STUDY OF THE CHEMICAL POTENTIAL OF WATER IN SMECTITE CLAYS

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The chemical potential of water in montmorillonite pores is studied using molecular dynamics simulations. Thermodynamic integration (TI) was employed as this method enables precise calculation of free energy differences between alchemical states and is well-established for studying hydration thermodynamics in layered materials. While Grand Canonical Monte Carlo (GCMC) simulations are commonly used to determine water adsorption isotherms and equilibrium water uptake in clays, TI offers the advantage of directly yielding the chemical potential at fixed hydration states, which is essential for systematic comparison of temperature effects and cation types[1].

Montmorillonite is described with the ClayFF force field, which is flexible and non-polarizable. Its structure consists of an octahedral layer sandwiched between two tetrahedral layers. Models with Ca^{2+} and Na^{+} interlayer cations are considered.

Water is modeled using the TIP4P force field, in which the charge of the oxygen atom is displaced by 0.14 Å along the bisector of the hydrogen-bond angle. Coulomb interactions are treated with the particle-particle particle-mesh method. The model imposes rigid bonds and angles.

The system is brought to the target conditions and equilibrated for 1 ns. Subsequently, thermodynamic integration is performed. The interaction between one water molecule and the rest of the system is gradually decoupled. First, the Coulomb term is linearly ramped down with the coupling parameter over 12 steps. Then, the van der Waals term is switched off. Each trajectory at a given value of the coupling parameter is run for 500 ps, which exceeds the time required for the studied molecule to diffuse between the montmorillonite layers. The chemical potential is computed using 32 distinct values of the coupling parameter.

The temperature dependence of the chemical potential is investigated. A comparison between the Na^{+} and Ca^{2+} forms reveals distinct temperature dependent behaviors, which are interpreted in terms of differences in interlayer structure and cation hydration.

1. Teich-McGoldrick, S.L. et al. Cygan Swelling Properties of Montmorillonite and Beidellite Clay Minerals from Molecular Simulation: Comparison of Temperature, Interlayer Cation, and Charge Location Effects // *J.Phys.Chem.C.* 2015. Vol. 119, Nr. 36. P. 20880-20891. https://doi.org/10.1021/acs.jpcc.5b03253.

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