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Surface mechanism of the boron adsorption on alumina in aqueous solutions

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ABSTRACT

The adsorption of boron (boric acid) from aqueous solutions on alumina has been investigated at pH 8.0, $I = 0.1$ M $NaClO_4$, $T = 22 \pm 3$°C, and under normal atmospheric conditions. The characterization of the adsorbed species was performed by Raman spectroscopy and the spectroscopic speciation was assisted by theoretical DFT calculations. Evaluation of the spectroscopic data points to the formation of inner-sphere surface complexes and indicates the formation of two different types of adsorbed boron species. The theoretical calculations corroborate the spectroscopic data and indicate that at low boron concentration the monodentate surface species dominates, whereas increased boron concentration favors the formation of a bidentate surface species. Assuming low coverage, the conditional formation constant for the monodentate surface species has been evaluated to be $\log \beta^* = 4.1 \pm 0.1$.

Keywords: Boric acid; Alumina; Raman spectroscopy; DFT calculations; Surface complexes; Formation constant

1. Introduction

Removal of toxic chemical species from contaminated waters by adsorption on solid surfaces (e.g. minerals or biomass by-products) is compared to other water treatment technologies (e.g. precipitation, ion exchange, and reverse osmosis) a cost-effective, with respect to design and operation simple approach, which is also insensible to toxic substances. Moreover, water treatment technologies based on adsorption meet environmental protection requirements [1].

Boron is a naturally occurring element that is found in oceans, sedimentary rocks, coal, shale, and some soils and is present mainly in the form of its oxygen compounds (e.g. borate minerals). In aqueous solutions, boron exists predominantly as boric acid, which is a very weak Lewis acid with a pK_a of approx. 9. Its dissociation is associated with the formation of $B(OH)_4^-$ and $H^+_{(aq)}$ through the addition of a water to a boric acid molecule [2,3]. It is also important to point out that, depending on the concentration of boric acid and solvent conditions, different polyborate species may be formed in solution by the condensation of several borate molecules. However, at boron concentrations below 0.025 $mol\,l^{-1}$, the aquatic chemistry of boron in solution is dominated by $B(OH)_3$ and $B(OH)_4^-$ [2–5].

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In natural waters, the concentration of boron is usually less than 1 mg l^{-1} and seldom exceeds the boron concentration in seawater, which is relatively high and averages around 4.5 mg l^{-1} [4]. However, depending on the hosting lithology, the boron concentration in regional ground waters can reach levels up to 8 mg l^{-1} [6]. Boron is also released, though to a lesser extent, from human activities. Borate mining and use of boron in various manufacturing industries are associated with industrial effluents that can contain boron up to several grams per liter (g l^{-1}) and consequently, such effluents have to be treated before discharge into natural water bodies [7].

Investigations show that the adsorption of boron (e. g. on alumina) is affected by both the distribution of boron species as well as the type and/or number of active sites of the adsorbent. Subsequently, the adsorption may vary with pH of the solution. The optimum pH for the removal of boron is about pH 8, which is close to the point-of-zero-charge (pzc) value of alumina (pzc ∼ 8) and is somewhat lower than the pK_a (about 9) of the boric acid, indicating that the optimum conditions for boron removal are given when the surface has no or a slight negative charge and boric acid is the predominant species in solution [8,9].

The nature of the adsorbed boron species as well as basic knowledge of the sorption mechanism at a molecular level are of fundamental importance to understand boron adsorption on solid surfaces and to develop effective boron removal technologies. In this context, information obtained by sophisticated spectroscopic methods [10–17] and computational modeling are major tools to elucidate the mechanism of boron interaction processes on surfaces [18,19]. However, only few studies have addressed the nature of the adsorbed boron species and the mechanism of the adsorption process by means of spectroscopy and computational modeling, and there is much room for further investigations.

This paper presents a study on the adsorption of boron on alumina by means of Raman spectroscopy, DFT calculations, and batch adsorption measurements. Characterization of the adsorbed species is performed by Raman spectroscopy and their validation is by theoretical calculations. Furthermore, the formation constant of the surface-bound boron species has been evaluated from the adsorption measurements. The present study aims to provide further insight into the boron adsorption on mineral surfaces.

