

Boron Adsorption Mechanisms on Oxides, Clay Minerals, and Soils Inferred from Ionic Strength Effects

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ABSTRACT

Prediction of anion adsorption behavior is enhanced by understanding the adsorption mechanism. This study was conducted to evaluate ionic strength effects on B adsorption and to infer B adsorption mechanisms on various surfaces. Boron adsorption on the Fe oxide goethite, the Al oxide gibbsite, the clay minerals kaolinite and montmorillonite, and two arid-zone soils was investigated as a function of solution pH (3–11) and ionic strength of the background electrolyte (0.01–1.0 M NaCl). Boron adsorption on the oxides and kaolinite increased from pH 3 to 6, exhibited a peak at pH 6 to 8.5, and decreased from pH 8.5 to 11. For B adsorption on montmorillonite and the soils, the adsorption maximum was located near pH 9. Ionic strength dependence, measured as the increase of the B adsorption maximum in 1.0 M NaCl solutions compared with 0.01 M NaCl solutions increased in the order: goethite (3%) < kaolinite (15%) < gibbsite (–30%) < montmorillonite (109%) ≈ montmorillonitic soil (116%) ≈ kaolinitic soil (129%). Shifts in zero point of charge were observed on goethite, gibbsite, and kaolinite following B adsorption. Ionic strength effect results suggest an inner-sphere adsorption mechanism for goethite, gibbsite, and kaolinite and an outer-sphere adsorption mechanism for montmorillonite and the soils. These mechanisms are also indicated by zero point of charge determinations, microelectrophoresis measurements, or both. The constant capacitance model, containing an inner-sphere adsorption mechanism, was able to describe B adsorption on goethite, gibbsite, kaolinite, and kaolinitic soil. The model was unable to describe B adsorption on montmorillonite and montmorillonitic soil because the computer optimizations diverged.

BORON is an important element in crop production. Boron deficiency is of concern in areas receiving plentiful rainfall while B toxicity may be a problem in arid areas (Keren and Bingham, 1985). Because the concentration range between plant deficiency and toxicity is narrow and plants respond only to the B activity in soil solution, understanding the mechanism of B adsorption on soil materials is necessary. Although organic matter plays an important role in B sorption, this study focused on soil minerals.

Anion exchange with surface hydroxyl groups has been invoked as the mechanism of B adsorption on Al and Fe oxide minerals (Sims and Bingham, 1968; McPhail et al., 1972). This type of ligand exchange is a mechanism by which anions become specifically adsorbed onto oxide mineral surfaces. Specifically adsorbing anions form inner-sphere surface complexes. Inner-sphere surface complexes contain no water molecules between the adsorbate anion and the surface

functional group (Sposito, 1984). The zero point of charge (ZPC) of variable-charge minerals is shifted to a more acid value following specific adsorption of anions. Boron adsorption lowered the ZPC of boehmite (Fricke and Leonhardt, 1950), pseudoboehmite (Alwitt, 1972), Al-hydroxide gel (Beyrouy et al., 1984), and magnetite (Blesa et al., 1984), indicating specific adsorption.

No information on the effect of B adsorption on the ZPC of clay minerals is available. Previous research has indicated that B adsorption occurs on the edges of the clay minerals illite (Couch and Grim, 1968) and montmorillonite (Keren et al., 1981). Ligand exchange with reactive surface hydroxyl groups on the broken edges has been suggested as the mechanism of B adsorption on clay minerals (Keren and Talpaz, 1984).

By studying the effects of ionic strength on ion adsorption, Hayes and Leckie (1987) were able to distinguish between inner- and outer-sphere metal ion surface complexes, while Hayes et al. (1988) were able to distinguish between inner- and outer-sphere anion surface complexes. Outer-sphere surface complexes contain at least one water molecule between the adsorbate anion and the surface functional group (Sposito, 1984). Studying Se adsorption, Hayes et al. (1988) suggested that SeO_4^{2-} , showing strong ionic strength dependence in its adsorption behavior, was weakly bonded as an outer-sphere surface complex, while SeO_3^{2-} , showing little ionic strength dependence in its adsorption behavior, was specifically adsorbed in a strong inner-sphere surface complex. These adsorption mechanisms were verified spectroscopically using extended x-ray absorption fine structure measurements (Hayes et al., 1987).

