

ADSORPTION DIAGRAMS OF n-ALKANES IN MULTISCALE KEROGEN POROSITY, DIFFUSION

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Introduction

Organic shale raises an important ecological and economical concern in the last decades. This unconventional hydrocarbon source is a mixture of n-alkane molecules trapped into connected or non-connected nanopores (<2nm), mesopores (2-50nm) and macropores (>50nm) of an organic disordered carbon structure called kerogen. At small pore sizes, the Darcy law fails to describe hydrocarbon diffusion into kerogen structures. Indeed, at nanoscale, confinement leads adsorption to show different behaviors from their bulk counterpart. Long alkanes are in a condensed liquid-like phase, while they are in gaseous phase for bulk. Thus, bulk viscosity becomes inappropriate to determine transport properties in nanopores. Small pore sizes with complex porous geometry open questions which have to be clarified in order to build a model able to predict various behaviors as production decline taking place during shale gas exploitation. We focused on adsorption mechanisms corresponding to the diffusion limiting factor at small pore scale. A thermodynamic study was performed to determine the alkane chain length distribution according to porous diameter.

Materials and Methods

A synthetic structure consisting of slit nano and mesopore shaped into dense kerogen was first used to extract qualitative adsorption behaviors. In a second time a realistic atomistic kerogen structure was used for quantitative calculation. This last structure was obtained by Hybrid Reverse Monte Carlo technique³, by fitting experimental radial distribution function of real kerogen samples. Mesoporosity was added from Microscopy 3D imaging tomography (figure 1.A) then relaxed by Molecular Dynamic using reaxFF force field⁴. Adsorption was performed by CBGCMC (Configurational Bias Grand Canonical Monte Carlo) simulations¹ based on coarse grained OPLS (Optimized Potentials for Liquid Simulations) potential² for methane, hexane and dodecane. For each alkanes, we determined adsorption isotherms in between T=300K and T=700K for pressure in between P=10⁻⁶ MPa and P=100MPa. We show that adsorption in nano and/or mesopores presents a clear selective adsorption behavior depending on alkane lengths, pore sizes and thermodynamical parameters as a function of pressure and temperature.

Results and Discussion

We first determined adsorption isotherms for methane, hexane and dodecane from T=300K upto 900K in a slit nano and mesopore in kerogen structure. Regarding chain lengths, adsorption isotherms present different behaviors. Short alkanes as methane are adsorbed in all pores, regardless pore sizes, at any given pressure and temperature. Adsorption isotherm increases monotonically with pressure and follow a Langmuir shape. Below T~500K at low P,

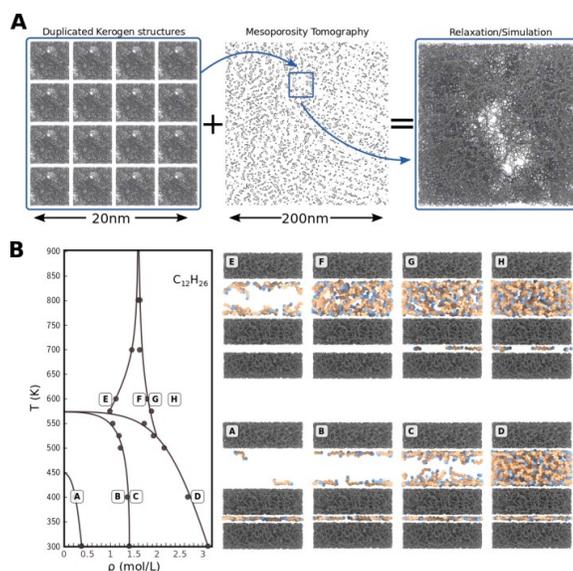


Figure 1 A) Duplicated nanoporous kerogen, mesoporosity is then inserted from tomography images. B) Temperature-Density adsorption diagram for dodecane. Adsorption in the different phases are shown at the right side.

hexane and dodecane are first adsorbed into nanopores. Mesopore remains empty upto the condensation pressure, then mesopores fill upon a very small pressure increase. This behavior is characterized by discontinuities on isotherms. At higher T, dodecane and longer alkanes show an opposite behavior. Above $T \sim 500\text{K}$ at low P, nanopores are disfavored, while mesopores adsorbed molecules. This pore size selectivity can be explained by large configurational entropy which dominate for long chains at large T. Interplay between kerogen porosity, alkane length and thermodynamics are shown in the adsorption diagrams, delimiting each behavior described for various alkanes regarding pressure and temperature (Figure 1.B). These diagrams have also been determined for the realistic nano/mesoporous kerogen and present a qualitative agreement with slit pores structure.

Conclusions

We show a selective alkane adsorption depending on pore sizes, alkane lengths, pressure and temperature of the system governed by a competing effect between alkanes adsorption energy and conformational entropy. These diagrams offer a thermodynamical map of alkane distribution into nano and mesoporosity and a better knowledge about molecules distribution in kerogen for various geological conditions.

References

1. Slepman, J. I., Frenkel, D. (1992). Configurational bias Monte Carlo: a new sampling scheme for flexible chains. *Mol. Phys.* 75, 50-70
2. Jorgensen, W.L., Tirado-Rives, J. (1988). The OPLS Force Field for Proteins. Energy Minimizations for Crystals of Cyclic Peptides and Crambin. *J. Am. Chem. Soc.* 110, 1657-1666
3. Bousige, C., Ghimbeu, C.M., Vix-Guterl, C., Pomerantz, E.A., Suleimenova, A., Vaughan, G., Garbarino, G., Feygenson, M., Wildgruber, C., Ulm, F.-J., Pellenq, R., Coasne, B. (2016). Realistic molecular model of kerogen's nanostructure. *Nature*. 576-582
4. Chenoweth, K., van Duin, A. C.T., Goddard III, W. A., (2008) ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. *J. Chem. Phys.* 112, 1040-1253