2. Materials and methods

All experiments were performed at room temperature ($T = 22 \pm 3$ ℃) under atmospheric conditions in aqueous solutions at pH 8.0 and constant ionic strength ($I = 0.1$ M $NaClO_4$). The experiments were performed in duplicate and the mean values have been used for data evaluation. The preparation of stock solutions was carried out by dissolution of a standard boron solution (99.99%, Aldrich Co.) in deionized water. All experiments were performed in 150 ml polyethylene screw capped bottles since preliminary experiments have shown that adsorbate sorption onto the screw-capped bottle walls was negligible. The adsorbent, alumina (Al_2O_3, 99.9%, 150 mesh, Aldrich Co.), was used without any further purification or other pre-treatment. The BET surface area was determined by N_2 adsorption and was found to be 169 $m^2 g^{-1}$. An average pore diameter of 6 nm was determined.

The boron concentration in solution was measured by photometry using azomethine-H as chromophoric agent. The potentiometric pH measurements were carried out by means of a glass electrode (Inolap) attached to a pH meter (WTW). The system was calibrated with buffer solutions (pH 2, 4, 7, and 10, Merck) before and after each measurement.

Experiments of the boron sorption on alumina were performed by addition of a boron stock solution to a suspension, which contained 1 g alumina in 100 ml of 0.1 M $NaClO_4$ aqueous solution. Several mixtures with a constant amount of alumina (1 g per 100 ml 0.1 M $NaClO_4$) and a variable boron concentration (0.1 mg l^{-1} < [B] < 7.0 mg l^{-1}) at pH = 8.0 were prepared. After three days of equilibration, the concentration of the non-complexed boron was determined by photometry using azomethine-H as indicator. For comparison, parallel measurements were made for solutions of similar composition in boron but without alumina (reference solutions).

Raman spectra were measured (alpha300 confocal Raman microscope, WITec, equipped with an iCCD camera—spectrograph yielding a spectral resolution of $\Delta v = 2\ cm^{-1}$) using a laser wavelengths $\lambda_{Laser} = 532$ nm. The moist solid samples were measured. Using the confocal Raman microscope specifically the signal from the mineral surface was probed. Raman spectra were collected at different locations (or along lines across the surface of the sample). At each spot, the Raman signal was collected for 30 s in order to obtain spectra at a good signal-to-noise ratio.

Computational methodology

A minimal model of two Al-centers (dimer of Al$(OH)_3$) was used to simulate the surface of amorphous alumina. The computations were carried out at the B3LYP/6-31G(d) level of theory as implemented in the program Gaussian03 [20]. Vibrational analyses (within the harmonic oscillator approximation) showed that the stationary points are minima on the potential energy surface.

3. Results and discussion

3.1. Raman spectroscopic investigations

For the Raman spectroscopic investigation, a series of adsorption systems with variable boron concentration (0.1–7 mg l^{-1} or 0.009–0.7 mmol l^{-1}) and constant alumina amount 1.0 g has been prepared and selected Raman spectra of the corresponding solid alumina phases are shown in Fig. 1 (for 200–1,000 cm^{-1}) and Fig. 2 (for 2,900–3,750 cm^{-1}), respectively. For comparison, Raman spectra of boric acid in solid form and in aqueous solution are shown as well. In Table 1, the frequencies extracted from the Raman spectra for boric acid (solid), for boric acid in solution, and for boric acid adsorbed on Al_2O_3 are summarized. It has to be noted that at the boron concentration range used in this study, no formation of polymeric boron species is expected [3–5].

Based on the Raman spectra of boric acid but also on literature data for boron compounds, the bands between 3,300 and 3,700 cm^{-1} correspond to the O–H stretching modes of the B–OH groups [10–12,14,15]. In contrast to aquatic boron species, which do not show well-resolved O–H stretching bands in the Raman spectra, adsorbed boron species and boron compounds in solid form show relatively strong, fairly well-resolved vibrational bands corresponding to O–H stretching modes. This is attributed to the restricted interaction of the O–H groups in the solid and adsorbed form with water molecules via hydrogen bridges, which results in the broadening or even the disappearance of the associated Raman peaks (see Fig. 2).

