

Functionalization of Bentonite by Intercalation of Surfactants

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The functionalization of bentonite by intercalation of surfactants dodecylamine, hexadecylamine, octadecylamine, and the octadecyltrimethylammonium cation is described. Products are characterized by elemental analysis, thermal analysis, FT-IR spectra, and powder X-ray diffraction analysis. Laminar amine-clay nanocomposites contain about one mol amine per (Si,Al)₄ clay unit, while the cationic surfactant show an intercalation rate of only 0.42 under the same conditions. The cation insertion is governed by ion exchange and the resulting stoichiometry corresponds to the cationic exchange capacity of the clay. The stoichiometry of amine nanocomposites, going beyond the cationic exchange capacity, is explained by the insertion of amine species stabilized in the interlaminar phase by both, the coordination of sodium ions and van der Waals interactions between neutral surfactants. Models for the nanocomposite interlaminar space, considering the interlaminar distances, the geometry of the guest and the area available in aluminosilicates sheets, are proposed.

Keywords: bentonite; intercalation; laminar clays; nanocomposites; surfactant

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INTRODUCTION

Natural clays are being widely studied as conventional materials specially because its abundance, low cost and relatively high purity [1]. The montmorillonites are laminar aluminosilicates where the isomorphous substitution of silicon by aluminum, which generates negatively charged lamina, is neutralized by alkali or alkaline earth cations located in the interlaminar spaces [2]. The modification of the interlaminar phase leaves considerable scope to the regulation of the clay properties by the exchange of interlaminar cations and or the intercalation of neutral species leading to the formation of composites with great potential for the development of new materials with scientific or technological interest. Thus, for example, applications of these type of materials, such as their use as template polymerization [3], in the removal of contaminants [4] or to stabilize metal nanoparticles [5] are often associated to the nature and spacing of the interlaminar phase in the nanoclays used as precursors.

In this work we describe the functionalization of the interlaminar space of bentonite by intercalation of the neutral surfactans, dodecylamine DDA, hexadecylamine HDA and octadecylamine ODA, and the cationic surfactant octadecyltrimethylammonium bromide, OTAB in order to contribute to a better understanding of the nature and structure of the interlaminar space. A model permitting to visualize the interactions and the packing density of the surfactants in the interlaminar phase is proposed.

EXPERIMENTAL

Bentonite (Sigma), was first purified by sedimentation techniques and converted to its sodium form by ionic exchange with 1 M sodium chloride (Merck p.a.). The salt excess was separated by dialysis (Sigma dialysis tubing cellulose membrane). The mean particle size after filtering the suspension through a membrane (Whatman glass micro fiber filters, GF/D) was $<3\ \mu\text{m}$. The structural formula of our montmorillonite $\text{Na}_{0.47}(\text{Al}_{1.58}\text{Fe}_{0.17}\text{Mg}_{0.25})(\text{Al}_{0.22}\text{Si}_{3.78}\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ was determined by Plasma Atomic Absorption Spectroscopy (Perkin Elmer ICP-OES OPTIMA 1000DV).

The clay cation exchange capacity (*cec*) determined directly by exchange of sodium with an ethylenediamine complex of Cu(II) [6] was 110 meq per 100 g of the clay. Dodecylamine DDA, hexadecylamine HDA, octadecylamine (ODA), and octadecyl trimethylammonium bromide (OTAB) were used as received (Aldrich).

The intercalation reaction was afforded by stirring at room temperature during three days a suspension of the Na-Bentonite in ethanol-H₂O (1:1) with an excess of the surfactant (1:3 mol per (Si,Al) unit of the clay). Solid products were separated by centrifugation, washed, and dried under vacuum. The elemental analysis (SISONS ES-1108), %: Found (calculated for [Bentonite(DDA)_{1.1} · 2.3(H₂O)]): C: 23.42(23.14); N: 2.083(2.249); H: 5.05(5.05). (Calculated for [Bentonite(HDA)_{0.94} · 3.0(H₂O)]): C: 25.60(25.60); N: 1.795(1.842); H: 5.49(5.49). (Calculated for [Bentonite(ODA)_{1.0} · 4.5(H₂O)]): C: 27.73(27.66); N: 1.710(1.792); H: 6.20(6.20). (Calculated for [Bentonite(OTAB)_{0.42} · 1.9(H₂O)]): C: 18.08(17.93); N: 0.979(0.996); H: 3.92(3.91).

