

## MOLECULAR SIMULATION STUDY OF KAOLINITE INTERCALATION

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### EXTENDED ABSTRACT

Kaolinite is a common 1:1 type clay mineral, consisted of layers which are built up from one tetrahedral silica sheet and one octahedral aluminium hydroxide sheet. The layers are held together by hydrogen bonds forming a distinct space between the layers and this causes the cleavage and softness of the mineral. The equilibrium basal spacing of kaolinite is around 0.72 nm. Depending upon the application, kaolinite is often modified from its natural state by physical or chemical treatments to enhance the properties of the material. Kaolinite can intercalate various molecules in their interlayer space. Strong polar molecules can expand the basal spacing by disturbing the intermolecular hydrogen bonds between the layers. The obtained mechanically stable complexes have well defined basal spacings. The separation of kaolinite layers by reactive guest molecules (e.g. dimethyl sulfoxide, urea, formamide, potassium acetate) has been studied both experimentally and theoretically. In this work, molecular simulations and X-ray diffraction experiments were used to investigate the properties of kaolinite/urea and kaolinite/potassium acetate complexes. Urea has the earliest practical application in synthesis of organocomplexes of kaolinite, and potassium acetate is the substance by which one of the largest basal spacings can be achieved in direct kaolinite intercalation. Molecular simulations are suitable tools to study the adsorption and intercalation of molecules in clays. In our simulations the kaolinite model was constructed according to its experimental crystal structure [1] using a recently published thermodynamically consistent force field (INTERFACE [2]) to describe its intramolecular and intermolecular interactions. The INTERFACE force field operates as an extension of common harmonic force fields (AMBER, CHARMM, GROMACS, OPLS, etc.) by employing the same functional form and combination rules to enable accurate simulations of inorganic-organic (as well as inorganic-biomolecular) interfaces. According to the literature [2], the INTERFACE force field performs well in comparison to experimental data and alternative force fields. The validity of the force field parameters has been tested for several materials, such as layered silicates and fcc metals. For the guest molecules standard force fields (CHARMM for urea and potassium acetate, and SPCE for water) were applied. The simulations were performed using the GROMACS [3] program suit. The basal spacings were determined by series of NpT (fixed number of molecules, constant pressure and temperature) Molecular Dynamics (MD) simulations.

In control experiments, high-grade Zettlitz kaolin was used and a dry manual or a mechanical grinding technique was employed for intercalation. The basal spacings were determined by X-ray diffraction analysis based on the well-defined 001 reflections.

We investigated the hypothetical loading vs. basal spacing diagrams obtained from the simulations for the kaolinite/guest molecule complexes: the results are in agreement with the expectations, the basal spacing increases with the content of the guest molecules. Stable regions were identified, where the calculated distance is almost constant in function of the intercalated molecule content. The Gibbs free energy for the simulated systems with kaolinite was also calculated, where possible, to locate more precisely the loading in the stable structures. The simulated basal spacing data for the kaolinite/urea and kaolinite/potassium acetate complexes are in good agreement with our experimental X-ray diffraction results and other experimental data available in the literature. From the two types of stable kaolinite/potassium acetate intercalate complexes identified in this study, the one with larger basal spacing is formed with incorporating water into the interlayer space (only this complex can be produced by the basic synthesis procedure in air atmosphere).

The structure of interlayer molecules of the complexes was characterized by density profiles and molecular orientation distributions of the guest molecules obtained from simulation data. Our examinations validated the supposed (single- or double- layered) arrangements of guest molecules and revealed the character of the hydrogen bonds between the guest molecules and the layer surfaces.

### REFERENCES

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