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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 $Zn(NO_3)_2$ and 2-, 3-, or 4-aminopyridine in 10 mM KNO_3 as background electrolyte suggested that soluble complexes ZnL^{2+} and $Zn(OH)L^+$ 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_3 or 3.3 mM $Ca(NO_3)_2$ 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^{2+} 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.

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^-) 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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Previous reports [3,8,9] suggest that the sorption of transition metals (Cu(II), Zn(II), Cd(II)) to montmorillonite can be suppressed by competition for surface sites by ligands, but the sorption data were modeled for only one of these [3]. In this study we have collected a range of data on the simultaneous sorption of Zn(II) and 2-, 3-, and 4-aminopyridine to three montmorillonites, and in modeling the results we have built on the models developed previously [1,2] for the sorption of the separate components. We conclude that although Zn(II)–aminopyridine complexes are formed in solution, and under alkaline conditions ternary complexes form at the surface of montmorillonite, these reactions do not contribute greatly to the sorption behavior. The most important effect is competition by the two sorbates for the permanent negatively charged sites of montmorillonite.

2. Materials and methods

2.1. Montmorillonite

Montmorillonite samples were the same as those used previously [1,2]. Na-montmorillonite (Wyoming) SWy-2 from Cook County, Wyoming, USA, and Ca-montmorillonite (Texas) STx-1 from Gonzales, Texas, USA were from the Clay Minerals Society [10]. Ca-montmorillonite (STx-1) was used as received and is called STx-Ca in this study. The other clay samples were treated with K^+ prior to use. A 250-g portion of SWy-2 was stirred for 36 h in 2 L of 200 mM KNO_3 solution. 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 (labeled STx-K). The surface areas and cation exchange capacities [10] were 31.80 $m^2 g^{-1}$ and 76.40 $cmol kg^{-1}$ for SWy-K, and 83.9 $m^2 g^{-1}$ and 84.4 $cmol kg^{-1}$ for STx-K and STx-Ca.

2.2. Reagents

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

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 4-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. Assays

Aminopyridines were measured by high performance liquid chromatography (HPLC) (Shimadzu liquid chromatograph, with an SPD-M10AVP Shimadzu diode array detector). A 150 × 4.6-mm polar Phenomenex HPLC column and guard column (Synergy 4 μ Polar-RP80A) was used, with a mobile phase of 3:2 (v/v) acetonitrile:water to which 0.01% NH_4OH was added, giving a pH of about 8.0. The wavelengths used for the analysis were 230 nm for 2- and 3-aminopyridine and 280 nm for 4-aminopyridine. Peak integration was carried out using LC-10 Version 1.60 software. Total zinc was measured by flame atomic absorption spectrophotometry (Varian AA10).

2.3.2. Sorption experiments and potentiometric titrations

Sorption experiments and titrations were conducted at a constant temperature of 25 °C in thermostated reaction vessels. Suspensions were continuously purged with oxygen-free humidified nitrogen to eliminate carbon dioxide. The background electrolyte was 10 mM KNO_3 for SWy-K and STx-K and 3.3 mM $Ca(NO_3)_2$ for STx-Ca. pH was measured with an Orion Ross Sure-Flow pH electrode, which was calibrated with NBS buffers at pH 4.01 and 6.86. In experiments with montmorillonite, suspensions with surface area 100 $m^2 L^{-1}$ were first preequilibrated overnight at the natural pH, after which aminopyridine and $Zn(NO_3)_2$ were added at the required concentrations, and the pH was adjusted to the starting value.

Acid–base titrations were conducted on solutions or suspensions containing one or more of montmorillonite, aminopyridine, and Zn(II), with 10 mM KNO_3 as background electrolyte. Following preequilibration of the montmorillonite (if applicable), aminopyridine and/or Zn(II) were added as required, and the pH was adjusted to approximately 10 by the addition of 100 mM KOH (Metrohm Dosimat 665), after which the system was titrated back to about pH 4 with 100 mM HNO_3, using an automated titration system. Successive additions of HNO_3 were made only after the pH drift was less than 0.002 min^{-1}. Titrations of suspensions typically took 2 d to complete.

Sorption edge experiments measured the effect of aminopyridine on the sorption of Zn(II), or vice versa, over a range of pH. The pH of a preequilibrated montmorillonite suspension was increased to 10 by the addition of KOH, and after 30 min aminopyridine and/or Zn(II) was added to the desired total concentrations. After a further 30 min a 4-ml sample was transferred into a polypropylene centrifuge tube, which was flushed with N_2 and then capped. The pH of the suspension was decreased in steps of about 0.5, and further 4 ml samples taken after 30 min equilibration at each pH. All the samples were then tumbled end on end for 2 d. The final pH of each sample was measured before it was centrifuged, and the supernatant solution assayed for aminopyridine or Zn as required.