Molecular Simulation of Aqueous Methane Between Na-Montmorillonite Clay Interlayers

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Introduction

- Because of its abundance and high energy density, natural methane is an important source of energy.
- **Aqueous methane** can form crystalline hydrates under specific T/P conditions. Methane molecules will be trapped in a lattice of smaller water molecules.
- Clay swelling occurs within clay surfaces due to an uptake of water from surrounding micro-pores (Rotenberg et al. 2007). This can inhibit the free flow of the oncoming fluid.
- Many methane reservoirs contain clays of various types with high degrees of swelling properties.
- Improper exploitation of reservoirs could result in rapid decomposition, wellbore instability, landslides and even collapse.

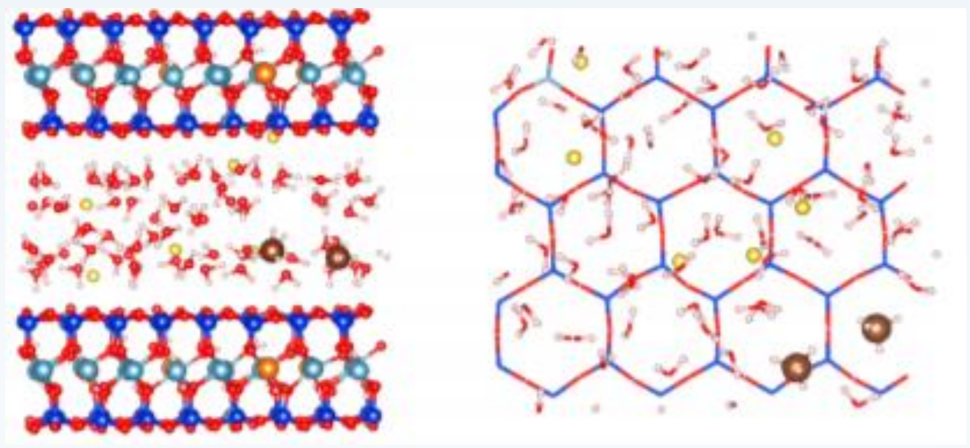

Fig. 1: Snapshot of simulation of hydrated methane vapor structure in the clay interlayer.

Objectives

- How do thermodynamic conditions effect the interactions between methane aqueous fluids and the surrounding clay surfaces?
- The parameters that were experimented with are temperature, pressure, and relative humidity. **Vary based on burial depth.**
- Data was used to analyze the swelling properties of Na-Montmorillonite clay.

Methods

- Peng-Robinson equation of state to find partial pressures of each species along with Widom's Insertion Monte Carlo simulations were used to find chemical potentials.
- **Towhee:**
  - The CLAYFF forcefield, clay minerals and water molecules (Cygan et al. 2004).
  - Methane, Jorgensen's OPLS all atom (OPLS-AA) model (Jorgensen et al. 1996).
- **Grand Canonical Monte Carlo (GCMC) Simulations:**
  - 10 million moves, basal spacing from 13 to 24 Å (insertions, deletions, translations, and rotations).
  - 30 million move continuing runs were performed to obtain water and methane contents.

Results

Key: T = Temperature, P = Pressure, RH = Relative Humidity, n = number of molecules

TABLE 1
Chemical Potentials at Various T/P/RH

T (K)	P (bar)	RH (%)	Chemical Potential -Water (KJ/mol)	Chemical Potential - Methane (KJ/mol)
300	20	5	−53.08 ± 0.01	−28.01 ± 0.02
300	20	10	−51.35 ± 0.04	−28.01 ± 0.02
300	20	20	−49.63 ± 0.05	−28.01 ± 0.02
300	30	10	−51.35 ± 0.04	−27.02 ± 0.02
300	30	20	−49.63 ± 0.05	−27.02 ± 0.02
300	50	20	−49.63 ± 0.05	−25.80 ± 0.03
300	50	30	−48.62 ± 0.03	−25.80 ± 0.03

