



Reconstitution of cutin monomers on smectite surfaces: adsorption and esterification



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ABSTRACT

This paper focuses on the physico-chemical interactions of cutin monomers with clay smectites. Adsorption of cutin monomers was measured, and esterification and reconstitution were studied using Fourier transformed infrared spectrometry (FTIR), X-ray diffraction (XRD) and mass spectrometry (MS) analyses. Adsorption of a common cutin monomer, ω -dihydroxypalmitic acid (diHPA) to smectite was found to be affected by its interactions with exchangeable cations. Inner-sphere complexation was observed for Fe^{3+} -montmorillonite, and nontronite. Outer-sphere complexes were observed for Ca^{2+} - and Wyoming Na^{+} -montmorillonite. XRD measurements showed that cutin monomers were intercalated between smectite layers, and MS results demonstrated their enhanced esterification on the smectite surfaces (as compared to monomer solution). This study suggests that cutin monomers can be reconstituted and esterified on the smectite surfaces to form stable organo-mineral complexes.

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1. Introduction

Plant cuticle, is a thin, predominantly lipid layer that covers all primary aerial surfaces of vascular plants (Jeffree, 1996). Residues and derivatives of the plant cuticle constitutes are commonly found in soil organic matter (SOM) (Kögel-Knabner, 2002; Nierop, 1998). In many plant species, cutin biopolymer is the major component of the cuticle, comprising from 30 to 85% of the cuticle's weight (Holloway, 1982). Cutin is an insoluble, high-molecular-weight biopolymer, which consists of inter-esterified cross-linked hydroxy-fatty acids and hydroxyepoxy-fatty acids (Kolattukudy, 1980, 2001). The major components of cutin are derivatives of C_{16} and C_{18} fatty acids, and to a lesser extent, *p*-coumaric acid. In many plant cuticles, the dominant cutin monomer is ω -dihydroxypalmitic acid (diHPA), which exists as a mixture of four different isomers 10,16-, 9,16-, 8,16- and 7,16-diHPA acid (Kolattukudy, 1980). The commonly dominant isomers are 9,16-diHPA acid and 10,16-diHPA acid (Kolattukudy, 2001). In the environment, cutin bio-decomposition is facilitated mainly by cutinase produced by fungi and bacteria (Kolattukudy, 2001).

Adsorption of high- and low-molecular-weight organic compounds on the common soil mineral montmorillonite saturated with different cations has been widely studied (Chefetz et al., 2011; Kang and Xing, 2007; Polubesova et al., 2008), and the catalytic properties of montmorillonite toward chemical reactions of organic compounds, such as

oxidation, esterification and organic synthesis have been demonstrated (Mittal, 2007; Mortland, 1970; Nagendrappa, 2011; Pinnavaia, 1983; Polubesova et al., 2010). However, little information is available on the reactions of fatty acids (i.e., cutin building blocks) with clays, which can model cutin monomer interactions with montmorillonite and other soil minerals. Self-assembly and esterification of diHPA and 9,10,16-trihydroxypalmitic acid (triHPA) have been observed on mica (Heredia-Guerrero et al., 2009, 2010). It has been suggested that the mid-chain secondary hydroxyl groups of acids reinforce the intermolecular hydrogen bonding ($\text{R}-\text{OH}\cdots\text{HO}-\text{R}$) within self-assembled layers, whereas the terminal primary hydroxyl groups trigger the formation of multilayers of acids via tail-to-head ($\text{R}-\text{OH}\cdots\text{HOOC}-\text{R}$) interactions. It was also shown that diHPA undergoes self-assembly on mica by forming an almost vertically oriented molecular layered pattern. This orientation of the monomers has been suggested to facilitate esterification reaction due to steric closeness of hydroxyl and carboxyl groups (Heredia-Guerrero et al., 2009). It is important to note however that the abovementioned studies with diHPA, triHPA and mica were conducted in ethanolic-chloroform solution and thus do not characterize interactions in the natural environment.

