DIVISION S-2—SOIL CHEMISTRY

Boron Adsorption on Aluminum and Iron Oxide Minerals[1]

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ABSTRACT

Boron adsorption behavior was investigated on various crystalline and x-ray amorphous Al and Fe oxide minerals. Adsorption increased at low pH, exhibited a peak in the pH range 7 to 8, and decreased at high pH. The magnitude of B adsorption was much greater for the x-ray amorphous materials. Since B adsorbs specifically on Al and Fe oxide minerals, the constant capacitance model containing a ligand exchange mechanism was used to describe its adsorption behavior. The constant capacitance model was able to represent B adsorption on all minerals over the entire pH range studied (3–12) using the same set of surface complexation constants. With the exception of amorphous Al oxide, B adsorption on these oxide minerals could be successfully described by optimizing only the B surface complexation constant. Other nonexperimental parameters were held fixed at values identical to those previously used in modeling phosphate, silicate, and selenite adsorption on Al and Fe oxide minerals.

BORON is an essential element in plant nutrition. Low concentrations are required for sufficiency while higher concentrations produce toxicity symptoms and marked yield decrement. Since the concentration range between deficiency and toxicity is narrow, reactions affecting B availability are of interest. Statistical analyses of B sorption behavior in whole soils have indicated that Al and Fe oxides play an important role. Bingham et al. (1971) found significant correlation between the Al_2O_3 content and B adsorption of four Mexican and six Hawaiian soils. El-rashidi and O'Connor (1982) found that a multiple regression equation including percent Fe_2O_3, organic C, and cation exchange capacity could explain 90% of

the variance in adsorbed B of 10 soils from New Mexico.

The adsorption behavior of B on various Al and Fe oxide minerals both crystalline and x-ray amorphous has been previously investigated (Scharrer et al., 1956; Hatcher et al., 1967; Sims and Bingham, 1968; McPhail et al., 1972; Choi and Chen, 1979). Scharrer et al. (1956) studied B fixation on Al_2O_3 and Fe_2O_3. They found that both minerals exhibited increasing B sorption with increasing pH. Adsorption peaks occurred at pH 6 to 7 for Al_2O_3 and pH 8 to 9 for Fe_2O_3 and were followed by a gradual decline. Sims and Bingham (1968) and McPhail et al. (1972) obtained similar adsorption behavior using x-ray amorphous hydroxy Fe and Al forms. Sims and Bingham (1968) found that B adsorption was maximum on freshly precipitated materials and decreased with increasing crystallinity resulting from aging. Choi and Chen (1979) studied B adsorption on an activated alumina of high surface area and found an adsorption peak near pH 8. McPhail et al. (1972) described their adsorption isotherm data using the Langmuir equation, while Choi and Chen (1979) used the Freundlich isotherm. Both sets of researchers obtained good fits of these equations to their data.

Sims and Bingham (1968) suggested that the mechanism of B adsorption may be anion exchange with hydroxyl ions. McPhail et al. (1972) also invoked this mechanism to explain their B adsorption data. This type of ligand exchange with surface reactive OH^- groups is a mechanism by which anions become specifically adsorbed onto oxide mineral surfaces. Specific adsorption of anions produces a shift in the zero point of charge, ZPC, of the mineral to a more acid value. A shift in ZPC was observed following B adsorption on boehmite (Fricke and Leonhardt, 1950), pseudoboehmite (Alwitt, 1972), aluminum hydroxide gel (Beyrouty et al., 1984), and magnetite (Blesa et al., 1984) indicating specific adsorption on these minerals.

The constant capacitance model (Stumm et al., 1970; Schindler and Gamsjäger, 1972; Stumm et al., 1976; 1980) is a chemical model which explicitly defines surface species and chemical reactions and includes the effect of pH on adsorption. The constant capacitance model uses a ligand exchange mechanism to describe adsorption and is thus appropriate for modeling specific adsorption. The model has been successful in describing adsorption of the specifically adsorbing inorganic anions fluoride, phosphate, silicate, and selenite (Sigg and Stumm, 1981; Goldberg and Sposito, 1984; Goldberg, 1985).

