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1 **Calculating Free Energy of Fluid-rock Interactions at Oil-shale Interfaces by**
2 **Molecular Dynamics Simulation**

3

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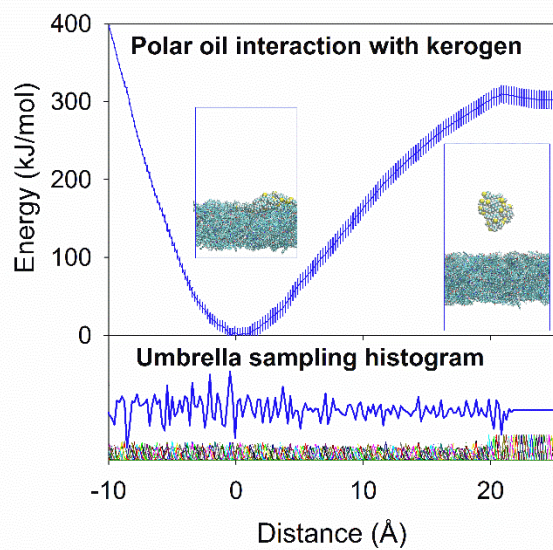
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15

16 **Abstract**

17 Understanding the fluid-rock interactions in shale nanopores is essential for the characterization
18 of the transport and storage of hydrocarbon in oil reservoir rocks of tight formations such as
19 shale. Due to the strong surface effect in nanospace and the heterogeneous nature of hydrocarbon
20 systems, it is a great challenge to study the oil-shale interfaces. Molecular Dynamics simulations
21 were applied to investigate the interaction of light oils with calcite and kerogen surfaces. Octane
22 and octanthiol were used as model molecules to represent non-polar and polar oil compounds. A
23 model molecule of kerogen fragment was implemented as the building block to construct
24 kerogen surfaces which is the major constituent of shale organics. Calcite (104) surface was used
25 due to its hydrophilic property of its surfaces and its ubiquitous presence in formation rocks,
26 especially in carbonate shales. Umbrella Sampling method together with Weighted Histogram
27 Analysis Method was employed to calculate the free energy profile of oil desorption on the
28 surfaces of kerogen and calcite. The effects of oil polarity, size of oil molecular cluster, and
29 water on the free energy were investigated. The results show that at molecular scale, the free
30 energy of desorption of oil molecules is significantly reduced from both kerogen and calcite
31 surfaces if water is presented. For polar oil molecule, the free energy of desorption is higher than
32 that of non-polar oil at both calcite and kerogen surfaces. The organic kerogen surface exhibits
33 stronger binding energies of oil molecules than the inorganic calcite. These findings suggest that
34 1) polar oil compounds require more effort to be recovered than non-polar ones, 2) oil clusters of
35 a smaller size are harder to be displaced than a larger size, and 3) the presence of water decreases
36 the free energy of desorption. This study provides energetic perspective of the interactions and
37 insights on the oil recovery in shale formations. The methodology presented in this study
38 demonstrates that MD simulation is capable to 1) evaluate the impact of different factors to the
39 oil recovery in shale play and 2) offer valuable implications for developing novel technologies of
40 oil recovery from unconventional shale.



43

44 **1 Introduction**

45 Ultra-tight formations, such as shale, bear abundant hydrocarbon fluid in poorly
46 connected nanoscale pores with extremely low porosity and permeability.^{1,2} The flow properties
47 of transport and storage of fluid confined in nanopores deviates substantially from those of its
48 bulk phase. This deviation is largely caused by the surface interactions within nanospace.³⁻⁵ The
49 interactions between the fluid and pore surface can affect a large portion of confined fluid
50 molecules depending on the pore size and interfacial interactions, which leads to dramatic
51 differences in the behaviors of fluid migration and storage in nanopores, compared to those of
52 bulk phase fluid.^{6,7} For instance, if the pore size decreases from 100 nm to 10 nm, the affected
53 volume of the fluid increases from 17% to 100% by the intermolecular interactions with surface
54 (assuming the affected radius is 3 nm) as shown in Fig 1. Significant amounts of hydrocarbon in
55 ultra-tight reservoirs are confined in the nanopores,⁸ mostly in organics and associated with
56 minerals.^{9,10} To understand how the hydrocarbon is stored in the formation rocks, it is vitally
57 important to understand the interfacial interactions between the hydrocarbon fluid and nanopore
58 surfaces in ultra-tight formation. Since oil recovery process is linked to the interfacial
59 interactions between oil molecules and nanopore surfaces, knowing how much energy is needed
60 to allow oil to be detached from the surface is fundamental to understand the transport and
61 storage behavior of oil in shale,¹¹ which can determine the favorable recovery techniques and
62 reservoir conditions for oil desorption in terms of thermodynamics. This approach can lead to
63 important implications for oil recovery efforts.