Purity as well as the intercalation degree of the products was monitored by powder X-ray diffraction. (Siemens D-5000, Cu-K α radiation). FT-IR spectra in the range 4000–250 cm⁻¹ (Bruker Vector 22 infrared Fourier transform spectrometer) using the KBr pellet. TG/DSC analyses (STA 625 PL Analyzer) were carried at a heating rate of 10°C/min under nitrogen stream. The morphology of the products was analyzed by Scanning Electron Microscopy (SEM) (Phillips XL-30 and Hitachi S400 with EDS system).

RESULTS AND DISCUSSION

The intercalation of surfactants into the bentonite leads to laminar solids as shown in Figure 1. The presence of the organic guest confined in this aluminosilicates was confirmed by FT-IR spectroscopy, thermal analysis and powder X-ray diffraction. The stoichiometry of the resulting organic-inorganic nanocomposites was determined by elemental analysis.

In Table 1, selected absorption bands from the FT-IR spectra of the free amines, the OTAB and the corresponding bentonite intercalates are reported. As observed for the nanocomposite [Bentonite(DDA)_{1.1} · 2.3(H₂O)], spectra of the free amine and amine confined in the bentonite are in general similar. In the spectra of intercalated amines, the symmetric and antisymmetric bands associated with NH₃⁺ stretching appear at frequencies of 3020 cm⁻¹ and in the range of 3110–3160 cm⁻¹, respectively, while those characteristic of the alkylammonium group are not observed. It is interesting to remark that the bands centered at 2920 cm⁻¹ and 2850 cm⁻¹ assigned to intercalated amine, compared to those of the free guest, are well resolved (see inset to Fig. 2), pointing to a well ordered trans conformation of the amine in the confined state [7].

In Figure 3 the thermal analysis of the Bentonite(HDA)_{0.94} · 3(H₂O) is shown. The melting point of the amine is observed as an endothermic



FIGURE 1 Scanning electron micrograph of [Bentonite(OTAB)_{0.42} · 1.9(H₂O)].

peak at 48°C. A second, more notorious, endothermic peak is observed at 428°C. Most organic material is lost between 180° and 500°C, agreeing approximately with the amine content in the sample (32%). The loss of amine appears to occur by two processes, centered with approximately the same mass loss [8].

TABLE 1 Selected Absorption Bands from the FT-IR Spectra of the Bentonite Nanocomposites

OTAB (cm ⁻¹)	Bentonite-OTAB (cm ⁻¹)	DDA-HDA-ODA (cm ⁻¹)	Bentonite-Amine (cm ⁻¹)	Assignment
719–730	721	720–730	722	modes methylene scissoring-roching
1463–1473	1473–1488	1463–1473	1460–1470	modes methylene scissoring-roching
2850–2918	2850–2926	2849–2920	2853–2926	Stretching sym-asm CH ₂
2870				Stretching sym-CH
2952		2955	2956	Stretching asym-CH
		3332		Stretching NH ₂
	3630		3630	O–H stretching