In this paper, we report the adsorption and transformation (i.e., esterification) of diHPA and triHPA by common soil smectite minerals in aqueous solutions. The main hypothesis of the study was that the mode of adsorption would be affected by the type of clay and exchangeable cation, hence we used nontronite and montmorillonite enriched with Fe^{3+} , Ca^{2+} and Na^{+} , as adsorbents. We postulate that adsorption of these acids will result in their esterification and oligomerization due

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to Brönsted acidity of clays and reduction in aqueous dielectric permittivity on the smectite surfaces (Sposito, 1984). The generated data may help explain potential reactions of cutin monomers with common soil smectites.

2. Experimental section

2.1. Chemicals and reagents

TriHPA (95% purity) was purchased from Tokyo Chemical Industry (Japan), and N,O-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA + TMCS; 99:1) was obtained from Fluka (Buchs, Switzerland); pyridine and ethyl acetate were purchased from Merck (Darmstadt, Germany). Heptadecanoic acid, oxalic acid, ammonium oxalate, chloroform methanol, HCl, NaOH and H₂SO₄ were purchased from Sigma-Aldrich Israel Ltd. (Rehovot, Israel).

2.2. Isolation of cutin monomers

Monomers of cutin were isolated from tomato (*Lycopersicon esculentum*) fruit cuticle using the previously reported method (Shechter and Chefetz, 2008). Briefly, tomato fruit peels were treated with oxalic acid and ammonium oxalate solution to remove non-cuticular matter. Waxes were then removed by Soxhlet extraction with chloroform/methanol. To obtain cutin monomers, the dewaxed tomato cuticles were hydrolyzed and then saponified with 1% KOH in methanol (W/W 70 °C, 8 h). For clean-up, the solution containing cutin monomers, was filtered (glass microfiber filter) and methanol was evaporated. The remaining monomers were re-dissolved in double-distilled water. Next, the pH of the solution was adjusted to 2.5 and the cutin monomers were isolated using liquid–liquid extraction with ethyl acetate. The organic phase containing the cutin monomers was removed, dried with sodium sulfate and kept at 4 °C. The identification of the dominant components of isolated cutin monomer solutions was performed using GC–MS; the concentrations of the dominant components were measured using GC–FID. The final cutin monomer isolate was composed mainly by diHPA (80%) whereas coumaric acid, hydroxyhexadecanoic acid and triHPA made up 7, 3.5 and 3%, respectively. These data are consistent with previous studies (Gérard and Osman, 2007; Hauff et al., 2010; Kolattukudy, 1980; Riley and Kolattukudy, 1975). Aqueous solutions of the monomers were prepared by evaporating the ethyl acetate and re-dissolving the materials in double-distilled water. The pKa values of diHPA and triHPA were calculated using Calculator Plugins (Marvin 6.1.0., 2013).

2.3. Preparation of clay sorbents

Wyoming Na⁺-montmorillonite (SWy1) and nontronite (NAu2) were obtained from the Source Clays Repository (Clay Minerals Society, 2013). The Fe₂O₃ content in SWy1 and NAu2 was 3.35 and 37.42%, respectively (Clay Minerals Society, 2013). The <2-μm fraction of the smectite was separated by sedimentation in distilled water and used for the experiments. The cation exchange capacity and exchangeable cation composition of SWy1 and NAu2 were determined using ammonium acetate method (Sumner and Miller, 1996). The cation exchange capacity was 0.78 ± 0.09 and 0.85 ± 0.09 mmol_c/g for SWy1 and NAu2, respectively. The exchangeable cation composition for SWy1 was: Ca²⁺ (37%), Na⁺ (41%), Mg²⁺ (21%) and K⁺ (1%). The exchangeable cation composition for NAu2 was: Ca²⁺ (30%), Na⁺ (56%), Mg²⁺ (13%) and K⁺ (1%). Homoionic Fe³⁺- and Ca²⁺-montmorillonites (hereafter FeWy1 and CaWy1, respectively) were prepared by sequential washing of the SWy1 with 1N FeCl₃ or CaCl₂, respectively. Excessive salts were removed by dialysis of the montmorillonite samples against distilled water until the supernatant solution