64 To probe the interfacial interactions at nanoscales, atomistic- and molecular-level
65 characterizations are needed. Both experimental and computational approaches have been

66 applied to study the hydrocarbon fluid behavior in shale at nanoscale. Extensive experimental
67 studies have been conducted on the shale formation to characterize the organic content^{12,13}, pore
68 structure^{9,14-16}, and petrophysics^{9,17-19}. These studies aimed to calibrate the empirical models in
69 reservoir engineering to describe the fluid flow^{20,21} and to provide implications for reservoir
70 assessment and production optimization.¹⁰ However, it is challenging to interpret the dynamics
71 and kinetics of interface interactions without knowing the molecular scale details given the
72 compositional and structural heterogeneity of shale formations. Understanding the shale systems
73 heavily relies on the characterization technologies to conduct experiments on surfaces and
74 interfaces²²⁻²⁴ such as Focus Ion Beam Scanning Electron Microscopy (FIB-SEM),^{19,25,26}
75 Transmission Electron Microscopy (TEM),^{26,27} Atomic Force Microscopy (AFM),^{1,20,28} X-ray
76 Diffraction (XRD),^{29,30} X-ray microtomography (Micro-CT),^{31,32} Nuclear Magnetic Resonance
77 (NMR),^{33,34} etc. Implementing these methodologies become challenging at molecular level and
78 even infeasible at atomic scale in order to characterize microscopic phenomena. Unlike
79 experiments, computational simulations can study physical phenomena over a wide range of
80 scale across space and time,³⁵ directly connecting the microscopic details of a system with
81 macroscopic properties of experimental interest.³⁶ Due to the intensive computation, Quantum
82 Mechanics (QM) simulations have strict limit on the size, time, and complexity of systems.³⁵⁻³⁷
83 Molecular and atomistic simulations, built on classical molecular mechanics (MM) such as
84 Monte Carlo (MC) and Molecular Dynamics (MD), are more appropriate than QM methods to
85 address the issues of size and complexity of hydrocarbon systems. MC methods are stochastic
86 approach, suitable for analyzing system equilibrium, while MD techniques are deterministic,
87 favorable to study both equilibrium and transport properties of a given system.^{36,37} Thus, this
88 study used MD in order to understand the energetics of fluid-rock interactions at nanoscale.

89 Currently, there are several studies using MD to investigate hydrocarbon fluid interactions with
90 shale minerals and kerogen such as 1) the adsorption, diffusion, and permeation of hydrocarbon
91 fluid in shale kerogen and kerogen analogue;^{7,38–44} 2) slippage, displacement, and adsorption of
92 hydrocarbon flow on quartz, calcite slits, and montmorillonite slits;^{45–48} 3) detachment of oil
93 cluster from silicate surfaces in surfactant solution.⁴⁹ These studies evaluated the effect of
94 nanopores on the properties of hydrocarbon fluid, such as bulk viscosity, contact angle, and
95 slippage. Liu et al 2012 stated that water can penetrate the oil—water interface and form surface
96 water layer on a hydrophilic silica surface, enhancing the oil detachment from the hydrophilic
97 surface. However, the energetic aspect of the hydrocarbon/shale interaction essentially remains
98 intact and hence limited kinetic information is reported.

99 The present study attempts to test the feasibility of computational approach to evaluate
100 the free energy profile of oil compounds desorption from shale surfaces. Calculation of free
101 energy profile by Umbrella Sampling widely used in computational biology and biochemistry.⁵⁰
102 is adopted in this study to investigate the oil interactions with shale media especially organic
103 kerogen to calculate the free energy changes during the adsorption and desorption processes. We
104 examine the surfaces of kerogen and calcite to evaluate the effect of four different variables
105 including oil polarity (polar vs non-polar oil), oil cluster size (single molecule oil vs 30-molecule
106 oil cluster), surface composition (inorganic calcite mineral vs organic kerogen), and surface
107 water (the presence vs the absence of surface water). Profiling the free energy surface of oil-rock
108 interactions in nanopores provides an insight of hydrocarbon behaviors in unconventional shale
109 reservoir, a multi-phased nano-porous system of rich organic content.

110

111 **2 Method**

112 2.1 Molecular models for oil, kerogen, and calcite

113 Crude oil is a mixture of widely varying polar and non-polar compounds as well as their
114 proportions. Typically, crude oil contains over 45% non-polar (e.g. alkanes and cycloalkanes)
115 and less than 15% polar species (e.g. N-, S-, O- and metal-containing compounds).^{51,52} Polar
116 components can significantly affect properties of hydrocarbon fluid in reservoir such as
117 viscosity, contact angle, interfacial activity, emulsion, and chemical stability.^{2,53,54} The oil-rock
118 interactions are largely attributed by the polar species,⁵⁵ particularly in shale since organic phases
119 usually retain more polar components than minerals². Thioalkanes are common sulfur
120 compounds found in crude oils.⁵⁶ Shale oil has high content of light oil (C₁-C₉).^{57,58} Therefore,
121 we selected 1-octanethiol (C₈H₁₈S) with a dipole moment of 2.9 D⁵⁹ and its non-polar
122 counterpart n-octane (C₈H₁₈) with no dipole moment as models for polar and nonpolar oil as
123 shown in Figure 2. In addition, to model small oil drop, we prepared two oil clusters consisted of
124 30 molecules of octanethiol and octane, respectively.