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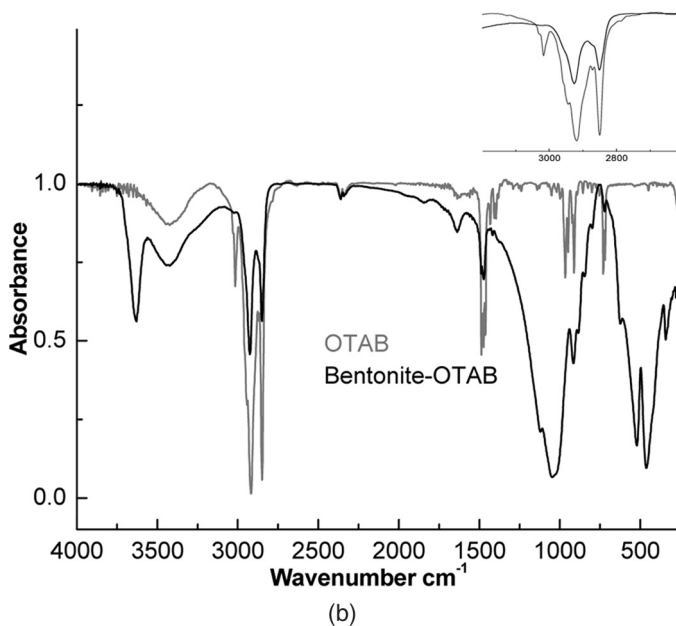
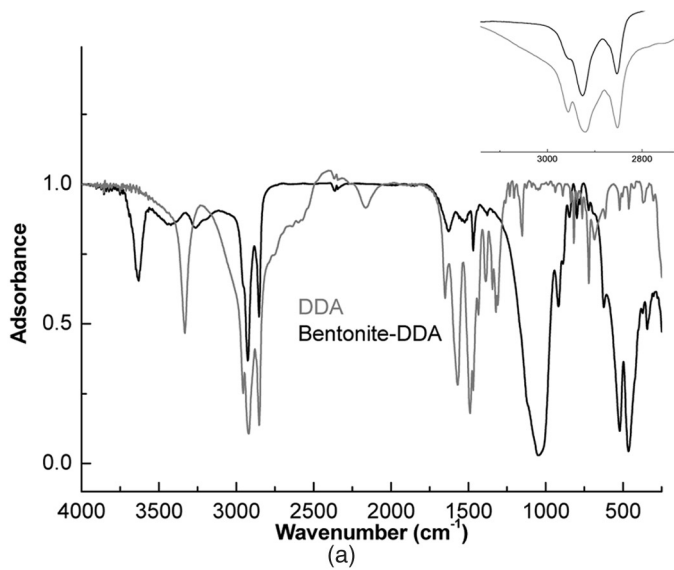


FIGURE 2 FT-IR spectrum of (a) Dodecylamine and [Bentonite(DDA)_{1.1}·2.3 (H₂O)]; (b) octadecyltrimethylammonium bromide and [Bentonite(OTAB)_{0.42}·1.9 (H₂O)].

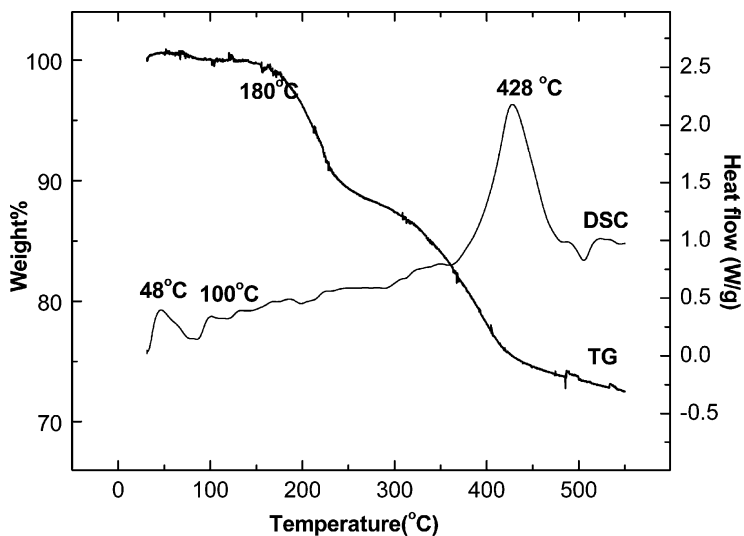


FIGURE 3 Thermal analysis of $[\text{Bentonite}(\text{HDA})_{0.94} \cdot 3.0(\text{H}_2\text{O})]$.

