Energetics of Interfacial Interactions of Hydrocarbon Fluids with Kerogen and Calcite using Molecular Modeling

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Abstract

The fluid-rock interactions are essential to characterize the behavior of petroleum fluids in reservoir formations. Such understanding is difficult to obtain due to the heterogeneous nature of hydrocarbon systems. This study investigated the interactions of light oil molecules with kerogen and calcite using Molecular Dynamics simulations. Specifically, octane and octanthiol were used as model molecules for non-polar and polar oil compounds; a kerogen fragment molecule was employed as the building block for kerogen, the major constituent of reservoir rock organics; calcite as a model system for hydrophilic materials in reservoir rocks. Umbrella Sampling method combined with the Weighted Histogram Analysis Method was deployed to calculate the free energy profiles of oil molecule desorption from kerogen and calcite surfaces. The effects of oil molecular polarity, size of oil molecular cluster, and the presence of water on the interfacial interactions were evaluated based on the free energy profile of desorption. The results show the free energy of desorption of oil molecules significantly decreases at both kerogen and calcite surfaces if water is presented. For the polar oil molecule, the free energy of desorption is higher than that of non-polar oil at both calcite and kerogen surfaces. The kerogen surface exhibits stronger binding energies of oil molecules than the calcite. These findings suggest that 1) polar oil compounds require more effort to be recovered than non-polar ones from the reservoir rocks, 2) isolated oil molecules or oil clusters of a smaller size are harder to be displaced from the surfaces than a larger size of molecular clusters, and 3) the presence of water decreases the free energy of desorption at both surfaces. The results provide an energetic perspective of the interfacial interactions for the oil recovery in reservoir formations. This study demonstrates that the capability of MD simulation in evaluating the impact of different factors on the interfacial interactions for the fundamental understanding of the oil recovery processes in petroleum reservoirs, which can provide valuable implications for developing novel technologies of oil recovery.

INTRODUCTION

Oil is the main energy source for our modern civilization and will remain as a major contributor of global energy in the foreseeable future.[1] However, only a portion of oil preserved in a reservoir can be recovered. Thus, it is imperative to improve the recovery efficiency of petroleum reservoirs. Current methods to improve oil production including primary, secondary, and tertiary oil recovery techniques can yield 30 to 60 % of the original oil in place, leaving up to 70% of the original oil in a reservior.[1,2]

The pressing demand of energy from modern civilization has spurred technical innovations to improve oil recovery, especially through tertiary oil recovery or enhanced oil recovery. However, there is a limited understanding of how hydrocarbon-bearing fluids interact with the materials in reservoir formations. This knowledge gap impairs the assessment of the economic potential of a hydrocarbon reservoir. For example, relative permeability, an essential parameter of fluid flow characteristics for formation evaluation, is measured by Special Core Analysis (SCAL) through conducting flow experiments on core plugs taken from a reservoir. However, SCAL results are often contradictory or cannot be properly implemented in the reservoir modelling and petrophysical evaluation.[3–5] A myriad of factors may complicate the results, including the hydrofracture geometries, networks of preexisting fractures, adsorption and desorption processes, non-Darcy multiphase flow, chemically and structurally heterogeneous formations, etc.[6]

The interfacial interactions between the fluid and rock play a key role in all these complications. As shown in Figure 1, if a pore has a less than 100 nm radius and the intermolecular interaction has an effective distance of 3 nm, a significant portion (12% – 100% volume) of confined fluid can be directly affected by the interfacial interactions. Therefore, to

64 further improve recovery efficiency, a fundamental understanding of the fluid-rock interactions
65 is indispensable.

66 To probe the interfacial interactions at nanoscales, molecular-level characterization is
67 necessary. Both experimental and computational approaches have been applied to study the
68 hydrocarbon fluid behavior in the rock at nanoscale. Extensive experimental studies have been
69 conducted on the reservoir formations to characterize the organic content[7,8], pore structure[9–12],
70 and petrophysical properties[11,13–15]. These studies aimed to calibrate the empirical models in
71 reservoir engineering to describe the fluid flow[16,17] and to provide a basis for reservoir
72 assessment and production optimization.[18] However, due to the compositional and structural
73 heterogeneity of reservoir formations, it is challenging to interpret the dynamics and kinetics of
74 interface interactions without knowing the molecular scale details. Current understanding of the
75 hydrocarbon systems heavily relies on the characterization technologies to conduct experiments
76 on surfaces and interfaces[19–21] such as Focus Ion Beam Scanning Electron Microscopy (FIB-
77 SEM),[15,22,23] Transmission Electron Microscopy (TEM),[23,24] Atomic Force Microscopy
78 (AFM),[16,25,26] X-ray Diffraction (XRD),[27,28] X-ray microtomography (Micro-CT),[29,30] Nuclear
79 Magnetic Resonance (NMR),[31,32] etc. Implementing these methodologies to characterize
80 microscopic phenomena becomes challenging at the molecular level. Unlike experiments,
81 computational simulations can study physical phenomena over a range of scales,[33] directly
82 connecting the microscopic details of a system to macroscopic properties of experimental
83 interest.[34] Due to the intensive computation, Quantum Mechanics (QM) simulations have strict
84 limits on the size, time, and complexity of the systems.[33–35] Molecular simulations, built on
85 classical molecular mechanics (MM) such as Monte Carlo (MC) and Molecular Dynamics (MD),
86 are more appropriate than QM methods to address the issues of size and complexity of the

hydrocarbon systems. MC methods are stochastic approach, suitable for system equilibrium, while MD techniques are deterministic, suitable for both equilibrium and transport properties of a given system.[34,35] Thus, this study used MD to investigate the energetics of fluid-rock interactions. Currently, there are several studies using MD to investigate hydrocarbon fluid interactions with kerogen and minerals, such as 1) the adsorption, diffusion, and permeation of hydrocarbon fluid in shale kerogen and kerogen analogue;[36–43] 2) slippage, displacement, and adsorption of hydrocarbon flow on quartz, calcite slits, and montmorillonite slits;[44–47] 3) detachment of oil cluster from silicate surfaces in surfactant solution.[48] These studies evaluated the effect of nanopores on the properties of hydrocarbon fluid, such as bulk viscosity, contact angle, and slippage with focuses on the phenomena of the interactions. For instance, Liu et al 2012 stated that water can penetrate the oil—water interface and form a surface water layer on a hydrophilic silica surface, enhancing the oil detachment from the hydrophilic surface.[48] However, there is a knowledge gap in the energetic aspect of the interactions, which is essentially underexplored. This lack of the knowledge on the thermodynamics of the interactions limits current understanding of the fundamental mechanism in hydrocarbon fluids interactions with reservoir formations.

The present study intends to examine the feasibility of the computational approach to evaluate the free energy profile of oil compounds desorption from the surfaces of reservoir rock materials. Umbrella Sampling, widely used in computational biology and biochemistry[49], was adopted to compute the free energy profiles of the oil interactions with the rock materials in the desorption. We studied the surfaces of kerogen and calcite to evaluate the effect of four different variables including oil polarity (polar vs non-polar oil), oil cluster size (a single molecule oil vs 30 molecules oil cluster), surface hydrophobicity (inorganic calcite mineral vs organic kerogen),

and surface water (the presence vs the absence of surface water). Probing the free energy changes in oil-rock interactions can provide insight into the thermodynamics of the surface wettability and hydrocarbon behaviors in reservoir formations.

