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Free energy calculations of cesium ion adsorption to the interlayer of montmorillonites using classical molecular dynamics

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The migration behavior of radionuclides in clay minerals used as buffer material must be clarified for the long-term safety of geological disposal of high-level radioactive waste. We can investigate diffusion/adsorption behavior of cesium ion and sodium ion in clay minerals and water systems at molecular scale using molecular dynamics simulation on a supercomputing system. In this study, we evaluate the free energy profiles of the cesium and sodium ions adsorption to the montmorillonite interlayer from bulk water in mesopore. We found that the free energies in the interlayer of Na-montmorillonite are smaller than those in the bulk water for the cesium and sodium ions, and the averaged free energy value for cesium in the interlayer is lower than that for sodium. This result shows that cesium ion is more strongly adsorbed to the interlayer of Na-montmorillonite than sodium ion. Moreover, we found differences in the shape of these free energy profiles in the interlayer. The free energy profile for the cesium ion has a spiky structure with many local minimums, although that for the sodium ion is almost uniform. These results suggest that the cesium ion forms the inner-sphere complex at these local minimums and the sodium ion forms the outer-sphere complex. Furthermore, we investigated salinity dependence on the free energy profiles. We confirmed that the affinities of both cations to Na-montmorillonite decrease with increasing salinity, and the adsorption mechanism of these cations does not depend on salinity. In the presentation, we discuss the free energy profiles with different layer charges, interlayer distances, etc.

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