



Change of organobentonite interlayer microstructure induced by sorption of aromatic and petroleum hydrocarbons—A combined study of laboratory characterization and molecular dynamics simulations



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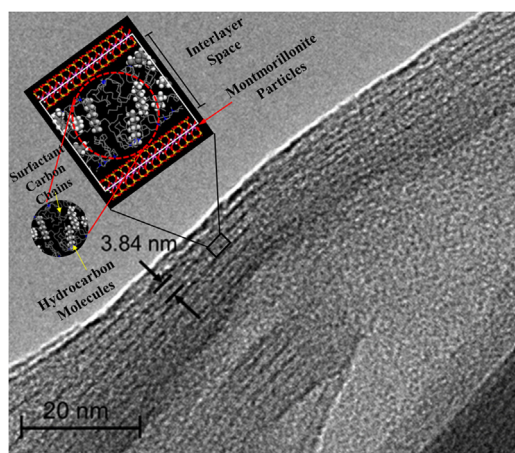
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HIGHLIGHTS

- Lab tests were conducted to quantify the change of microstructure of bentonite due to successive intercalation.
- The XRD and TEM results confirmed the interlayer expansion of bentonite due to primary and secondary sorption.
- Molecular simulations were conducted to study the microstructure of clay/surfactant/sorbate hybrids.
- FT-IR results indicated a rearrangement mechanism of surfactant chains within the organoclay interlayers after secondary sorption.
- Both experimental and simulation results yield insights into the engineering behaviors of organic-modified clays.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the impact of secondary sorption of hydrocarbons on the interlayer morphology of organic surfactant modified montmorillonites was studied. Montmorillonites intercalated with two quaternary ammonium surfactants, hexadecyltrimethylammonium (HDTMA⁺) and bis (hydrogenated tallow alkyl) dimethyl ammonium were chosen as the soil sorbents to uptake naphthalene and gasoline. Laboratory characterization using X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) were carried out, and molecular dynamics (MD) simulations were performed. The successive interlayer expansion of montmorillonites due to the intercalation of surfactants and hydrocarbons were measured by XRD and TEM. FT-IR was employed to verify the intercalation of organic surfactants and sorbates. Additionally, the MD modeling was conducted to demonstrate the interlayer microstructure of organoclays and to quantify interactions between minerals, surfactants,

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and sorbates. The experimental and simulation results validated the transitions of montmorillonite interlayer expansion due to the successive intercalation of organic surfactants and sorbates, yielding insights into the understanding of the microstructures of sorbate/surfactant/clay hybrids and their physical-chemical and mechanical behaviors.

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1. Introduction

Organoclays are of engineering interest because of their enhanced physical and chemical properties [1,2]. Most commonly, montmorillonite is used as a base clay to prepare organoclays through interlayer cation exchange [3]. Synthesized organoclays typically exhibit higher sorptivity and retention capacity of organic compounds, decreased surface charge, decreased permeability for non-polar liquids and lower compressibility when compared to base clays [1,4–7]. Organoclays, especially intercalated surfactant/clay hybrids, are widely used as: (1) sorptive materials for waste containment and groundwater remediation, (2) additives in rheological control agents, and (3) drilling fluids because they are easier to synthesize, more available and their properties are relatively known [8–12].

Previous studies demonstrated that the intercalation of organic surfactant into alluminosilicates such as montmorillonite is through cation exchange or primary adsorption [13]. The arrangement of intercalated surfactants in the organoclay interlayer is controlled by the charge density of base clay, the percentage of exchanged cations and the surfactant type [14]. Using hexadecyltrimethylammonium (HDTMA⁺)-a single chain quaternary ammonium cation as an example, the intercalated aliphatic carbons on the HDTMA cations tend to form layered structures such as lateral monolayers (basal spacing 13–15 Å), lateral bilayers (basal spacing 17.7–19.8 Å), and pseudo-trilayers or paraffin monolayers (basal spacing >22 Å) [14–16]. The increased surfactant loading often lead to the higher packing density of surfactants per unit basal area, highly ordered chain arrangements, and consequently, increased interlayer spacing occupied by liquid-like surfactants [17]. Many studies have indicated that the physical-chemical properties of organoclays including hydrophobicity, sorptivity, strength, compressibility and thermal stability are controlled by the microstructure of interlayer surfactants [18–22].