METHODS

Molecular models for oil, kerogen, and calcite

Crude oil is a mixture of a wide range of polar and non-polar compounds with varying proportions, composition, and molecular weight. Typically, crude oil contains over 45% non-polar (e.g. alkanes and cycloalkanes) and less than 15% polar species (e.g. N-, S-, O- and metal-containing compounds).[50,51] Polar components can significantly affect properties of hydrocarbon fluid in reservoir such as viscosity, contact angle, interfacial activity, emulsion, and chemical stability.[52–54] The oil-rock interactions are largely attributed by the polar species,[55] particularly in organic phases which usually retain more polar components than minerals[52]. Thioalkanes are common sulfur compounds found in crude oils.[56] Crude oil, especially from shale, can has a high content of light oil (C_1-C_9).[57,58] Therefore, we selected 1-octanethiol ($C_8H_{18}S$) with a dipole moment of 2.9 D[59] and its non-polar counterpart n-octane (C_8H_{18}) as the models for polar and nonpolar oil respectively in our simulations as shown in Figure 2. In addition, to model a small oil drop, we prepared two oil clusters consisted of 30 molecules of octanethiol and octane for polar and non-polar oil droplets respectively as shown in Figure 3(c).

Reservoir rocks have complex microstructures and mineralogy and contains various amount of inorganic and organic constituents. Major mineral phases include clays, quartz, and carbonates (calcite and dolomite).[60] Due to its simple structure and ubiquitous presence in formation rocks, the calcite (104) face was chosen as a mode for hydrophilic surface of reservoir

rocks. The calcite (104) is a flat stoichiometric surface. It is one of most common mineral faces occurred in both geological and biological systems and has been well studied both computationally and experimentally.[61] The key organic phase in shale involved in the interactions with hydrocarbon fluid is kerogen.[52,62,63] Despite the complexity of kerogen in reservoir formations[64], many studies used graphene to represent kerogen[36,42,43,65–68]. The differences between graphene and kerogen, such as bonding environment of functional groups[69,70] and surface morphology[64], give rise to different chemical and mechanical properties and interfacial interactions. These deviations can lead to inaccurate modeling with respect to experimental measurements[70,71]. To capture fundamental properties of kerogen, we employed a molecular fragment $C_{22}H_{13}ON$ directly derived from type II kerogen to build kerogen surfaces,[37] which is the most common kerogen in hydrocarbon-bearing shale formations.[64] The kerogen molecule has five benzene rings, a secondary amine, and a phenol group, making this kerogen molecule a polar compound. To create kerogen surfaces, 511 kerogen molecules were randomly added into a computational supercell (18,907 atoms in total), quenched from 3000 to 300 K. The surface was then created by inserting a vacuum space between the kerogen and lastly a stabilization and a relaxation of the surface were followed at 300 K using an NVT ensemble.

The calcite (104) surface in Figure 3(b) was built with 1620 $CaCO_3$ molecule units with a dimension of approximately 7 × 7 × 2 nm with 8,100 atoms. The kerogen surface in Figure 3(a) was built with 511 $C_{22}H_{13}ON$ molecule units with a dimension of approximately 8 × 8 × 3 nm and 18,907 atoms as shown. Because of the ubiquitous presence of water in the reservoir formations, water molecules were added to the fluid. To ensure the oil molecules surrounded by water, 7,250 and 10,000 water molecules were added to the calcite surface of single oil molecule

or oil cluster, respectively, while 7,500 and 10,000 water molecules were placed on kerogen surfaces of single oil molecule or oil cluster, respectively.

A previous experimental study indicates the calcite (104) surface exhibits neutral charge due to the stoichiometry and alternating of Ca^{2+} and CO_3^{2-}.[72,73] Kerogen surfaces can be negatively charged due to the deprotonation of functional groups, such as OH and NH. However, classical MD models only simulate interatomic interactions by empirical potentials for bond length, angle, and dihedral, whereas formation and breaking of covalent bonds are not considered unless specified by force field. Both calcite and kerogen surfaces maintain electrical neutrality owing to the charge balance of each model molecule. Layers of alternating Ca^{2+} and CO_3^{2-} on the calcite (104) create a flat surface, while the benzene rings and polar functional groups of kerogen molecule yield highly heterogenous surfaces of kerogen.

Molecular Dynamics (MD) Simulation and Gibbs Free Energy Profiles

MD simulations in this study were deployed using software package GROningen MAchine for Chemical Simulations (GROMACS).[74] All simulations employed three-dimensional periodic boundary conditions. The OPLS-AA force field was used to describe oil molecules and kerogen.[75] The SPC potential is used to describe water molecule.[76] A previously developed force field was used for calcite.[77] All these potentials have been tested and are capable of producing satisfactory results on bulk and interfacial properties, which are consistent with experimental data.[78–80] Newton's equations of motion were integrated using the leap-frog scheme with a timestep of 1 fs, fast Smooth Particle-Mesh Ewald (SPME) electrostatics, Verlet cutoff-scheme, and temperature coupling using a Nose-Hoover extended ensemble with a coupling

constant of 0.1 ps. Simulations were visualized by Visual Molecular Dynamics (VMD) package.[81]

The potential of mean force for the oil interactions with different surfaces was computed by Umbrella Sampling and the Weighted Histogram Analysis Method (WHAM).[82,83] Gromacs package was used to carry out Umbrella Sampling simulations by running separate simulation windows along the reaction coordinate individually. These windows were generated by extracting a series of configurations from a pulling simulation that drew the oil into or away from the surfaces along the designated reaction coordinate.

In each simulation window, umbrella potential, a biased harmonic potential, was applied to the system. For each individual simulation window, a constraint potential with a force constant 9000 $kJ \cdot mol^{-1} \cdot nm^{-1}$ for 0.1 ns to equilibrate the system was first applied, then an umbrella potential with a force constant 9000 $kJ \cdot mol^{-1} \cdot nm^{-2}$ was deployed for 0.1 ns up to 0.2 ns to obtain probability distribution of the given reaction coordinate. With enough sampling overlaps between simulation windows in the entire reaction coordinate space, a free energy profile curve can be calculated by combining data from each window using WHAM.[82,84]

An analysis routine to estimate the errors of the energy profiles was developed using LOESS algorithm in RStudio.[85,86] This method took the energy profile and employed the bootstrap technique to calculate the confidential intervals at 95% confidence level. The computed errors are listed as shown in Table 1 denoted by brackets. The fluctuation of free energy profile, as shown in Figure S1, is consistent with the size of the estimated error bar.

RESULTS AND DISCUSSION

Free energy surfaces in Figures 4-7 show how the system energy changes as a function of the distance between oil compounds and surfaces with respect to their centers of mass. When the oils molecules are close to the surfaces, the energy increases due to repulsive interactions. When the oils gradually move away from the surface, the energy first reaches the minimal point, at which the adsorption occurs at the surfaces. An absence of the minimum suggests zero desorption energy. As the distance continuously increases, the energy increase until the system reaches the energy plateau where no additional energy is required to desorb the oil molecules from the surfaces.