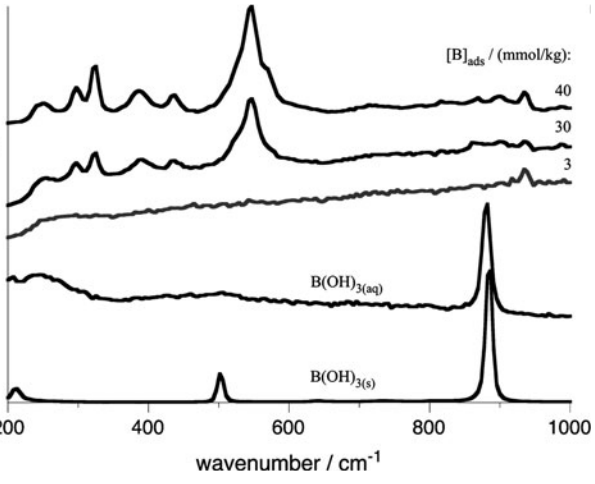

Fig. 1. Raman spectra of boron adsorbed to alumina (at pH 8) in comparison to the Raman spectra of boric acid in solid form and in aqueous solution for the spectral range <1,000 cm^{-1}.

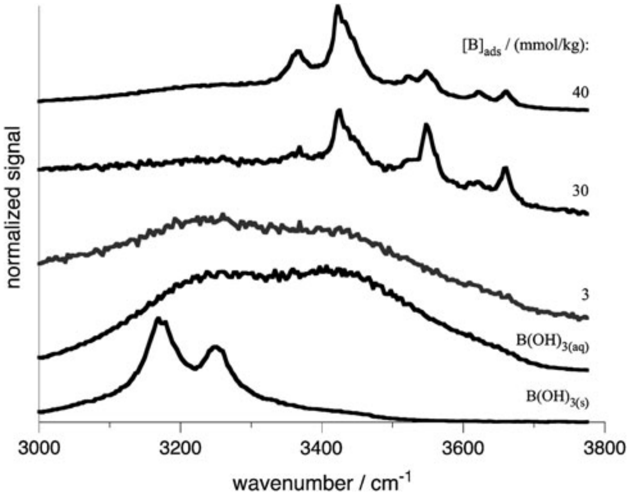

Fig. 2. Raman spectra of boron adsorbed to alumina (at pH 8) in comparison to the Raman spectra of boric acid in solid form and in aqueous solution for the spectral range >2,900 cm^{-1}.

The absorption bands between 800 and 1,000 cm^{-1} correspond to the symmetric O–BOH stretching modes, whereas the strong absorption bands at 547 cm^{-1} which predominates in the spectra of the boron species adsorbed on alumina may be attributed to the Al–O–B stretching. Comparing the spectra of the solid form and the solution with the results obtained from the adsorbed boron, it is further seen that the degenerated symmetric stretching vibration (around 890 cm^{-1}, see Table 1 and Fig. 1) is split into three vibrations (869, 900, and 935 cm^{-1}, respectively). Assuming the formation of an inner-sphere complex between alumina and boron, mono- or bidentate binding might be possible (see Fig. 3). Due to the adsorption to alumina, the symmetry of the $B(OH)_3$ is lowered to C_{2v} and three vibrational modes are now found in the Raman spectra. From the splitting of the symmetric stretching vibration, no further conclusion on the formation of mono- or bidentate surface complexes can be drawn, since both are of C_{2v} symmetry and consequently identical splittings of the vibrational mode can be expected. However, a major advantage of Raman spectroscopy compared to IR spectroscopy is its applicability for aqueous samples. A close evaluation of the O–H-vibrational modes adds additional information (see Fig. 2). According to the Raman spectra obtained at $v > 3{,}000$ cm^{-1}, two different surface species with distinct spectroscopic patterns can be identified. At boron concentrations below 30 ppm, the species with Raman bands at 3,660, 3,547, and 3,422 cm^{-1} is predominant, whereas in the Raman

Table 1
Raman wavenumbers in cm^{-1} (relative intensity)