The purpose of this work is to test the ability of the constant capacitance model to describe B adsorption on Al and Fe oxide minerals. With the exception of the work by Choi and Chen (1979), literature data sets were insufficient (never containing more than six data points) for testing the model. For this reason B adsorption experiments were conducted using various crystalline and x-ray amorphous Al and Fe oxide minerals under changing conditions of solution pH.

MATERIALS AND METHODS

Boron adsorption behavior was studied on a variety of adsorbents. Samples of $Al(OH)_3$, Al_2O_3, and Fe_2O_3 were ob-

Table 1. Numerical values of nonadjustable parameters used in the model.

Solid	Specific surface area $(10^4 \, m^2 \, kg^{-1})$	Maximum adsorption density $(mol \, m^{-3})$	Suspension density $(kg \, m^{-3})$
Al-oxides			
Gibbsite	0.20	ndt	200
α-alumina	0.09	ndt	200
Alon	6.96	0.191	10
Aluminium oxid C	9.69	0.270	40
Pseudoboehmite	22.7	0.298	6.4
Amorphous aluminum oxide	16.3	0.289	5.2
Fe-oxides			
Hematite	1.64	0.189	100
Goethite	3.12	0.0981	25
34% Goethite/maghemite	5.57	0.154	20
64% Goethite/maghemite	7.42	0.259	40
Amorphous iron oxide	11.2	0.224	6.4

† Boron adsorption could not be detected under the experimental conditions used.

tained from Fischer Scientific Co. and found to be essentially pure gibbsite, α-alumina, and hematite, respectively, using x-ray diffraction analysis. It was found that the hematite sample was contaminated with sulfate to such an extent that it released up to 1.7 mg SO_4^{2-} g^{-1} of hematite to aqueous solution. Since it was felt that the presence of high SO_4^{2-} concentrations would interfere with the B adsorption experiments, the hematite was purified using a modification of the method of Jurinak (1966). Following the digestion at pH 4.0 the oxide was resuspended, collected on a filter paper, rinsed with distilled deionized water, and dried at 105°C before use. A fumed alumina, alon, was obtained from Cabot Corp. and a sample of aluminium oxid C was supplied by Degussa. Both of these aluminas were identified as δ-Al_2O_3 using x-ray diffraction.

X-ray amorphous Al and Fe oxide samples were prepared using a modification of the method developed by McPhail et al. (1972) and freeze-dried. For the Al oxide synthesis, $AlCl_3$ was substituted for the nitrate salt and the shaking time was increased to 15 min. In the Fe oxide synthesis, the concentrations of $Fe(NO_3)_3$ and NaOH were doubled and the heating time in the water bath increased to 15 min. Pseudoboehmite was synthesized using the method of McLaughlin et al. (1981). The final boiling step was omitted. X-ray diffraction patterns of this material showed the characteristic broad peaks of pseudoboehmite located at the same positions as the peaks of boehmite. Goethite was synthesized according to the procedure of McLaughlin et al. (1981) and verified by x-ray diffraction analysis to be predominantly such.