Interactions of oil molecules with kerogen surface

The free energy profiles in Figure 4 and Table 1 show the energy changes as a function of the distance between oil compounds and kerogen surface in the presence of water. The desorption energies are 17.0 ± 2.0 kJ/mol and 16.5 ± 3.3 kJ/mol for non-polar and polar single oil molecule and 371± 12.4 kJ/mol and 209 ± 7.0 kJ/mol for non-polar and polar oil clusters, respectively. In the absence of water, it is challenging to maintain oil molecules as a cluster at or above 300 K. To stabilize the oil cluster, a series of Umbrella Sampling simulations were carried out under lower system temperatures to extrapolate the desorption energy to 300 K (detail was discussed in Figure S3). The desorption energies of the oil clusters on kerogen surfaces are 437 ± 13.5 kJ/mol for both polar and non-polar (Figure S3). For the single oil molecule, the desorption energies on kerogen in Figure 5 and Table 1 are 23.3 ± 3.5 kJ/mol and 39.5 ± 9.5 kJ/mol for non-polar and polar, respectively.

220 ***Interactions of oil molecules with calcite (104) surface***

221 The free energy profiles in Figure 6 shows how free energy changes as a function of the
222 distance between oil compounds and the calcite (104) surface in water. Unlike the rest free
223 energy profiles (described later), they exhibit a distinct pattern: as the distance increase, the free
224 energy quickly decreased and then stayed at the same value as the molecule is further away from
225 the surface. Such patterns indicate near zero energy of the desorption of oil molecules on the
226 calcite surface in the presence of water.

227 For comparison, the same systems without water were simulated, of which the free
228 energy profiles are depicted in Figure 7. The results show that 33.6 ± 3.9 kJ/mol and 18.0 ± 5.5
229 kJ/mol are required to desorb polar and non-polar oil molecules from the calcite surfaces
230 respectively, and 222 ± 36 kJ/mol and 198 ± 42 kJ/mol to desorb polar and non-polar oil clusters,
231 respectively. A detailed analysis of the trajectory (Figure S4) suggests that the polar molecule
232 was bound to the calcite surface through the thiol functional group –SH, which confirms a
233 previous study on the adsorption of simple organic molecules on calcite (104).[87] In addition, the
234 thiol group –SH of polar oil appears to favor the sites of Ca^{2+} site of calcite (104) surface,
235 whereas the non-polar oil shows no preference of absorption sites.

236

237 ***Effect of surface composition on the desorption energy***

238 Our study shows that, in general, oil molecules have stronger interactions with kerogen
239 than with calcite regardless of surface environment and oil molecular polarity. Kerogen is an
240 organic compound and usually oleophilic, whose surface property depends on the specific
241 functional groups. The kerogen model in this study contains functional groups such as hydroxyl

(–OH) and thiol (sulfhydryl, –SH) groups which inherently exhibit a strong affinity with hydrophilic surfaces while the rest strongly interact with hydrophobic surfaces. On the other hand, calcite, especially the (104) face, is strongly hydrophilic with ionic species Ca^{2+} and CO_3^{2-} on the surface. Therefore, water can be more easily desorbed from the kerogen surface than from the calcite surface, leading to higher desorption energy for oil molecules at the kerogen surface and weak desorption at the calcite surface. Another factor that contributes to the difference between kerogen and calcite is the surface area: calcite has a low surface area which weakens its sorption capacities,[88] whereas kerogen is porous and waxy according to experimental observations.[64,89] Thus, the effective surface area on kerogen would be much higher than calcite, leading to a higher desorption capacities for oil.

As a result of their different surface properties, the desorption energy at kerogen surface is higher than at the calcite surface: 5.3 to 17 kJ/mol higher for a single oil molecule and 210 to 372 kJ/mol higher for the oil cluster (7.0 to 12.4 kJ/mol per molecule for the oil cluster). The difference in the desorption energies of both single molecule oil and oil cluster implies that oil recovery from organic phases of reservoir rock can take more energy than from these highly hydrophilic surfaces of inorganic mineral phases such as calcite.

Effect of molecular polarity

Our study shows that the polar oil has a stronger interaction with the kerogen and calcite surfaces than non-polar oil. At kerogen surface, molecular polarity plays an imperative role in the energetics of the oil desorption. These phenomena can be explained by the dipole interactions. Since there is no free ion in the systems, the intermolecular interactions are

dominated by permanent dipole interaction, or Keesom interaction. As shown in Figure S5 (a) and (c), the thiol functional group (–SH, yellow) of the polar oil tend stay in close proximity to the functional groups of kerogen molecules such as amine (–NH–, blue) and hydroxyl (–OH, red) upon contact at the interface, which confirms the expected dipole interactions. Unlike the polar oil, non-polar oil molecules have no dipole moment, therefore a weaker desorption energy than the polar oil molecules is expected. Thus, the interactions of the polar oil molecule with kerogen surface is stronger than that of non-polar.[90] As shown in the Table 1, the desorption energies of the single molecule oil show that the polar oil molecule requires energy about two times of the energy of non-polar per molecule in the absence of water. The desorption energies of single polar and nonpolar oil molecules are approximately the same in the presence of water. For the oil cluster, our calculation indicates that polar oil cluster requires the similar desorption energies as the non-polar oil cluster. These results suggest that the effect of polarity is complicated by kerogen surface property and the presence of water.

At the calcite (104) surface, polar oil molecules consistently require higher desorption energies than its counterpart non-polar oil owing to the molecular dipole of the polar oil and the hydrophilic nature of the calcite surface. Although previous studies suggested that calcite (104) is overall non-polar because the alternating Ca^{2+} and CO_3^{2-} are closely packed and charge balance is maintained,[91,92] the electrostatic interaction between ionic species at the calcite surface and the functional group at the polar molecule favors the adsorption of the polar oil molecules. Therefore, the desorption energy for the polar oil molecule is approximately two times of the desorption energy for the non-polar oil molecule and the desorption energy for the polar oil molecular cluster is approximately 10% higher than the desorption energy for the non-polar oil cluster in the absence of water.

Effect of surface water

Our study shows that the presence of surface water reduces the oil desorption energy on all surface conditions, promoting oil desorption in all these cases. As discussed previously, the calcite surface is hydrophilic, while kerogen is both hydrophilic and hydrophobic. The surface water can easily be attracted to the calcite surface and kerogen hydrophilic functional groups. Both water and polar oil molecules have similar dipole moments 2.9 D and 2.27 D,[59,76] respectively. Water molecules compete with polar oil molecules for adsorption at surfaces with a hydrophilic character, and consequently reducing the desorption energy of the oil molecules at the surfaces. The interactions of waters with the calcite (104) surfaces were much stronger than with kerogen surfaces, suggesting a weaker hydrophilic nature of kerogen surface than the calcite surface. The affinity between calcite and water is stronger than that between calcite and oil, resulting in a strong oil-repellent surface of calcite in the presence of water. As shown in Table 1, kerogen surface with water requires much lower energies to desorb oil. For polar oil, the surface water brought a reduction of 50% - 60% on desorption energy to desorb polar oil compound and 15% - 30% reduction for non-polar oil compound. The energy differences between non-polar and polar oil also demonstrate the crucial role of molecular polarity on the fluid-rock interactions. Given the strong hydrophilicity of calcite, the calcite surface becomes oleophobic, jettisoned all the surface oil, in the presence of water. The result provides a fundamental understanding of the role of water in interactions of oil molecules and reservoir materials and in oil recovery.

