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Monte Carlo and molecular dynamics simulations of methane in potassium montmorillonite clay hydrates at elevated pressures and temperatures

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Abstract

The structure and dynamics of methane in hydrated potassium montmorillonite clay have been studied under conditions encountered in sedimentary basin and compared to those of hydrated sodium montmorillonite clay using computer simulation techniques. The simulated systems contain two molecular layers of water and followed gradients of 150 bar km^{-1} and 30 K km^{-1} up to a maximum burial depth of 6 km. Methane particle is coordinated to about 19 oxygen atoms, with 6 of these coming from the clay surface oxygen. Potassium ions tend to move away from the center towards the clay surface, in contrast to the behavior observed with the hydrated sodium form. The clay surface affinity for methane was found to be higher in the hydrated K-form. Methane diffusion in the two-layer hydrated K-montmorillonite increases from $0.39 \times 10^{-9}\ \text{m}^2\,\text{s}^{-1}$ at 280 K to $3.27 \times 10^{-9}\ \text{m}^2\,\text{s}^{-1}$ at 460 K compared to $0.36 \times 10^{-9}\ \text{m}^2\,\text{s}^{-1}$ at 280 K to $4.26 \times 10^{-9}\ \text{m}^2\,\text{s}^{-1}$ at 460 K in Na-montmorillonite hydrate. The distributions of the potassium ions were found to vary in the hydrates when compared to those of sodium form. Water molecules were also found to be very mobile in the potassium clay hydrates compared to sodium clay hydrates.

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1. Introduction

The structure and mobility of aqueous and organic fluids in swelling clay minerals are crucial to the location and migration of petroleum hydrocarbons in the soil.

Clays are layered aluminosilicates with structures and interlayer pores that are ideal for studying fundamental properties of confined fluids. They are found in terrestrial environments and marine sediments, and form a basic component of soil. 2:1 clays are made up of sheets of octahedrally coordinated cations sandwiched between two sheets of tetrahedrally coordinated cations. The internal pores are saturated by hydroxyl groups and several molecular layers of absorbed water. Negative layer charges arise from isomorphic cation substitution of the tetrahedral and octahedral cations. These layer charges are balanced by charge compensating counterions such as Na^+ and K^+ and tend to form ionic solutions with water molecules found in hydrated clays thereby forcing the clay layers apart and resulting in swelling. A number of studies have been performed to highlight and understand how swelling clay minerals play a crucial role in oil and gas production and exploration [1,2]. In addition, there have been several simulations and experimental studies directed at understanding the structure and dynamics of interlayer species in clays [3–6]. Sposito et al. [4,5] reported the simulation of radial distribution function for interlayer water in lithium, sodium and potassium montmorillonite. Sutton and Sposito [7] also used molecular simulation to investigate the interlayer water structure of Cs-smectite hydrates. Understanding the structure and behavior of these interlayer species will help alleviate the problem of borehole instability

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commonly associated with the uptake of water by smectite from drilling fluids. Previous work has shown that sorption of water by different smectite clays is dependent on the size and charge of the hydrating counterion which is largely responsible for the swelling behavior of clays [8–10].

However, most of these previous works have focused largely on clay–water-cation systems, with few comparable studies existing on the interaction of hydrocarbons and organics fluids with interlayer species. In a recent study, Park and Sposito [11] used simulation techniques to investigate the effect of montmorillonite surfaces on methane hydrate formation and proposed the occurrence of methane hydrate in natural sediment in presence of clay surfaces at ambient condition.

One of our aims in this work is to use simulation techniques to investigate the underlying mechanism of smectite clay swelling in the presence of organic fluids. We determine the structure and mobility of methane in the interlayer region of potassium montmorillonite hydrated clay and monitor the impact of hydrophobic molecules on the microscopic properties of other interlayer species. We compared our results with previous studies on sodium montmorillonite hydrated clay [12,13] and investigate the difference between the role of K^+ and Na^+ ions as clay swelling inhibitors in the presence of organic molecules.

