kinetics

Figs. 5 and 6 compare the effect of chloride salts, nitrate salts, and Tris with HCl or HNO_3 on the initial dissolution kinetics of the soda-lime (Fig. 5) and borosilicate (Fig. 6) glasses. The element concentrations (B, Ca, Na, and Si) are followed by ICP-AES during 2.5 h, and the normalized leached fractions (g m^{-2}) of glass are computed according to:

$$\text{NL}_i = \frac{C_i}{x_i \times S/V}$$

where C_i is the concentration of element i and x_i its mass fraction in the glass, S/V is the ratio of powder surface over alteration volume. In order to assess the congruency of the dissolution, normalized leached fractions for all elements of the glass are reported in Fig. 7 in the case of the dissolution in pure water.

The soda-lime glass is nearly not altered, the normalized leached fractions after 2.5 h of lixiviation reach about 0.05 g m^{-2} for Si, 0.065 g m^{-2} for Ca, and 0.4 g m^{-2} for Na. The dissolution is incongruent since Na is released faster than Si and Ca. It is interesting to note that Ca and Si are almost congruently released (Fig. 7). This indicates that Ca^{2+} ions are retained in the leached layer formed after the departure of Na^+ ions. Moreover, KCl , KNO_3 , Tris/HCl , or Tris/HNO_3 bearing solutions show no difference

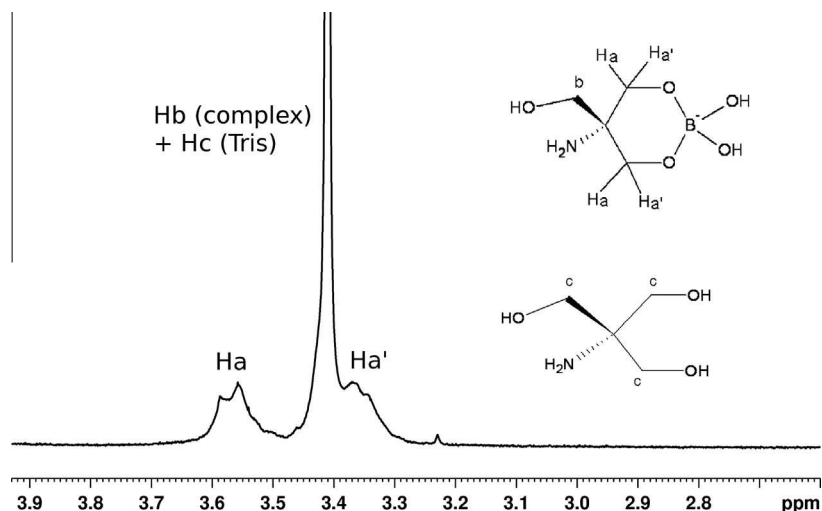


Fig. 3. ^1H NMR of the Tris/boron 1/1 solution at $\text{pH} 10.0$.

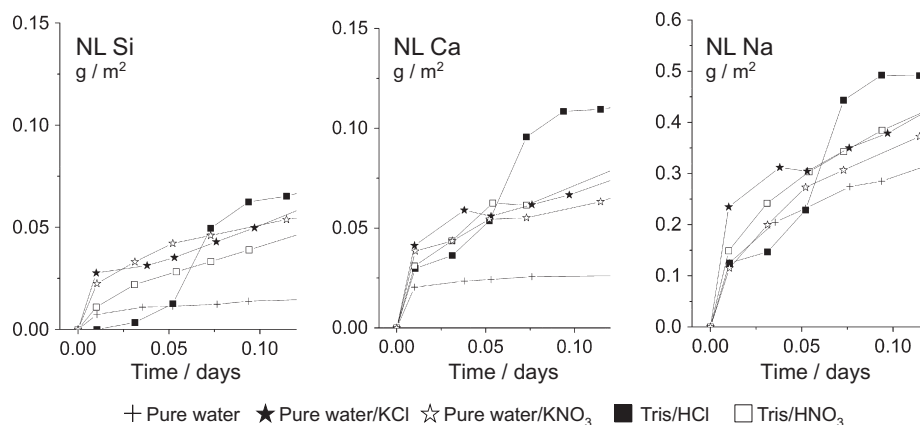


Fig. 5. Normalized leached fraction based on Si, Ca and Na for the NSC14 glass altered in different solutions (4×10^{-2} M) with Tris ($7.3 < \text{pH} < 7.4$) and without Tris ($6.1 < \text{pH} < 6.8$). $T = 80^\circ\text{C}$ and $S/V = 0.6 \text{ cm}^{-1}$.

