



## Research Paper

## Facile modification of montmorillonite by intercalation and grafting: The study of the binding mechanisms of a quaternary alkylammonium surfactant

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## ABSTRACT

Modified clays are among the most investigated organic-inorganic hybrid materials. Traditionally, they are prepared via reaction of the clay mineral with an organic substrate that can be bonded by cation exchange or by covalent grafting. However, the possibility of bonding one organic substrate to the clay mineral via these two mechanisms simultaneously has not been deeply investigated. In this study, a simple modification of a clay mineral was investigated via the reaction of a quaternary alkylammonium surfactant that possesses an alkoxysilane group [(3-trimethoxysilylpropyl)octadecyldimethylammonium chloride] (TPODAC) with raw bentonite that contains montmorillonite (Mt) as the main phase (~90%) and acid-activated bentonite (H5-Mt). The structures, morphologies, and compositions of natural and modified montmorillonites were investigated via various methods, which evidenced successful organic modification. The surface area of Mt. ( $50 \text{ m}^2 \text{ g}^{-1}$ ) was as expected for sodium bentonite. After acid activation, an increase of the BET area ( $120 \text{ m}^2 \text{ g}^{-1}$ ), a decrease of the cation-exchange capacity (CEC), and a loss of crystalline order were observed. The presence of TPODAC in the hybrid materials was evidenced by three IR absorption bands at approximately  $2930 \text{ cm}^{-1}$ ,  $2860 \text{ cm}^{-1}$ , and  $1475 \text{ cm}^{-1}$ . Negligible leaching of TPODAC from the hybrid materials in aqueous media at pH 3, 7, and 10, in hydrophobic media, and in high-ionic strength media were observed, thereby demonstrating the excellent chemical stability of these materials. A quantitative evaluation of the contribution of each binding mechanism of TPODAC in the hybrid materials was conducted by applying a surfactant-mineral interaction model in which grafting, cross-linking, and cation exchange mechanisms were proposed. The amounts of surfactant in the hybrid materials that were predicted by the model were in agreement with the results that were obtained via TGA.

## 1. Introduction

Organoclays (OCs) are hybrid materials that result from the association of clay minerals (such as montmorillonite, vermiculite, and saponite) with surfactants, polymers, and/or other organic compounds. Cationic surfactants such as quaternary ammonium salts have been mainly used for the modification of clay minerals. However, in the past few years, alternatives such as zwitterionic surfactants (SB16 and SB12) and non-conventional non-ionic surfactants (C10E3 and Brij 56) that involve other interaction mechanisms in addition to cation exchange have been proposed (Guégan, 2019). The exchange of inorganic cations that are naturally present in clay minerals by quaternary alkylammonium cationic surfactants has been widely used to modify the surface properties (Xi et al., 2004; Xi et al., 2007; He et al., 2010; Naranjo et al., 2013; Parolo et al., 2014; Martín et al., 2019; Slaný et al., 2019;

Mekhzoum et al., 2020). A disadvantage of this modification is that this reaction is typically reversible and the surfactants, which are electrostatically bound to the mineral layers, can be easily released in aqueous media. This could be avoided if the organic substrates and the mineral were covalently bonded (Jaber and Miehé-Brendlé, 2009).

Grafting bonding has been used to obtain organic-inorganic hybrid materials (He et al., 2005; Paul et al., 2011; Qin et al., 2014), where the components are linked by covalent bonds, thereby avoiding the leaching of the organic substrates when the hybrid materials are used in aqueous media (Jaber and Miehé-Brendlé, 2009). In addition, grafting bonding can occur on the crystal surface, on the layer surface (inter-layer expansion occurs) and mainly on the external broken edges (the basal space remains unchanged) (He et al., 2005; Jaber and Miehé-Brendlé, 2009; Parolo et al., 2014; Guégan, 2019). Despite its advantages, this treatment has been applied less extensively than cation

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