

Theoretical and experimental study of montmorillonite intercalated with tetramethylammonium cation

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ABSTRACT

Structural and vibrational features of Na-montmorillonite and montmorillonite intercalated with tetramethylammonium cation (TMA⁺) were characterized theoretically and experimentally. Theoretical study was performed using density functional theory with inclusion of dispersion corrections. The analysis of the hydrogen bonds in the calculated models has shown that the Na⁺ cations coordinated by six water molecules (Na-M model) are bound to montmorillonite layers by moderate hydrogen bonds between water molecules and basal oxygen atoms of the tetrahedral sheets. Hydrated Na⁺ cations are stabilized by relatively strong hydrogen bonds among water molecules. In the intercalate model, the TMA⁺ cation is fixed in the interlayer space by weak hydrogen bonds between the methyl groups and basal oxygen atoms of montmorillonite layers. The calculated vibrational spectra are in a good agreement with the measured infrared spectra. The detailed analysis of the simulated vibrational spectra allowed unambiguous identification of corresponding bands in the measured spectra and their assignment to the particular vibrational modes. For example, calculations clearly distinguished between AlMgOH and AlAlOH stretching vibrations and also between the coupled vibrations of the methyl groups of the TMA⁺ cations.

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1. Introduction

Clay mineral montmorillonite is an intensively studied material due to its broad range of possible industrial applications. Montmorillonite, a member of the smectite group, has layered structure consisting of two tetrahedral sheets linked to an octahedral sheet through sharing of apical oxygens. The octahedral sites are occupied mainly by Al(III) but partly substituted with Fe(III) and Mg(II). The tetrahedra contain Si(IV) as central atoms with some Al(III) substitution. Isomorphic substitutions prevail in the octahedral sheets generating negative excess layer charge (for smectites in the range of 0.4–1.2|e| per O₂₀(OH)₄). This layer charge is compensated by exchangeable, typically hydrated cations (Na⁺, K⁺, Ca²⁺, or Mg²⁺ in natural samples). The amount of water in interlayer space varies in dependence on external conditions. They can easily sorb/release a lot of water accompanied by a radical expansion/shrinking of the volume.

The surfaces of natural smectites have predominantly hydrophilic character [1]. Thus, non-polar organic compounds, which often contaminate water resources and soils, are not effectively sorbed by smectites. The ability of smectites to swell and

replace interlayer cations is often used to modify their hydrophilic character. The replacement of inorganic with organic cations via ion-exchange mechanism converts clay surfaces to hydrophobic. As a result, organoclays become effective sorbents also for non-polar organic contaminants giving them a potential usage in environmental applications and technologies [2–5]. Organoclays found also applications as ingredients in varnishes, fireproof coats, lubrication grease or as nano-fillers in polymer–clay nanocomposites [6,7].

The potential of organoclays as effective sorbents is under extensive investigation. Most often they are prepared using quaternary ammonium cations [(CH₃)₃NR]⁺ or [(CH₃)₂NRR']⁺, where R and R' are hydrocarbon chains [8]. One of the most intensively studied intercalated clays is prepared by intercalation of tetramethylammonium cation into smectite [9–11]. This intercalate can also be used as a precursor for preparation of organoclays with larger organic cations.

Detailed knowledge on the organoclay structure, degree of intercalation, orientation and distribution of organocations in the interlayer space can help in choosing suitable surfactants for preparing materials with predetermined properties. Several experimental techniques are used for organoclays characterization. For example, interlayer distance in clay minerals and/or organoclays (*d*₀₀₁ spacing) is determined by X-ray diffraction (XRD) methods. This value was used for prediction of the arrangement of alkylammonium cations in the interlayer space [12]. Cations with

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short alkyl chains are supposed to be arranged in monolayers, longer chain alkylammonium ions in bilayers with the alkyl chain axes parallel to the silicate layers or in pseudotrimolecular assemblies. Among spectroscopic methods, NMR and IR techniques were used to investigate the conformation of alkylammonium cations in organoclays [13–18]. The positions of the stretching CH_2 vibrations are sensitive to the arrangement of the hydrocarbon chains. The narrow bands near 2918 and 2850 cm^{-1} assigned to $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ vibrations, respectively, have been reported as characteristic for highly ordered all-trans conformations. A shift to higher wavenumbers indicates an increase in the number of gauche conformers reflecting the ‘disorder’ of the chains.

In spite of intense spectroscopic research of the organoclays, e.g. by IR and Raman spectroscopy [4,19–22] or UV–vis spectroscopy [23], many important questions remain open, or obtained experimental data have not been completely interpreted yet because of complex character of the studied organoclay materials. Thus, the methodology of molecular modelling, from quantum-chemical (QM) to empirical force-field (FF) methods along with molecular dynamics (MD) or Monte Carlo (MC) approach are found as a suitable complement to experimental studies [24–26]. Application of these methods in combination with realistic models of studied systems offers pure comprehensive information including about the bonding relations in organoclays, interaction energies, types of interactions between the clay layers and the guest cations, and also about thermodynamic and mechanical characteristics of the clays and/or organoclays. Infrared vibrational spectra can be calculated to significantly support their interpretation. Moreover, calculations on suitable models can help in planning of experiments for preparation of organoclays of required properties. The classic MD–FF method was used in several papers to investigate the interactions of various alkylammonium cations with minerals such as montmorillonite or mica [27–31]. Some studies [32–35] provided relations between the cation size and basal spacing. In contrast to the FF methods, no direct molecular simulations on organoclays based on quantum-chemical methods have been used so far. Only several QM studies were published on the clay minerals intercalated with small organic molecules. The systems kaolinite-dimethylsulfoxide, kaolinite-dimethylselenoxide, and kaolinite-N-methylformamide were modelled by means of density functional theory (DFT) approach [36–40] showing how small molecules are organized in the interlayer space, the nature of their binding to the layers, and the energy of formation of intercalated systems. Moreover, vibrational spectra have been simulated and used in the analyses of experimental data.

