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Inconsistency in the triple layer model description of ionic strength dependent boron adsorption

Sabine Goldberg [*]

USDA-ARS, George E. Brown Jr. Salinity Laboratory, 450 W. Big Springs Road, Riverside, CA 92507, USA

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Abstract

Understanding anion adsorption mechanisms is necessary to allow prediction of anion adsorption behavior. This study was conducted to evaluate the ability of the triple layer model, a chemical surface complexation model, to describe the effect of changes in solution ionic strength (0.01–1.0 M NaCl) and solution pH (3–11) on B adsorption by the iron oxide, goethite, the aluminum oxide, gibbsite, the clay minerals, kaolinite and montmorillonite, and two arid zone soils. Ionic strength dependence of adsorption suggests an inner-sphere adsorption mechanism for goethite, kaolinite, montmorillonite, and the two soils and an outer-sphere adsorption mechanism for gibbsite. The triple layer model, containing an inner-sphere adsorption mechanism, was able to describe B adsorption on goethite, kaolinite, montmorillonite, and the two soils. The model was able to describe B adsorption on gibbsite using an outer-sphere adsorption mechanism. A problematic inconsistency exists in the triple layer model description of ionic strength dependent B adsorption between the type of B surface complex defined in the model and the ionic strength dependence of the model result. That is, postulating an inner-sphere adsorption mechanism in the triple layer model resulted in an ionic strength dependence appropriate for the formation of outer-sphere surface complexes and vice versa. Additional tests of the ability of the triple layer model to describe ionic strength dependent adsorption of additional ions are needed to establish whether the inconsistencies are limited to the B system or are of concern in other triple layer model applications.

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Keywords: Surface complexation modeling; Inner-sphere surface complex; Outer-sphere surface complex; Goethite; Gibbsite; Kaolinite; Montmorillonite; Soil

1. Introduction

Boron is an important element in plant nutrition. Boron toxicity may be a problem in arid areas, while B deficiency is of concern in areas receiving plentiful rainfall [1]. The B solution concentration range between plant deficiency and toxicity is narrow. Plants respond only to the B activity in soil solution and not to B adsorbed on soil minerals [2]. For this reason, understanding of the mechanism of B adsorption on soil materials is essential.

Boric acid is a very weak monobasic acid with a $\mathrm{p}K_a$ of 9.2 and a trigonal geometry. It acts as a Lewis acid by accepting a hydroxyl ion to form the borate anion:

$$H_3BO_3 + H_2O \leftrightarrow B(OH)_4^- + H^+. \tag{1}$$

The borate anion has a tetrahedral geometry. Direct experimental evidence for the presence of both trigonal and tetrahedral B on the surface of amorphous Fe oxide was provided by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy [3,4].

Ligand exchange with surface hydroxyl groups has been invoked as the mechanism of B adsorption on Al and Fe oxide minerals [3,5,6] and clay minerals [7]. Ligand exchange is a mechanism whereby anions become specifically adsorbed onto mineral surfaces forming inner-sphere surface complexes. Inner-sphere complexes contain no water molecules between the adsorbing anion and the surface functional group; while outer-sphere complexes contain at least one

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[*] Fax: +1-951-342-4962.
E-mail address: sgoldberg@ussl.ars.usda.gov.

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water molecule between the adsorbing anion and the surface functional group [8]. Adsorbed B formed both inner-sphere and outer-sphere surface complexes on amorphous Fe oxide as observed by ATR-FTIR spectroscopy [4].

The effects of ionic strength on adsorption have been used previously to distinguish between inner-sphere and outer-sphere metal [9] and anion [10] surface complexes on goethite. Selenate showing strong ionic strength dependence in its adsorption behavior was considered weakly bonded as an outer-sphere surface complex, while selenite [10], lead and cadmium [9] showing little ionic strength dependence in their adsorption behavior were considered specifically adsorbed as strong inner-sphere surface complexes. Extended X-ray absorption fine structure (EXAFS) measurements were used to verify the adsorption mechanisms for the selenium species [11]. Using the reasoning of Hayes and co-workers [9–11], Goldberg et al. [12] interpreted their ionic strength dependent B adsorption results to indicate the formation of inner-sphere B surface complexes on goethite, gibbsite, and kaolinite and outer-sphere B surface complexes on montmorillonite and two soils. In a more detailed evaluation of ionic strength effects on ion adsorption, McBride [13] indicated that ions forming inner-sphere surface complexes can show ionic strength dependent adsorption which increases with increasing solution ionic strength. The explanation for this is the principle of mass action. Increased ion adsorption results because of the increased solution activity of the counter ion of the background electrolyte available to compensate the surface charge generated by specific ion adsorption. Reinterpretation of the data of Goldberg et al. [12] using the mass action principle indicates an outer-sphere adsorption mechanism for B on gibbsite and inner-sphere adsorption mechanisms for B on goethite, kaolinite, montmorillonite, and soils.

