

Structure and dynamics of citrate ions in Mg/Al layered double hydroxide: ^{13}C NMR and molecular dynamics simulation studies

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Chemical interaction between naturally occurring organic species and minerals or dissolved cations is often dominated by carboxyl sites, but the molecular scale behavior is poorly understood. Here we describe a combined experimental and molecular modeling study designed to understand the structure and dynamics of these interactions taking the citrate-hydrotalcite system as an example. Hydrotalcite [here, $(\text{Mg}_3\text{Al})(\text{OH})_8\text{A}^- \cdot n\text{H}_2\text{O}$] is a layered double hydroxide (LDH) with positive structural charge with which citrate interacts via Coulombic attraction and H-bonding.

The citrate-hydrotalcite was prepared by ion exchange with the corresponding nitrate-hydrotalcite from aqueous solution at pH = 11.5 and 65°C. The water content was varied by controlling the relative humidity (R.H.) conditions. Basal spacings from powder XRD, compositional analysis and TGA/DTA confirm complete citrate for nitrate exchange. Compositional analysis indicates that citrate is present as the -3 anion, consistent with the solution used for the ion exchange. ^{13}C CP-MAS NMR spectra show well-resolved peaks for the backbone C-sites in citrate, except that signal for the central carboxylic C-site overlaps those of the terminal ones. There is no evidence for cross-linking of the citrate with the Mg/Al LDH. The decreasing NMR peak widths and increasing basal spacing with increasing R.H. imply increasing dynamical averaging of the citrate sites in a progressively more water-rich interlayer.

A series of short NPT-molecular dynamics (NPT-MD) runs, carried out to determine suitable lattice parameters for the simulated system, were followed by long production runs in the microcanonical (NVE) ensemble. The MD results offer fresh insight into the structure, nature of the H-bonding and conformations of interlayer citrate and are compared with those of sodium citrate in bulk solution.

Colloid formation and cesium mobility in Hanford sediment columns leached with simulated tank waste

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We studied Cs mobility and the alteration and transformation of minerals in Hanford sediments under conditions similar to a Hanford tank leak. Our objectives were to investigate (1) the nature and location of feldspathoids and zeolite precipitated in the sediments, and (2) the extent to which Cs was retained by the sediment matrix.

Hanford sediments were packed into 10-cm long columns and leached with simulated tank waste consisting of 1.4 m NaOH, 0.125 m NaAlO₄, 3.7 m NaNO₃, and 1.3E10⁻⁴ m Cs at 22 and 50°C. We monitored outflow solution composition with time for 25 days, and the columns were then segmented into four 2.5 cm layers. The colloidal fractions in these segments were characterized in terms of mineralogy, particle morphology, Cs content, and short-range Al and Si structure.

We found that the nature of the minerals formed in the column depended on the experimental conditions. Zeolite A and chabazite precipitated at 22°C, whereas cancrinite and sodalite formed at 50°C. Cesium retention in the column was lowered in the high ionic strength solution due to competition from Na for the exchange sites. Increasing the temperature lowered Cs retention by altering the distribution and number of sorption site, reducing the Cs for Na selectivity, and through formation of cancrinite and sodalite.