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Research paper

Spectroscopic evidence and molecular simulation investigation of the bonding interaction between lysine and montmorillonite: Implications for the distribution of soil organic nitrogen

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ABSTRACT

Clay minerals, widespread in natural soil environment, play important roles in the distribution of organics and their utilization by plants and microorganisms. Interface interactions of clay minerals and amino acids are essential for soil and life sciences. The bonding interaction between montmorillonite and lysine was studied systematically and comprehensively in this paper. The montmorillonite-lysine complexes were characterized by X-ray diffraction (XRD), attenuated total reflectance Fourier-transform infrared spectra (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and molecular simulation investigation. The results of XRD showed that interlayer spacing of montmorillonite increased or decreased with different amounts of lysine indicating two different bonding interactions. Amino acids adsorbed onto montmorillonite through the bonding interaction of electrostatic attraction between negatively charged surface of montmorillonite and $-NH_3^+$ at the end of lysine on interlayer adsorption aspect as confirmed by XPS and ATR-FTIR spectroscopy. For edge adsorption aspect, the adsorption was through the bonding interaction between $-COO^-$ group and $>AlOH_2^+$ / $>SiOH_2^+$ groups. Electron localization function calculations for O, Si and Al atoms further demonstrated the bonding interaction of $-NH_3^+$ groups and the $-Si-O^-$ groups intuitively. These findings give more understandings on the adsorption and distribution of amino acids in different sites of clay minerals.

1. Introduction

Dissolved soil organic nitrogen with low-molecular weight, uptake by plant roots in nature soil environment has drawn much attention in recent years (Qualls and Richardson, 2003; Persson and Näsholm, 2010; Cao et al., 2013). Amino acids constitute a potentially significant source of soil nitrogen and can be assimilated directly by plant (Persson and Näsholm, 2010; Warren, 2006). However, amino acids could be absorbed by soil solid phase very easily which would affect the distribution and utilization of organics by plant and microorganism (Qualls and Richardson, 2003). The amino acids adsorbed by soil solid phase, accounting for > 92% of total soil amino acids, are predominantly in soil organic nitrogen (Cao et al., 2013). Therefore, it can be inferred that the interaction between amino acids and soil solid phase is a significant factor that affects the distribution and bioavailability of amino acids.

Clays are important component of the soil solid phase (Liu et al., 2010). Adsorption of clays is a potentially important process in the natural environment because it can lead to removal of some free amino acids from the natural solutions, sediments and soils (Ramos and Huertas, 2013). And the adsorption of clay minerals may affect amino acids transport processes in the natural environment, such as the bioavailability of amino acids by plant (Jones and Kielland, 2002). Meanwhile, the adsorbed amino acids will serve as a long-term nitrogen source (Jones et al., 2004). As basic elements of life material, nutrition of plant and microorganism, amino acids have a close relationship with mineral clays once they penetrated into the clay layers (Henry and Jefferies, 2003). However, to the author's knowledge, investigations relevant to the bonding interaction between lysine and the edge-/interlayer-surface of montmorillonite have not been well documented.

To investigate the clay-amino acids interaction system, it's essential to know the dissociative forms of amino acids in the reaction solution or the surface of clay minerals. Lysine is an alkaline polar amino acid and comprised of basic amino groups and acidic carboxyl groups. Depending on the degree of protonation of these functional groups

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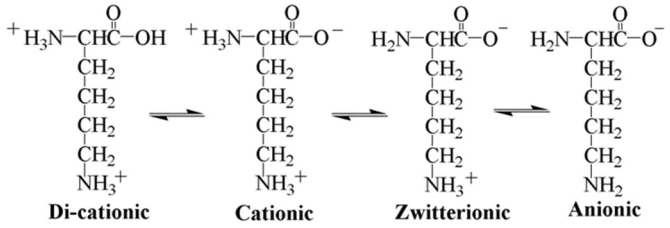

Fig. 1. Different dissociation states of dissolved lysine with different pH.

($-NH_2 \leftrightarrow -NH_3^+$, $-COOH \leftrightarrow -COO^-$, as shown in Fig. 1), the net charge of the amino acid molecule transforms from neutral or positive to negative in aqueous solution (Kitadai et al., 2009). Therefore, different dissociation states of amino acids show different bonding interaction behaviors, including electrostatic attraction or electrostatic repulsion, covalent bonding and hydrogen bonding (Kitadai et al., 2009; Gao et al., 2008; Lambert, 2008). The potential removal of clay minerals for amino acid adsorption in the natural environments has been studied in laboratory experiments at several pH conditions and varying concentrations in recent years (Ramos and Huertas, 2013; Cuadros et al., 2009; Kitadai et al., 2009). However, the results of these works mainly focused on the adsorption of amino acids by clay minerals, rarely involved in bonding interaction between specific functional groups of amino acids and specific atoms of edge-/interlayer-surface of montmorillonite.

