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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_3 or 3.3 mM $Ca(NO_3)_2$ 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^-). X-ray diffraction data and sorption kinetics suggest that sorption occurs not only at external X^- 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 pK_as. 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^{2+} is much more effective than K^+ in competing with protonated aminopyridines for the X^- sites.

Keywords: Montmorillonite; Kaolin; Kaolinite; 2-Aminopyridine; 3-Aminopyridine; 4-Aminopyridine; Extended constant capacitance model; ATR-FTIR; XRD

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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space of 2:1 clay minerals is known to change the basal spacing of the clays [6–12]. Thus determination of such changes by XRD can provide qualitative information on the type of the interaction between the organic molecule and the montmorillonite. For instance, by taking measurements of basal spacing of montmorillonite Yermiyahu et al. [13] concluded that congo red, a cationic dye, was primarily located in the interlayer region. Other studies suggest that sorption of organic molecules to montmorillonite can decrease [14,15] or increase [2,3,8,12,16] the basal spacing of the clay, or leave it unchanged [7].

Previous investigations of the interaction between aminopyridines and montmorillonite [2–4] have been limited primarily to infrared (IR) spectroscopic and X-ray diffraction (XRD) studies. In this paper we combine sorption, IR spectroscopic, and XRD data with surface complexation modeling to deduce the mode of interaction between 2-, 3-, and 4-aminopyridine and montmorillonite. Interpretation of some of the data is assisted by comparison with the sorption of aminopyridines to kaolinite, a nonexpanding clay.

2. Materials and methods

2.1. Clays

Clay samples were from the Clay Minerals Society Source Clays Repository: Na-montmorillonite (Wyoming) SWy-2 from Cook County, Wyoming, Ca-montmorillonite (Texas) STx-1 from Gonzales, Texas, and kaolin KGa-1b from Washington, Georgia. STx-1 has Ca as the principal exchange cation; as received it is called STx-Ca in this study. SWy-2 was treated with K^+ prior to use: 250 g of SWy-2 was stirred for 36 h in 2 L of 200 mM aqueous KNO_3. The suspension was then dialyzed against distilled water, with the water replaced several times each day until the concentration of K^+ (measured by atomic absorption spectroscopy) was less than 0.1 M. Finally the suspension was freeze-dried to produce the sample called SWy-K in this study. The same method was used to prepare K-saturated Texas montmorillonite (called STx-K) and K-saturated kaolinite (KGa-K). The surface areas and cation exchange capacities [17] were 31.8 $m^2\,g^{-1}$ and 76.4 $cmol\,kg^{-1}$ for SWy-K, 83.9 $m^2\,g^{-1}$ and 84.4 $cmol\,kg^{-1}$ for STx-K and STx-Ca, and 10.05 $m^2\,g^{-1}$ and 2.0 $cmol\,kg^{-1}$ for KGa-K.

2.2. Reagents

Water was Milli-Q reagent grade (Millipore, Bedford, MA).

Stock solutions of 2-, 3-, and 4-aminopyridine (100 mM) were prepared by dissolving pure solid (Sigma–Aldrich, Australia 99+% for 2-aminopyridine, 99% for 3-aminopyridine, 98% for 4-aminopyridine) in water. Fresh stock solutions were prepared at least once per month.

HNO_3 solution (0.100 M) was prepared from Convol HNO_3 (BDH Laboratory Supplies, England), and 0.100 M KOH from Convol KOH (BDH Laboratory Supplies, England). All other reagents were of analytical reagent grade.

2.3. Experimental methods

2.3.1. X-ray diffraction

Suspensions of montmorillonite (300 $m^2\,L^{-1}$) in aqueous 2-aminopyridine (0–30 mM) were equilibrated at selected pHs for 24 h. Each suspension was then centrifuged, and the paste oven-dried at 60 °C for 20–30 h. A slurry prepared by grinding a small amount of the dried paste with isopropyl alcohol was placed onto a quartz single crystal and left for about 1 h until the isopropyl alcohol had evaporated, leaving a well-dried sample that was analyzed with a Phillips PW 1710 X-ray diffractometer.

2.3.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

7.50 g of SWy-K was added to 50 ml water and stirred overnight under nitrogen at 25 °C. The pH of the suspension was then adjusted to about 10 with KOH, and a sufficient amount of the selected aminopyridine added to the suspension to give an initial concentration of 10 mM. After a further equilibration time of at least 3 h a 5-ml sample of the suspension was taken and centrifuged at 7000*g* for 10 min. FTIR spectra of the cell, supernatant, and paste were taken separately as described below. The pH of the suspension was then adjusted down to a new value, the system equilibrated for at least 3 h, a 5 ml sample taken, and the process repeated.

A Bruker Equinox 55 FTIR spectrometer equipped with a deuterated triglycine sulfate, DTGS, detector was used to collect the IR spectra. Samples were analyzed by use of a Dicomp/ZnSe DurasamplIR 9-bounce ATR accessory (SensIR Technologies). For each sample 500 scans were collected from the cell, supernatant, and paste over the wavelength range from 700 to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1}. Approximately 1 mm thickness of paste was applied uniformly to the ATR crystal before measurement of the paste spectrum. A polymethyl methacrylate lens with an *O*-ring gasket was pressed over each sample to prevent drying or CO_2 absorption during measurements. Supernatant spectra were collected and subtracted from the paste spectra to remove any contribution from ligands remaining in solution.

Spectra (500 scans) were also taken of montmorillonite suspensions at several pHs. The montmorillonite spectrum with pH closest to that of the aminopyridine/montmorillonite paste was subtracted in order to obtain the spectrum of the sorbed aminopyridine species. Care was taken to remove the spectral contribution due to interlayer water as completely as possible. ATR-FTIR spectra of 10 mM solutions of each aminopyridine were also collected at pH values between 3.5 and 10.