125 The mineralogy of shale is highly complicated, which contains inorganic and organic
126 constituents. Inorganic phases consist of three major minerals: clays, quartz, and carbonates
127 (calcite and dolomite)¹⁴. Due to its simple structure, we chose calcite (104) face as a hydrophilic
128 mode of shale inorganic surface. The calcite (104) is a flat stoichiometric surface, which is one
129 of most common mineral faces occurred in both geological and biological systems and has been
130 well studied both computationally and experimentally.⁶⁰ The key organic phase in shale involved
131 in the interactions with hydrocarbon is kerogen.^{2,61,62} Despite the complexity of kerogen in
132 reservoir formations⁶³, many studies used graphene to represent kerogen^{7,43,44,64-67}. The
133 differences between graphene and kerogen, such as bonding environment of functional
134 groups^{68,69} and surface morphology⁶³, give rise to different chemical and mechanical

135 properties^{69,70}. Changing surface properties can drastically alter the interfacial interactions with
136 hydrocarbons, leading to different simulation results. To capture fundamental properties of
137 kerogen, we employed a molecular fragment C₂₂H₁₃ON derived from type II kerogen to build
138 kerogen surfaces,³⁸ which is the most common kerogen in hydrocarbon-bearing shale
139 formations⁶³. The kerogen molecule has five benzene rings, a secondary amine, and a phenol
140 group, resulting in a polar compound. To create kerogen surfaces, 511 kerogen molecules were
141 randomly added into a computational supercell (18,944 atoms in total), quenched from 3000 to
142 300 K (ramp), and the surfaces were created by inserting a vacuum space between the kerogen and
143 then stabilization and relaxation of the surface were followed at 300 K using an NVT ensemble.

144 The calcite (104) surface in Figure 3(b) was built with 1620 CaCO₃ molecule units with a
145 dimension of approximately 7 × 7 × 2 nm with 8,100 atoms. The kerogen surface in Figure 3(a)
146 was built with 511 C₂₂H₁₃ON molecule units with a dimension of approximately 8 × 8 × 3 nm
147 with 18,907 atoms as shown. Because of the ubiquitous presence of water in the reservoir
148 formations, water molecules were added to the fluid. To ensure the complete submergence of
149 their interactions within water, 7,250 and 10,000 water molecules were added to the calcite
150 surface of single oil molecule or oil cluster, respectively; while 7,500 and 10,000 water
151 molecules were placed on kerogen surfaces of single oil molecule or oil cluster, respectively.

152 A previous experimental study indicates calcite (104) surface exhibits neutral charge due
153 to the stoichiometry of Ca²⁺ and CO₃²⁻.^{71,72} Kerogen surfaces can be negatively charged due to
154 the deprotonation of functional groups, such as OH and NH. However, classical MD models only
155 simulate interatomic interactions by empirical potentials for bond length, angle, and dihedral,
156 whereas formation and breaking of covalent bonds are excluded unless specified by force field.
157 Both calcite and kerogen surfaces maintain electrical neutrality owing to the charge balance of

158 each model molecule. Layers of alternating Ca^{2+} and CO_3^{2-} on calcite (104) created a well-
159 organized surface of neutral charge, while the benzene rings and polar functional groups of
160 kerogen molecule yielded a highly heterogenous surfaces of kerogen.

161

162 2.2 Molecular Dynamics (MD) Simulation and Gibbs Free Energy Profiles

163 MD simulations in this study were deployed using software package Groningen
164 MAchine for Chemical Simulations (GROMACS).⁷³ All simulations were under the three-
165 dimensional periodic boundary conditions. The OPLS-AA force field was used to describe oil
166 molecules and kerogen.⁷⁴ The SPC potential is used to describe water molecule, which exhibits a
167 dipole moment of 2.27 D, comparable to the experimental measurement 1.85 D.⁷⁵ A previously
168 developed force field was used for calcite.⁷⁶ All these potentials have been tested and are capable
169 of producing satisfactory results on bulk and interfacial properties, which are consistent with
170 experimental data.⁷⁷⁻⁷⁹ For a typical umbrella simulation, 1 ns simulation was used for the
171 system to reach equilibrium. Newton's equations of motion were integrated using the leap-frog
172 scheme with a timestep of 1 fs, fast Smooth Particle-Mesh Ewald (SPME) electrostatics, Verlet
173 cutoff-scheme, and temperature coupling using a Nose-Hoover extended ensemble with a
174 coupling constant of 0.1 ps. Simulations were visualized by Visual Molecular Dynamics (VMD)
175 package.⁸⁰

176 The potential of mean force for the oil interactions with different surfaces was computed
177 by Umbrella Sampling and the Weighted Histogram Analysis Method (WHAM).^{81,82} Gromacs
178 package was used to carry out Umbrella Sampling simulations by running separate simulation

179 windows along the reaction coordinate individually. The simulation windows were generated by
180 simulations pulling the oil into or away from the surfaces regardless of the presence of water.