Effect of oil clustering

Our study shows that oil clusters require lower desorption energies per molecule than a single oil molecule. For instance, the desorption energy of a single molecule of polar oil is 4.6 to 25.2 kJ/mol higher than the desorption energy per molecule of the oil cluster, which is an increase of 37% to 340% of desorption energy per molecule in the oil cluster. This difference is mainly caused by the number of oil molecules that directly interact with the surface. Not all the molecules in the 30-molecule clusters directly interact with the surfaces, while the single molecule always interacts with the surfaces, which leads to the smaller desorption energies per molecule of a molecular cluster. Although the oil molecular clusters are too small to be comparable with oils in the porous medium in reservoir rocks, the trend quantified in this study suggests that as the pore size decreases, recovering the oil confined in the pores becomes more challenging.

CONCLUSIONS

This study demonstrated that Molecular Dynamics simulation is capable of calculating the free energy surface of desorption of single oil molecules and oil molecular clusters at calcite and kerogen surfaces. The results provide fundamental understandings of the interfacial interactions and valuable implications for oil recovery in reservoirs. The main conclusions are as follows.

(1) Hydrophobicity of the surface of reservoir materials has a significant effect on the desorption of the oil molecules from the surfaces, leading to a higher free energy cost for

oil displacement from organic phases of reservoir rock than from the highly hydrophilic surfaces of inorganic mineral phases such as calcite.

(2) The polarity of oil molecules strongly affects the interfacial interactions at both the kerogen and calcite surfaces. The polar oil molecules require more energy to be recovered from both surfaces than non-polar ones. For complex hydrocarbon fluid systems, having a large portion of polar compounds in the oil poses a great challenge. In order to effectively model the interactions between oil and the reservoir materials and to produce reliable results, an accurate description of the polarity of oil molecules is necessary.

(3) The presence of water at interface plays a fundamental role in the interactions between oil molecules and reservoir materials. Because of its large dipole moment, water facilitates the oil desorption by interacting with hydrophilic surfaces or sites of either organic kerogen or inorganic minerals.

(4) Single oil molecule or small oil molecule cluster dispersed in small nanopores tend to be more challenging to be recovered than large oil molecular clusters due to the stronger interactions of oil molecules with the surfaces.

The success of implementing the free energy methods to study the simple hydrocarbon fluid systems paves the way for building more realistic simulations for complex systems by varying temperatures, adding fluid components (e.g. electrolytes, methane, carbon dioxide, and large oil compounds) and introducing other major inorganic phases such as clay minerals and quartz.

ASSOCIATED CONTENT

Supporting Information

Supporting text 1: Code for error estimation performed by RStudio

Supporting text 2: Trajectories of pertinent molecular dynamics simulations

Figure S1: Free energy surfaces of oil drop of polar or non-polar oil on calcite surface with water.

Figure S2: Free energy surfaces of 30-molecule oil drops interacting with kerogen surface under different temperatures.

Figure S3: Desorption energies of 30-molecule oil drops on kerogen surfaces under different temperatures.

Figure S4: Snapshot of the simulation trajectory of calcite surface interaction with polar oil molecule in the absence of water.

Figure S5: Snapshot of the simulation trajectory of kerogen surface interaction with polar oil molecule in the absence of water at different time step

Table S1: Desorption energies of oil drops on kerogen surface under different temperatures in the absence of water.

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Notes

There are no conflicts to declare.

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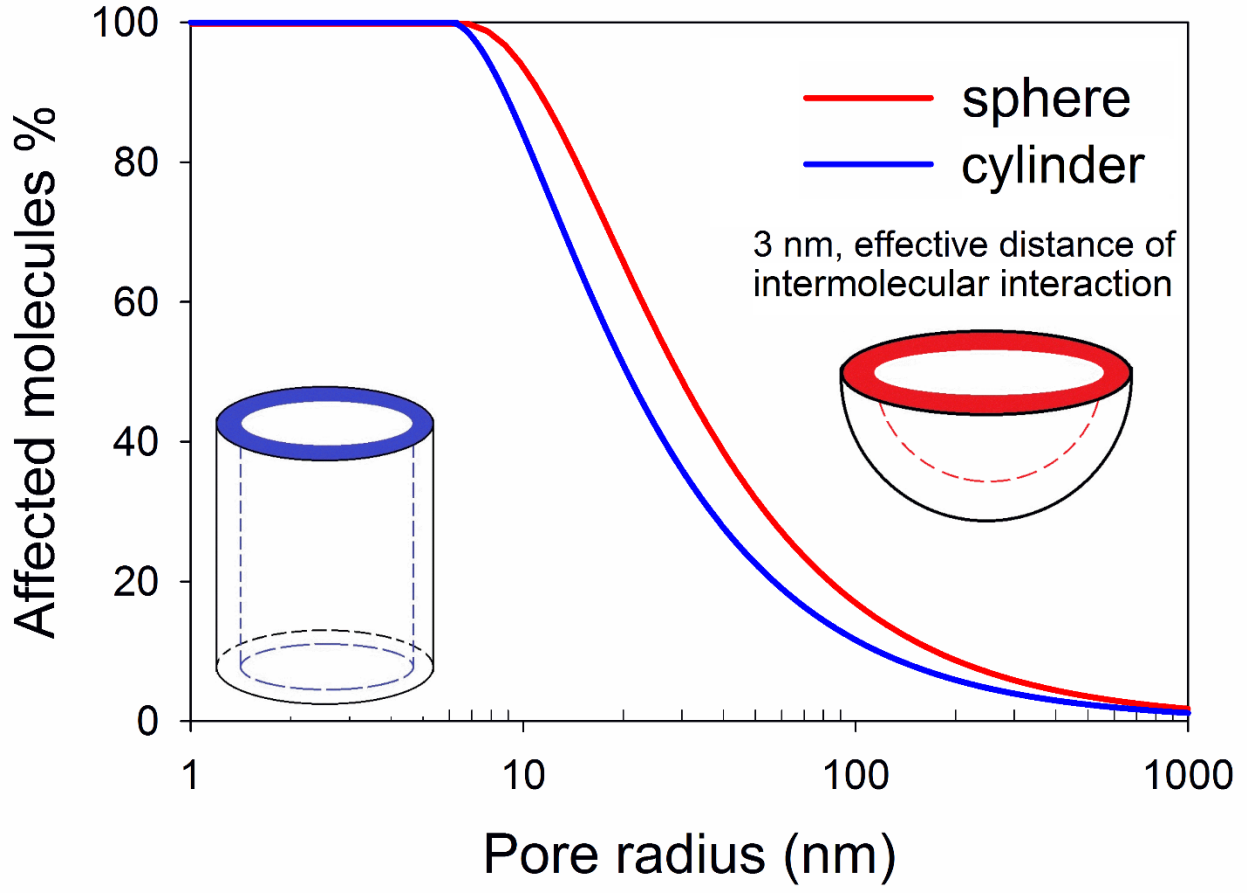