Surface complexation models such as the constant capacitance model and the triple layer model are chemical models that explicitly define surface complexes and chemical reactions and consider the charge on both the adsorbing anion and the adsorbent solid. The constant capacitance model has been used successfully to describe B adsorption on various Al and Fe oxides, clay minerals, and soils [12,14–17]. The constant capacitance model considers all ions to adsorb specifically forming inner-sphere complexes unaffected by changes in solution ionic strength since the model uses the constant ionic medium Reference State. Solution ionic strength effects can be included by considering activity coefficients for the solution species. The triple layer model can consider both inner-sphere and outer-sphere surface complexes and has been successful in describing ionic strength dependent selenium [10], molybdenum [18], and arsenic [19] adsorption by soil minerals.

For heavy metals, adsorption behavior with ionic strength is a function of the type of background electrolyte [20]. In $NaNO_3$ solutions, Cd, Pb, Co, and Zn adsorption exhibited very little ionic strength dependence. In NaCl solutions, Cd and Cu adsorption decreased strongly with increasing ionic strength. In $NaClO_4$ solutions, Cd, Co, and Ni adsorption increased somewhat with increasing ionic strength. In order to accurately describe heavy metal adsorption in $NaNO_3$ and $NaClO_4$ solutions using the triple layer model, Criscenti and Sverjensky [20] invoked the formation of metal surface complexes that included the background electrolyte anion. Since such surface species were not necessary to describe heavy metal adsorption in NaCl, these authors recommended use of this background electrolyte for metal adsorption studies.

The objective of the present study was to evaluate the ability of the triple layer model to describe the ionic strength effects on B adsorption behavior by oxides, clay minerals, and soils from a background electrolyte of NaCl using the data published previously by Goldberg et al. [12].

2. Materials and methods

Boron adsorption behavior was studied on goethite (α-FeOOH), gibbsite (α-$Al(OH)_3$), kaolinite (KGa-2, poorly crystallized kaolinite), Na-montmorillonite (SWy-1, Wyoming bentonite), Arlington soil (classified as coarse-loamy, mixed, thermic Haplic Durixeralf), and Bonsall soil (classified as fine, montmorillonitic, thermic Natric Palexeralf). Synthesis methods for the oxide minerals were described by Goldberg et al. [12]. The clay minerals were obtained from the Clay Minerals Society's Source Clays Repository (University of Missouri, Columbia) and used without any pretreatment. The soil samples consisted of the <2-mm fraction of subsurface (25–51 cm) layers of each soil series.

Trace impurities in the oxides and clay minerals and dominant clay minerals in the soils were determined by X-ray diffraction as described in detail by Goldberg et al. [12]. Specific surface areas were determined using N_2 adsorption for oxides and clay minerals and ethylene glycol monoethyl ether (EGME) adsorption for soils (see Goldberg et al. [12] for method details and parameter values).

Experimental details for determining B adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration) are given by Goldberg et al. [12]. Samples of adsorbent were added to centrifuge tubes and equilibrated with aliquots of a 5.0 $\mathrm{g\,m^{-3}}$ B solution in NaCl background electrolytes (0.001, 0.01, 0.05, 0.1, and 1 M). The supernatants were analyzed for pH, filtered, and analyzed for B concentration using the colorimetric azomethine-H method described by Bingham [21].

The triple layer model [22] was used to describe B adsorption behavior on the adsorbents. The computer program FITEQL 3.2 [23] was used to fit surface complexation constants to the experimental adsorption data. In the present application of the triple layer model to B adsorption, the following surface complexation reactions were considered:

$$\mathrm{SOH_{(s)} + H^+_{(aq)} \leftrightarrow SOH^+_{2(s)}}, \tag{2}$$

$$\mathrm{SOH_{(s)} \leftrightarrow SO^-_{(s)} + H^+_{(aq)}}, \tag{3}$$

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