The constant capacitance model is a chemical surface complexation model that uses a ligand exchange mechanism to describe specific anion adsorption (Stumm et al., 1980). The model explicitly defines inner-sphere surface complexes and chemical reactions and considers the charge on both the adsorbate and the adsorbent. The constant capacitance model has been used successfully to describe B adsorption on various Al and Fe oxides via ligand exchange with surface hydroxyl groups (Goldberg and Glaubig, 1985), clay minerals via ligand exchange with aluminol groups (Goldberg and Glaubig, 1986a), and soils (Goldberg and Glaubig, 1986b) as a function of solution pH.

The objectives of our study were to: (i) investigate the ionic strength effects on B adsorption behavior by oxides, clay minerals, and soils; (ii) evaluate the nature of the adsorbed B surface complexes using the ionic strength data; and (iii) investigate the ability of

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Table 1. Characterization of adsorbent materials used in this study

Oxides and clays	Surface area†	Trace impurities	Dominant minerals
	m ² g ⁻¹		
goethite	42.5	hematite	
gibbsite	66.5	bayerite	
KGa-2 kaolinite	19.3	chlorite	
SWy-1 montmorillonite	18.6	mica	
Soils			
Arlington	103.1		montmorillonite, vermiculite, kaolinite
Bonsall	105.7		kaolinite, illite, montmorillonite

† Oxide and clay surface area determined using a N₂ adsorption isotherm; soil surface area determined using ethylene glycol monoethyl ether adsorption.

the constant capacitance model to describe B adsorption on soil minerals.

MATERIALS AND METHODS

Boron adsorption behavior was studied on various adsorbents. Goethite (α -FeOOH) and gibbsite [α -Al(OH)₃] were synthesized according to the procedures described by McLaughlin et al. (1981) and Kyle et al. (1975), respectively, and verified as such by x-ray diffraction. Samples of kaolinite (KGa-2, poorly crystallized kaolinite) and Na-montmorillonite (SWy-1, Wyoming bentonite) were obtained from the Clay Minerals Society's Source Clays Repository (Univ. of Missouri, Columbia). The clay minerals were used without any pretreatment. Subsurface (25–51-cm) samples of the Arlington (coarse-loamy, mixed, thermic Haplic Durixeralf) and Bonsall (fine, montmorillonitic, thermic Natric Palixeralf) soil series consisted of the < 2-mm fraction. Although the Bonsall soil is classified as montmorillonitic, the clay mineralogy of the particular subsample used in this study was dominated by kaolinite. Organic C content of the soil samples was low ($\leq 0.2\%$) as determined by the method of Nelson and Sommers (1982).

Trace impurities in the oxides and clay minerals were determined using x-ray diffraction powder mounts (see Table 1). Dominant clay minerals in the soils were determined by converting x-ray diffraction peak areas obtained using oriented mounts directly to clay mineral contents as described by Klages and Hopper (1982). Specific surface areas of the oxides and clay minerals were determined using a single-point Brunauer-Emmett-Teller (BET) N₂ adsorption isotherm obtained with a Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, NY). Specific surface areas of the soil samples were determined using ethylene glycol monoethyl ether as described by Cihacek and Bremner (1979). Table 1 presents mineralogical data and specific surface area values for all materials.

Boron adsorption experiments were carried out in batch systems to determine adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration). Samples of adsorbent (0.375 g for oxides, 0.75 g for montmorillonite, 2.5 g for kaolinite, and 5.0 g for soils) were added to 50-mL polypropylene centrifuge tubes and equilibrated with aliquots (25 mL for clays and soils and 15 mL for oxides) of a 0.001, 0.01, 0.05, 0.1, or 1.0 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 additions that changed the total volume by $\leq 2\%$. The samples were centrifuged at a relative centrifugal force of 7800 \times g for 20 min. The decantates were analyzed for pH, filtered through a 0.45- μ m Whatman filter, and analyzed for B concentration using a Technicon Auto Analyzer II (Technicon Industrial Systems, Tarrytown, NY) and the azomethine-H method described by Bingham (1982).