646

647 Figure 1. Effect of intermolecular interaction on the fluid confined in nanostructures.

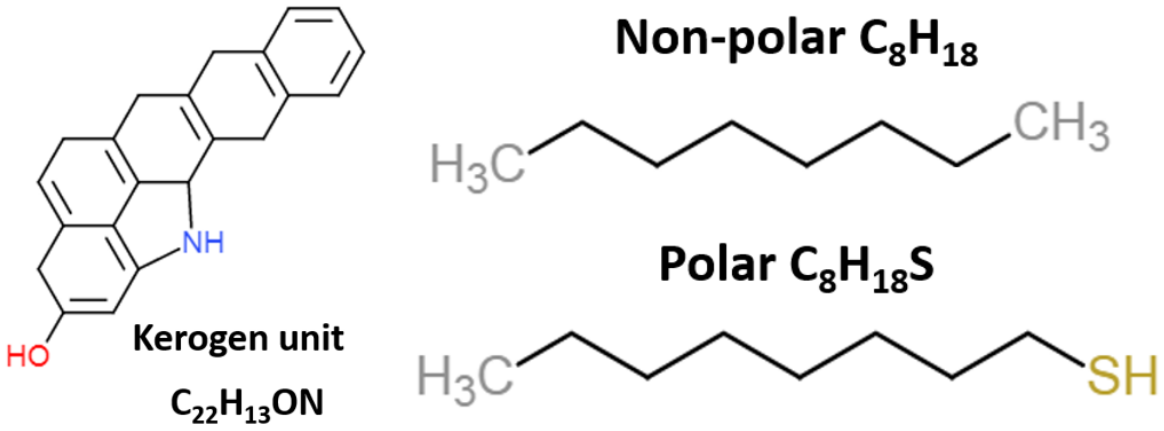


Figure 2. Molecular structure of type II kerogen fragment (left), non-polar oil n-octane (right top), and polar oil 1-octanethiol (right bottom).

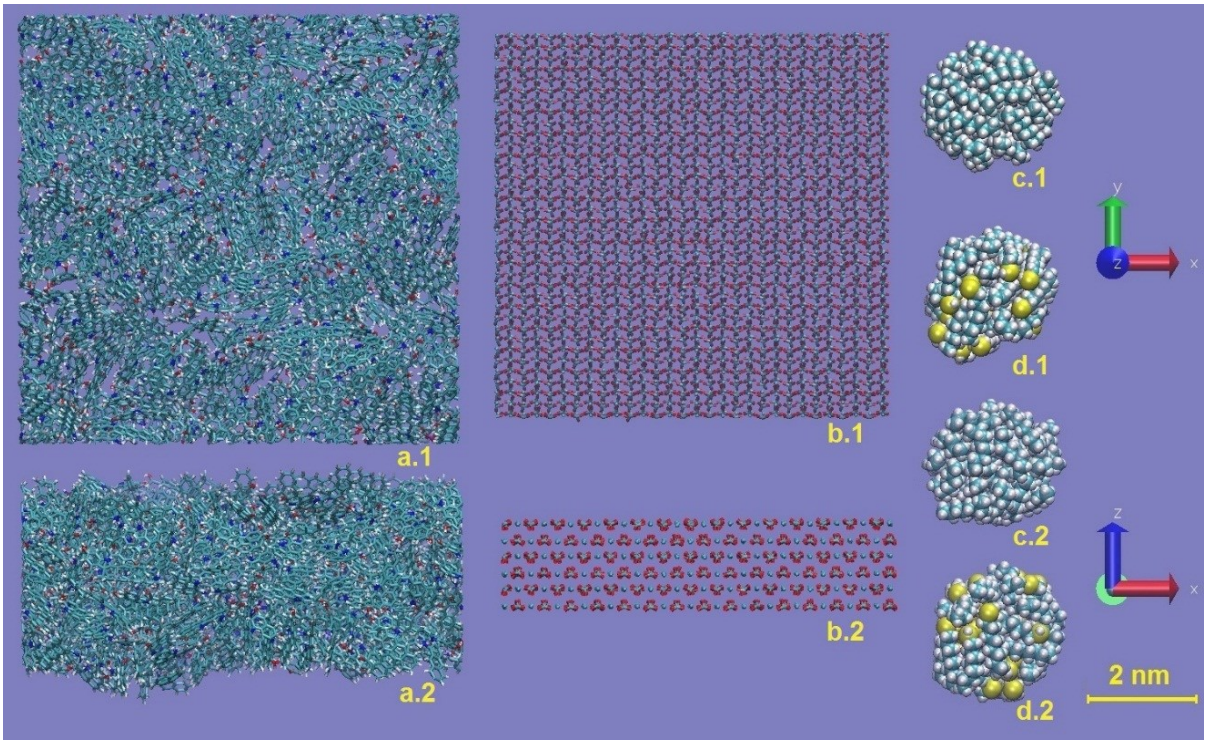


Figure 3. Kerogen slab (a), calcite (104) slab (b), 30-molecule non-polar oil cluster (c), and 30-molecule polar oil cluster (d). “x.1” and “x.2” denote different orientations.

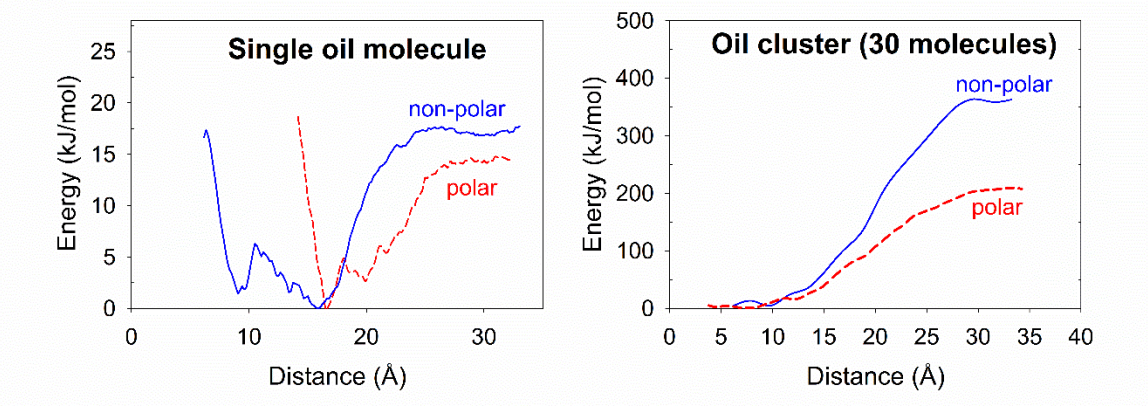
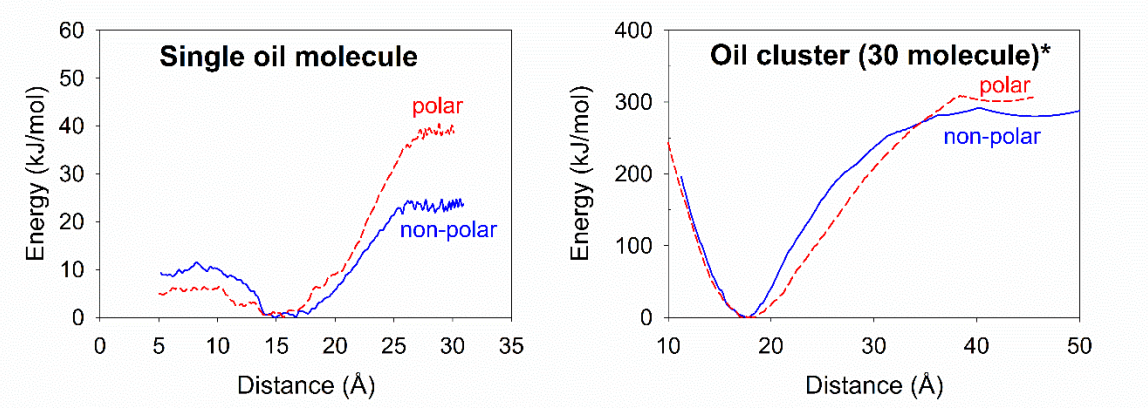


