

# Cosorption of Zn(II) and 2-, 3-, or 4-aminopyridine by montmorillonite

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## Abstract

Data from acid–base titrations at 25 °C of Zn(NO<sub>3</sub>)<sub>2</sub> and 2-, 3-, or 4-aminopyridine in 10 mM KNO<sub>3</sub> as background electrolyte suggested that soluble complexes ZnL<sup>2+</sup> and Zn(OH)L<sup>+</sup> form, where L represents aminopyridine. Zinc–hydroxyaminopyridine complexes have not been reported previously. The cosorption of Zn(II) with each of the aminopyridines to K-saturated Wyoming (SWy-K) and Texas (STx-K), and Ca-enriched Texas (STx-Ca) montmorillonites 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 background electrolyte. Comparison with previous data for sorption of Zn(II) and the aminopyridines separately and surface complexation modeling of the cosorption data showed that under acid conditions competition between Zn<sup>2+</sup> and aminopyridinium ions for the permanent negatively charged sites of montmorillonite results in suppression of the uptake of each sorbate by the other, but only when a large excess of the competing sorbate is present. Under alkaline conditions the sorption of Zn(II) was not affected by the presence of even a large excess of aminopyridine, but the sorption of 4-aminopyridine in particular was slightly enhanced when a large excess of Zn(II) was present. The enhancement was attributed to the formation of metal-bridged ternary surface complexes at the variable-charge sites on the edges of the montmorillonite crystals.

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## 1. Introduction

This paper is concerned with the simultaneous sorption of basic aromatic molecules and a transition metal to the clay mineral montmorillonite, which is a common component of soils, and also finds use as a sorbent for organic and inorganic materials.

The aminopyridines are aromatic compounds that carry both ring nitrogens and amino nitrogens. They can serve simple models for a range of pyridine derivatives found in nature and industry as analytical reagents, drugs, dyes, pesticides, alkaloids, etc. In a previous paper [1] we showed that 2-, 3-, and 4-aminopyridine bind under acid conditions by ion exchange to the permanent negatively charged sites (X<sup>-</sup>) of the silica-like faces of montmorillonite, both on

the external surfaces and in the interlayer spaces, but do not appear to interact with the pH-dependent surface hydroxyl groups (SOH) on the edges of montmorillonite crystals.

By contrast, Zn(II) sorbs under acid conditions to the permanent negatively charged sites of montmorillonite by ion exchange, but under alkaline conditions it forms inner-sphere complexes with the variable-charge sites at the crystal edges [2].

Because the aminopyridines and Zn(II) bind to the same montmorillonite sites at low pH we can expect that each might suppress the sorption of the other, but their behavior at higher pH will depend on the extent to which the sorbates form soluble complexes or ternary surface complexes. It has been reported for a number of metal–ligand pairs that complex formation can lead to either enhancement [3,4] or suppression [3,5–7] of the sorption of metal ions by clay minerals.

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