Thermogravimetric analysis of this goethite using the Du Pont 990 Thermal Analyzer coupled with a 951 Thermogravimetric Analyzer (TGA) module showed a weight loss value differing by only 2% from the calculated theoretical weight loss for pure goethite. Weight loss values were determined graphically using the procedure of Karathanasis and Hajek (1982). Two additional precipitates were synthesized which were found by x-ray diffraction analysis to consist of a coprecipitate of goethite and maghemite. A solution of equal parts of 0.275 M $FeCl_2$ and 0.875 M NaOH was heated in a water bath for 20 min at 70°C, cooled to room temperature, filtered, and dried at 105°C. The product was found to contain 64% goethite using thermogravimetric analysis. Upon reduction of the initial solution concentrations to 0.11 M $FeCl_2$ and 0.35 M NaOH the synthesis technique yielded a solid which was predominantly maghemite having a goethite content of 34%. Thermogravimetric analysis was found to be a convenient and quantitative method for measuring percent goethite in these mixtures. Specific
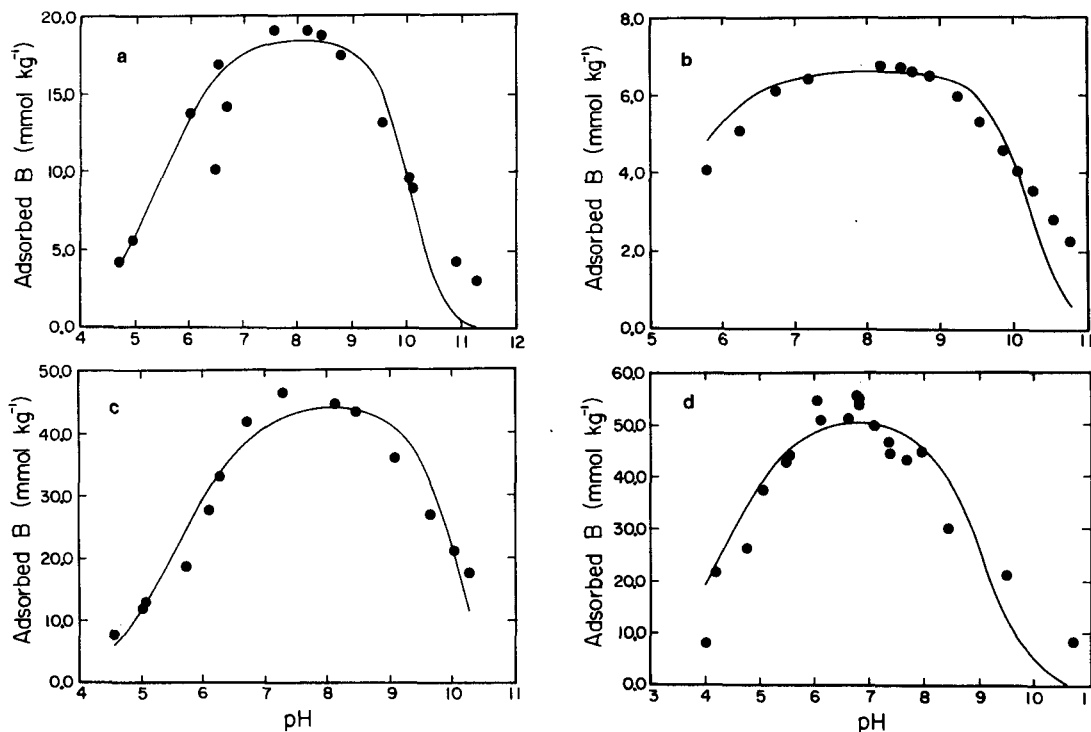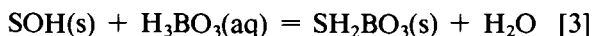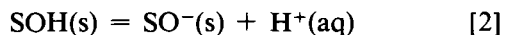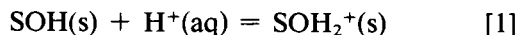
Fig. 1. Boron adsorption on Al oxides: (a) alon, (b) aluminium oxid C, (c) pseudoboehmite, and (d) amorphous Al oxide. Circles represent experimental data. Model results are represented by solid line.

surface areas of all minerals studied were determined using N_2 adsorption. A multi-point BET adsorption isotherm was determined using a Cahn electrobalance model RG. The samples were outgassed at 100°C. Surface area values are listed in Table 1.

Boron adsorption experiments were carried out in batch systems. Appropriate amounts of solid (see Table 1) were added to 50-mL polypropylene centrifuge tubes and equilibrated with 10 or 25 mL of a 0.1 M NaCl solution by shaking for 20 h on a reciprocating shaker. This solution contained 5.0 g B m^{-3} and had been adjusted to the desired pH values using 1 M HCl or 1 M NaOH. Optimal additions of acid and base were determined in preliminary analyses and changed the total volumes by <2%. The samples were centrifuged at 12 500 rpm for 30 min in a Servall superspeed centrifuge. The decantates were analyzed for pH, filtered, and analyzed for B concentration. Boron was determined using a Technicon Auto Analyzer II and the Azomethine-H method described by Bingham (1982).