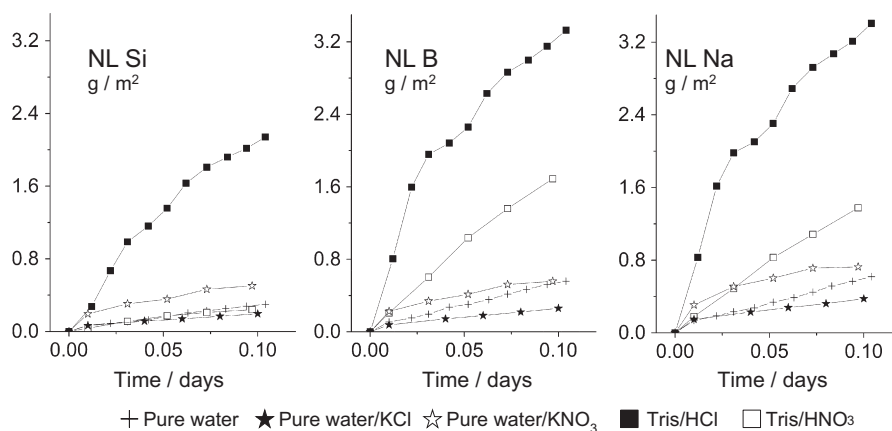


Fig. 6. Normalized leached fraction based on Si, B and Na for the NSB18 glass altered in different solutions (4×10^{-2} M) with Tris ($7.3 < \text{pH} < 7.4$) and without Tris ($6.1 < \text{pH} < 6.7$). $T = 80^\circ\text{C}$ and $S/V = 0.2 \text{ cm}^{-1}$.

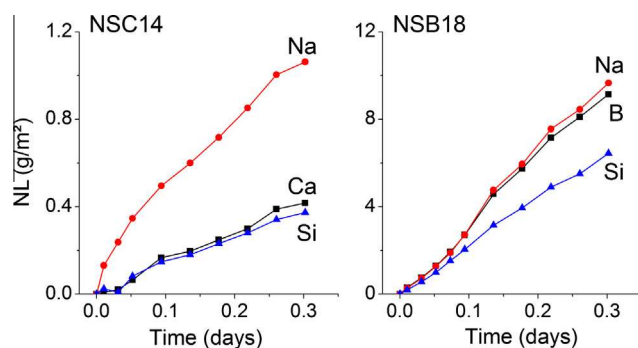


Fig. 7. Normalized leached fractions based on Si, Ca and Na for the NSC14 glass (left) and based on Si, Na and B for the NSB18 glass (right), for dissolution experiments carried out in pure water ($6.1 < \text{pH} < 6.8$).

regarding the dissolution rate of this glass. The Na release rate is maintained, while the Si and Ca release rates are slightly increased, by a factor of about 2, with respect to pure water. This latter phenomenon is attributed to an ionic strength effect and is discussed later.

The borosilicate glass dissolves more rapidly than the soda-lime glass when we consider the Si release rate, in pure water or in salt-containing solutions. The dissolution is accelerated in Tris-containing solutions (Fig. 6). In the following, we first present the kinetics without Tris, then the effect of Tris addition.

In pure water and KCl or KNO_3 bearing solutions, the normalized leached fraction based on Si is about 0.2 g.m^{-2} after 2.5 h, compared to 0.05 g.m^{-2} for the NSC14 glass in the same conditions. Beside, the Na release rate is very comparable to that of the NSC14 glass, with NL_{Na} reaching about 0.4 g.m^{-2} as well. The normalized leached fraction based on boron is intermediate between NL_{Na} and NL_{Si} (Fig. 7). It indicates that B–O–B and Si–O–B bonds are hydrolyzed at a higher rate than Si–O–Si bonds as expected [27] but not as fast as Na^+/H^+ ion exchange. Furthermore, the fast hydrolysis of B/Si–O–B bonds is the cause of the faster release rate of Si in this glass, according to previous studies on the dissolution of sodium borosilicate glasses [16,28–30]. Hydrolyzed boron leaves behind silanol groups and diminishes the connectivity of the glass network, accelerating the release of Si by hydrolysis. On the opposite, considering the NSC14 glass that has similar SiO_2 and Na_2O contents (Table 1), the Ca^{2+} ions seem not to be exchangeable with protons at this neutral pH, and Si is not released as fast. At last, no effect of the ionic strength can be put in evidence in these kinetics, presumably because of the higher dissolution rate of this glass that overcomes any ionic strength effect, and because it would be within the error bar (that is $\pm 5\%$ of the value).