181 In each simulation window, umbrella potential, a biased harmonic potential, was applied
182 to the system. For each individual simulation window, we first applied a constraint potential with
183 a force constant $9000 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{nm}^{-1}$ for 0.1 ns to equilibrate the system, then deployed an
184 umbrella potential with a force constant $9000 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{nm}^{-2}$ for 0.1 ns up to 0.2 ns if necessary to
185 obtain probability distribution of the given reaction coordinate. With sufficient windows to
186 overlap the entire reaction coordinate space, a free energy profile curve can be calculated by
187 combining data from each window using WHAM.^{81,83}

188 The error analysis on energy profiles was performed by R using LOESS algorithm.^{84,85}
189 This method fitted the dataset of each energy profiles and deployed bootstrap technique to
190 calculate confidential interval of 95%. The computed errors listed as shown in Table 1 denoted
191 by brackets. The fluctuations of free energy profile lines as shown in Figure S1 were consistent
192 with the size of the error bar.

193

194 **3 Results**

195 Free energy surfaces in Figures 4-7 exemplify how the system energy changes as a
196 function of the distance between oil compounds and surfaces. When the oils approach surface,
197 the energy required becomes large due to repulsive interactions. When the oils gradually move
198 away from the surface, the energy reaches the minimal point which is the state of adsorption of
199 the oil at the surfaces. As the distance continuously increases, the energy increase until system

200 reaches the energy plateau region where no additional energies are required to maintain distance
201 between the oils and the surfaces.

202

203 3.1 Interactions of oil molecules with kerogen surface

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

215

216 3.2 Interactions of oil molecules calcite (104) surface

217 The free energy profiles in Figure 6 shows how free energy changes as a function of the
218 distance between oil compounds and calcite (104) surfaces in water. Unlike the rest free energy
219 profiles (described later), they exhibit a distinct pattern: as the distance increase, the free energy
220 quickly decreased to minimal and maintained at the same level to form a flatland. Such patterns

221 indicate near zero energies for the desorption of oil molecules on the calcite surface in the
222 presence of water.

223 For comparison, an identical set of systems without water were simulated, of which the
224 free energy profiles are depicted in Figure 7. The results show that 33.6 ± 3.9 kJ/mol and $18.0 \pm$
225 5.5 kJ/mol are required to desorb polar and non-polar oil molecules from calcite surfaces
226 respectively, and 222 ± 36 kJ/mol and 198 ± 42 kJ/mol to desorb polar and non-polar oil clusters,
227 respectively. According to the simulation output trajectory (Fig. S4), the polar molecule was
228 bound to the calcite surface through the thiol functional group $-SH$, which confirms a previous
229 study on the adsorption of simple organic molecules on calcite (104).⁸⁶ In addition, the thiol
230 group $-SH$ of polar oil appears to favor the sites of Ca^{2+} of calcite (104) surface, whereas the
231 non-polar oil shows no preference of absorption sites.

232

233 **4 Discussion**

234 4.1 Surface effect (kerogen vs calcite)

235 The simulation results suggest that the desorption energy of oil on calcite surfaces are
236 consistently lower than on kerogen surfaces, suggesting stronger interactions of the oil molecules
237 with kerogen than calcite. The desorption energy is 5.3 to 17 kJ/mol higher for a single oil
238 molecule and 210 to 372 kJ/mol higher for the oil cluster (7.0 to 12.4 kJ/mol per molecule for the
239 oil cluster) at kerogen surface than at the calcite surface regardless of molecular polarity. Both
240 single molecule oil and oil cluster requires higher desorption energy from kerogen than calcite,
241 indicating oil recovery from organic phase of shale requires more energy than the hydrophilic
242 inorganic calcite surface.

243 Another factor that contributes to the difference between kerogen and calcite surfaces is
244 the surface morphology. Calcite (104) surface is well-structured, which has low surface area.
245 Therefore, calcite has low sorption capacities.⁸⁷ The kerogen surface is porous and waxy based
246 on the experimental observations.^{63,88} The effective surface area on kerogen would be much
247 higher than calcite, leading to stronger interactions and a higher desorption energy for oil.

248

249 4.2 Effect of oil polarity

250 Molecular polarity plays imperative role in the energetics of oil desorption. For oil
251 adsorbed on the calcite surfaces, polar oil molecules consistently require higher desorption
252 energies than its counterpart non-polar oil owing to the molecular dipole of both polar oil and the
253 hydrophilic nature of calcite surface. The desorption energy for polar oil molecule is about two
254 times of the desorption energy for non-polar oil molecule and the desorption energy for polar oil
255 molecular cluster is about 10% higher than the desorption energy for non-polar oil cluster in the
256 absence of water. However, the effect of polarity is complicated on kerogen surfaces. The
257 desorption energies of the single molecule oil show that the polar oil molecule requires energy
258 about two times of the energy of non-polar per molecule in the absence of water; whereas the
259 desorption energies of polar and nonpolar oil molecules are approximately the same in the
260 presence of water. For 30-molecule oil cluster, our calculation indicates that polar oil cluster
261 requires the same desorption energies as the non-polar oil cluster.