The secondary sorption in organoclays may lead to a further modification of their microstructures, and consequently, the modification of their engineering properties including sorptivity, permeability, and strength. At the microscale, organoclays synthesized from long-chain surfactants have a decreased surface area as the large organic surfactant molecules may block the surface sites of clays [23,24]. However, the increased loading of surfactants can prop up the interlayer space and create an organophilic phase for the secondary sorption of non-polar molecules [25]. Similarly, the intercalated sorbates (in addition to the surfactants) may further increase the interlayer spacing [26,27] and facilitate the sorption of even larger sorbates. The slightly enhanced sorptivity or the increased soil-water distribution coefficient was observed for organoclays after secondary sorption and was explained as result of the increased organic partitioning phase and interlayer spacing [28].

Several studies indicated that the interlayer expansion and swelling of the bulk volume of organoclays were observed when interlayer sorption of hydrocarbon molecules of diesel oil, gasoline, kerosene occurred [8,26,29]. A study by Benson et al. [5] demonstrated that the permeability of organoclay could be lowered by six orders of magnitude when permeated with fuels. The decreased permeability was related to the high swelling tendency

of the organoclay in fuels. In another study by Lo and Yang [30] it was observed that organoclays exposed to hydrocarbon or fuels exhibited much improved self-healing ability under freeze-thaw and dry-wet cycles as well as less susceptibility to volumetric deformations and cracking.

Both experimental and simulation techniques have been performed to examine the interlayer microstructure of intercalated phases and their interactions. Microstructural properties of some organoclays were characterized by X-ray diffraction (XRD) [31–33], Fourier transform infrared spectroscopy (FT-IR) [34], Raman spectroscopy [35,36], transmission electron microscopy (TEM) [75,37,38] and scanning electron microscopy (SEM) [39]. In addition to the above laboratory characterization techniques, computational approaches such as MD simulations allow us to reproduce the interlayer microstructure of organoclays and quantify the interactions between mineral, water and organic phases at the nano-scale level [15,25,38,40–43]. These previous studies addressed the following issues regarding the clay/surfactant hybrids: (1) the mechanisms of primary sorption (or intercalation by cation exchange) of organic surfactants in clays, especially the governing factors (e.g., clay charge density, percentage of exchanged cation and cation types); (2) the microstructure of the intercalated cationic surfactants in the interlayer of synthesized clays and the expansion of interlayer occurred due to intercalation. (3) The affinity of organic sorbates toward the synthesized clay/surfactant hybrids, typically interpreted from the organic carbon content or basal spacing of the synthesized clays.

Many studies were conducted to investigate the transition of the interlayer microstructure from natural bentonite to surfactant modified bentonite [11,19,26,27]. However, most of the previous studies, if not all of them, focused on the intercalation of cationic surfactants and base clays or the primary cation exchange process. Limited information regarding the impact of organic sorbates on the organoclays interlayer morphology are available. Additionally, although many studies quantified the sorption of the organic compounds onto synthesized organoclays at the batch scale, at the molecular level, our understanding of the interactions between intercalated surfactants and organic sorbates is still limited. Consequently, the fundamental understanding of the impact of secondary sorption of organic sorbates on the interlayer microstructure and resultant bulk properties of organoclays merits examination. This study was conducted to systematically quantify: (1) the interactions between mineral phase (alluminosilicates), surfactants and hydrocarbon sorbates; (2) the interlayer expansion of montmorillonite due to consecutive intercalation of surfactant and hydrocarbons; (3) and the surfactant arrangement and re-arrangement before and after hydrocarbon sorption. Aromatic hydrocarbons and gasoline hydrocarbons were chosen as the organic sorbates, and two intercalated, partitioning organoclays were chosen as sorbents. A comprehensive study using the laboratory characterization (XRD, TEM, and FT-IR) and the molecular simulation were conducted to quantify the impact of the primary and secondary sorption on the organoclay microstructure. The obtained results were expected to yield insights into: (1) the impact of hydrocarbon sorbates on the interlayer surfactant re-arrangement; (2) ease of sorbate intercalation and the magnitude of interlayer expansion due to the secondary sorption; and (3) the

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