Zero points of charge and/or electrophoretic mobilities were determined for all adsorbents by microelectrophoresis using a Zeta-Meter 3.0 system (Zeta Meter, Long Island City, NY). The electrophoretic mobilities of suspensions containing 0.01% solid in 0.001 M NaCl for oxides and in 0.01 M NaCl for clays and soils were determined at various pHs. The ZPCs were obtained by interpolating the data to zero electrophoretic mobility. Electrophoretic mobility measurements were also determined for all materials in the presence of 5 and 250 g B m⁻³. Boron solutions are monomeric at concentrations ≤ 0.025 M (Cotton and Wilkinson, 1980).

The constant capacitance model (Stumm et al., 1980) was used to describe B adsorption behavior on the adsorbents. The computer program FITEQL (Westall, 1982) was used to fit intrinsic B surface complexation constants to the experimental adsorption data using the model assumptions and procedure described in detail by Goldberg and Sposito (1984a). Surface reactions, intrinsic conditional equilibrium constants, mass balance, and charge balance were analogous to those for the application of the constant capacitance model to B adsorption on Al and Fe oxides (Goldberg and Glaubig, 1985), clay minerals (Goldberg and Glaubig, 1986a), and soil samples (Goldberg and Glaubig, 1986b). The surface site density was obtained from maximum B adsorption. Numerical values of the intrinsic protonation constant $K_+(int)$ and the intrinsic dissociation constant, $K_-(int)$ (Table 2) were obtained from a literature compilation of experimental values for Al and Fe oxides (Goldberg and Sposito, 1984a). The intrinsic protonation constants were initially fixed at $\log K_+(int) = 7.31$, $\log K_-(int) = -8.80$ for goethite, $\log K_+(int) = 7.38$, $\log K_-(int) = -9.09$ for gibbsite and the clays (Goldberg and Sposito, 1984a), and $\log K_+(int) = 7.35$ and $\log K_-(int) = -8.95$ for the soils (Goldberg and Sposito, 1984b). For montmorillonite and the soils it was subsequently necessary to optimize $\log K_+(int)$ and $\log K_-(int)$ together with the B surface complexation constant using the FITEQL program. The value of the capacitance density was fixed at $C = 1.06$ F m⁻². The constant capacitance model is very insensitive to this empirical parameter (Goldberg and Sposito, 1984a).

RESULTS AND DISCUSSION

Zero points of charge occurred at pH 8.5 for goethite, pH 9.6 for gibbsite, and pH 3.3 for kaolinite (Fig. 1). Electrophoretic mobilities of montmorillonite and the soils were negative even at pH 2. Thus the ZPCs could not be determined without dissolving these solids. Figure 1

Table 2. Surface complexation constants obtained from the FITEQL program.

Solid	$\log K_B(int)^\dagger$	$\log K_+(int)^\ddagger$	$\log K_-(int)^\S$
goethite	4.94	¶	¶
gibbsite	4.92	¶	¶
kaolinite	4.98	¶	¶
Bonsall soil	4.81	8.47	#
Arlington soil		no convergence	
montmorillonite		no convergence	

$$\dagger K_B(int) = \frac{[SH_2BO_3]}{[SOH][H_3BO_3]}$$

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

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

¶ Log $K_B(int)$ was optimized while holding $\log K_+(int)$ constant. $\log K_+(int) = 7.31$, $\log K_-(int) = -8.80$ for goethite. $\log K_+(int) = 7.38$, $\log K_-(int) = -9.09$ for gibbsite and kaolinite.

Indicates that this constant was insignificantly small [$\log K_-(int) < -31$].