262 These phenomena can be explained by the dipole interactions. Since there is no free ion
263 in the systems, the intermolecular interactions are controlled by permanent dipole interactions, or
264 Keesom interaction. As shown in Fig S5 a and c, the thiol functional group (–SH, yellow) of

265 polar oil tend to be in proximity to the functional groups of kerogen molecules such as amine (–
266 NH–, blue) and hydroxyl (–OH, red) upon contact at the interface, which confirms the
267 anticipated dipole interactions. Unlike polar oil, non-polar oil molecules have no dipole moment
268 and therefore a weaker desorption energy than the polar oil molecules. Thus, the affinity of the
269 polar oil molecule with both calcite and kerogen surfaces is stronger than non-polar.⁸⁹ This
270 postulation implies that the polar content of shale oil can significantly affect the oil/rock
271 interactions in shale by changing the chemical environment at the interfaces.^{53,90–92} This finding
272 suggests that a high polar content in hydrocarbon fluid can bring additional challenges to oil
273 recovery in tight formations of unconventional shale plays.

274 In the absence of water, similar desorption energies for non-polar and polar oil clusters
275 on kerogen surfaces were similar, which suggests that the molecular polarity has insignificant
276 impact on the interactions between the oil cluster and kerogen surface. As shown in Fig S5, it is
277 possible that the polar oil molecular clusters were formed primarily by the strong dipole
278 interactions between their functional groups thiol –SH, which reduces the exposure of functional
279 groups to the kerogen surfaces and therefore lead to a bonding that is mainly contributed by the
280 interactions of non-polar group of polar molecule with kerogen surface. Another possible
281 explanation is due the heterogenous nature of kerogen surface. The kerogen molecule is a large
282 compound with five non-polar benzene rings and two polar functional groups –OH and –NH–.
283 Therefore, it is possible that the affinity between non-polar groups of kerogen with non-polar oil
284 is similarly strong as the polar groups of kerogen to polar oil.

285 Moreover, calcite (104) plane cannot be treated as non-polar surface, especially at
286 nanoscale. Previous studies suggested that calcite (104) is overall non-polar because the
287 alternating Ca^{2+} and CO_3^{2-} are closely packed and maintain charge balance.^{93,94} Our study shows

288 that at molecular level the calcite (104) is clearly favors the adsorption of the polar oil than non-
289 polar oil due to the dipole moment possessed in each Ca^{2+} and CO_3^{2-} pair.

290

291 4.3 Effect of surface water and oil cluster

292 The presence of surface water reduces the oil desorption energy on all surface conditions,
293 promoting the oil desorption for all the cases. As discussed previously, calcite is hydrophilic,
294 while kerogen has both hydrophilic and hydrophobic functional groups. The surface water can
295 easily be attracted to the calcite surface and kerogen hydrophilic functional groups. Both water
296 and polar oil molecules have similarly potent dipole moments 2.9 D and 2.27 D, respectively.
297 Water molecules compete with polar oil molecules for adsorption at surfaces with hydrophilic
298 character, and consequently reducing the desorption energy of the oil molecules at the surfaces.
299 The interactions of waters on calcite (104) surfaces were much stronger than on kerogen
300 surfaces, suggesting a weaker hydrophilic nature of kerogen surface than the calcite surface. The
301 affinity between calcite and water is stronger than that between calcite and oil, resulting in a
302 strong oil-repellent surface of calcite in the presence of water.

303 Our result shows that oil clusters of smaller size require higher desorption energies per
304 molecule than a single molecule of oil. The desorption energies required per molecule for oil
305 clusters are substantially smaller than those of single molecules. For polar oil, the desorption
306 energy of single molecule of oil is 4.6 to 25.2 kJ/mol higher than the desorption energy per
307 molecule in oil cluster, which is 37% to 340% increment of desorption energy per molecule in
308 oil cluster. This difference is mainly attributed to the number of oil molecules that directly
309 interact with the surface. Not all the molecules in the 30-molecule clusters directly interact with

310 the surfaces, while the single molecule always interacts with the surfaces, which leads to the
311 smaller desorption energies per molecule.

312

313 **5 Summary and concluding remarks**

314 Molecular Dynamics Simulation is demonstrated to be capable to calculate the energetics
315 of oil/rock interactions at the interfaces. The effects of surface, oil polarity, presence of surface
316 water, numbers of oils in oil molecular cluster on the desorption free energy suggest that 1) the
317 waxy and porous structure of kerogen has a significant contribution to the higher desorption
318 energies owing to the large surface area and strong dipole moments of functional groups than
319 calcite; 2) polar oil compounds require more effort to be recovered than non-polar from both
320 kerogen and calcite surfaces. If the presence of polar content is substantial, it is necessary to treat
321 shale oil as polar mixtures instead of non-polar for effective oil recovery; 3) an single oil
322 molecule or oil molecules larges dispersed in nanopore tends to be more challenging to be
323 recovered than large oil molecular cluster due to stronger interactions with the surfaces than
324 clustered oil molecules; 4) water facilitates the oil desorption by reducing the binding energy
325 between oil and shale rocks, either kerogen or inorganic calcite. Given the desorption process in
326 this study is reversible and is the reserved process of adsorption, the amount of energy required
327 for desorption is the same for adsorption. This study illustrates a computational approach of
328 atomistic scale using realistic models and advanced free energy methods to investigate the
329 energies involved in the oil/rock interactions at fluid-rock interfaces, offering valuable
330 implications for oil recovering from tight reservoirs especially in unconventional shale play.

