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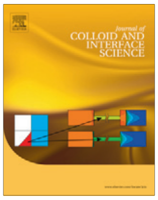

Surface complexation reactions of inorganic anions on hydrotalcite-like compounds

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ABSTRACT

Complexation reactions of environmentally important inorganic anions such as nitrate, chloride, sulfate, arsenate, and phosphate on the surface of hydrotalcite-like compounds (HT) were investigated to understand the role of HT in the immobilization of hazardous anions in an alkaline environment. The effects of surface complexation reactions on the solid state properties of HT were also evaluated to understand their stability. Synthetic HT was used for the adsorption and post-adsorption experiments. The obtained adsorption isotherms showed that the order of selectivity of HT for anions was $NO_3 < Cl < SO_4 \ll AsO_4 < PO_4$. To distinguish the adsorption mechanisms (inner-sphere complexes or outer-sphere complexes) of these anions, zeta potential measurements and infrared absorption spectroscopic analysis were performed. The results indicated that NO_3 and Cl were adsorbed as diffuse ions on the outer surfaces of the HT, while SO_4 formed outer-sphere complexes with a strong electrostatic interaction. Moreover, AsO_4 and PO_4 formed inner-sphere complexes via a ligand substitution reaction on the HT surfaces. And it was suggested that oxyanions with low ionic potential, such as AsO_4 and PO_4, had a tendency to form inner-sphere complexes with the HT surfaces. The formation of inner-sphere complexes shifted the isoelectric point and the surface charge of the HT. Furthermore, the solubility of the HT was reduced by the inner-sphere complexes with PO_4 and AsO_4. It was revealed that the formation of inner-sphere complexes on the HT surfaces contributed to the stabilization of the HT, as well as a decrease in the mobility of these anions.

1. Introduction

Hydrotalcite-like compounds (HT), which are also referred to as layered double hydroxides (LDHs), are well known as anionic clays due to their anion-exchange properties [1]. The general formula for HT is:

$$[Mg^{2+}_{1-x}Al^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$$

where x is equal to the Al/(Mg + Al) molar fraction and ranges from 0.17 to 0.33, and A^{n-} is the interlayer anion with a valence of n [2,3]. The brucite-like trioctahedral layers have a positive charge due to the isomorphic substitution of Al^{3+} for Mg^{2+}, and anions are intercalated into the interlayer to maintain electroneutrality. It has been thought that the interlayer anions can be exchanged for other anions with higher selectivity. Miyata [4] represented the order of anion selectivity derived from the selectivity coefficients as follows:

$$I^- < NO_3^- < Br^- < Cl^- < F^- < OH^- \text{for monovalent anions}$$

$$SO_4^{2-} < CO_3^{2-} \text{for divalent anions}$$

This anion selectivity depends on the diameter of the non-hydrated anion and its valence [4].

Recently, HT have attracted considerable attention because of their extremely high anion-exchange capacities of about 3 meq/g [4,5], which are comparable to organic anion-exchange resins. Therefore, HT have been utilized as adsorbents in the removal of various pollutants from aqueous solutions. The adsorption characteristics of inorganic anions such as borate, nitrate, fluoride, phosphate, sulfate, chromate, arsenate, and selenate have been investigated (e.g., Refs. [6,7]). However, the adsorption mechanisms have not been fully elucidated, especially the surface complexation reactions, as pointed out by Goh et al. [7].

The adsorption modes of ions on mineral surfaces are mainly divided into outer-sphere and inner-sphere surface complexes. In general, the chemical interactions in inner-sphere complexes are stronger than those of outer-sphere complexes [8]. These differences in binding strengths influence the mobilities of ionic species in the environment. Hence, a distinction between outer-sphere and inner-sphere complexes is significant in evaluating the degree of anion fixation after adsorption onto HT. However, it has been mostly assumed that the adsorption mechanisms of anions onto HT are based on the formation of outer-sphere complexes in the interlayer by anion-exchange reactions.

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In this context, this study focused on surface complexation reactions on the HT surfaces in order to examine the adsorption mechanisms of anions onto HT. Environmentally important inorganic anions such as nitrate (NO_3), chloride (Cl), sulfate (SO_4), arsenate (AsO_4), and phosphate (PO_4) ions were used as the adsorbates in the experiments. To distinguish the inner-sphere complexes from the outer-sphere complexes of these anions, zeta potential measurements and infrared absorption spectroscopic analysis were performed. Furthermore, the effects of complexation reactions on the solid state properties of HT were also evaluated.

2. Materials and methods

2.1. Synthesis of HT

The HT were synthesized with reference to the procedure of previous investigations [2,3]. Briefly, 50 mL of an aqueous solution containing $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$, with a Mg/Al molar ratio of 3 and a total metal ion concentration of 0.8 mol/L, was continuously added to 50 mL of 0.2 mol/L Na_2CO_3 solution in a polypropylene reactor. The solutions were stirred vigorously at room temperature. The pH was maintained at a constant value of 10 by the simultaneous addition of 2 mol/L NaOH solution during precipitation. The pH of the suspension was measured with a pH meter (TOA DKK HM-20P with calibrated pH glass electrode). The total volume of the resulting suspension was adjusted to 200 mL by adding distilled water. Then, the suspension was aged hydrothermally using a Teflon lined stainless steel crucible at 150 °C for 48 h in a thermostatic oven. After the hydrothermal treatment, the obtained solid products were collected by centrifugation and washed with distilled water. The washed products were dried for 48 h using a vacuum freeze drier. In the HT preparation, the use of glassware was completely avoided to prevent contamination with silicate ions.