This is for the first time that the DFT approach is used in the simulation of the structure and vibrational spectrum of TMA^+ -montmorillonite. The calculations were performed in coordination with the experimental measurements of IR spectra. The aim of the study is characterization of the structure and interactions of the TMA^+ cations and montmorillonite layers at the molecular level and the interpretation and analysis of measured IR data by means of calculated vibrational density of states.

2. Materials and methods

2.1. Experimental details

Montmorillonite separated from the SAZ-1 bentonite (Cheto, AZ, USA) obtained from the Source Clays Repository of the Clay Minerals Society was used in the experiments. Its structural formula $\text{Na}_{1.22}\text{K}_{0.01}(\text{Al}_{2.59}\text{Fe}_{0.16}\text{Mg}_{1.26})(\text{Si}_{8.0})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ shows that the substitutions occur only in the octahedral sheets.

Infrared spectra were collected by a Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer from Thermo Scientific.

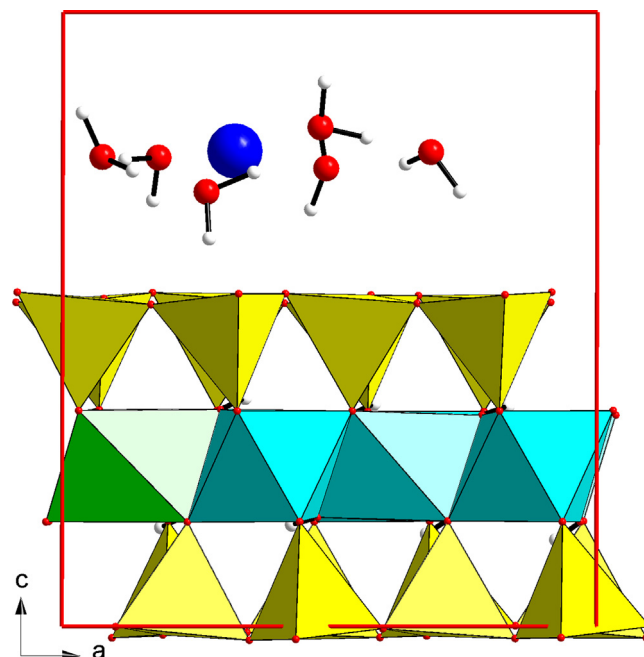


Fig. 1. Optimized structure of computational Na-M model.

The KBr pressed disk technique (1 mg of sample and 200 mg of KBr) was used to measure spectra in the mid-infrared region ($4000\text{--}400\text{ cm}^{-1}$). Spectra were obtained by co-addition of 64 scans at a resolution of 4 cm^{-1} . Spectral manipulations were performed using the Thermo Scientific OMNIC™ software package.

XRD patterns were measured on powder specimens in order to obtain the d_{001} spacings. The measurements were performed using a Bruker D8 Advance diffractometer with a Goebel mirror. The patterns were recorded in the range $1.5^\circ\text{--}72^\circ$ (2θ) using a step of 0.05° 2θ .

2.2. Computational models

Compositional variety and structural complexity of clay minerals usually require certain simplifications of the models used in molecular simulations, especially when quantum chemical methods are used. Owing to a lack of detailed structural data on the SAZ-1 montmorillonite used in the experiment, structural models for the calculations were derived from the monoclinic structure of Wyoming montmorillonite with structural formula of $\text{Na}_{0.75}(\text{Al}_{3.5}\text{Mg}_{0.5})(\text{Si}_{7.75}\text{Al}_{0.25})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ [41]. The structural models used in the calculations have simplified composition only with $\text{Al}^{3+}/\text{Mg}^{2+}$ substitution in the octahedral sheets (this simplification is in accordance with a composition of SAZ-1 montmorillonite used in experiments). Similar models with the same composition of the layers have also been used in a theoretical study of hydration steps of several cations in the interlayer space [25]. The model of montmorillonite with exchangeable Na^+ cation hydrated by six water molecules (Na-M) was used as an initial structure for simulations and preparation of models with intercalated TMA^+ cation (Fig. 1). The Na-M model has structural formula $(\text{Na}_{0.5}\text{Al}_{3.5}\text{Mg}_{0.5})(\text{Si}_8)\text{O}_{20}(\text{OH})_4 \times 6\text{H}_2\text{O}$ and starting cell parameters $a = 10.34\text{ \AA}$ twice greater than the original a vector from the work by [41], $b = 8.97\text{ \AA}$, $c = 9.95\text{ \AA}$, and $\beta = 99.5^\circ$. The model of the montmorillonite intercalated with TMA^+ cation (TMA-M) was constructed from the optimized Na-M model by replacing the $[\text{Na}(\text{H}_2\text{O})_6]^+$ with the TMA^+ cation. The starting cell parameters were $a = 10.472\text{ \AA}$, $b = 9.077\text{ \AA}$, $c = 15.099\text{ \AA}$, and $\beta = 95.85^\circ$ (Fig. 2). Additionally, calculations were also performed on the isolated

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