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Residence times for protons bound to three oxygen sites in the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polyoxocation

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Abstract

Although, the kinetic reactivity of a mineral surface is determined, in part, by the rates of exchange of surface-bound oxygens and protons with bulk solution, there are no elementary rate data for minerals. However, such kinetic measurements can be made on dissolved polynuclear clusters, and here we report lifetimes for protons bound to three oxygen sites on the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (**Al$_{13}$**) molecule, which is a model for aluminum-hydroxide solids in water. Proton lifetimes were measured using ^1H NMR at pH ~ 5 in both aqueous and mixed solvents. The ^1H NMR peak for protons on bound waters (η-H_2O) lies near 8 ppm in a 2.5:1 mixture of H_2O/acetone-d_6 and broadens over the temperature range −20 to −5 °C. Extrapolated to 298 K, the lifetime of a proton on a η-H_2O is $\tau^{298} \sim 0.0002$ s, which is surprisingly close to the lifetime of an oxygen in the η-H_2O (~0.0009 s), but in the same general range as lifetimes for protons on fully protonated monomer ions of trivalent metals (e.g., $Al(H_2O)_6^{3+}$). The lifetime is reduced somewhat by acid addition, indicating that there is a contribution from the partly deprotonated **Al$_{13}$** molecule in addition to the fully protonated **Al$_{13}$** at self-buffered pH conditions. Proton lifetimes on the two distinct sets of hydroxyls bridging two Al(III) (μ_2-OH) differ substantially and are much shorter than the lifetime of an oxygen at these sites. The average lifetimes for hydroxyl protons were measured in a 2:1 mixture of H_2O/dmso-d_6 over the temperature range 3.7–95.2 °C. The lifetime of a hydrogen on one of the μ_2-OH was also measured in D_2O. The τ^{298} values are ~0.013 and ~0.2 s in the H_2O/dmso-d_6 solution and the τ^{298} value for the μ_2-OH detectable in D_2O is $\tau^{298} \sim 0.013$ s. The ^1H NMR peak for the more reactive μ_2-OH broadens slightly with acid addition, indicating a contribution from an exchange pathway that involves a proton or hydronium ion. These data indicate that surface protons on minerals will equilibrate with near-surface waters on the diffusional time scale.

1. Introduction

Geochemists are coming to rely heavily on computer methods of predicting reaction pathways in the Earth because so many of the key environments are difficult to sample. Particularly important are the reactions between minerals and aqueous solutions, as these reactions control the overall solution chemistry and the rates of mineral transformations. However, our ability to simulate such reactions is limited by a lack of experimental data at a suitable scale. Data are needed on *elementary* reactions, meaning reactions that proceed in solution as written on the molecular scale.

Work on aluminum-hydroxide molecules such as the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (**Al$_{13}$**) polyoxocation can be helpful in constraining the dynamic nature of functional groups at mineral surfaces. This molecule (Fig. 1) is among the best characterized aqueous oligomers, as the reactivities of structural oxygens (Phillips et al., 2000; Casey et al., 2000), the acid–base chemistry (Furrer et al., 1992), the dissolution rates (Amirbahman et al., 2000; Furrer et al., 1999) and pathways for oxygen-isotope exchanges (Rustad et al., 2004) are all known. From this work, we know that the 12 equivalent bound water molecules (η-H_2O) exchange with bulk solution in milliseconds when the

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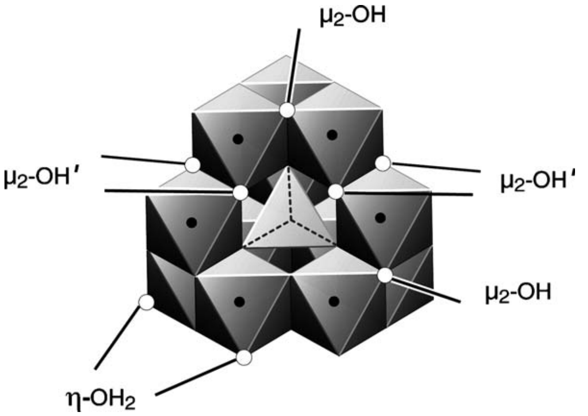

Fig. 1. Polyhedral representation of the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ ion (**Al₁₃**), which has the ε-Keggin structure and three sets of structurally distinct protons on the fully protonated molecule.

molecule is fully protonated (pH < 6.5). The two structurally distinct sets of hydroxyl bridges within a single **Al₁₃** molecule (μ₂-OH, μ₂-OH′) exchange at rates that differ by a factor of $\sim 10^3$. At 298 K exchange of oxygen isotopes with bulk water occurs at characteristic times of $\tau^{298} \sim 1$ min and $\tau^{298} \sim 17$ h, assigned as $\mu_2\text{-OH}^{fast}$ and $\mu_2\text{-OH}^{slow}$, respectively, although assignment to structural sites remains uncertain. Metal substitution into the core tetrahedral site causes enormous changes in reactivities of these hydroxyl bridges, but not the bound waters, which are virtually unchanged (Casey and Phillips, 2001; Lee et al., 2002a).