2.2. Calcination of HT

Previous studies [2,9] confirmed that the calcinations of HT at 500 °C will undergo transformation into Mg–Al mixed oxides that would revert to the original layered structure in the presence of water and anions through a rehydration reaction. Through this reaction, rehydrated HT with hydroxide ions in the interlayers can be ideally derived. To obtain oxides with mixed Mg–Al, synthesized HT were calcined in a muffle furnace at 500 °C for 2 h. The calcined HT samples were recovered without grinding and were used in anion adsorption experiments as the precursors of HT.

2.3. Anion adsorption experiments

Batch adsorption experiments were carried out for anion adsorption onto HT. Reagents of $NaNO_3$, NaCl, Na_2SO_4, Na_2HAsO_4, and Na_2HPO_4 were used as sources of each adsorbate anion. The adsorption experiments of each anion were tested separately. To minimize the influence of carbon dioxide, de-aerated distilled water was used. Solutions with a constant volume of 40 mL and having various initial concentrations of anions ($\leqslant$10 mmol/L) were prepared and mixed with 40 mg of calcined HT in 50 mL polypropylene centrifuge tubes. The suspensions were dispersed in an ultrasonic bath for 2 min and then placed in a shaker for 24 h at 25 °C. For NO_3 ions adsorption, the adsorption experiments were conducted under light shielding. After adsorption, the equilibrium pH values of the suspensions were measured with a pH meter. The suspensions were then separated by centrifugation, and the supernatant solutions were filtered through a 0.2 μm PTFE membrane filter. The obtained filtrate was analyzed for remaining anion and metal ion concentrations. Some colloidal aluminum was maybe contained in the filtrate.

The concentrations of nitrate ions were analyzed by absorption spectrophotometry using a JASCO V-550. The concentrations of chloride ions were analyzed by ion chromatography using a Metrohm 861 Advanced Compact IC. The concentrations of magnesium, aluminum, sulfur, arsenic, and phosphorus were analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES) using a SHIMADZU ICPE-9000.

2.4. Characterization of HT samples

The Mg/Al molar ratio of rehydrated HT was determined as follows. Precisely, 10.0 mg of rehydrated HT was dissolved in 100 mL of 1 mol/L HNO_3. Then, the solution was diluted to one-tenth with ultrapure water. The obtained solution was analyzed for magnesium and aluminum concentrations using a SHIMADZU ICPE-9000 (ICP-AES).

Rehydrated HT and anion-adsorbed HT were characterized by powder X-ray diffraction (XRD), attenuated total reflection Fourier-transform infrared (ATR-FTIR), and zeta potential measurements. The XRD profiles of the samples were collected using a Rigaku RINT 2100 powder diffractometer with Cu Kα radiation (λ = 0.15406 nm) at 30 kV and 20 mA in the 2–70° range, with a scanning rate of 1°/min. The ATR-FTIR spectra of rehydrated HT, anion-adsorbed HT powder, and solutions containing each anion were recorded using a JASCO FT/IR-6200 spectrometer with a diamond crystal from 400 to 4000 cm^{-1}. The zeta potential measurements of the HT suspensions with adsorbed anions were carried out using a MALVERN Zetasizer NanoZS90 at 25 °C. The concentrations of suspended solids were adjusted to 1.0 g/L. Concurrently, the pH values of the suspensions were also determined, and the pH was changed using an autotitrator (MALVERN MPT-2) by the addition of 0.1 mol/L HNO_3 solution.

2.5. Speciation and activity analysis

The speciation, activity, and saturation calculations were determined by using PHREEQC code [10], and the thermodynamic database THERMODDEM [11] was used in the calculations. The extended Debye-Hückel equation [8] was used for calculating the activity coefficients.

3. Results and discussion

3.1. Adsorption isotherms

The adsorption isotherms of inorganic anions (NO_3, Cl, SO_4, AsO_4, and PO_4) onto HT are shown in Fig. 1. The amounts of adsorbed anions are expressed in mmol/g-calcined HT, which does not reflect the equivalent of anionic valence. The equilibrium pH rose with increasing amounts of anion adsorption, in every anion system. This indicates that hydroxide ions in the HT interlayer were released into the bulk solution by adsorption of the other anions. The results in Fig. 1 showed that the order of anion selectivity of HT is $NO_3 < Cl < SO_4 \ll AsO_4 < PO_4$. Hence, the resulting orders of selectivity based on the mole amounts are consistent with the results of Miyata [4]. If the anions are intercalated into the HT interlayers with the same chemical species as the dissolved anions in the bulk solution (pH 10.6–11.4), NO_3 and Cl display an exchange efficiency of only about 15% of the theoretical anion-exchange capacity of HT (6.10 meq/g-calcined HT). Therefore, the rest should be compensated by hydroxide ions. And sorbed SO_4 amounts for 30% of the total anion exchange capacity. In particular, AsO_4 and PO_4 ions showed great affinity for HT.