331

332 **Conflicts of interest**

333 There are no conflicts to declare.

334

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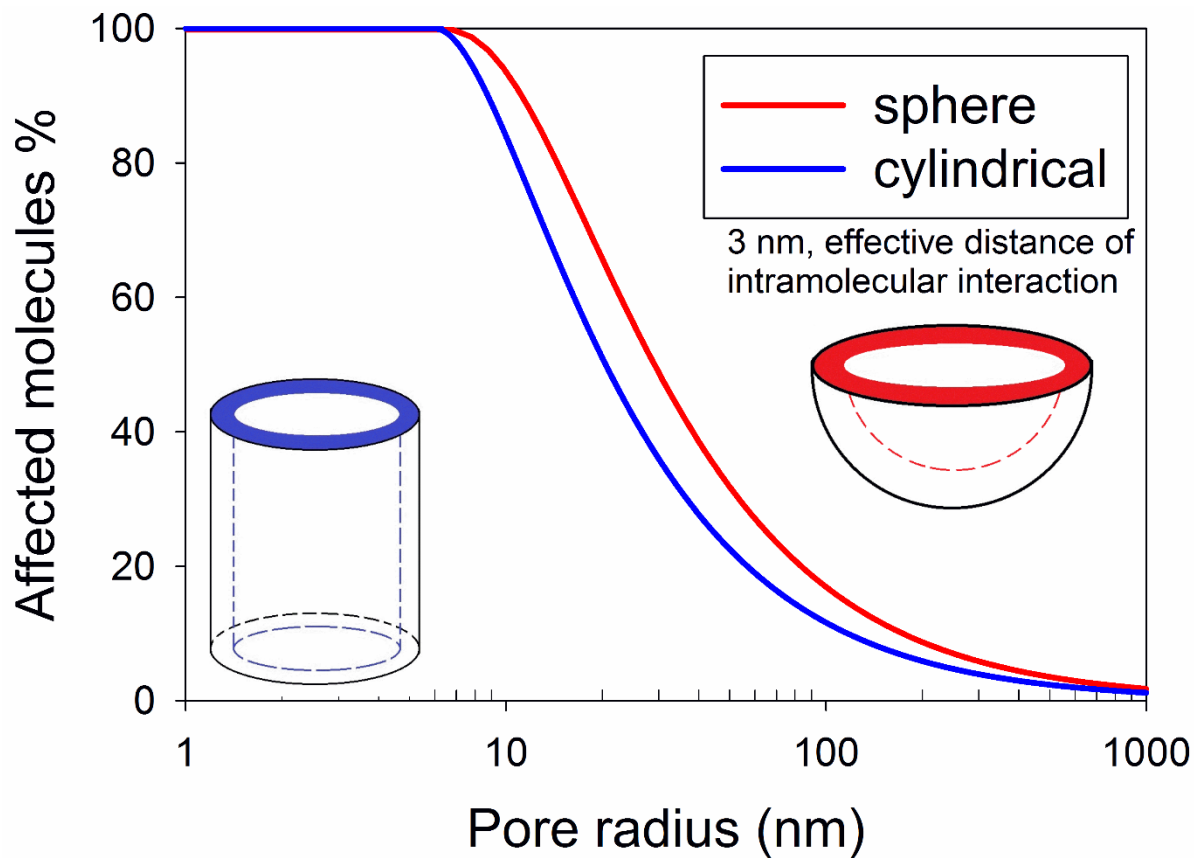
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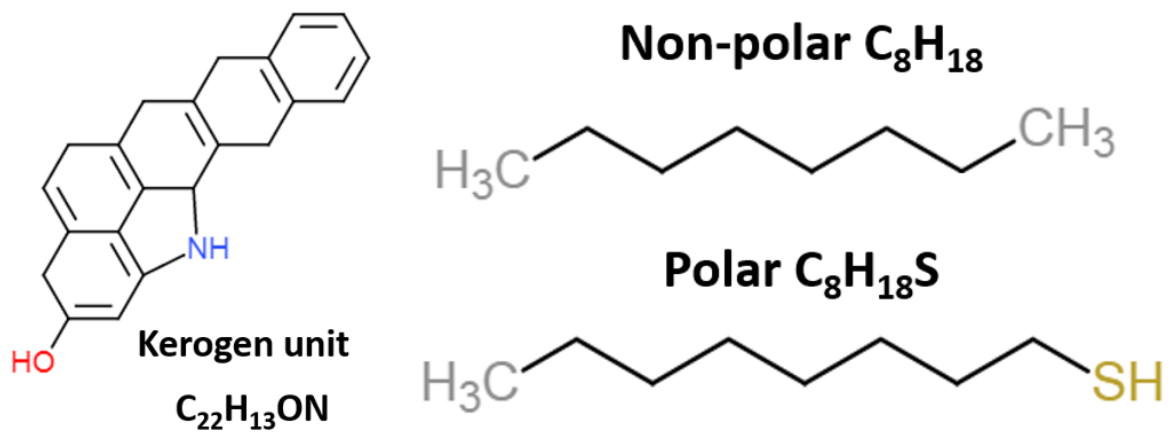
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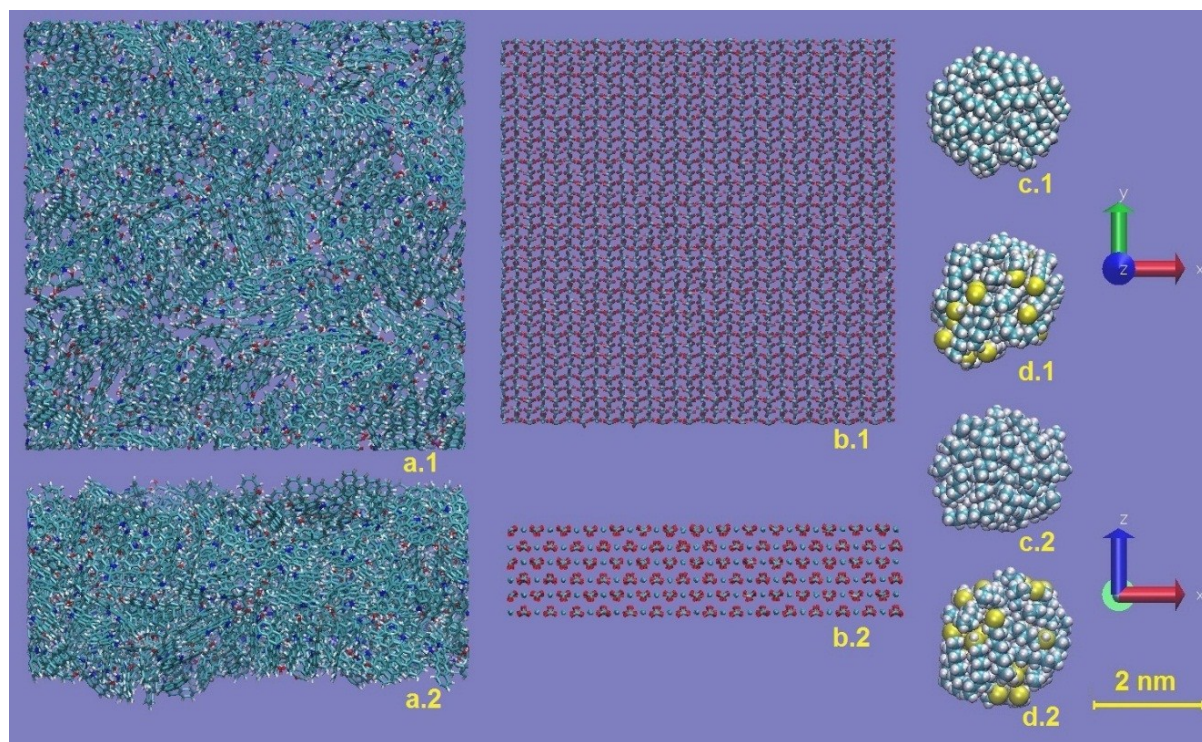
Figure 1. Effect of intermolecular interaction on the fluid confined in nanostructures.