The constant capacitance model (Stumm et al., 1980) was used to describe the B adsorption data. The computer program FITEQL (Westall, 1982) was used to fit intrinsic surface equilibrium constants to the experimental data. The computer program MICROQL (Westall, 1979) was used to speciate the chemical system and to check goodness of fit of the model. A detailed description of the model assumptions and the fitting procedure used is provided in Goldberg and Sposito (1984).

In the application of the model to B adsorption the following surface reactions are defined:

$$SOH(s) + H^+(aq) = SOH_2^+(s) \qquad [1]$$

$$SOH(s) = SO^-(s) + H^+(aq) \qquad [2]$$

$$SOH(s) + H_3BO_3(aq) = SH_2BO_3(s) + H_2O \qquad [3]$$

where SOH(s) represents 1 mole of reactive surface OH$^-$ bound to a metal ion, S (Al or Fe), in the oxide mineral.

Following are the intrinsic conditional equilibrium constants describing the surface reactions:

$$K_+ \text{ (int)} = \frac{[SOH_2^+]}{[SOH][H^+]} \exp(F\psi/RT) \qquad [4]$$

$$K_- \text{ (int)} = \frac{[SO^-][H^+]}{[SOH]} \exp(-F\psi/RT) \qquad [5]$$

$$K_B(\text{int}) = \frac{[SH_2BO_3]}{[SOH][H_3BO_3]} \qquad [6]$$

where R is the molar gas constant, T is the absolute temperature, and square brackets indicate concentrations (mol m^{-3}). The mass balance equation for the surface functional group, SOH, is:

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SH_2BO_3] \qquad [7]$$

and the appropriate charge balance equation is:

$$\sigma = [SOH_2^+] - [SO^-] \qquad [8]$$

where again square brackets indicate concentrations (mol m^{-3}) and the net surface charge, σ, has units of moles of charge per cubic meter. The chemical equilibrium problem formulated above can be solved using a system of simultaneous equations.

Values for the intrinsic protonation-dissociation constants $K_+(\text{int})$ and $K_-(\text{int})$ can be calculated from batch titration data of net surface charge. The calculation procedure is described in Goldberg and Sposito (1984). In this study numerical values of the intrinsic protonation-dissociation constants were obtained from a literature compilation of experimental data for Al and Fe oxides (see Table 1, Goldberg and Sposito, 1984). These two constants were also fit simultaneously with the B surface complexation constant

K_B(int) using the FITEQL program. Table 1 lists values of experimental parameters.

RESULTS AND DISCUSSION

Boron adsorption as a function of pH is shown in Fig. 1 for four Al oxide minerals. The shapes of the adsorption curves for alon, aluminium oxid C, and and pseudoboehmite are very similar showing adsorption peaks in the pH range 7 to 8. Boron adsorption on the amorphous Al oxide exhibited a lower adsorption peak in the pH range 6 to 7. Boron adsorption was highest for the materials of highest specific surface area and of lowest crystallinity: amorphous Al oxide (Fig. 1d) and pseudoboehmite (Fig. 1c). This behavior agrees with the observations of Sims and Bingham (1968) that B adsorption is highest for amorphous materials. Reactivities of gibbsite and α-alumina toward B were so low that B adsorption could not be measured under our experimental conditions. The lack of reactivity of these materials is not surprising given their extremely low surface areas (see Table 1) and correspondingly low total concentration of OH^- groups.

