QUANTIFYING THE INTERFACIAL INTERACTIONS OF KEROGEN, WATER, AND HYDROCARBON AT DIFFERENT THERMAL MATURITY LEVELS AND ITS IMPACT ON FLUID MOBILITY

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ABSTARCT

Wettability of organic-rich mudrocks has significant impacts on multiphase fluid flow and hydrocarbon recovery. Since kerogen can constitute a significant volumetric fraction of mudrocks, the wettability of kerogen can considerably affect the wettability of organic-rich mudrocks. In a recent project, we showed using a combination of experimental methods and molecular simulation studies that kerogen type, thermal maturity, and reservoir temperature conditions affect the contact angle of water droplet on kerogen surface. This indicates that the wettability of kerogen is variable with its geochemistry and reservoir conditions. However, these studies do not consider the impact of having a third phase hydrocarbon in the reservoir system. Moreover, wettability affects the distribution of fluids in the porous media and the relative fluid mobility of reservoir fluids. However, the impact of kerogen wettability on fluid mobility is yet to be understood at a molecular level.

Therefore, in this research project, we plan to use molecular dynamics (MD) simulations to determine the impact of kerogen geochemistry and reservoir conditions on three phase contact angles of water and hydrocarbon on kerogen surface. We also use MD simulations to determine the impact of wettability on mobility of fluids in kerogen pores. We use realistic molecular models of kerogen. The chemical structure and composition of these molecular models are verified against experimental data for kerogen including Fourier transform infrared (FTIR) measurements, X-ray photoelectron spectroscopy (XPS) measurements and X-ray fluorescence (XRF) measurements. The results obtained from MD simulation will be verified against experientially measured three-phase contact angles on kerogen surface. Furthermore, wettability of kerogen surface impacts the interaction between the fluid and the kerogen pores and, therefore, affects the relative permeability/mobility of different fluids in the kerogen pore space. In this work, we simulate water and oil transport through the kerogen pores of varying hydrophilicities by using MD simulations to determine the impact of kerogen wettability on the fluid mobilities.

INTRODUCTION

Wettability of organic-rich mudrocks impacts the multiphase and multicomponent transport in organic-rich mudrocks. Therefore, it is important to understand the factors affecting the wettability of organic-rich mudrocks for developing reliable models for fluid transport in mudrocks and for reliable formation evaluation. Organic-rich mudrocks are composed of inorganic minerals such as quartz, calcite, feldspar, and clay minerals; and organic matter such as kerogen, bitumen, and pyrobitumen. The properties of these inorganic minerals are well known and understood. Among the types of organic matter, kerogen is an important component of organic-rich mudrocks volumetric concentrations of 5–40%. However, the properties of kerogen (e.g., Wettability) are still not understood clearly. Moreover, the wettability of

kerogen and organic-rich mudrocks has a significant impact on the relative permeability and fluid mobilities of different reservoir fluids. Therefore, understanding the kerogen wettability and the impact of wettability on fluid mobility of water and hydrocarbon, is important to understand the forces required in enhanced oil recovery to displace hydrocarbons in the reservoir.

The composition of kerogen evolves from hydrogen-rich organic matter into hydrogen-poor residual carbon with increase in thermal maturity (Baskin 1997). In addition to evolution in composition of kerogen, the chemical structure of kerogen transforms aliphatic carbon-rich to aromatic carbon-rich structures (Vandenbroucke 2003; Vandenbroucke 2007). In a recent experimental and MD simulation study, the geochemistry of kerogen (kerogen type and thermal maturity), as well as reservoir temperature was found to have a significant impact on the wettability of kerogen (Jagadisan and Heidari 2019; Jagadisan and Heidari 2020). Increase in oxygen-to-carbon ratio and decrease in aromatic carbon content was found to make kerogen water-wet, while decrease in oxygen-to-carbon ratio and increase in aromatic carbon content was found to make kerogen oil-wet. Moreover, increase in reservoir temperature was found to make the kerogen more water-wet due to decrease in surface tension between kerogen and water drop. However, in these studies the impact of wettability in three phase water-oil-kerogen was not tested.