At present, the interaction mechanism of amino acids and clay minerals has been studied by ATR-FTIR (Norén et al., 2008; Sebben and Pendleton, 2015). ATR-FTIR was reported to allow direct investigation of the interface and the surface chemistry of the adsorbate in situ (Kitadai et al., 2009). In addition, surface techniques such as XPS, were reported to be used to study the changes of the nitrogen groups of organic molecules adsorbed onto montmorillonite, due to the high sensitivity of the N1s binding energy of adsorbed bases (Lombardi et al., 2006; Petraki et al., 2005). Ahmed et al. studied the surface interaction of glycine and diamond-like carbon using XPS (Ahmed et al., 2013). The adsorption and reaction of the glycine were studied on the polar single crystal surface of zinc oxide by XPS (Gao et al., 2014). Furthermore, molecular simulation has been an important tool in study of interface interaction due to its visibility at the scale of molecule and electron cloud could show the bonding interaction more directly and vividly (Asl et al., 2016). A number of facets regarding arginine-glycine-aspartate (RGD)-bismuth ferrite (BFO)-(111) membrane interactions and reactivity have elucidated on a molecular level by molecular simulation (Li et al., 2016). However, there are few reports covering the experimental method and simulation method simultaneously on interactions of amino acids and clay minerals.

The objective of the present study was to investigate the bonding interaction between lysine and montmorillonite using XRD, ATR-FTIR, XPS, and molecular simulation investigation from adsorption, bonding to electron transfer. The present study is expected to have significant relevance in understanding the interaction and distribution of amino acids on different sites of clay minerals.

2. Materials and methods

2.1. Materials

The montmorillonite (Mt, for short) was obtained from Sanding Technology Co., Ltd., Zhejiang of China. The structural formula of the Mt sample was calculated according to Sun et al., 2007. Lysine stock solution (1.0 mol·L^{-1}) was prepared through dissolving 146.20 g lysine powder (min. 98% TLC; Sigma-Aldrich) into 1000 mL ultrapure water. Aliquots were taken from the stock solution and diluted with ultrapure water to obtain concentrations of 0.025 to 1.0 mol·L^{-1} (0.025, 0.050, 0.10, 0.25, 0.50 and 1.0 mol·L^{-1}).

2.2. Batch adsorption experiments

Lysine solution (30 mL) was mixed with 300 mg Mt in conical flasks. The pH was adjusted in each sample with suitable amount of 1 mol·L^{-1} HCl or NaOH solution to a final pH value of 9.0. The pH value was chosen since our preliminary experiment showed a high adsorption at this pH value. The mixtures were stirred at 120 rpm for 12 h at 25 ± 1 °C to achieve adsorption equilibrium. Then, the suspension was centrifuged at 8000*g* for 10 min. The obtained precipitates were washed three times with ultrapure water and allowed to air dry for 24 h. The control group without Mt was prepared to quantify the possible loss of lysine likely due to biodegradation. There was no sign of lysine loss with time in the control group, indicating no biodegradation occurred in the Mt suspension in the course of whole experiment.

2.3. X-ray diffraction analysis

X-ray diffraction patterns of lysine-Mt complex powder were obtained by a PANalytical X'Pert Pro diffractometer (radius: 240.0 mm) equipped with an X'Celerator detector, Cu K_α radiation of 1.54 Å, operated at 40 kV and 40 mA, detection range 2θ = 3°–80°. The scan step size and time per step were 0.03° and 10.16 s, respectively.

2.4. ATR-FTIR analysis

2.4.1. ATR-FTIR measurements of lysine in aqueous solution

The solution of lysine with different pH was determined by a drop-type pH meter (PHS-3CW; Bante instrument Co., Ltd., Shanghai, China) immediately before ATR-FTIR analysis. The sample was analyzed by in situ infrared spectroscopy using an Attenuated Total Reflection (ATR) Fourier Transform Infrared Spectroscopy (ATR-FTIR, Frontier) with a diamond ATR accessory. Spectra ranging from 400 to 4000 cm^{-1} were obtained by co-addition of 64 scans with a resolution of 1 cm^{-1} and a mirror velocity of 0.6329 cm·s^{-1}. Background spectra were determined on the ATR accessory without a sample in ambient. A spectrum of ultrapure water was also determined and subtracted from the spectrum of each lysine solution (subtraction factor = 0.96–1).

2.4.2. ATR-FTIR measurements of lysine-Mt complex suspensions

Each lysine-Mt complex suspension (a mixture of 5 mL 0.50 mol·L^{-1} amino acid solution of different pH and 50 mg of Mt) was prepared and stirred for 12 h. 200 μL suspension was spread evenly on the ATR accessory after the background spectrum was determined.

The spectra of the lysine-Mt complex include the portions of the amino acids interacted with Mt, the non-interacted amino acids, water, and the Mt. In order to obtain the spectrum of the lysine interacted with Mt, we proceeded according to Kitadai et al. (2009).

2.5. XPS measurements

X-ray photoelectron spectroscopy (XPS) spectra of survey scan, N1s and C1s of Mt and Mt-lysine (pH 9.00) samples were obtained on a Kratos Axis spectrometer equipped with an energy analyzer. The Al-Kα line was used as radiation source at the emission voltage at 15 kV and 5 mA. Raw spectra were smoothed before being fitted using software XPSpeak software using a Shirley base line and a Gaussian-Lorentzian peak shape.

2.6. Electron localization function calculation

Materials Studio (version 5.0, Accelrys Software Inc., San Diego, CA, USA, 2009) was used as the simulation software. Simulation process is divided into three parts: Monte Carlo calculations, molecular dynamics simulations and quantum chemical calculations. According to the foregoing dynamics calculations, use ONETEP and CASTEP modules based on density functional theory to calculate molecular dynamics

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