Research paper

Adsorption of lactate and citrate on montmorillonite in aqueous solutions

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ABSTRACT

Lactate and citrate were adsorbed on montmorillonite surface from aqueous solutions from pH values 2 to 12 in the presence of 10 mmol L^{-1} KNO_3. The adsorbed molecules were characterized using Attenuated Total Reflectance Fourier transform Infrared (ATR-FTIR) spectroscopy at pH values 4, 6 and 8. Macroscopic adsorption measurements indicate that the adsorption of both ligands is highly pH dependent. ATR-FTIR results indicate that lactate is likely adsorbed by nonspecific electrostatic interactions, since no changes were found in peak position and shape of carboxyl group stretches. Nevertheless, ATR-FTIR results suggest that citrate is adsorbed in the >AlOH groups as an inner-sphere surface complex at low pH. The macroscopic adsorption behavior of the ligands was modeled as a function of pH by using the Diffuse Layer Model (DLM) for lactate and the Triple Layer Model (TLM) for citrate. Surface complexation of lactate and citrate was described with the complex >AlLac (logK = 11.25) and the complex >AlCit^{2-} (logK = 10.58) respectively.

These findings are of relevance for the evaluation of the catalytic effect that takes place during the dissolution of clay minerals in the presence of low-molecular-weight organic ligands.

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1. Introduction

The nature of bonding between organic species and mineral surfaces may play a role in catalyzing the reaction of mineral dissolution due to the formation of surface-organic complexes and the increase in the solubility of structural cations (Johnson et al., 2004a,b; Yoon et al., 2004). However, the catalytic mechanism is still under debate (Cama and Ganor, 2006; Drever and Stillings, 1997; Drever and Vance, 1994; Golubev and Pokrovsky, 2006; Li et al., 2006; Oelkers and Schott, 1998; Pokrovsky et al., 2009; Stillings et al., 1998).

Low-molecular-weight (LMW) organic acids can absorb onto mineral surfaces either by specific chemical interactions (chemisorption) to form inner-sphere complexes or by nonspecific interactions (physisorption) via hydrogen bonding and/or electrostatic interactions to form outer-sphere complexes (Axe and Persson, 2001; Filius et al., 1997). Among the LMW organic acids, lactate and citrate play a significant environmental role because of their prevalence in soil, sediments and aerosols resulting from exudation by plant roots, production by fungi, and discharge by microorganisms (Gadd, 1999; Ryan et al., 2001). Extensive work has been done to characterize the type and structure of surface complexes of simple organic acids with minerals (Axe and Persson, 2001; Cornell and Schindler, 1980; Evanko and Dzombak, 1998; Filius et al., 1997; Johnson et al., 2004a,b; Jonsson et al., 2010; Kubicki et al., 1999; Yoon et al., 2004). However, the adsorption mode of lactate has been only studied in metal oxides. Cornell and Schindler (1980) suggested that lactate was adsorbed as monodentate

inner-sphere complexes, whereas Filius et al. (1997) found that lactate adsorbs predominantly as outer-sphere complexes. Awatani et al. (1998) examined the adsorption of lactate on titanium oxide and concluded that lactate adsorbs in a bidentate fashion involving hydroxyl and carboxyl groups. These results may suggest that the structures and binding modes of lactate at mineral/water interfaces vary depending on the type of absorbent. On the other hand, citrate adsorption has been studied before in clays, but the adsorption mode is still unclear. Kubicki et al. (1999) found that citrate was adsorbed on montmorillonite by outer-sphere complexation. Lackovic et al. (2003) modeled citrate adsorption on illite with two bidentate outer-sphere complexes, but they did not provide spectroscopic information.

