

CHEMICAL REACTION KINETICS AND BONDING MECHANISMS OF BORON ADSORPTION AND DESORPTION ON ALUMINA

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Abstract

Boron (B) is a plant nutrient which is essential for adequate plant growth, yet, the range between B deficiency levels and toxicity levels is rather narrow. It is generally accepted that B adsorption reactions with soil components, particularly metal oxides, most often regulate the amount of B in the soil solution available for plant uptake. The reaction mechanisms of B adsorption on oxide soil components have not been clearly identified or fully characterized.

Pressure-jump relaxation kinetic experiments were conducted to measure the rates and determine the reaction mechanism for B adsorption on an alumina γ - Al_2O_3 surface from boric acid (BA)/borate (BT) solutions. Relaxation times τ were measured from pH 7.0 to 9.7 in alumina suspensions with 0.012 mol L^{-1} total B. A plot of τ^{-1} vs. BT plus surface site concentration yielded an adsorption rate constant (k_f^{int}) of $3.3 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ and a desorption rate constant (k_r^{int}) of $1.8 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$. The ratio $k_f^{\text{int}}/k_r^{\text{int}}$ yielded an equilibrium constant ($\log K_{\text{KIN}}^{\text{int}}$) of 8.26, in agreement with the intrinsic equilibrium constant for $\text{B}(\text{OH})_4^-$ adsorption ($\log K_{\text{BIS}}^{\text{int}} = 7.69$) obtained from adsorption isotherms.

Four surface complexation models were tested for their ability to model equilibrium and kinetic data simultaneously: the constant capacitance model, the diffuse layer model, a Stern model variant, and the triple layer model (TLM). Modeling of data from both kinetic and static experiments was only successful using the TLM under the assumption that both BA and BT were adsorbed via ligand exchange on neutral alumina surface sites. Water is the leaving ligand in both exchange reactions. The TLM indicated that BT is the predominant adsorbed species throughout the pH range 7.0 to 10.8.

Horizontal attenuated total reflectance Fourier transform infrared (HATR-FTIR) spectroscopy experiments were conducted to test the kinetic model conclusions. Spectra of B/alumina suspensions indicated that B does indeed undergo ligand exchange reactions with surface hydroxyl groups on the oxide surface. However, the HATR-FTIR spectra indicated that three-coordinate BA is the predominant form of adsorbed B at pH 4.3.