When Tris is added to the solution with HCl or HNO_3 , the normalized leached fractions based on Na and B increase by a factor of about 4 (Tris/ HNO_3) or 8 (Tris/HCl) after 2.5 h. Na and B are congruently and preferentially released at a higher rate, while Si hydrolysis rate is either unchanged (Tris/ HNO_3) or increased by a factor of about ten (Tris/HCl). In the dissolution experiments with

the NSC14 glass, it is shown that Tris has no effect on the release of Si, Ca, nor Na. Thus, the increase in the B and Na release rates is the consequence of an accelerating effect of Tris on the B release rate, likely linked to its complexing properties toward boron. The differences in the kinetics between the Tris/HCl and Tris/HNO₃ solutions, especially concerning the Si release rate, are not well understood. It would be expected that the faster hydrolysis of B/Si–O–B bonds and of Na departure accelerate the release of Si. This is indeed the case for the Tris/HCl solution but not for the Tris/HNO₃ solution, that also has a less important leaching effect on B and Na.

4. Discussion

The dissolution experiments performed in this study are carried out in static conditions at low S/V (about 0.1 cm^{−1}) and over a very short time period (2.5 h). Thus, only the initial dissolution regime is investigated, before the formation of any condensed or reprecipitated alteration layer. The two chosen glasses have similar SiO₂ and Na₂O contents, but one contains CaO (NSC14) and the other B₂O₃ (NSB18). In pure water at neutral pH, the release of Ca is low and congruent with that of Si (Fig. 7). Either Ca²⁺ ions are very slowly exchanged with H⁺ ions (at a similar or lower rate than Si–O–Si hydrolysis), or Ca²⁺ ions are ion exchanged and immediately trapped in the leached silicate layer. The slow leaching of Ca²⁺ ions and their beneficial effect on the glass chemical durability have been observed for many years [31,32]. An interpretation is that Ca²⁺ ions, unleached or trapped in the leached layer, cross-link the silicate units and reduce the mobility of H₂O, yielding to lower depths of leached layer as found by SIMS [31]. In the borosilicate, the release of B is faster than that of Si, consistently with the high boron solubility (high affinity term). As a consequence, the release of Si is four times more rapid than in the soda-lime glass. The departure of boron breaks the network connectivity and creates both open pathways for water and numerous silanol bonds, accelerating the Si release in solution [16,30]. It is interesting that Na⁺ ions are released to the same extent in both glasses, but interpretation of that is subtle as Na⁺ ions do not play the same structural role in the two compositions. In particular, a fraction of Na⁺ ions are in a charge-compensating position near BO₄[−] units in the borosilicate glass: by ¹¹B MAS NMR, nearly 65% of boron are in BO₄ units in this glass, charge compensated by nearly 65% of the Na⁺ ions (because the Na₂O equals the B₂O₃ content) (our own data, not shown, and [33]). These charge-compensating Na⁺ ions are expected to be released slower than the network modifying Na⁺ ions [27]. It may explain while the Na release rate is not much faster in the borosilicate compared with the soda-lime glass.

The dissolution experiments performed on the NSC14 glass put in evidence an effect of the ionic strength that accelerates by a factor of about two the release of Si and Ca. Such an effect has been recognized for amorphous silica [34,35] and for quartz [36]. For instance, silica dissolution kinetics is increased by 20 in 0.05 M NaCl solution at pH 5.7 [34], while further addition of NaCl does not further enhance the kinetics. Moreover, this effect is maximum at neutral pH [35]. Our experimental conditions are thus particularly sensitive to the ionic strength. Two causes are invoked to explain the effect: (i) the ionic strength decreases the potential of the charged double layer at the glass-water interface, thus increasing the number of the ionized silanol groups, that are more active toward hydrolysis than the protonated silanol groups [35] and (ii) the solvated cations attracted to the negatively charged glass surface modify the water properties in the interfacial region and in particular increase the frequency of water nucleophilic attack on Si–O–Si bonds [34,36,37].