Spectroscopy methods are well suited for probing the structure and binding in metal–carboxylate complexes in aqueous solutions and at interfaces. Carboxylate groups of organic ligands have characteristic infrared-active vibrational bands that are sensitive to changes in proton and metal coordination. ATR-FTIR spectroscopy is one of the most direct methods used to distinguish different structures of organic adsorbents at mineral/water interfaces under in-situ conditions. It has been widely used to investigate organic ligand/clay surface complexation (Kang and Xing, 2007; Kubicki et al., 1997, 1999; Lackovic et al., 2003; Specht and Frimmel, 2001). Wet samples obtained in the adsorption reactions can be directly mounted on the ATR cell without any preparation that may affect the surfaces or adsorbed complexes. Thus, ATR-FTIR is able to provide information about the binding mode of ligands usually by comparing the IR spectra from adsorbed species with corresponding solution species. However, ATR-FTIR results do not always provide definitive information on different coordination geometries for surface complexes. In order to better understand the ligand–montmorillonite interactions, the experimental results obtained must be integrated with a surface

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complexation model, which establishes the stoichiometry of the adsorption reactions and provides a thermodynamic characterization of the equilibria involved.

We focused on montmorillonite in the present study because of its prevalence in soils and sediments. Moreover, montmorillonite dissolution mechanism and reactivity have been widely investigated in previous work (Amram and Ganor, 2005; Baeyens and Bradbury, 1997; Bauer and Berger, 1998; Cama et al., 2000; Furrer et al., 1993; Huertas et al., 2001; Metz et al., 2005a,b; Ramos et al., 2011; Rozalén et al., 2008, 2009a,b; Zysset and Schindler, 1996).

In this work we study the adsorption mechanism of lactate and citrate onto montmorillonite using the batch equilibrium adsorption method and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy. The results of the complete adsorption study are used to develop a surface complexation model that explains the dependence of the adsorption of organic ligands onto the surface of montmorillonite. The results of this study allow making quantitative predictions that can facilitate evaluation of the potential role of mineral surface chemistry in several geochemical processes involving the interactions of organic molecules and mineral surfaces.

2. Materials and methods

2.1. Materials

The clay material used in all experiments was a bentonite from the La Serrata — Cortijo de Archidona deposit located at Cabo de Gata (Almeria, SE Spain). This bentonite is approximately 92% montmorillonite; the remainder consists of accessory/companying minerals (quartz, feldspars, micas, calcite, amphibole) and volcanic glass (for a detailed characterization of the sample and methods see Ramos et al. (2011)). The adsorption experiments were performed on the <4 µm fraction, collected by repeated sedimentation–suspension cycles in deionized water, and then exchanged with K^+. The calculated structural formula of the K-smectite (based on one unit cell) corresponds to a montmorillonite (Newman and Brown, 1987):

$$K_{0.95}Mg_{0.02}Ca_{0.01}\left(Al_{2.79}Fe^{3+}_{0.35}Mg_{0.86}\right)(Si_{7.84}Al_{0.16})O_{20}(OH)_4.$$

Only 0.34 K^+ ions per half formula unit are exchangeable which indicates the presence of a small proportion of non-swelling layers. X-ray diffraction (XRD) patterns recorded on powder specimens and on oriented and glycolated mounts indicate that the sample is composed of a dioctahedral smectite with approximately 10–15% non-swelling layers. No accessory phases were detected. The specific surface area was measured by BET using 5-point N_2 adsorption isotherms after degassing the sample for two days at 110 °C under vacuum. The specific and edge surface areas were, respectively, 111 and 6.5 $m^2 g^{-1}$, with an associated uncertainty of 10%.

The organic carbon content determined by the wet oxidation method on the <4 µm fraction (Mingorance et al., 2007) yielded 2.57 ± 0.27 g C kg^{-1} (0.26 ± 0.03%), which is consistent with the value 0.35 ± 0.05% obtained for bulk FEBEX bentonite (Fernandez et al., 2004). Although the presence of organic carbon could affect to the adsorption results, the clay was used as adsorbent without any pretreatment. Previous works suggest that the process of removal of organic carbon may affect the mineral surface more than the presence of organic carbon (Brown and Brindley, 1980).

