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# Surface complexation modeling of the sorption of 2-, 3-, and 4-aminopyridine by montmorillonite

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## Abstract

The sorption of 2-, 3-, and 4-aminopyridine on K-saturated Wyoming (SWy-K) and Texas (STx-K) and Ca-enriched Texas (STx-Ca) montmorillonite was measured at 25 °C with 10 mM KNO<sub>3</sub> or 3.3 mM Ca(NO<sub>3</sub>)<sub>2</sub> as the background electrolyte. The aminopyridines adsorbed to montmorillonite at low pH, but not at high pH. Extended constant capacitance surface complexation models (ECCMs) and attenuated total reflectance-FTIR data indicate that aminopyridines sorb to the silica-like faces by cation exchange, forming outer-sphere complexes between aminopyridinium ions and permanent negatively charged surface sites (X<sup>-</sup>). X-ray diffraction data and sorption kinetics suggest that sorption occurs not only at external X<sup>-</sup> sites but also at those in the interlayer spaces. Differences in the sorption behaviors of 2-, 3-, and 4-aminopyridine result from differences in their p*K<sub>a</sub>*s. The extent of sorption of aminopyridines by the montmorillonite samples (SWy-K > STx-K > STx-Ca) results from the higher cation-exchange capacity of SWy-K, and from the fact that Ca<sup>2+</sup> is much more effective than K<sup>+</sup> in competing with protonated aminopyridines for the X<sup>-</sup> sites.

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## 1. Introduction

Compounds containing pyridine rings are widely distributed in nature and have several important applications, including analytical reagents, drugs, dyes, pesticides, and alkaloids. Aminopyridines have two nitrogen atoms, each of which has a lone pair of electrons. The ring nitrogen atom is known to be more basic than the amino nitrogen [1] and consequently protonation of aminopyridine is expected to take place on the ring nitrogen atom. It has been suggested [2,3] that both 2- and 3-aminopyridine sorb to clay minerals by coordinating to Lewis acid sites or exchangeable cations, with the ring nitrogen atom involved rather than amino nitrogen. On the other hand, Busca et al. [4] proposed that 2-aminopyridine was held to iron oxide by multiple bonding

through both the amino group and the ring nitrogen, while 3- and 4-aminopyridine were bound only through the ring N. They compared the IR spectra of adsorbed 2-aminopyridine with that for adsorbed aniline and found similar changes in bands corresponding to NH stretching and deformation frequencies supporting the idea that the amino nitrogen of 2-aminopyridine plays an important part in the binding to iron oxide layers.

Montmorillonite crystals have two different regions which have been implicated in sorption [5,6]. The external regions (faces plus edges) carry both permanent negatively charged sites and sites with pH-dependent charges. The interlayer region has permanent negatively charged sites resulting from isomorphous substitution, with the surface charge compensated by hydrated interlayer cations.

In principle aminopyridines can sorb either to external active sites or in the interlayer space of montmorillonite. Intercalation of cations or organic species into the interlayer

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