TABLE 2
Water and Methane Contents at Various T/P/RH

T (K)	P (bar)	RH (%)	Equil. Basal Spacing (Å)	n - water	n - methane
300	20	5	15.5	36	4
300	20	10	16.0	45	3
300	20	20	17.0	78	1
300	30	10	16.1	44	5
300	30	20	17.0	70	2
300	50	20	17.4	75	3
300	50	30	17.9	91	1

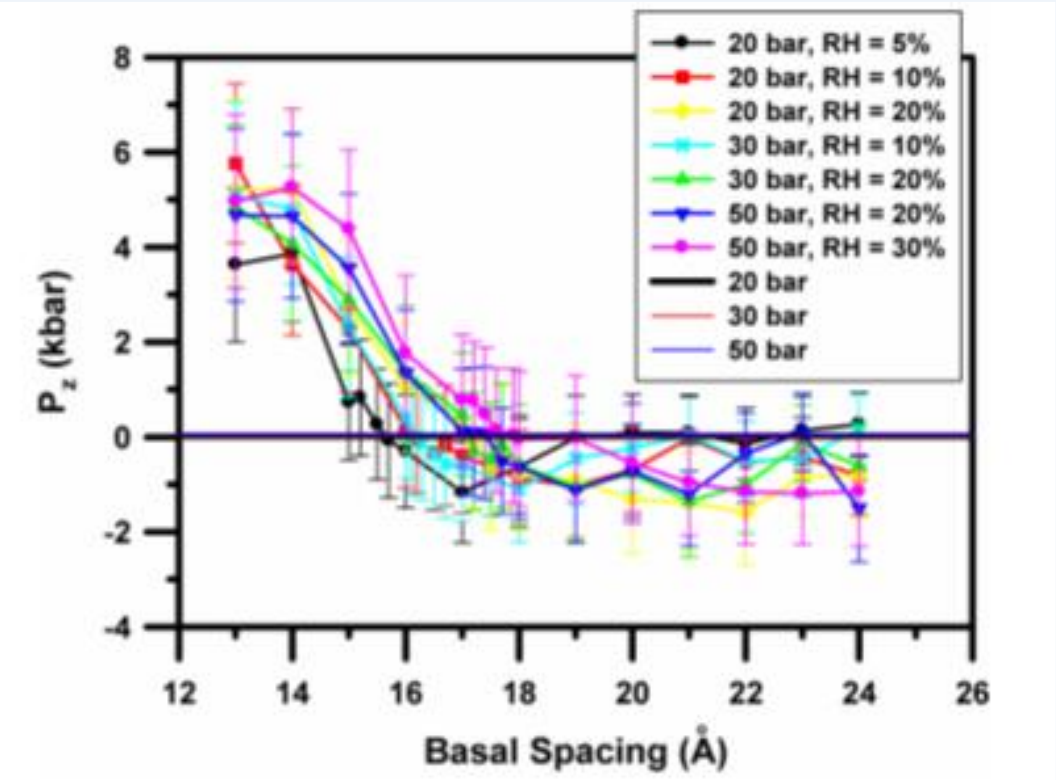

Fig. 2: Normal pressure curves as a function of basal spacing of Na-montmorillonite under various T/P/RH conditions.

- A higher chemical potential is attributed to higher degrees of intercalation.
- increase in P and RH would lead to more water and methane molecules entering the clay interlayer.
- Equilibrium basal spacing is the height of the clay interlayer at which the confined aqueous methane fluids are thermodynamically stable

Conclusions

- Higher relative humidity and low pressure will allow **water** to enter the interlayer.
- Lower relative humidity and higher pressure will allow **methane** to enter easier.
- It can be assumed that initial clay swelling properties are dominated by water adsorption.
- For practical application of the results, analysis would have to be made on each specific case as necessary.

Future Work

- In future experiments, it would be valuable to explore the swelling properties of other common clay minerals.
- Trends could be confirmed using different parameters (different depths) or with other molecule types.

Selected References

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