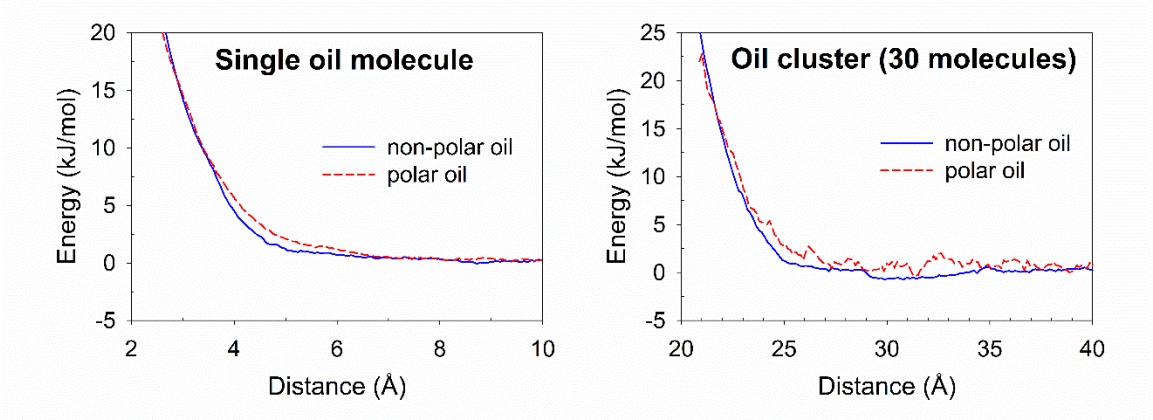
Figure 4. Free energy surfaces of single molecule of polar or non-polar oil on kerogen surface with water (left); Free energy surfaces of oil drop of 30 polar or non-polar oil molecules on kerogen surface with water (right).



661

662 Figure 5. Free energy surfaces of single molecule of polar and non-polar oil on kerogen surface without
663 water (left); free energy surfaces of oil drop of 30 polar or non-polar oil molecules on kerogen surface
664 without water (right). *indicates the simulations were prepared at 200K due to the technical issues as
665 described in the discussion.

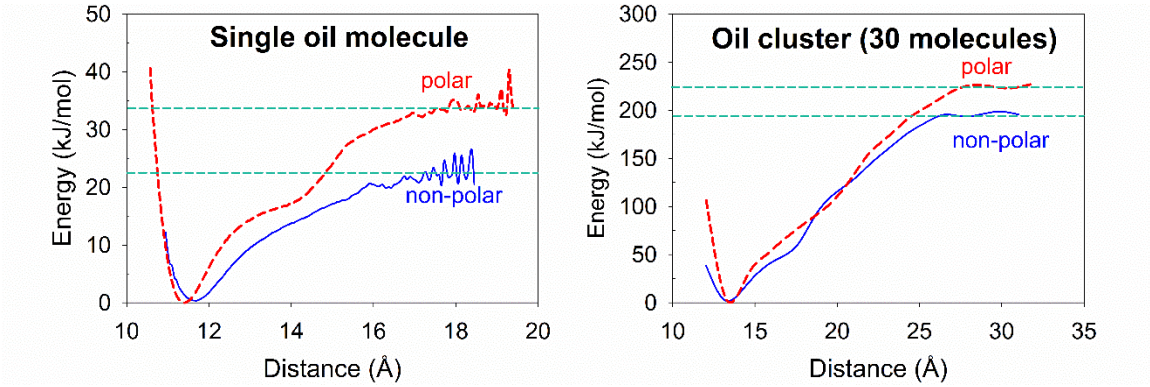
666



667

668 Figure 6. Free energy surfaces of single molecule and 30-molecule cluster of polar or non-polar oil on
669 calcite surface in the presence of water.

670



671

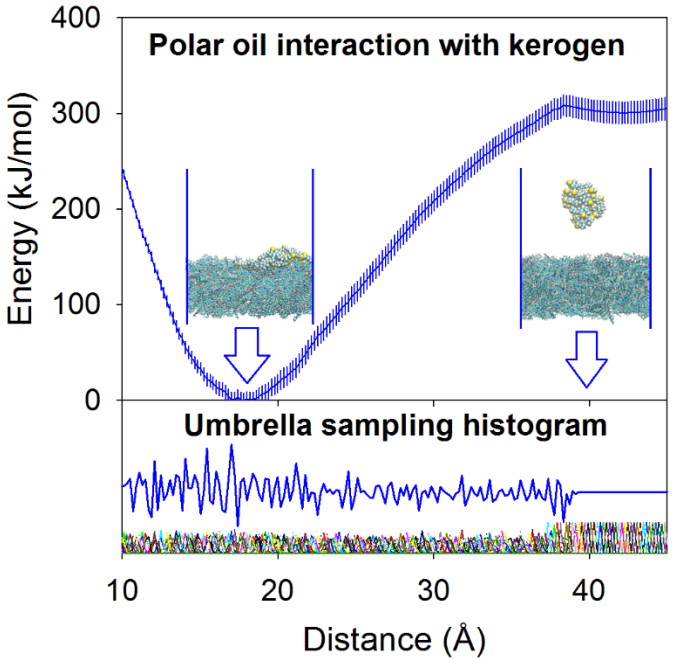
672 Figure 7. Free energy surfaces of single molecule of polar or non-polar oil on calcite surface without
673 water (left); free energy surfaces of oil drop of polar or non-polar oil on calcite surface without water
674 (right).

675

Table 1. Desorption energy of single molecule oil droplet and 30-molecule oil drop on calcite and kerogen surface under 300 K. The ( ) denotes the errors propagated from the output data of WHAM.