2.2. Batch adsorption experiments

Adsorption edges of lactate and citrate were carried out at room temperature using the batch equilibrium method at room temperature. Potassium nitrate was added to the solutions as background electrolyte. For lactate individual suspensions were prepared for every point of the

adsorption series. For lactate adsorption, a quantity of 0.023 g of montmorillonite was added to 20 mL of 10 mmol L^{-1} KNO_3 in a polyethylene bottle. The suspensions were stirred for 3–4 min and left to equilibrate for 24 h. A volume of 0.3 mol L^{-1} lactic acid stock solution was added to reach a total ligand concentration of 0.15 and 1.5 mmol L^{-1}. A control sample without clay was prepared to quantify the potential loss of lactate due to other processes. The pH was adjusted in each sample with an appropriate amount of 1 mol L^{-1} HCl or KOH solution to cover a pH range from 2 to 11. After 5 h the pH was measured in each bottle and an aliquot of 10 mL was withdrawn and filtered through a 0.22 µm Durapore membrane to analyze the lactate remaining in the solution.

Citrate adsorption was more limited than lactate adsorption, thus we used the solid:solution ratio approximately 6–7 times higher to obtain a better measurement in citrate concentration before and after adsorption experiments. A quantity of 0.58 g of montmorillonite was suspended in 100 mL of 10 mmol L^{-1} KNO_3 solution. The suspension was stirred for 3–4 min and equilibrated for 24 h. Then a volume of citrate stock solution was added to reach a total ligand concentration of 0.15 and 1.5 mmol L^{-1} and the pH was adjusted to 2 by adding 1 mol L^{-1} HCl solution. Every 20 min the pH was measured and a 5 mL aliquot was withdrawn while stirring. The pH was then increased in steps of approximately 1 unit using an appropriate amount of 1 mol L^{-1} KOH solution. The 5 mL aliquot was immediately filtered through a 0.22 µm Durapore membrane and the solution was analyzed for citrate.

Lactate and citrate concentrations in the supernatants were measured by ion chromatography using a Metrohm 761 Compact Ion Chromatograph with a Metrosep Organic Acids column. The eluent was prepared with 0.5 mmol L^{-1} sulfuric acid/15% acetone. The detection limit is 0.9 ppm for lactate and citrate. The associated error was 3%.

There was no indication of decreasing of lactate or citrate concentration over time in the control solutions, indicating that no bacterial degradation took place in the clay suspensions during the experiments. The adsorption of lactate and citrate from solutions 0.15 mmol L^{-1} was reported in Ramos et al. (2011) only to show qualitatively the amount and pH of ligand adsorption. The analysis and modeling of these results are the objectives of the present study.

2.3. Infrared spectroscopy

All reactions of lactate and citrate with montmorillonite were conducted in acid-washed 30 mL glass vials with polytetrafluoroethylene (PTFE) caps. A volume of 10 mL of 10 mmol L^{-1} KCl (background electrolyte) at desired pH (4, 6 or 8) was added to each vial with 0.625 g of smectite. KCl was used for FTIR experiments instead KNO_3 to avoid the strong absorbance introduced by the nitrate anion in the spectral region of interest. The IR adsorption experiments were performed at three different pH conditions, acid, near neutral and basic, which according to the results of the adsorption edges correspond to ligand adsorbed, partially adsorbed and desorbed, respectively. The suspensions were stirred for 3–4 min and allowed to equilibrate for 24 h. After equilibration, 2.5 mL of 125 mmol L^{-1} ligand solution was added to each vial to reach a total ligand concentration of 25 mmol L^{-1} and a total solid/ solution ratio of 50 g L^{-1}. With the ligand concentration used in batch experiments no band was observed in the spectra due to the low amount of ligand adsorbed. It was necessary to increase ligand concentration up to 25 mmol L^{-1}. Every suspension had a replicate at the same pH without ligand as a reference in the spectral analysis. All the suspensions were stirred and allowed equilibrating for 5 h at room temperature. To separate the supernatant from the wet paste of the montmorillonite–ligand complex, the suspensions were filtered through a 0.22 µm Durapore membrane. A part of the precipitated complex was washed with a background solution containing 10 mmol L^{-1} of KCl. Every paste of the montmorillonite–ligand complex (with and without washing) was removed from the filter with a spatula and placed in a horizontal flat ATR cell. The sample holding region was sealed with a