# Bulk and Interfacial Properties of Alkanes in the Presence of Carbon Dioxide, Methane, and Their Mixture

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## Introduction

The emissions of CO2 into the atmosphere play an important role in global warming and lead to key environmental problems. Interestingly, enhanced oil recovery (EOR) methods have been employed for CO2 storage and improving oil recovery. Usually impurities such as CH4 are present along with the CO2 removed from exhaust gases of power plants and industrial processes.

In this work, molecular dynamics (MD) simulations are performed to study the bulk and interfacial properties of systems containing alkanes (our model oil), CH4, and CO2 under geological conditions. Linear, branched, and cyclic alkanes (C7-C19) are considered for this work. Furthermore, theoretical analysis based on the predictive Peng–Robinson equation of state (EoS) in combination with density gradient theory (DGT) was used for comparison with the simulation results.

## Simulation Model and Methods

The 2-phase simulation setup used in this work is provided in Figure 1 [1,2]. The simulation box has dimensions of about 50 × 50 Å in directions parallel to the interface. Alkanes, $CH_4$, and $CO_2$ are modeled using the transferable potentials for phase equilibria (TraPPE) force field. A 10 ns equilibration MD simulation in the *NPT* ensemble is followed by a 6 ns production run in the *NVE* ensemble. The equations of motion are integrated using the leap-frog algorithm with a time step of 1 fs.

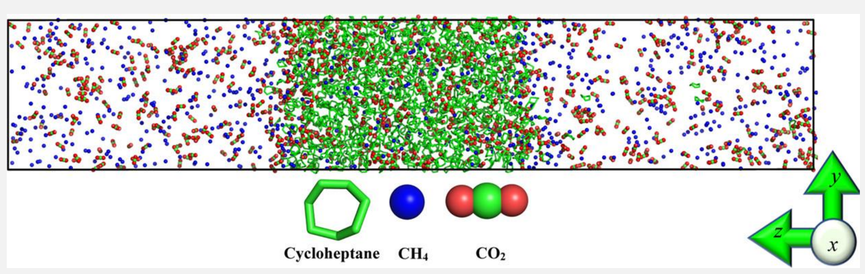


**Figure 1.** Equilibrium snapshot of the CH4+CO2+alkane (cycloheptane) system at 323 K and 100 bar.

## Results

### Bulk Properties

Density profiles show preferential dissolution in the alkane-rich phase and accumulation in the interfacial region of $CO_2$ from the $CH_4/CO_2$ mixture.

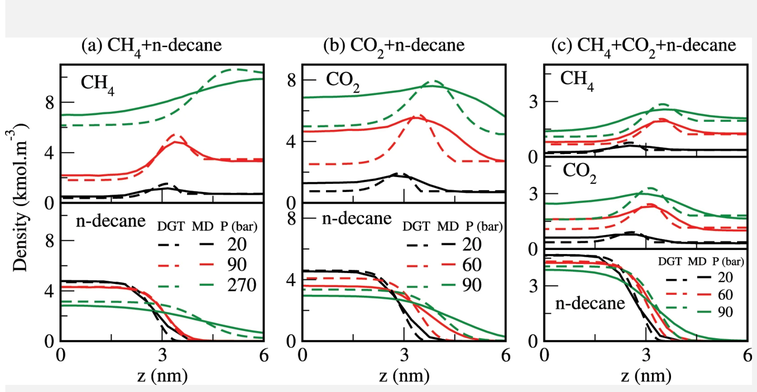


**Figure 2.** Atomic density profiles of CH4, CO2, and decane.

In general, mole fractions of CO2 and CH4 increase with increasing pressure and decreasing temperature.

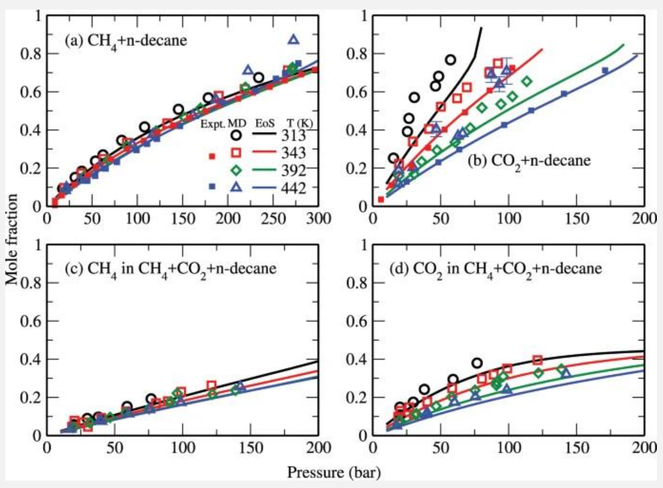


**Figure 3.** Mole fractions of CH4 and CO2 in the decane-rich phase.

### Bulk Properties

Swelling results are, in general, consistent with the behavior observed for the solubility data.