611

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

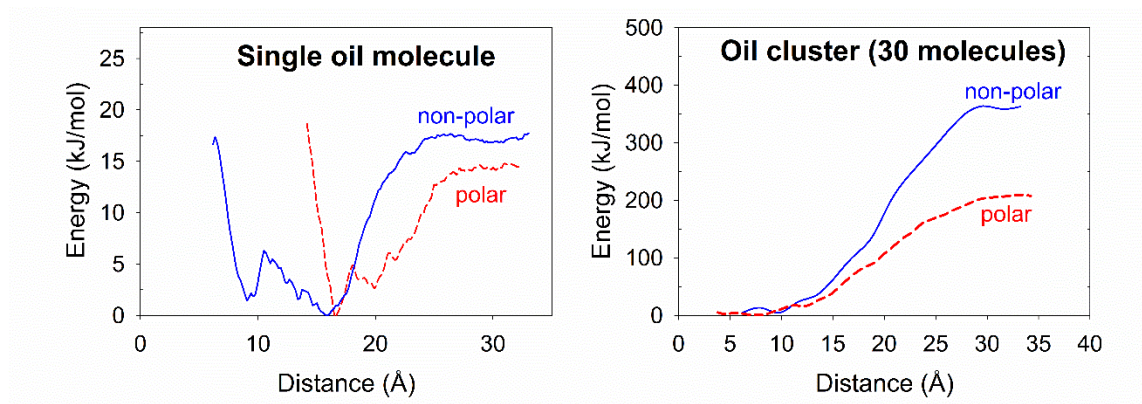
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616 Figure 3. Kerogen slab (a), calcite (104) slab (b), 30-molecule non-polar oil cluster (c), and 30-molecule
617 polar oil cluster (d). “x.1” and “x.2” denote different orientations.