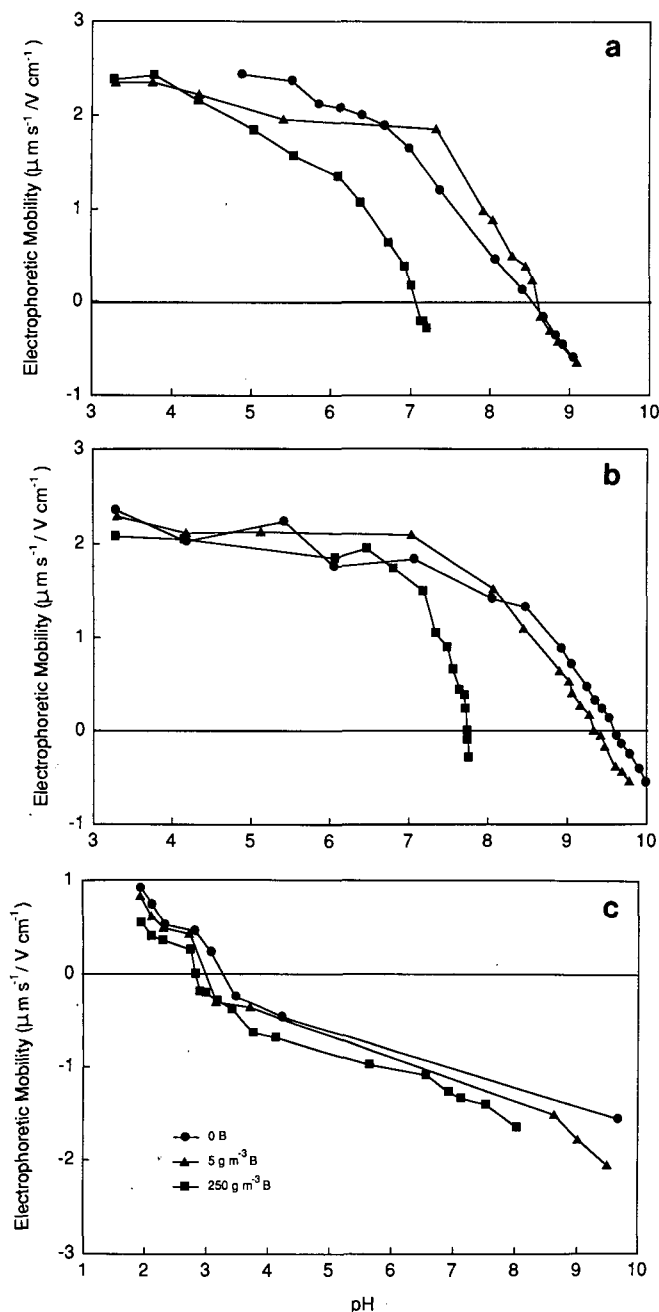


Fig. 1. Electrophoretic mobility as a function of pH and total B concentration in NaCl solution: (a) goethite, (b) gibbsite, and (c) kaolinite.

presents the shifts in ZPC obtained on adsorption of B onto goethite, gibbsite, and kaolinite. The ZPCs shifted to increasingly lower pH values with increasing B concentration. On addition of 250 g B m^{-3} , the ZPC shifted from pH 8.5 to 7.1 for goethite (Fig. 1a), from pH 9.6 to 7.7 for gibbsite (Fig. 1b), and from pH 3.3 to 2.8 for kaolinite (Fig. 1c). Shifting of the ZPC and reversal of the electrophoretic mobility with increasing ion concentration are characteristics of specific ion adsorption behavior (Hunter, 1981). The observed changes in ZPC are indicative of inner-sphere surface complexation of B on goethite, gibbsite, and kaolinite. Electrophoretic mobilities for montmorillonite and the soils were negative at

all pH values and for all B additions. Since ZPCs or reversals of electrophoretic mobility were not observed, no information on the mechanism of B adsorption can be inferred for these materials.

Figure 2 shows B adsorption as a function of pH and ionic strength for all materials investigated. Boron adsorption on all materials exhibited a parabolic adsorption envelope. Boron adsorption initially increased as the solution pH increased. An adsorption maximum was reached at an intermediate pH value and B adsorption subsequently declined as the pH continued to increase. The adsorption peaks were found at pH 6 to 8 for gibbsite (Fig. 2b), pH 7.5 to 8.5 for goethite (Fig. 2a), pH 8 to 8.5 for kaolinite (Fig. 2c), and pH 9 to 10 for montmorillonite (Fig. 2d), Bonsall soil (Fig. 2e), and Arlington soil (Fig. 2f). Scatter in the adsorption data at pH < 4 and > 9 is probably due to adsorbent dissolution.

