

Structure and stability of montmorillonites intercalated with *n*-butylammonium cations (*n* = 1-4) – DFT study.

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Modification of clay minerals by organic cations is a subject of great interest because of the possibility to develop new materials with the specific properties for new technological applications (e.g. polymer-clay nanocomposites, sorbents, deposits of radioactive waste, fireproof coats, etc.). Especially montmorillonite (Mnt) is suitable candidate for modification because of its swelling and ability to replace exchangeable cations. Knowledge on the structure and properties of organoclays is essential for their preparation and applications. Organomontmorillonites can be characterized by different physicochemical methods including infrared (IR) spectroscopy. In spite of the intense spectroscopic research of the organoclays, many important questions remain open or experimental data have not been completely interpreted yet because of the complex structure of the studied organoclay materials. In such situation molecular simulations can effectively complement experimental data.

This work is focused on the structure, dynamics, and stability of four *n*-butylammonium cations in the montmorillonite interlayer space and on the surface (mono-, di-, tri-, and tetra-butyl ammonium cations, *n*BA, where *n*=1-4). The structures of intercalates and surfaces are modeled by using periodic models and DFT approach. Preliminary results showed that the stability of the *n*BAM structures decreased with the increasing number of butyl chains in order 1BAMnt > 2BAMnt > 3BAMnt > 4BAMnt. The interaction energies were in a good correlation with the strength of the hydrogen bonds formed between cations and montmorillonite surfaces. Power spectra, calculated from the first principle molecular dynamics, helped in the interpretation of the complex IR spectra of *n*BA-organoclays.

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