Molecular Dynamics Simulation of a new effective inhibitor for CO_2 hydrate formation

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Introduction

- The production of gas hydrates is a serious challenge in natural gas processing and transportation, which prompts to the intensive research and development of gas hydrate inhibitors, ranging from thermodynamic inhibitors (THI) and kinetic inhibitors (KHI).
- Current experimental results in our group introduce the hydrate-inhibitory behavior of Triethylenetetramine (TETA), a very promising amine for CO2 hydrates. The high hydrophilicity of TETA, caused by its primary and secondary amino groups, has prevented water molecules from rearranging for hydrate formation in the CO2-hydrate system.
- Motivated by the result, this project aims to qualitatively understand and examine the potency of TETA from the microscopic perspective with the assistance of molecular dynamics (MD) simulations.

Methodology

- The simulation box for each simulation is made of 5 different layers. From left to right: a layer with CO2 molecules in gas (1), a water block with dissolved CO2 and TETA molecules (2), a second hydrate slab (3), the same water and CO2 box is also repeated on the right side of the hydrate slab (4,5). Three different simulation boxes with different concentrations of TETA (50, 125, 250 molecules dissolved in each water/CO2/TETA block) were prepared.
- Regarding the force fields used in the simulations, the TIP4P/ICE model (Abascal et al., 2005) was used for water, while the TETA was parametrized by the general Amber force field (Wang et al., 2004). Moreover, the CO2 molecule was parameterized considering all the oxygen atoms, using TraPPE (Transferable Potentials for Phase Equilibria) model (Potoff & Siepmann, 2001).
- All simulations were conducted through GROMACS package.

Results

1. The number of gas hydrates formed during *NPT* simulations

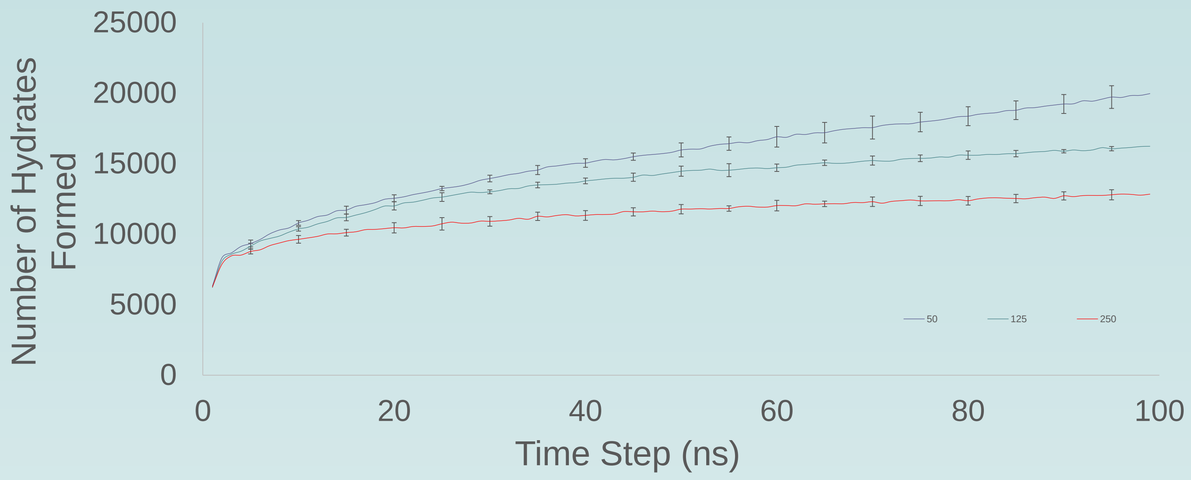
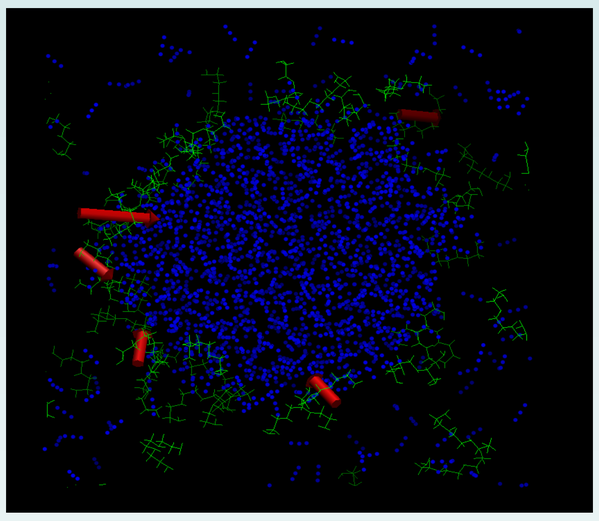


Figure 1. The number of gas hydrates existed during the *NPT* simulation at three different concentrations of TETA (50/125/250 molecules)