The effect of ionic strength on B adsorption is also indicated in Fig. 2. Ionic strength was varied by two orders of magnitude, from 0.01 to 1.0 M NaCl. When the surface is positively charged at low pH, increases in ionic strength decrease the potential in the plane of adsorption and thus decrease B adsorption due to the effect of high concentrations of anions near the positively charged surface. When the surface is negatively charged at high pH, increases in ionic strength increase the potential in the plane of adsorption and thus increase B adsorption due to the effect of high concentrations of cations near the negatively charged surface (Barrow et al., 1980). Ionic strength dependence was best evaluated by observing the shift in magnitude of the B adsorption maximum. The materials exhibited diverse behavior in their ionic strength dependence. Goethite, gibbsite, and kaolinite showed relatively little ionic strength dependence of the B adsorption maxima, suggesting the formation of inner-sphere surface complexes. Inner-sphere adsorption mechanisms for these materials had already been indicated by the electrophoretic mobility measurements discussed above. Montmorillonite and soils, on the other hand, exhibited greater ionic strength dependence of the adsorption maxima suggesting the formation of outer-sphere surface complexes and outer-sphere adsorption mechanisms. Ionic strength dependence of the adsorption maxima was measured as the percentage increase in B adsorption maximum in 1.0 M NaCl solutions compared with 0.01 M NaCl solutions. Ionic strength dependence increased in the order: goethite (3%) < kaolinite (15%) < gibbsite (-30%) < montmorillonite (109%) \approx Arlington soil (116%) \approx Bonsall soil (129%).

The constant capacitance model was used to describe B adsorption on the materials studied. The model assumes an inner-sphere adsorption mechanism for the B surface complex. The model uses the constant ionic medium reference state and thus does not consider the ionic strength of the background electrolyte. The constant capacitance model was able to describe B adsorption on goethite, gibbsite, kaolinite, and the kaolinitic Bonsall soil. The model was unable to describe B adsorption on the montmorillonite and the montmorillonitic Arlington soil. Table 2 provides values of the surface complexation constants obtained using the FITEQL computer program (Westall, 1982). Boron adsorption on goethite, gibbsite, and kaolinite was described with the model when only the B surface complexation constant, $K_B(\text{int})$, was optim-