Figure 2 shows B adsorption as a function of pH for three Fe oxide minerals. The shapes of these adsorption curves are similar to those for the Al oxide minerals showing adsorption peaks near pH 8. Again as for the Al oxide minerals, the highest amount of adsorption was exhibited by the amorphous material. Following the SO_4^{2-} removal treatment the adsorption maximum and the shape of the B adsorption curve on hematite were essentially unaltered. Thus it appears that borate ions may adsorb on specific sites not occupied by SO_4^{2-} ions as suggested by Bingham and Page (1971) to explain similar adsorption behavior on an allophanic soil. However it is equally likely that $B(OH)_4^-$ ions adsorb with greater affinity and can therefore readily replace SO_4^{2-} ions on the hematite surface. Sposito (1984) indicates that SO_4^{2-} anion adsorption may occur via outer-sphere complex formation. Boron adsorption behavior of the two mixed goethite/maghemite solids was similar to the goethite sample (see Table 1).

Reproducibility of some of the adsorption maxima was evaluated. Maximum adsorption in mmol kg^{-1} was: 18.6 ± 0.59 for alon, 6.78 ± 0.035 for aluminium oxid C, 45.0 ± 15.0 for amorphous Al oxide, and 1.84 ± 0.071 for hematite. The large standard deviation for the amorphous oxide can be attributed to the fact that the replicates were synthesized in two separate batches. This difference between precipitates formed using the same procedure indicates the large variability inherent to amorphous oxide minerals. It was found that adsorption on aluminium oxid C, pseudoboehmite, hematite, and goethite increased on a per gram basis with decreasing solid suspension density. This indicates that B saturation on these materials had not been attained. For this reason reproducibility was tested only for replicates having identical solid suspension densities.

Maximum B adsorption per unit surface area was calculated for each material. The variability of this parameter was large and therefore no statistically significant (95% level of confidence) differences were
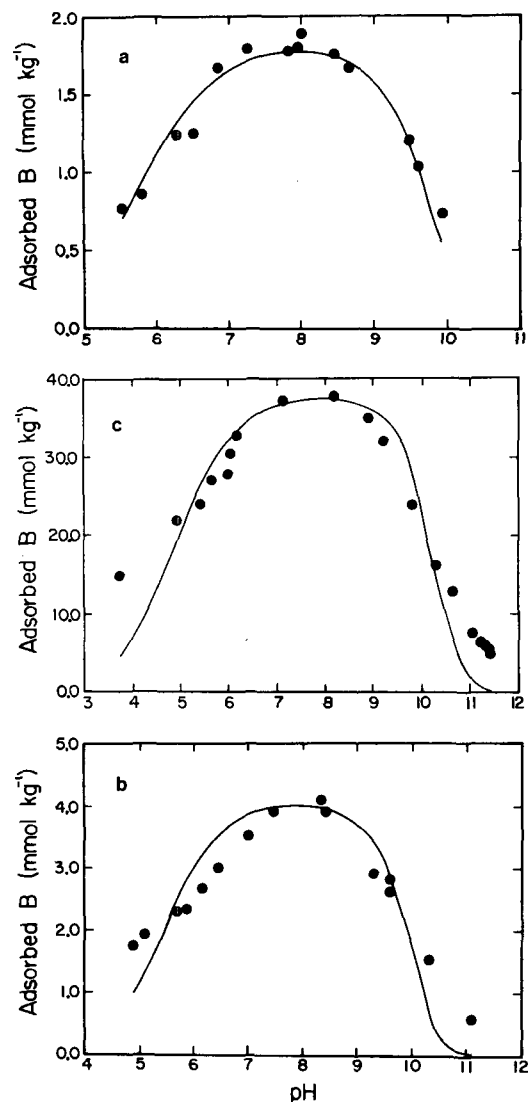

Fig. 2. Boron adsorption on iron oxides: (a) hematite, (b) goethite, and (c) amorphous iron oxide. Circles represent experimental data. Model results are represented by solid line.

found. However, the amorphous Al and Fe oxide materials exhibited the highest density of adsorbed B on a surface area basis. This is reasonable as the amorphous materials are expected to have a higher density of reactive OH^- groups.