2. The agglomeration of TETA molecules between water and gas hydrates.



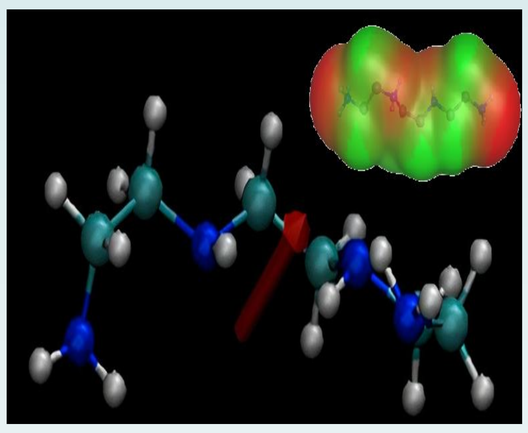


Figure 2. Left: Dipole moment of some TETA molecules within a representative CO2 nanobubble. Right: Hydrophilic (Red) and Hydrophobic (Green) regions with a TETA molecule

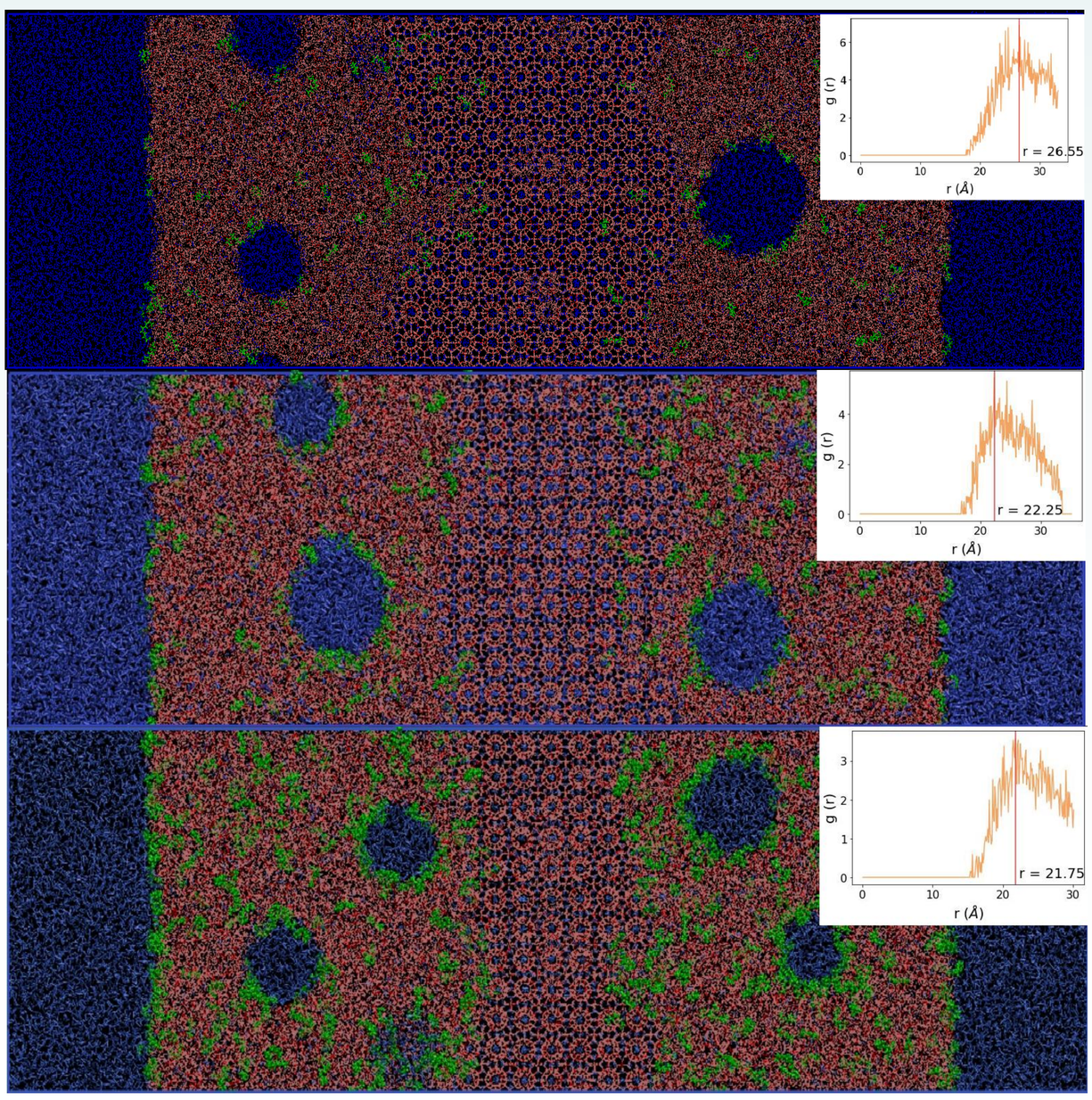


Figure 3. Last snapshot of each simulation box (50/125/250 TETA molecules) respectively

Conclusion

- The concurrent melting and forming of gas hydrates from the three snapshots confirm the observations of our previous experimental research, which shows that increasing concentration of TETA inhibitors will lead to longer induction time for gas hydrates.
- One TETA molecules' layer covers each CO2 nanobubble and their dipole moments are perpendicular to the surface of CO2 nanobubbles.
- TETA molecules agglomerate on the interface layer between water and CO2 gas hydrates, making strong hydrogen bonds to the water molecules using their hydrophilic amino groups. This result confirms our previous results, suggesting that hydrogen bonding between TETA and water is the major factor which distracts water molecules from the formation and stabilization of CO2-water hydrates

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References

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