Timescales for dynamic conversion of functional groups determine how we should view their structures and even their stoichiometries. Consider, as an example, the $AlOH^{2+}(aq)$ ion, which contains four bound water molecules in the inner-coordination sphere of the Al(III) and a single bound hydroxyl (see Swaddle et al., 2005). The bound hydroxyl interconverts back-and-forth to a water molecule by protonation/deprotonation $\sim 10^5$ times a second (Fong and Grunwald, 1969). Thus, on the timescale of a reaction that takes minutes to hours (e.g., polymerization and dissolution), it might be better to view the $AlOH^{2+}(aq)$ ion as having five bound ligands, each one having the 4/5 the character of a bound water and 1/5 the character of a bound hydroxyl. The bound ligands are not static.

In this paper, we extend the earlier work of Akitt and Elders (1988) and Akitt (1989) and report rates of proton exchange from each of the different oxygen sites in the **Al₁₃** molecule (Fig. 1). Several authors have argued that molecules like the **Al₁₃** are useful for understanding some mineral surfaces, such as aluminum-hydroxide solids and clays (see Casey and Swaddle, 2003) because the **Al₁₃** is structurally similar to aluminum-hydroxide solids (Bradley et al., 1993; Phillips et al., 2000). It polymerizes to form a gel that ages to bayerite (see Bradley et al., 1993; Furrer et al., 2002) and the proton charge density of **Al₁₃** (0.32 C/m²; +7 charge over a sphere with radius of 0.53 nm) is comparable to that of aluminum-hydroxide solids (0.16–0.48 C/m²; Hiemstra et al., 1999). Thus, understanding proton residence times on the **Al₁₃** should be useful in understanding proton residence times at the surfaces of more complex and heterogeneous materials, such as aluminous clays, which should nonetheless expose structurally similar stoichiometries to the aqueous solution.

2. Materials and methods

2.1. Starting material

Synthesis of $Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}(SeO_4)_4](H_2O)_x$ (**Al₁₃**) crystals was accomplished using the method of Furrer et al. (1992). For the variable-temperature experiments, 23 mg of **Al₁₃** selenate crystals were ground with excess $BaCl_2$ (~13 mg) and extracted with 500 μL of distilled water. This $BaCl_2$ solution metathetically dissolves the salt, precipitates the selenate, and releases the oligomer cation intact to solution. The resulting solution containing the **Al₁₃** cation was filtered through a 0.22 μm membrane filter into a 5-mm (o.d.) NMR tube. For measurements at low temperature, 200 μL of acetone-d_6 (dimethylketone: C_2D_6O) was added to the filtrate in order to depress the freezing point of the solution to as low as −20 °C. However, further additions of acetone-d_6 significantly decreases the solubility of **Al₁₃** in solution, which makes experiments at temperatures below −20 °C difficult. For the kinetic experiments performed above room temperature, a 2:1 mixture of water and dmso-d_6 (dimethylsulfoxide: C_2D_6SO) was used to raise the boiling point of a neat H_2O solution.

The pK_a of the **Al₁₃** molecule is near $6 < pK_a < 6.5$ (Furrer et al., 1992; Lee et al., 2002b) so extraction of this amount of the salt into water yields a solution near pH ~ 5 because a small fraction of waters bound to the **Al₁₃** deprotonate. To measure pH, glass electrodes were calibrated in the appropriate solvent on the concentration scale and pH values were measured at 298 K. For the experiments in which pH was varied, aliquots of HCl (0.1 M HCl) diluted with an appropriate amount of acetone-d_6 or dmso-d_6 were added to an amount of stock solution as the electrode response was measured.

2.2. ^1H NMR spectroscopy

All NMR measurements were conducted with a Bruker Avance NMR spectrometer based on an 11.7 T magnet located at the University of California Davis, NMR facility. ^1H NMR spectra were recorded at 500.1 MHz using a low-temperature 5-mm probe in locked mode (acetone-d_6 or dmso-d_6). A pulse width of 4 μs corresponding to a 33° tip angle ($\pi \approx 22$ μs based on the bulk water signal) was used with a relaxation delay of 1 s. Two hundred scans were recorded over a sweep-width of 7.5 kHz. Sample temperature was determined with a copper–constantan thermocouple placed inside a separate NMR tube but with similar geometry and with the same solvent mixture as