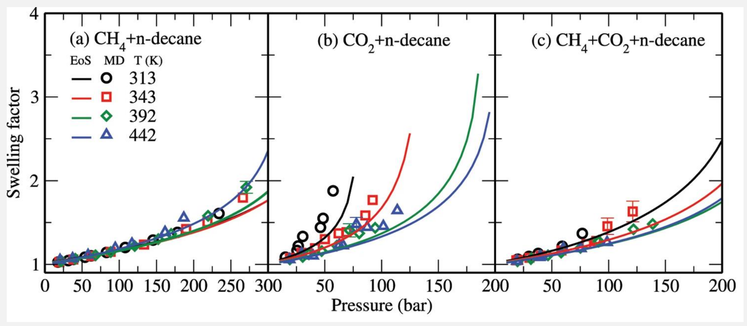


**Figure 4.** Swelling factor of the alkane-rich phase.

Radial distribution functions (RDFs) show that $CO_2$ molecules are positioned relatively closer to alkane. The magnitude of the first peak is relatively higher in the cycloalkane systems.

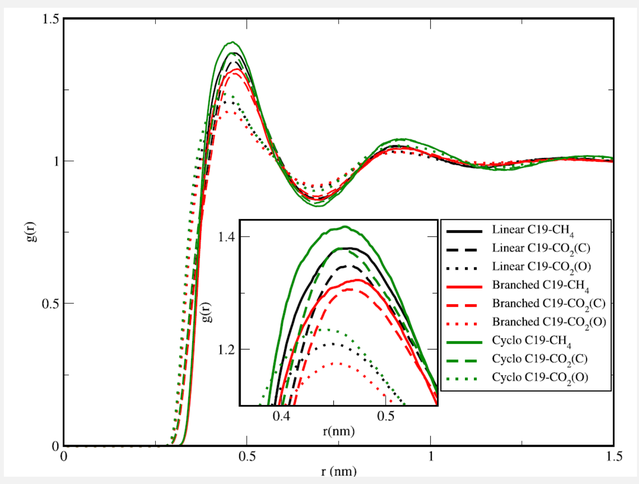


**Figure 5.** RDfs between alkane and CH4/CO2 in the bulk liquid phase at 323 K and 100 bar.

### Interfacial Properties

Interfacial tension (IFT) values of the $CO_2$+alkane system increase with the addition of $CH_4$.

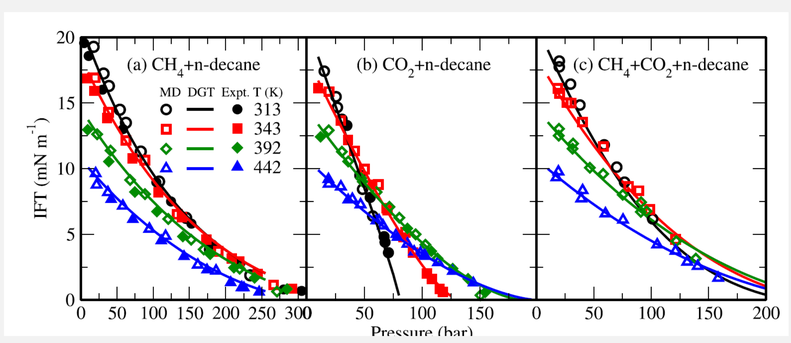


**Figure 6.** IFTs of decane+CH4/CO2 systems.

The relatively higher surface excess of the CO2+alkane system results in a steeper decrease in its IFT as a function of pressure

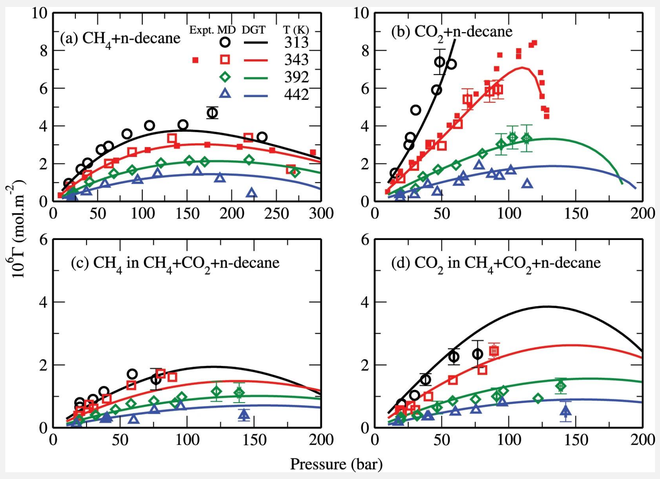


**Figure 7.** Surface excess of CH4 and CO2.

## Conclusions

- Preferential dissolution in the alkane-rich phase and accumulation in the interfacial region of $CO_2$ from the $CH_4/CO_2$ mixture.
- IFT values of the $CO_2$+alkane system increase with the addition of $CH_4$.
- Cyclization effects are more important than branching effects for the bulk and interfacial properties.
- MD results agree with theoretical analysis based on the predictive Peng–Robinson EoS in combination with DGT.

## References

1. Choudhary, N., Nair, A. K. N., Ruslan, M. F. A. C., & Sun, S. (2019). Bulk and interfacial properties of decane in the presence of carbon dioxide, methane, and their mixture. Scientific reports, 9(1), 1-10.
2. Choudhary, N., Ruslan, M. F. A. C., Nair, A. K. N., & Sun, S. (2021). Bulk and interfacial properties of alkanes in the presence of carbon dioxide, methane, and their mixture. Ind. Eng. Chem. Res., 60(1), 729-738.

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