Desorption energy (kJ/mol)		Kerogen with water	Kerogen	Calcite with water	Calcite
Non-polar oil	Single molecule	17.0 (2.0)	23.3 (3.5)	0	18.0 (5.5)
	Cluster - total	372 (13.8)	438 (13. 5)	0	198 (42)
	Cluster - per molecule	12.4 (0.46)	14.6 (0.45)	0	6.6 (1.4)
Polar oil	Single molecule	16.5 (3.3)	39.5 (9.5)	0	33.6 (3.9)
	Cluster - total	210 (11.4)	438 (13.5)	0	222 (36)
	Cluster - per molecule	7.0 (0.38)	14.6 (0.45)	0	7.4 (1.2)

677 **TOC**


Polar oil interaction with kerogen
Energy (kJ/mol)
400
300
200
100
0
Umbrella sampling histogram
10
20
30
40
Distance (Å)

678

Supporting Information

Energetics of Interfacial Interactions of Hydrocarbon Fluids with Kerogen and Calcite using Molecular Modeling

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Supporting Information

Code for error estimation performed by RStudio

```
library(bootstrap)
attach(dat)

B<-150
boot.fit<-matrix(0,B,length(x))

for (i in 1:B){
set.seed(i)
indx <- sample(1:178,size=178,replace=T)

fit <- loess(y~x,dat[indx,],span=0.30)

boot.fit[i,] <- predict(fit,x)
}

FUN<-function(x){
quantile(x,prob=c(.025,.975),na.rm=T)  # calcutlate 95% CI
}
boot.CI<-apply(boot.fit,2,FUN)

y_2.5<-boot.CI[1,]
y_97.5<-boot.CI[2,]
```

Video links of pertinent simulation trajectories

100 ps MD trajectory of a polar oil molecule interaction with kerogen surface
https://youtu.be/lTlvF7TlyMg

100 ps MD trajectory of a polar oil molecule interaction with frozen kerogen surface
https://youtu.be/P2AXQOT4W1E

1 ns MD trajectory of a polar oil molecule interaction with frozen kerogen surface
https://youtu.be/iL8cv0Mprcg

100 ps MD trajectory of a non-polar oil molecule interaction with kerogen surface
https://youtu.be/zmdeLdsBWsQ

100 ps MD trajectory of a polar oil molecule interaction with calcite (104) surface
https://youtu.be/crq9xLuhihk

100 ps MD trajectory of a non-polar oil molecule interaction with calcite (104) surface
https://youtu.be/B0WEq0kv7yA

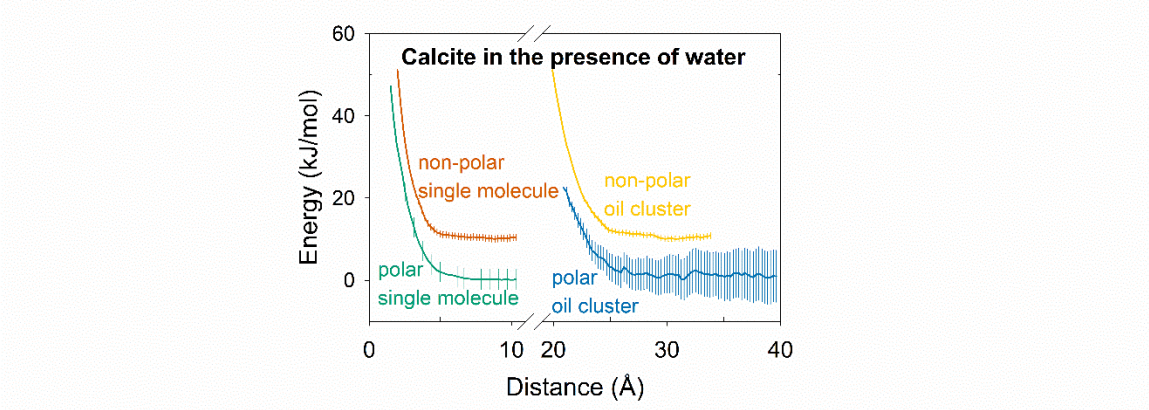

Figure S1. Free energy surfaces of a single molecule and cluster of 30 polar or non-polar oil molecules on calcite (104) in the presence of water. The free energy surfaces are plotted as a function of distance between the oil molecule / oil cluster and calcite surface with respect to their centers of mass. The density of displayed data is reduced for visual clarity.

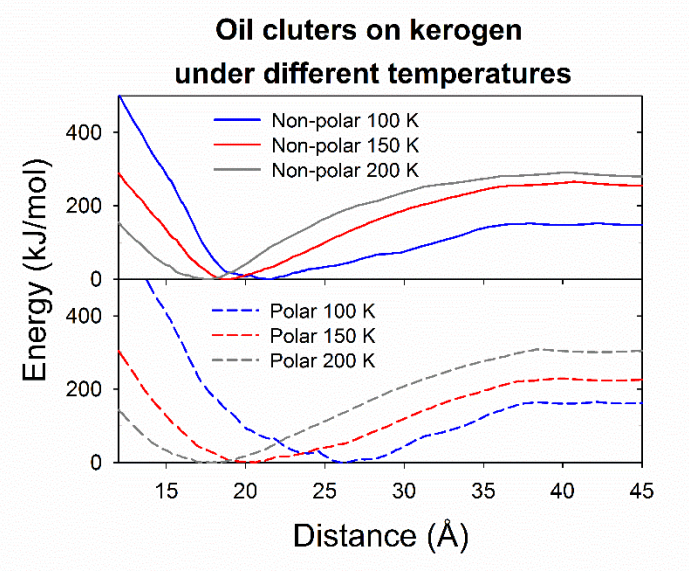

Figure S2. Free energy surfaces of cluster of 30-molecule polar and non-polar oil molecules on kerogen surface under different temperatures. The free energy surfaces are plotted as a function of distance between the oil cluster and kerogen surface with respect to their centers of mass. According to the data point pattern, the correlation between desorption energy and temperature can be formulated using the same linear equation as shown in Figure S3 for both polar and non-polar oil. The error bars are smaller than the symbol size.

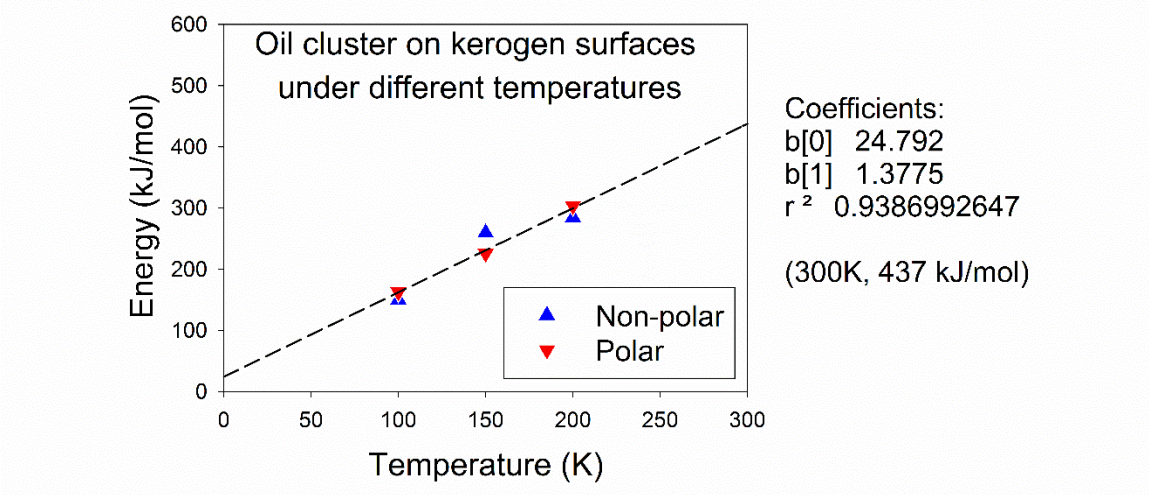

Figure S3. Desorption energies of 30-molecule oil clusters on kerogen surfaces under different temperatures. The non-polar and polar oil drops exhibit linear relationship between temperature and desorption energy (with a R-squared value of 0.9387). The non-polar and polar oil drops follow the same correlation between desorption energy (E_d in kJ/mol) and temperature (T in K):

$$E_d = 1.38 \cdot T + 24.8$$

The energy required for oil drop desorption from kerogen surface increases when the system temperature rises. As shown in Figure S5, a close examination on the interface of oil and surface reveals that oil molecule is strongly attached to the kerogen surface. The same correlation of energy and temperature suggested that the intermolecular bonding between kerogen and oil are so strong that the effect of oil polarity is negligible in such interactions.

