

CATION AND ANION ADSORPTION BEHAVIOR ON OXIDE SURFACES

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Abstract

The chemical and physical behavior of solid particles in an aqueous medium are affected by the interactions present at the solid-aqueous interface. Chemical reactions (e.g., cation and anion adsorption) and physical observations (e.g., electrokinetics) elucidate the nature of the interface; however, these experiments generally result in contradicting data. This research found that the inconsistencies are due to an overlapping of a pH-dependent solubility phenomena on the solid-aqueous phase interactions. This is particularly significant in potentiometric titration analyses that measure the proton adsorption isotherms with respect to pH.

This dissertation critically challenges current theories on the pH-dependent behavior of oxides with respect to cation exchange capacity, anion exchange capacity, potential determining ions, inert electrolytes, electrokinetics, and surface charge models. Methodologies and models commonly used in solid-aqueous interface research are critically reviewed based on Al and Si oxide studies, and a modification of the potentiometric titration procedure was developed, called the backtitration technique. The backtitration technique results in accurate proton adsorption isotherms due to the adjustments made for the variable solubility of the solid phase. This in turn allows development of proton adsorption models with an entirely new set of data. Specifically, an Al oxide is easily modeled with pH and salt-dependent reactions competing with salt-dependent reactions. The maximum number of sites is readily determined from the data without any further mathematical manipulations. Furthermore, the proton isotherms are stoichiometrically related to the cation and anion isotherm behavior. This allows predictions on cation and anion adsorption behavior based on the proton adsorption isotherm model.

It is strongly suggested that the Boltzmann distribution term in models using intrinsic equilibrium constants is merely tracking the solubility behavior of the solid phase. It is hypothesized that the oxide surface is neutral at all times; the charged behavior observed in electrokinetic studies is induced by the applied electric field that shears the aqueous counterions in one direction and the oxide surface in the opposite direction. In the absence of an applied electric field the

oxide particles are neutral, and the only surface reactions present are ion exchange reactions.