Theoretical Studies with Density Functional Theory (DFT) on Ca/ Na Montmorillonite: Structure, Forces and Swelling Properties

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Outline

• Research Background
• Methods
• Results
• Conclusions and applications
Research Background

- Swedish KBS-3 disposal concept

Fig 1. Swedish KBS-3 repository design
Research Background

• Structure of Ca/Na-bentonite

Figure 2. Structure of bentonite buffer
Research Background

Fig 3. Schematic picture of a stack of montmorillonite lamella
Research Background

• Swelling ability of bentonite\textit{(smectites)}

\textbf{Fig 4.} Free swelling tests with pure montmorillonites. \textit{Birgersson et al. 2009}
Research Background

Fig 5. Height of test samples versus time measured for free swelling in deionised water. Birgersson et al. 2009
Methods

Theories

➢ Most popular methods:

• Hypernetted Chain Approximation (HNC)
• Modified Gouy-Chapman Theory (MGC)
• Density Functional Theory (DFT)
Methods

- HNC---Integral Equation Method
- MGC---Poisson-Boltzmann Theory (PB)
- PB and DFT

Fig 6. (a) PB picture. (b) DFT picture
\[ i(r) = b \exp\{ z_i e(r) \} \]

Ornestion-Zernick (O.Z.) equation

\[ h(r_{1,2}) = c(r_{1,2}) + h(r_{2,3})c(r_{1,3}) dr_3 \]

Total  Direct  Indirect

1-2: direct effect
3-2: indirect effect
Methods

• Restricted Primitive Model (RPM)

Fig 7. Schematic picture of two charged walls immersed in a bulk solution
Fig 8. Schematic picture of two clay platelets system being in equilibrium with pure water
Fig 9. Monte Carlo method for calculating pi (π)
Results: Structures

Density distributions for Monovalent Counterions

Fig 10. Density profiles $n(z)$ in mol dm$^{-3}$ for a system with two planar, charged walls in equilibrium with pure water and with only monovalent counterions between surfaces. The surface charge density is 0.267 C m$^{-2}$, ion size $d=4.25\,\text{Å}$, surface separations $h=3, 5, 10$ Å.
Results: Forces

Net osmotic pressure for monovalent counterions

\[ P = \frac{RT}{z} \]

\[ z = h + d \]

Surface charge: \[ 0.267 \text{C/m}^2 \]

Ion diameter: \[ d = 4.25 \text{Å} \]

HNC: Hypernetted Chain Approximation

WCA: Weighted Correlation Approximation

Fig 11. As Fig 10. Double layer net osmotic pressure.
Results: Forces

Fig 12. but for the system with only divalent counterions, the surface charge density is varied from 0.13 to 0.05 C m\(^{-2}\), \(d=4.0\text{Å}\)
Results: Forces

Fig 12. As Fig 11. but the fraction of surface charge neutralized by monovalent counterions is indicated in figure. The surface charge density is 0.11 C/m^2.
fraction of sodium ≈ 30%

**Fig 13.** Relative number of layers per particle as a function of surface coverage when the Ca\(^{2+}\) ions exchanged by Li\(^+\), Na\(^+\), K\(^+\), Cs\(^+\) and Mg\(^{2+}\) ions (Schramm and Kwak, 1982a).

From (Jasmund and Lagaly, 1993)
Conclusions and applications

• Simulations agree quite well with the MC data
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