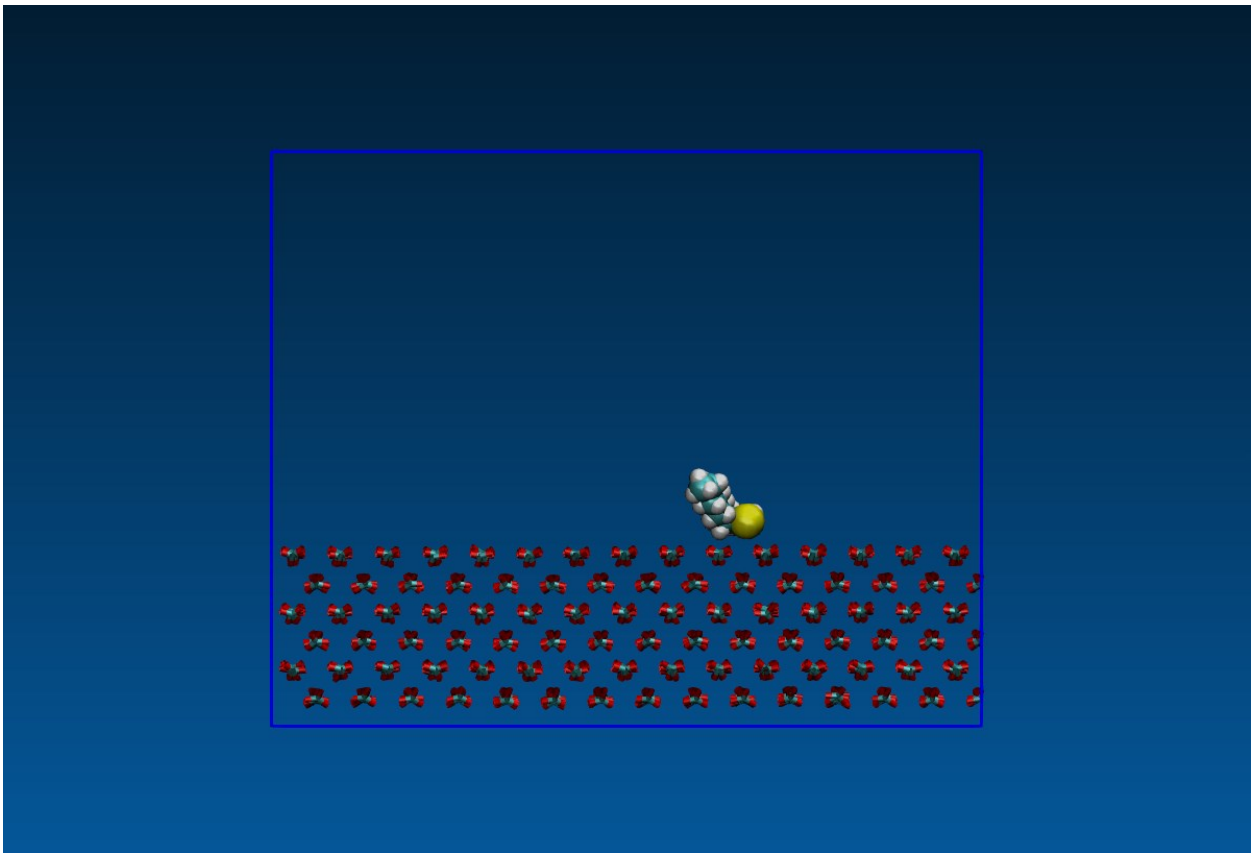

Figure S4. Snapshot of the simulation trajectory of calcite surface interaction with a polar oil molecule in the absence of water.

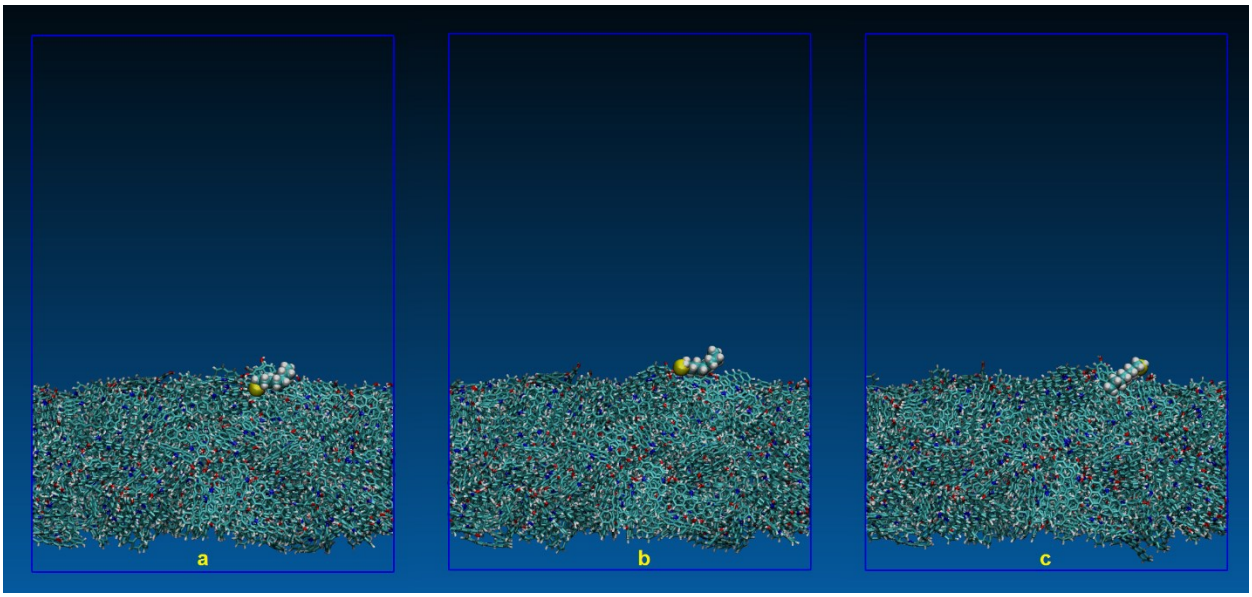

Figure S5. Snapshot of the simulation trajectory of kerogen surface interaction with a polar oil molecule in the absence of water at different time step. (a) and (b) depict strong interactions between polar oil functional group –SH and kerogen functional groups –NH– and –OH, whereas (c) illustrates strong interactions between non-polar carbon chain of polar oil and non-polar benzene rings of kerogen.

Table S1. Desorption energies of 30-molecule oil clusters on kerogen surfaces under different temperatures in the absence of water.

Desorption energy in kJ/mol [error]		
Temperature	Non-polar	Polar
100 K	150.5 [2.5]	163 [3]
150 K	260 [5.5]	226 [3]
200 K	285 [5.5]	304 [5]