At last, the Tris molecules accelerate the dissolution kinetics of the borosilicate glass, but not of the soda-lime silicate glass. The

kinetic effect of Tris on the dissolution of soda-lime glasses has been studied in the context of bioactive glass research, with simulated body fluid (SBF) solutions with or without Tris/HCl [15]. Tris-containing SBF solutions at neutral pH were found to accelerate the dissolution of these glasses. This effect was attributed to the complexation of Tris with Ca²⁺ ions rather than with silicon ions, because Tris does not promote the dissolution of pure silica glass (in water at neutral pH, [2]) and because similar conclusions were drawn for the dissolution of apatite-wollastonite type glass-ceramics [12]. However, a later study on bioactive glass-ceramics of the SiO₂–Na₂O–CaO system concluded to the enhancing effect of Tris on the dissolution of the crystalline part of the glass-ceramics, and not of the soda-lime residual glass (in SBF as well as in water, [13]). The present study confirms the absence of any effect of Tris on soda-lime silicate glass at neutral pH.

From the dissolution kinetics experiments in this study, the accelerating effect of Tris on the dissolution of the borosilicate glass is attributed to the complexation properties of Tris toward boron. The Tris–boron complexation may increase the chemical potential gradient of boron between the glass and the solution, and thus the thermodynamic driving force for the B release (affinity term in the B–O hydrolysis rate). Glass corrosion promoted by the selective extraction of boron has also been observed in the case of E-glass fibers corroded in solutions of oxalic acid, malonic acid, and glyoxylic acid [5] and assigned to the formation of strong complexes of boron with the acid in solution. Complexation in solution with Si has also been invoked as a driving force for the glass dissolution, to explain the accelerated effect of some sodium acid salts, in particular sodium citrate, on the dissolution of silicate glass [2,3]. These complexes have, however, not been characterized so far. On the other hand, another possible mechanism is the surface complexation, that is, the adsorption of the organic species on specific surface sites – boron sites in this case. Such a complexation may either accelerate or decelerate the dissolution depending on the desorption rate of the complex from the surface. Citrate may actually act in this way according to a study with varying concentration of citrate [4]. The present study does not provide any direct evidence of such an action. But, as boron is highly soluble in water, we think that the complexation in solution is not the predominant effect. Boron is already well stabilized in pure water, so that thermodynamic affinity for its release is very high without Tris. Thus, Tris molecules may rather act by adsorbing on boron sites and removing boron from the glass surface (increase of the Si–O–B hydrolysis rate).

5. Conclusion

The structure of the Tris–boron complex has been directly determined by ¹¹B and ¹H NMR and corresponds to the bidentate 1:1 complex proposed by Michov [20] on the basis of pH measurements. From quantitative analysis of the ¹¹B NMR spectra for different pH and Tris/boron ratios, apparent pK values are −1.78 and 7.55 for Tris–boric and Tris–borate formation, respectively, in the range of constants for other polyol:B complexes. Parallel dissolution experiments on a soda-lime silicate glass and a sodium borosilicate glass put in evidence the specific effect of the Tris–boron complexation on the dissolution kinetics of the borosilicate glass, at neutral pH. In the Tris/HCl solution, the release rate of boron is increased by a factor of about 8, pulling out sodium ions and causing a significant increase of the Si release rate. The effect is slightly less marked in the Tris/HNO₃ solution, although the faster extraction of boron and sodium is noticed. The Tris–boron complexation in solution may be a factor in increasing the dissolution kinetics, but as the solubility of boron in water is high even without Tris, it is more probable that the surface complexation and

removal of boron is the involved mechanism in accelerating the kinetics. From this study, one may conclude that it is dangerous to systematically add Tris buffer in leaching studies, because it interferes with the dissolution kinetics. On the second hand, the presence of polyalcohols in the body fluid may be useful to complex boron and help its dissolution and release. This is essential for the rapid dissolution of borosilicate fibers and their biosolubility after inhalation.

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