was free of chlorides, and the electrical conductivity of the solution was similar to that of distilled water. All samples were freeze-dried and stored in a desiccator. For CaWy1, Ca²⁺ was 95% of the total sum of exchangeable cations measured using ammonium acetate method (Sumner and Miller, 1996). For FeWy1, surface iron was extracted several times with a mixture of 0.5 M HCl and 1 M KCl. Iron was above 95% of all extracted cations.

2.4. Batch sorption experiments

Adsorption of diHPA by SWy1, NAu2, FeWy1 and CaWy1 was measured in batch using aqueous solutions containing cutin monomers. To estimate the effect of pH, diHPA adsorption at the initial concentration of 75 mg/L was determined at a pH range from 3 to 8 (pH was adjusted using 0.01 M HCl or NaOH). Adsorption isotherms were measured for all clays at constant pH of 4.2; diHPA was introduced at concentration ranged from 1 to 180 mg/L. All background solutions contained NaN₃ (100 mg/L) to inhibit microbial activity. The final clay concentration in the suspension was 1 g/L. The suspensions were equilibrated in the dark at 25 °C for 72 h (based on preliminary kinetic measurements). Then, suspensions were centrifuged for 15 min at 12,000 g, and aliquots of the supernatants were removed for diHPA analysis. Bi-solute adsorption experiments were conducted by adding triHPA as a competitor at a constant concentration of 100 mg/L to the background solutions containing elevated concentrations of diHPA (1–180 mg/L). Experimental conditions were identical to those described for the single-solute batch method.

The concentrations of diHPA and triHPA were measured by GC, following silylation of the fatty acids (Hauff et al., 2010). Briefly, aliquots of supernatants were dried under stream of N₂ and re-dissolved in a mixture of pyridine and BSTFA + TMCS (25/75, v/v) at 70 °C for 30 min. Heptadecanoic acid was added before the drying as an internal standard. The concentration of silylated fatty acids was measured using an Agilent 6890N GC equipped with FID. The method was validated by measuring known concentrations of triHPA. The Rxi-5Sil MS capillary column (30 m × 0.25 mm internal diameter, 0.25-μm film thickness) was used with He as the carrier gas at a flow rate of 2 mL/min. The N₂ make-up gas flow rate was 50 mL/min. The injector and detector temperatures were 250 and 280 °C, respectively. The oven was maintained at 60 °C for 1 min, and then the temperature was increased to 280 °C at a rate of 10 °C/min.

Both diHPA and triHPA exhibited minor sorption to the tubes (<0.5%), and negligible loss due to the volatilization. The adsorbed amounts of fatty acids were calculated from the difference between their initial and final concentrations in the supernatant. Each adsorption isotherm was constructed from 24 data points. The curves demonstrating pH dependent diHPA adsorption were fitted to the sigmoidal function (Eq. (1)).

$$Q = \frac{a}{1 + 10^{pH-b}} + c \quad (1)$$

where Q is the adsorbed concentration of diHPA (mg/g), which approaches to the maximal value ($a + c$, mg/g) at low pH values, and approaches to the minimal value (c , mg/g) at high pH, and b is the pH at the inflection point of the isotherm.

The isotherms were fitted to Langmuir and Freundlich models and to the dual mode model (Eq. (2)) using MATLAB curve fitting toolbox.

$$Q = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} + K_D \cdot C_e \quad (2)$$

where Q is the adsorbed concentration of diHPA (mg/g), Q_{\max} is the maximal adsorbed amount of the first monolayer (mg/g), K_L (L/mg) calculated for the Langmuir component of the dual mode model

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