Boric acid (solid) D_{3h}	Boric acid (solution, pH 8)	Adsorbed on Al_2O_3 (40 ppm) C_{2v}	
137 (4)			
213 (10)		245 (14)	
		297 (20)	
		320 (30)	
		386 (20)	
		437 (18)	
502 (22)	506 (11)		Sym. B–O–H bending
		547 (55)	Al–O–B?
642 (1)			
737 (1)		714 (14)	
		816 (15)	
887 (100)	882 (34)	869 (17)	Symmetric B–O stretching in trigonal BO_3
		900 (18)	
		935 (18)	
1,171 (4)			B–O–H bending
1,258 (1)			In-plane
1,314 (1)			Bending
1,384 (3)			B–O–H
	1,644 (10)		
	2,144		
3,172 (14)			
3,250 (10)	3,266 (94)		
		3,365 (59)	
3,429	3,419 (100)	3,422 (100)	B–O–H stretching
		3,522 (37)	
		3,547 (40)	
		3,621 (23)	
		3,660 (23)	

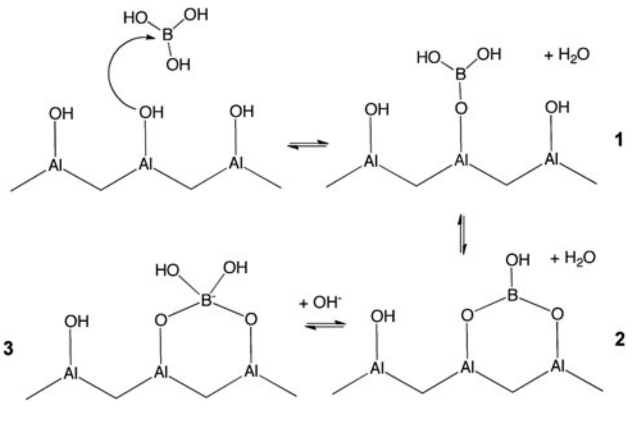

Fig. 3. Schematic illustration of the boron binding on alumina.

spectra of the samples with boron concentration of 40 ppm additional peaks at 3,621, 3,522, and 3,365 cm^{-1} become significant. Although, both species are present in the investigated samples, it is clear that increased boron concentration favors the formation of one adsorbed species. According to the literature, the adsorption of boron on alumina occurs through the formation of inner-sphere complexes [9]. The adsorption reaction and the three different modes of binding are schematically given in Fig. 3.

Among the three different surface complexes shown in Fig. 3, complexes 1 and 2 are expected to be predominant, whereas complex 3 is expected to dominate in the alkaline pH region ($pH > 9$) and hence is not taken into account within this study. Based on the literature data, which in the case of chromate surface complexes indicate that at increased concentrations the formation of the bidentate inner-sphere complex is favored [21], we have assigned the peaks at 3,657, 3,547, and 3,425 cm^{-1} to the trigonal monodentate inner-sphere complex (1). The trigonal monodentate inner-sphere complex (1) is the dominant species at low surface coverage. At high surface coverage, the formation of the bidentate inner-sphere complex (2) is favored and hence the peaks at 3,624, 3,524, 3,425, and 3,370 cm^{-1} correspond to bidentate species.

3.2. Computational modeling

To further support the suggested formation of the above-mentioned surface species, modeling of boric acid absorption on aluminum oxide has been performed by means of computations, which were carried out at the B3LYP/6-31G(d) level of theory as implemented in the program Gaussian03 (20). Initial approach of a boric acid molecule on the surface is expected to form the coordination complex **i** (see Fig. 4), in which the boric acid acts as a Lewis base on an Al site and also forms a hydrogen bond with an O-atom of the surface. In the gas phase, this process is predicted to be exothermic by 18.4 kcal/mol, and makes it 2.7 kcal/mol more exothermic than the computed adsorption of water (in the gas phase). Coordinated complex **i** can isomerize to monodentate form **ii** by formally dissociating the proton of the OH bridge on the surface in a process that is predicted to be exothermic by 6.9 kcal/mol. Isomerization of **i** to the bidentate form is slightly less exothermic (5.8 kcal/mol) (see Table 2).