Powder X-ray diffraction analysis reveals that intercalated products are pure phases with diffractogram characteristics for ordered laminar species, in which a notorious increment of the interlamellar space in

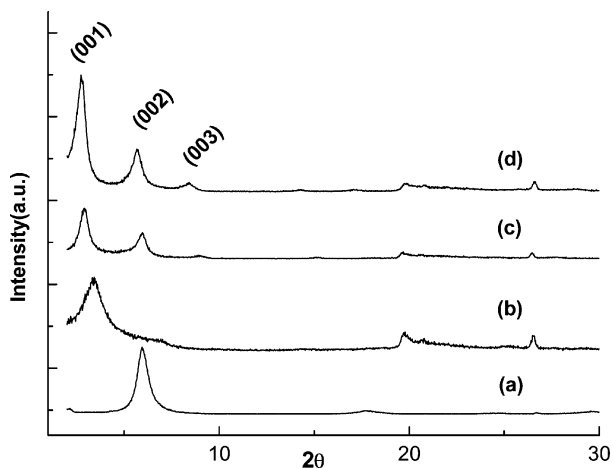


FIGURE 4 X-ray diffraction patterns of (a) Na-Bentonite; (b) $[\text{Bentonite}(\text{DDA})_{1.1} \cdot 2.3(\text{H}_2\text{O})]$; (c) $[\text{Bentonite}(\text{HDA})_{0.94} \cdot 3.0(\text{H}_2\text{O})]$; (d) $[\text{Bentonite}(\text{ODA})_{1.0} \cdot 4.5(\text{H}_2\text{O})]$.

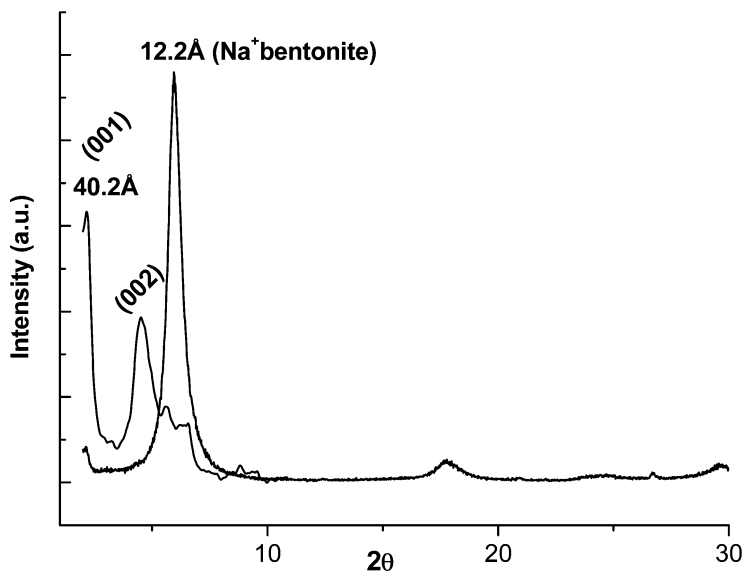


FIGURE 5 X-Ray diffraction pattern of (a) Na-Bentonite and (b) [Bentonita (OTAB)_{0.42} · 1.9(H₂O)].

the clay is observed. In Figures 4 and 5, the diffraction patterns of the obtained organic-inorganic nanocomposites are compared with that of the pristine clay. In these products, the interlaminar distances, determined from the position of the corresponding (001) diffraction peaks, reach values in the range 27 Å to 32 Å for the amines and 40 Å for the OTAB. Moreover, the detection of *00l* reflections with *l* > 1 in the refraction patterns reveals a one-dimensional order higher in the intercalates than in the pristine clay.