Common logarithms for the surface complexation constants obtained from the application of FITEQL to the experimental data are given in Table 2. The first three columns of constants in this table list values of log K_+(int), log K_-(int), and log K_B(int) obtained by fitting all three constants simultaneously. The last column of constants in Table 2 lists values of log K_B(int) obtained by using the values of log K_+(int) = 7.38, log K_-(int) = −9.09 for Al oxide and log K_+(int) = 7.31, log K_-(int) = −8.80 for Fe oxide minerals (see the literature compilations in Table 1 of Goldberg and Sposito, 1984). It should be noted that under these conditions log K_B(int) is the only parameter that was optimized by the FITEQL program. All other parameters were fixed at the identical values which had been used in previous modeling studies of phosphate, se-

Table 2. Surface complexation constants obtained from FITEQL.†

Solid	Log K_+(int)	Log K_-(int)	LogK_B(int)	Log K_B(int)‡
		Al-oxides		
Alon Aluminium	7.33	−9.60	4.98	5.13
oxid C Pseudoboeh-	7.16	−10.26	5.08	5.56
mite Amorphous aluminum	7.86	−8.54	5.52	5.09
oxide	5.93	−7.40	4.83	5.92
Averages	7.07 ± 0.82	−8.95 ± 1.25	5.20 ± 0.49	5.43 ± 0.39
		Fe-oxides		
Hematite	7.71	−8.64	5.15	4.88
Goethite Amorphous	7.86	−8.92	5.66	5.25
iron oxide	7.46	−8.91	5.72	5.63
Avg	7.68 ± 0.20	−8.82 ± 0.16	5.51 ± 0.31	5.25 ± 0.38
Overall avg	7.33 ± 0.67	−8.90 ± 0.89	5.28 ± 0.35	5.35 ± 0.36

† All intrinsic surface complexation constants were obtained using concentrations in mol L^{-1}.

‡ Log K_B(int) was optimized while holding log K_+(int) and log K_-(int) constant.

lenite, and silicate adsorption (Goldberg and Sposito, 1984; Goldberg, 1985).

Averages of values for log K_+(int) and log K_-(int) data obtained by FITEQL are not statistically different at the 95% level of confidence from those of the literature compilations. Average values of log K_B(int) in the last two columns of Table 2 are not statistically different at the 95% level of confidence. The standard deviations of the common logarithms of both sets of B adsorption constants are considerably smaller than those obtained by Goldberg and Sposito (1984) for the common logarithms of the formation constants for phosphate complexes on oxide minerals. Aluminum and Fe oxide minerals exhibited similar B adsorption behavior in that the common logarithms of the surface complexation constants for the two types of oxides were not significantly different.

The constant capacitance model is well able to describe B adsorption data fitting a smooth curve through the experimental points (Fig. 1 and 2). In all cases except for amorphous Al oxide (Fig. 1d) the closer fit was obtained by optimizing only the B surface complexation constant and is shown in Fig. 1 and 2. For amorphous Al oxide optimization of solely log K_B(int) gave a very poor fit. Therefore the model fit shown in Fig. 1d was obtained by optimizing all three surface complexation constants simultaneously.

CONCLUSIONS

Boron adsorption on various crystalline and x-ray amorphous oxide minerals increased at low pH, exhibited a peak in the pH range 7 to 8, and decreased at high pH. The magnitude of B adsorption decreased with increasing crystallinity of the solid. The presence of SO_4^{2-} did not limit B adsorption on hematite indicating either lack of site competition between these anions or higher adsorption affinity for $B(OH)_4^-$. The constant capacitance model was able to represent B adsorption behavior over the entire pH range studied using the same set of surface complexation constants.

Values of the protonation-dissociation constants and the B surface complexation constant for Al and Fe oxide minerals were not significantly different. Except on amorphous Al oxide, the model successfully described B adsorption on all materials under changing conditions of solution pH using only one adjustable parameter: the B surface complexation constant. All other parameters not determined experimentally were fixed at the identical values used in previous modeling studies of phosphate, silicate, and selenite adsorption.

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