As may expected from the similar geometries around the B-atom, the computed OH stretching vibrations in **ii** and **iii** are very similar and lie in the area of 3,790–3,820 cm^{-1}. In comparison, the computed OH stretch vibration for boric acid is 3,801 cm^{-1}, which is about 100 cm^{-1} higher than the observed stretching vibration in the vapor phase. The results of the computations support the assignment of the Raman bands carried out (vide supra). However, these findings differ from those described in a recent study based on experimental sorption data and CD-MUSIC modeling, which has shown that boron binds mainly as trigonal bidentate inner-sphere complex [22]. The disagreement could be ascribed to the relatively small differences in the formation enthalpies of the two surface species (i) and (ii).

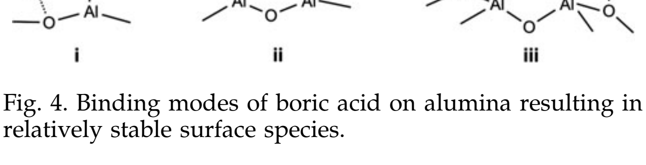

Fig. 4. Binding modes of boric acid on alumina resulting in relatively stable surface species.

3.3. Formation constants of the surface complexes

The corresponding adsorption experiments have been performed at pH 8 because at this pH, which is close to the pzc value of the adsorbent, alumina presents the highest adsorption capacity for boric acid. In addition, pH ~8 is the characteristic pH value of natural waters in contact with carbonaceous geological matrices (e.g. seawater and lake waters) [9]. The sorption of boric acid on alumina occurs through the formation of inner-sphere surface complexes and schematically the sorption of $B(OH)_3$ by the solid surface is illustrated in Figs. 3 and 4. These complexes are formed by the interaction of the boric acid ($B(OH)_3$), which is the predominant boron species under the given conditions in solution, with the surface active groups (hydroxy-groups) of the alumina surface [22,23]. Hereby, the surface of the alumina particles acts as Lewis base and binds boric acid (Lewis acid) through the oxygen active sites [9,22,23]. For the evaluation of our experimental adsorption data, we assume the formation of the mono-dentate complex (1) because of the conditions the corresponding adsorption experiments have been carried out (e.g. pH < 9 and relatively low surface coverage). In terms of a chemical equation, the adsorption reaction of boric acid on alumina is described by Eq. (1)

$$B(OH)_3 + \equiv S\text{–}OH \leftrightarrow \equiv S\text{–}O\text{–}B(OH)_2 + H_2O \tag{1}$$

and the corresponding equilibrium constant is given by Eq. (2)

$$\beta^* = \frac{[\equiv S\text{–}O\text{–}B(OH)_2]}{[B(OH)_3]\cdot[\equiv S - OH]} \tag{2}$$

where β^* is the formation conditional constant and $[\equiv S\text{–}O\text{–}(BOH)_2]$ is the concentration of the surface complexed boron and equals to the total boron concentration (initial boron concentration) minus the non-complexed aquatic boron concentration determined by photometry. At the given pH (pH 8.0), boron in aqueous solutions exists predominantly as boric acid. $[\equiv S\text{–}OH]$ is defined as the total concentration of active sites on the solid surface minus the complexed active sites $[\equiv S\text{–}OH] = [\equiv S\text{–}OH]_{tot} - [\equiv S\text{–}O\text{–}B(OH)_2)]$. The total concentration of active sites

Table 2
Relative enthalpies (ΔH, kcal/mol) at the B3LYP/6-31G(d) level of theory

Species	ΔH
i	0.0^{a}
ii	-6.9
iii	-5.8

[a] Relative to −1192.5712 a.u.