As observed from data in Table 2, the magnitude of the interlaminar distance depends on the surfactant chain length. All reactions were performed with the same surfactant/clay ratio, 3 mol per (Si,Al) unit of the clay; however, the stoichiometry of the products (Table 2) is

TABLE 2 Interlaminar Distances in Organo-Bentonite Nanocomposites

Composite	Δd Å	Length chain amine Å
Bentonite(DDA) _{1.1} ·2.3(H ₂ O)	27.0	18.0
Bentonite(HDA) _{0.94} ·3.0(H ₂ O)	31.2	22.0
Bentonite(ODA) _{1.0} ·4.5(H ₂ O)	32.1	25.0
Bentonita(OTAB) _{0.42} ·1.9(H ₂ O)	40.0	24.2

not always the same. For the amines the intercalation rate reaches approximately one mol per clay unit, while only 0.42 mol tetralkylammonium ions can be intercalated under the same conditions. These results can be better understood by considering the cation exchange capacity of our clay. Bentonite is a 2:1 type layered clay in which one Al, Mg octahedral sheet is sandwiched by two Si,Al tetrahedral sheets. The exchangeable cation capacity, *cec*, which corresponds to the amount of Mg and tetrahedral Al in the clay and which is also determined directly by exchange with ethylenediamine complex of Cu(II) ions, is in our case 0.47 mol per (Si,Al)₄ unit. Because of the similarity of the amount of intercalated tetraalkylammonium cation and the *cec* value, the driving force for the intercalation reaction appears to be mainly determined by the cation exchange. However, in the case of the neutral surfactants, where the exchange of sodium is not possible, the stabilization of the products appears to be achieved by at least two types of interactions, namely, the coordination of interlamellar sodium cations and van der Waals interactions between amine alkyl chains. Indeed, in the thermal analysis of the composite [Bentonite(HDA)_{0.94}·3(H₂O)] mentioned above (Fig. 3), two kind of intercalated amine molecules may be clearly distinguish. Approximately one half would be coordinated by the sodium cations, probably the fraction lost at higher temperatures, and the other one inserted between the formers. Taking in account the observed interlamellar distances and molecular models considering both, the stoichiometry of the composites and the space available in the aluminosilicate sheets [9], the arrangement of the guests in the interlamellar phase may be illustrated by the schemes in Figure 6. Thus, the intercalation of OTAB leads to a nanocomposite with some free space in the interlamellar phase, possible due to the steric hindrance produced by the

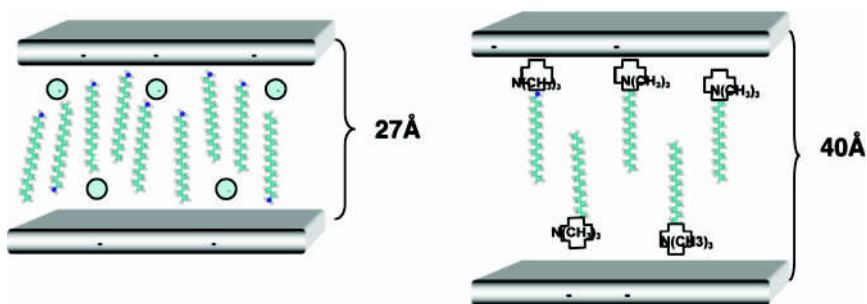


FIGURE 6 Schematic structure of the interlamellar phase in Bentonite-Surfactant nanocomposites.

surfactant heads, the trimethylammonium groups. This agrees with results obtained working with amines in an acid medium where a relatively high intercalation degree, (between 0.5 and 3.0 mol per clay unit) is also detected [10].

CONCLUSIONS

The intercalation of conventional surfactants like long-chain amines and their trimethylammonium salts leads to laminar nanocomposites. The interlaminar distances as well as the stoichiometry of the products depend mainly on both the structure and the charge of the surfactant. Intercalation of charged species is governed by cation exchange, the maximal stoichiometry being determined by the *cec* of the clay. Pillared products are obtained where part of the interlaminar space remains unoccupied. Intercalation of neutral surfactants leads to nanocomposites with interlaminar spaces in which the surfactant, stabilized by van der Waals interactions, is strongly compacted. These results contribute to the understanding of the nature of organo-clays and may prove useful when designing new nanocomposites, optimizing the manifold applications of this kind of products.

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