Moreover, wettability of organic rich mudrock impacts the distribution of fluids in the pore space (Anderson 1987). Therefore, wettability of kerogen and organic-rich mudrocks could affect the fluid mobility of different fluids present in the reservoir. For instance, hydrophilicity increases the interaction between water molecules and kerogen pore walls and influences water mobilities in the pore space in two ways. On one hand, the hydrophilic interaction could increase the capillary force, helping the uptake of water molecules. The imbibition capillary force increases dramatically with decreasing pore sizes. When the pore size is narrowed down to the subnanometer scale, as in the case of kerogen pores, water molecules inside the kerogen pores will have greater probability to form hydrogen bonded networks, which plays an important role for water transport in the confined environment (Suk and Aluru 2010). On the other hand, stronger interaction between water molecules and the kerogen pore walls results in increased friction and consequently reduces the flow velocity (Xu et al. 2018). Larger proportion of water molecules will interact with the pore wall as the pore size decreases, and thus the friction effect becomes more pronounced. Therefore, it is necessary to understand and investigate the effect of kerogen wettability on relative mobility of water and hydrocarbons. Understanding the interfacial forces between fluid and kerogen surface enables making better decisions for composition of fracture fluids required to change the surface tensions, and the forces required in enhanced oil production for displacing hydrocarbon and, thereby, optimizing production.

In this project, we plan to use realistic molecular models of kerogen developed by Ungerer et al. (2015) as inputs to the molecular simulation model. These the composition and structure of these kerogen molecules are verified against the elemental and functional analysis from X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and ^{13}C nuclear magnetic resonance (NMR) documented by Keleman et al. 2007. We use these models to determine three-phase (oil-water-kerogen) contact angle and wettability of kerogen. We then determine the impact of wettability of kerogen on fluid mobilities of water and oil in kerogen pores by simulating water transport using MD simulations through the pores constructed from kerogen sheets of different type and thermal maturity, and, therefore, differing wettability.

METHOD

Molecular models for kerogen developed by Ungerer et al. (2015) are used as inputs for simulations. We first condense kerogen molecular model units to a flat kerogen structure, till their density values converge to those obtained from experimental measurements. To study the three-phase wettability on kerogen surface, the oil is modeled as decane. The oil droplet is then placed on the flat kerogen surface surrounded by water molecules and the contact angle is simulated on each kerogen surface. The contact angle is then calculated at equilibrium.

Furthermore, in order to determine the impact of kerogen wettability on fluid mobility, we first create a kerogen pore space by creating pore space between two sheets of kerogen. We then calculate the water flux in the kerogen pore space for pressure drop (ΔP) ranging from 100 to 600 MPa. Based on the slope of the curve, we then determine the water mobilities in the kerogen pore space and quantify the impact of kerogen wettability on water mobility.

Preparation of the kerogen surface. In order to construct a smooth kerogen surface structure for the simulation of water droplets, five kerogen molecules of the same type and thermal maturity is placed in a simulation cell of size 50x50x50 Å. The consistent-valence forcefield (CVFF) (Dauber-Osguthorpe et al., 1988) is used to perform MD simulations. The sequence of MD simulations to generate condensed kerogen structures is adopted from Zhao et al. (2018). We use LAMMPS simulator (Plimpton, 1995) to perform the molecular dynamics simulations. Then, fix wall command is used on LAMMPS to create frictional walls with Lennard-Jones 12/6 potential (Lennard-Jones, 1924). The walls are placed on the two sides of the kerogen molecule along the Z-axis direction, with a fixed wall on the top and a moving wall at the bottom of the molecules. The molecules are then condensed in Z-axis direction till the density reaches 1.1 – 1.35 g/cc which is the density of pure kerogen (Okiongbo et al., 2005; Jagadisan et al., 2017). Subsequently, the energy of the kerogen was minimized using a number (N), volume (V), and temperature (T) ensemble, with a Nosé thermostat at a temperature of 298 K for 200 ps.

Contact angle simulation. A droplet of oil consisting of decane molecules is placed on the flat surface of the condensed kerogen structure. The oil droplet is then surrounded by water molecules. **Figure 1** shows the arrangement of oil and water molecules are initially arranged on the top of the flat kerogen structure and the oil cube is surrounded by three water cubes with different sizes. The number of water and decane molecules is determined by the sizes of the cubes and the water and oil densities under the condition of 300 K and 1 bar. The arrangement of molecules and the simulations are implemented using the platform of LAMMPS (large-scale atomic/molecular massively parallel simulator). Then, the energy of the system is minimized to optimize the molecular geometry. We use CVFF force field for decane and kerogen molecules and TIP3P water model for water molecules (Jorgensen et al., 1983) to then perform constant temperature and volume (NVT) simulations. The electrostatic potential and van der Waals (vdW) potential represented the nonbonding interactions. Lennard-Jones 9−6 electrostatic potential (Lennard-Jones, 1924) is used to perform the vdW interaction. Periodic boundary conditions are applied in the x- and y- and z-directions. As the simulation reaches to an equilibrium state, the contact angle formed by the oil droplet is measured, while the water molecules form a continuous phase surrounding the oil droplet. Each simulation was performed for 800 ps. The initial 600 ps is used to reach equilibrium. The remaining 200 ps of the simulation time is used to get the MD trajectory data, which is used to calculate the contact angle. **Figure 2** shows the workflow used in this paper to determine the three-phase contact angle and wettability of kerogen.

