Introduction & aim

Molecular simulations are suitable tools to study the adsorption and intercalation of molecules in clays. In this work, a recently proposed thermodynamically consistent force field for inorganic compounds (INTERFACE [1]), which enables accurate simulations of inorganic-organic interfaces, was tested for a two-sheet type clay mineral.

All-atom NpT molecular dynamics simulations were used to describe the characteristics (basal spacing, loading, molecular orientations) of some intercalate complexes of kaolinite.

Control experiments

- Material: high-grade Zettlitz kaolin, urea, potassium acetate
- Kaolinite/urea, kaolinite/potassium acetate intercalation compounds synthesized by grinding [2]
- X-ray diffraction analysis: Phillips PW3710 type diffractometer

Simulation Method

NpT MD simulations were used with the GROMACS [3] program suit. Basal spacings were determined for kaolinite at various guest molecule loadings.

Stable states of the intercalation compounds were identified where the guest molecule content undergoes a substantial change within a narrow range of the calculated basal spacing.

Force fields used in the simulations

Urea, Potassium acetate: CHARMM
Water: SPC/E
Kaolinite: INTERFACE

The INTERFACE force field:
- extension of common harmonic force fields (same functional form and combination rules),
- flexible models,
- enables accurate simulations of inorganic-organic interfaces,
- validity of the force field parameters has been tested for: layered silicates (mica, montmorillonite, pyrophyllite), silicates and aluminates in cement, other inorganic compounds, such as FCC metals, sulfates, phosphates, hydroxyapatite.
- energy expression:

\[ E_{\text{pot}} = \sum_i K_i |r_i - r_0| + \sum_i \sum_j |r_i - r_j|^{12} - \sum_i \sum_j |r_i - r_j|^{6} \]

Validation of the INTERFACE force field

Stable basal spacing and urea content

Results

Two types of stable kaolinite/potassium acetate intercalate complexes were identified, the one with larger basal spacing is formed with the incorporation of water into the interlayer space. The structure of interlayer molecules is characterized by density profiles and molecular orientation distributions for both cases.

Snapshots and density profiles for different types of kaolinite/potassium acetate intercalate complexes

- Kaolinite 69.6 m/m
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- Kaolinite 80.3 m/m
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- Kaolinite 69.2 m/m
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Structural analysis

- Density profiles indicate that at the higher basal spacing two well separated fluid layers develop.
  - \( d_{298} = 1.10 \text{ nm} \): the acetate ions try to turn with their dipole moment vectors to the Gibbsite-like sheet but most of the molecular planes are constrained in more or less parallel alignment with the clay layers.
  - \( d_{298} = 1.41 \text{ nm} \): the orientation distributions become more diffuse; there will be enough space for molecules to realize orientations nearly parallel to the z axis as well.

Conclusion

The INTERFACE force field proved to be appropriate for predicting the material properties of kaolinite. Simulations agree well with experiments concerning the key characteristics of the selected intercalate complexes of kaolinite. Our examinations confirmed some supposed (single- or double- layered) arrangements of guest molecules and revealed the character of interactions between the guest molecules and the layer surfaces. The need of interlayer water in the kaolinite/potassium acetate intercalation compound, which can be produced by the basic synthesis procedure in air atmosphere, was verified.