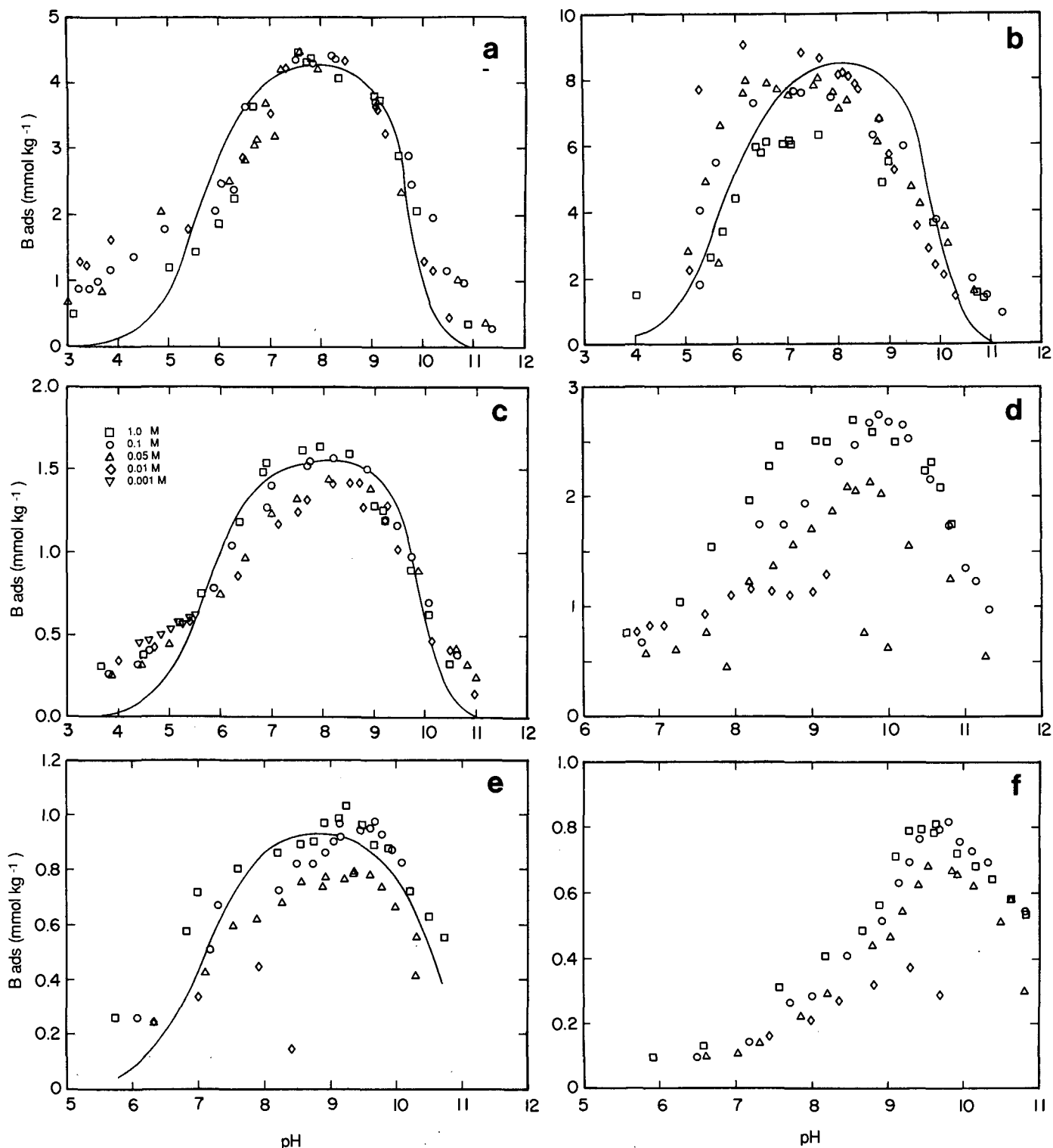


Fig. 2. Boron adsorption as a function of pH and ionic strength in NaCl solution: (a) goethite, (b) gibbsite, (c) kaolinite, (d) montmorillonite, (e) kaolinitic Bonsall soil, and (f) montmorillonitic Arlington soil.

ized (see Fig. 2a, 2b, and 2c). Simultaneous optimization of the protonation-dissociation constants and the B surface complexation constant was required to describe B adsorption on the kaolinitic Bonsall soil (see Fig. 2e).

The model was unable to describe B adsorption on the montmorillonite and the montmorillonitic Arlington soil since convergence of the FITEQL program could not be

obtained (see Table 2). The fact that no convergence was obtained for these materials would suggest that the inner-sphere adsorption mechanism assumed by the constant capacitance model is inappropriate. Thus the lack of model convergence indirectly suggests an outer-sphere adsorption mechanism for montmorillonite and montmorillonitic soil. The possibility that the lack of convergence is

due to computational difficulties cannot be ruled out. The good fit of the model to B adsorption on goethite, gibbsite, kaolinite, and kaolinitic soil suggests that inner-sphere surface complexation is the appropriate adsorption mechanism for these materials. The numerical values of the B surface complexation constants for these materials were very similar in magnitude (see Table 2), suggesting a common adsorption mechanism.

Based on our ionic strength dependence and ZPC results, B forms inner-sphere surface complexes on the Fe oxide goethite and the Al oxide gibbsite. Specific adsorption via ligand exchange had been suggested previously as the B adsorption mechanism for oxides (Sims and Bingham, 1968; McPhail et al., 1972). Shifts in ZPC following B adsorption had also been observed previously for Al oxide (Fricke and Leonhardt, 1950; Alwitt, 1972; Beyrouy et al., 1984) and Fe oxide (Blesa et al., 1984). Previous research had suggested specific adsorption via ligand exchange as the mechanism of B adsorption on clay minerals (Keren and Talpaz, 1984). Our ionic strength results indicate an inner-sphere adsorption mechanism for kaolinite clay and an outer-sphere adsorption mechanism for montmorillonite clay. An inner-sphere adsorption mechanism for B on kaolinite is also indicated by our ZPC data. Kaolinite clay has a greater proportion of pH-dependent edge sites than does montmorillonite clay, where the charge is mainly permanent and located on the basal planes. The predominant basal charge on montmorillonite clay may spill over to affect the edges (Secor and Radke, 1985,) perhaps allowing only the formation of weak outer-sphere surface complexes. Direct spectroscopic experimental evidence is necessary to verify the B adsorption mechanisms suggested by our indirect experimental results.

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