($[\equiv S\text{–}OH]_{tot}$) corresponds to the total number of the surface sites available for complexation and is determined using the Langmuir isotherm. Evaluation of the Langmuir isotherm results in the estimation of the maximum amount of adsorbate (e.g. boric acid) adsorbed per mass adsorbent (alumina) under the given conditions. On the other hand, this corresponds to the total concentration of active sites on the solid surface available for the adsorption of boric acid (e.g. $[\equiv S\text{–}OH]_{tot}$). Taking the logarithm and rearranging Eq. (2) results in Eq. (3)

$$\log\left(\frac{[\equiv S\text{–}O\text{–}B(OH)_2]}{[\equiv S\text{–}OH]}\right) = \log\beta^* + n \cdot \log[B(OH)_3] \qquad (3)$$

The intercept of the line described by Eq. (3) corresponds to the logarithmic value of the conditional formation constant ($\log\beta^*$) and the value of the slope corresponds to the stoichiometric factor of $[B(OH)_3]$, which here by definition equals to unity. Fig. 5 presents the experimental data in a $\log([\equiv S\text{–}O\text{–}B(OH)_2]/[\equiv S\text{–}OH])$-$\log[B(OH)_3]$ diagram. Linear regression analysis of the experimental data obtained at pH 6 based on Eq. (3) results in a $\log\beta^*$ of 4.1 ± 0.1 and in slope of 1.1 ± 0.1. The latter value, which is close to unity, proofs that Eq. (1) proposed for the surface complexation of boron by alumina is consistent. Moreover, the $\log\beta^*$ for the surface complex of boron on alumina is similar to the corresponding $\log\beta^*$ of boron on iron(oxy) hydroxide [24].

The conditional formation constant (β^*) equals to the thermodynamic formation constant under the given conditions and is a measure of the chemical affinity of the adsorbent surface (alumina) for the adsorbate molecules (boric acid). Increased values of the formation constant of surface complexes indicate higher affinity and/or selectivity of the adsorbent surface for the specific adsorbate molecules. The value determined in this study for the surface complexes of boric acid on alumina ($\log\beta^* \sim 4$) is characteristic for the interaction of boric acid with hydroxo-moieties of metal-oxide surfaces [24]. The chemical affinity of a certain contaminant is almost similar for the hydroxo-moieties present on a metal-oxide surface and therefore the number of the hydroxo-moieties, which is linearly related to surface area of the adsorbent, is the key parameter governing the adsorption on metal-oxide surfaces. Hence, increasing the surface area of the adsorbent is the main goal of recent studies [25,26].

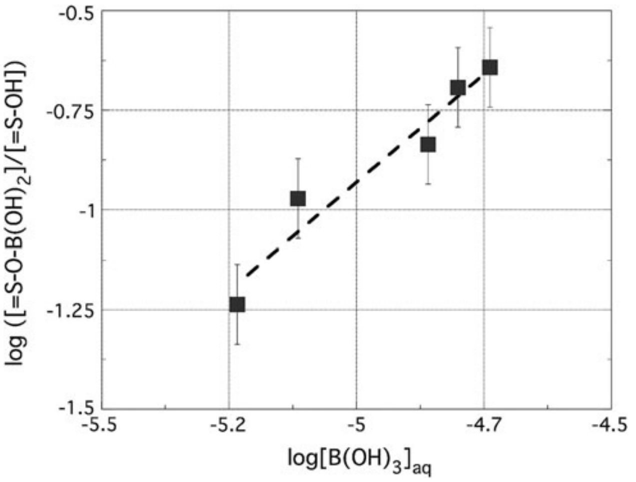

Fig. 5. $\log([(=S\text{–}O\text{–})_2BOH]/[(=S\text{–}OH)_2])$ as a function of $\log[B(OH)_3]$. Experimental data were obtained from photometric measurements in aqueous solutions containing 0.1 g l^{-1} alumina, 0.1 M $NaClO_4$ as background electrolyte and carried out at 25 ± 3°C under normal atmospheric conditions.

4. Conclusions

Based on the results obtained from this study it can be concluded that:

- According to Raman spectroscopy, two different adsorbed boron species (e.g. a monodentate and a bidentate surface complex) are formed on the alumina surface. The monodentate surface complex predominates at low boron coverage, whereas the formation of the bidentate surface complex is favored at increased boron coverage.
- The spectroscopic data are corroborated by theoretical calculations, which indicate that the formation of the monodentate surface complex is a thermodynamically favored process.
- The formation constant for the monodentate surface complex has been evaluated experimentally and is found to be $\log\beta^* = 4.1 \pm 0.1$. This value is similar to formation constants of boric acid complexes on other metal oxides, indicating that the surface area plays a key role in the adsorption on metal-oxide surfaces.

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