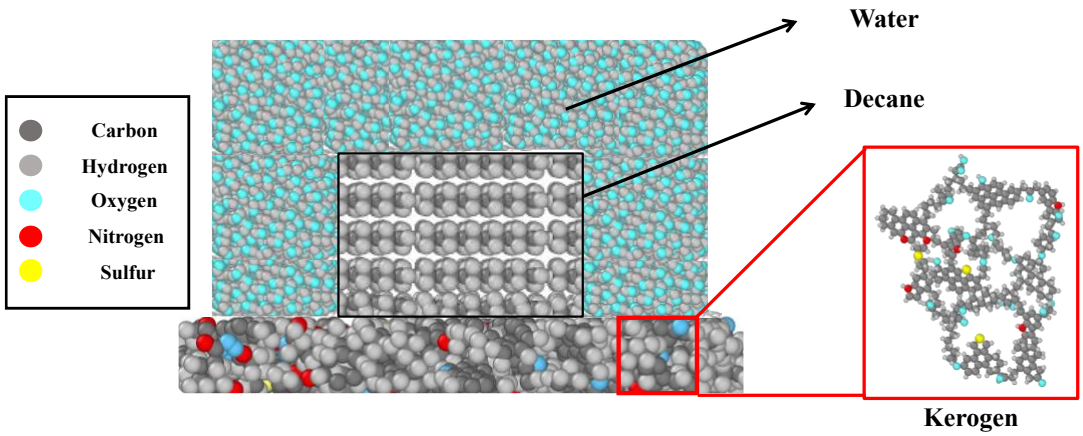


Figure 1: Simulation system with an oil (decane) cube surrounded by water on top of the kerogen II-A surface and atomic views of kerogen, decane, and water molecules on right.

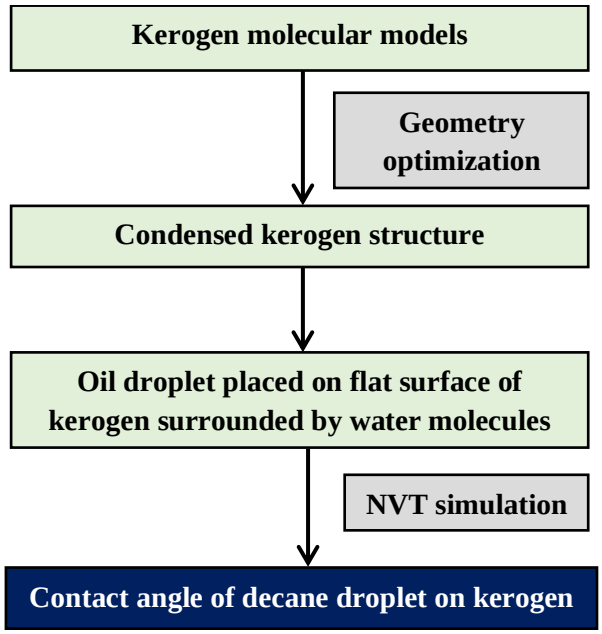
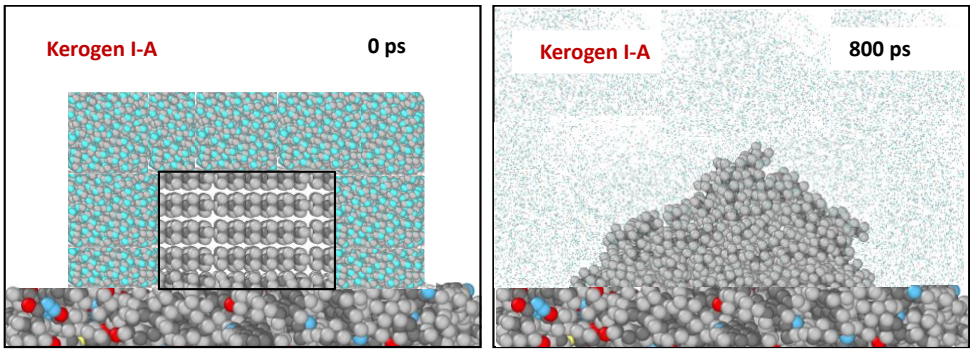


Figure 2: The proposed workflow to obtain three-phase contact angle formed by oil droplet on kerogen surface.