2. Methods

A combination of constant stress Monte Carlo (MC) and constant volume molecular dynamics (MD) methods using the codes MONTE and DLPOLY was used in the simulation [14,15]. Skipper and Sposito et al. [10,14] have developed methodology for investigating clay minerals while the general principles of these simulations techniques have been described by Frenkel and Smit [16].

The model clay mineral is a "Wyoming"-type smectite clay, of composition $[Al_{28}Mg_4][Si_{62}Al_2]O_{160}(OH)_{32}^{6-}$, with 6 charge compensating potassium cations, 4 methane particles, and 64 water molecules corresponding to a two-layer hydrate system.

The simulation cell in the Monte Carlo runs is composed of opposing 21.12 × 18.28 Å^2 clay mineral particles. This simulation cell was doubled in the direction normal to the clay sheets for the molecular dynamics runs, thus allowing us a cutoff distance of 9 Å in the minimum image convention used in the MD program DLPOLY. Temperature and pressure conditions corresponding to specific burial depth up to 6 km were introduced in the simulation to reproduce the pressures and temperature encountered in a typical petroleum-rich sedimentary basin. A compacting stress gradient of 150 $\mathrm{bar\,km^{-1}}$ and a geothermal gradient of 30 $\mathrm{K\,km^{-1}}$ were used in the simulations [2].

In the simulation cell, water and methane molecules were initially arranged randomly, while the potassium counterions were assigned positions opposite the clay negative charge sites. The interlayer species were then selected randomly to move for over 5 million MC steps. This gave information on total potential energy of the system, interlayer species positions including orientations, and clay layer spacing.

The equilibrium configurations obtained from MC calculations were then used as starting configurations in the MD simulations. The MD simulations were performed with a timestep of 0.5 fs for up to 800 ps using an NVT ensemble. Interlayer molecular configurations were stored every 1000 steps and used for results analysis. The simulation used Ewald summation technique with 3-dimensional periodic boundary conditions.

The potential model used for the water molecules is based on the TIP4P model of Jorgensen at al. [17] where water was treated as a rigid molecule with four intermolecular interaction sites. Methane was represented by a single Lennard–Jones in the OPLS model [18], and the interactions involving the clay mineral with interlayer species follow the methods described by Boek et al. [19]. These interactions are pairwise additive involving Coulomb and Lennard–Jones 6–12 potential of the form

$$U(r) = \sum\left(\frac{q_i q_j}{r_{ij}} - \frac{A_{ij}}{r_{ij}^6} + \frac{B_{ij}}{r_{ij}^{12}}\right), \tag{1}$$

where U is the potential energy of the system, the indices i and j indicate charge sites on each of the two interacting species, q is the effective charge on a site, r_{ij} is the intermolecular site separation, and A and B represent the van der Waals attractive and short-range repulsive terms, respectively. The potential parameters employed in the simulation follow those used in previous studies for Na-montmorillonite [13] while the additional interaction parameters used are K–O/O$_w$: $A = 1.17 \times 10^3$, $B = 6.33 \times 10^5$; K–K: $A = 2.25 \times 10^3$, $B = 6.68 \times 10^5$; K–CH$_4$: $A = 2.67 \times 10^3$, $B = 2.39 \times 10^6$, with the units of kcal Å^6 mol^{-1} and kcal Å^{12} mol^{-1} for A and B, respectively.

The self-diffusion coefficients for the interlayer species were calculated using 3D Einstein relation:

$$D = 1/6\mathrm{d}/\mathrm{d}t\left\langle\left|r(t-t_0)\right|^2\right\rangle, \tag{2}$$

where $\langle|r(t-t_0)|^2\rangle$ is the mean-square displacement, t is the simulation elapsed time and t_0 is arbitrary starting point. The slope of plots of the mean-square displacement against simulation time $20 < (t - t_0) < 200$ after equilibration was used in obtaining the diffusion coefficients.

3. Results and discussion

Two-layer hydrate K-montmorillonite simulations were performed with 64 water molecules, 4 methane, and 6 potassium ions as interlayer species. Five different sets of simulation were carried out with each set simulated at different temperature and pressure that correspond to burial depths of 0, 1, 2, 3 and 6 km under gradients of 150 $\mathrm{bar\,km^{-1}}$

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