PRELIMINARY RESULTS

Figure 3 shows the MD simulation results of contact angle formed by decane droplet on kerogen surface with water as the third phase at initial and equilibrium state after 800 ps (at the minimum energy of the system). The results show that the contact angle measured for kerogen I-A is 58°. Similar results would be obtained for other kerogen samples to quantify the three-phase wettability of kerogen. Impact of kerogen type and thermal maturity on three-phase contact angle of oil droplet would be determined.



(a) **(b)**

Figure 3: (a) Initial configuration of water and decane droplet and (b) Equilibrium condition of decane droplet on type I kerogen surface at 300K.

FUTURE WORK

Task 1: Quantify the contact angle of different hydrocarbons on the wettability of kerogen:

Organic-rich mudrocks can contain various compositions of hydrocarbons in the pore spaces. However, the previous work showed only the impact of decane wettability on kerogen surface. Therefore, we plan to expand the previous work on determining three-phase contact angle of kerogen for other hydrocarbon molecules in addition to decane.

Task 2: Quantify the impact of kerogen wettability on apparent flux and permeability of water using MD simulations:

We create a kerogen pore by creating a space between two flat kerogen surfaces of type I, type II and type III kerogen molecules at different thermal maturities (i.e. different wettability). We then place water molecules at the two ends of kerogen pores. **Figure 4** shows the schematic used to simulating the water flux in the kerogen pore space. We then apply a differential pressure (ΔPs) between the water molecules at the two ends of the pore space ranging from 100 to 600 MPa.

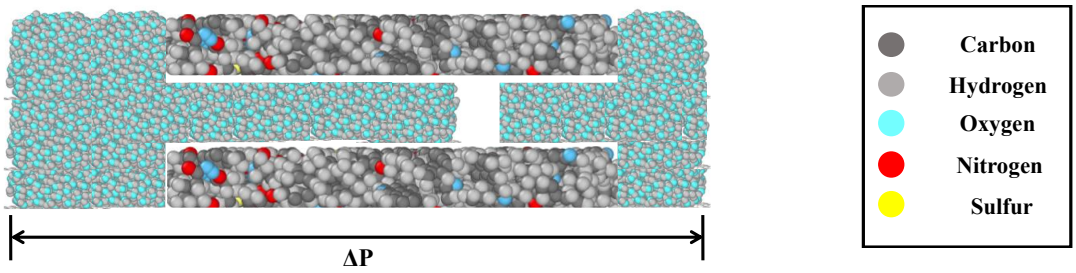


Figure 4: Representative snapshots of the water stream inside the kerogen pore during the flowing process under the corresponding ΔP.

We then calculate the water flux for each kerogen pore space to determine the impact of kerogen hydrophilicity and hydrophobicity on the water flux based on the slope of the water flux curve versus the differential pressure. The flux is calculated as the number of water molecules passing through the kerogen pore space at steady state or equilibrium state of the system.

Task 2: Quantify the impact of kerogen wettability on apparent flux and permeability of oil (decane) using MD simulations:

We propose to quantify the impact of kerogen wettability on oil flux and apparent mobility/permeability using simulating the flow of decane through the kerogen pores using MD simulations. For this purpose, we place decane molecules at the two ends of kerogen pores and apply a differential pressure between the two ends of the kerogen pore space ranging from 100 to 600 MPa determine the impact of wettability on oil flux.

Task 3: Quantify the effects of temperature on water and oil flux on kerogen surface using molecular simulations:

Temperature variation has been shown to affect the contact angle of water droplet on kerogen surface in a recent publication (Jagadisan and Heidari 2020). Thus, temperature can have an impact on the fluid mobilities of water and oil in the pores of organic-rich mudrocks. Therefore, we propose to model and quantify the effect of reservoir temperature on the fluid flux in the kerogen pores using molecular dynamics simulations.

Task 4: Quantify the force required to displace water and oil from the kerogen pores using molecular simulations:

Wettability of kerogen and organic-rich mudrocks can potentially have significant impacts on the relative permeability and fluid mobilities of different reservoir fluids. Moreover, fluid mobility and permeability of reservoir fluids can impact the forces required to displace these reservoir fluids though the kerogen pores. Understanding the forces required to displace the reservoir fluids is important for designing enhanced oil recovery methods and optimizing production. We, therefore, quantify the forces required to displace water and hydrocarbons in the reservoir using MD simulations.

ACRONYMS

CVFF	Consistent-valence Forcefield
MD	Molecular Dynamics Simulation
NMR	Nuclear Magnetic Resonance
NVT	Number (N), volume (V), and temperature (T) ensemble
vdW	van der Waals
XPF	X-Ray Photoelectron Spectroscopy

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