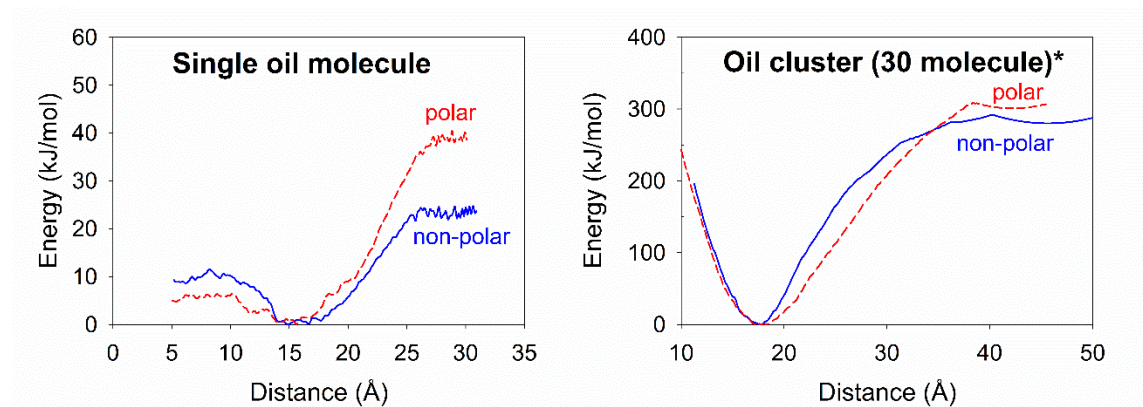
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620 Figure 4. Free energy surfaces of single molecule of polar or non-polar oil on kerogen surface with water
621 (left); Free energy surfaces of oil drop of 30 polar or non-polar oil molecules on kerogen surface with
622 water (right).

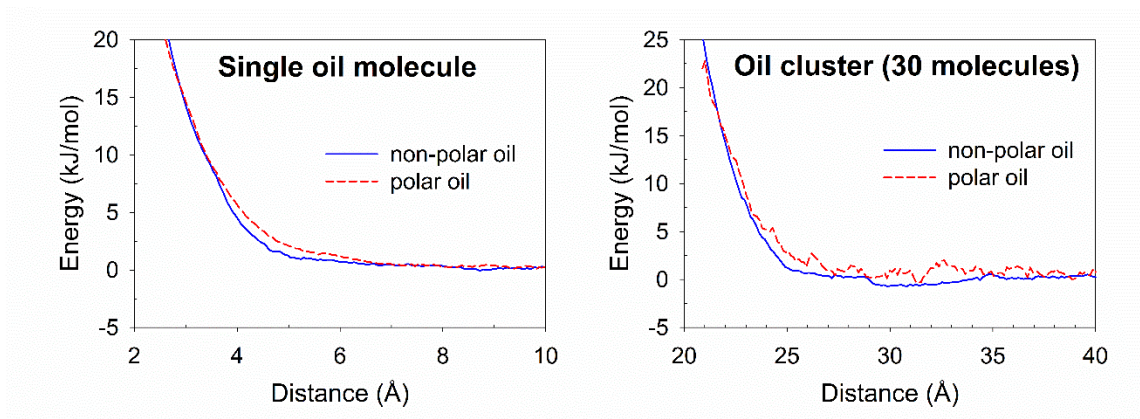
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625 Figure 5. Free energy surfaces of single molecule of polar and non-polar oil on kerogen surface without
626 water (left); free energy surfaces of oil drop of 30 polar or non-polar oil molecules on kerogen surface
627 without water (right). *indicates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

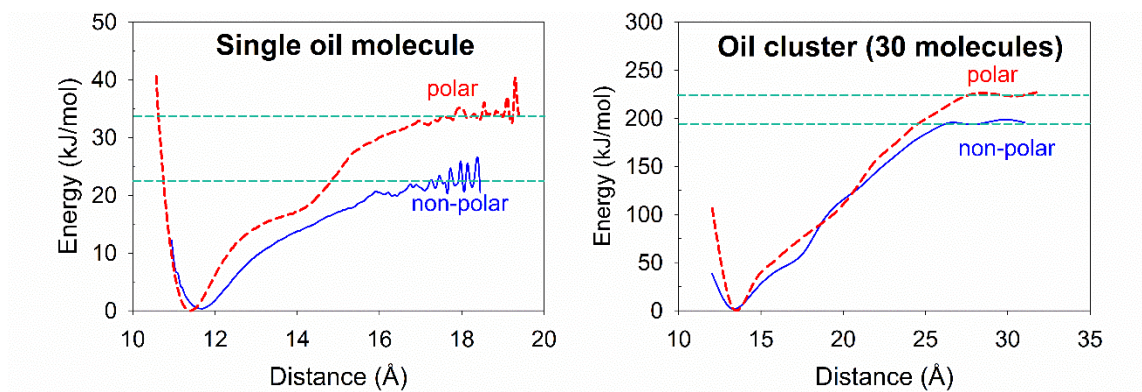
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630

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

633



634

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

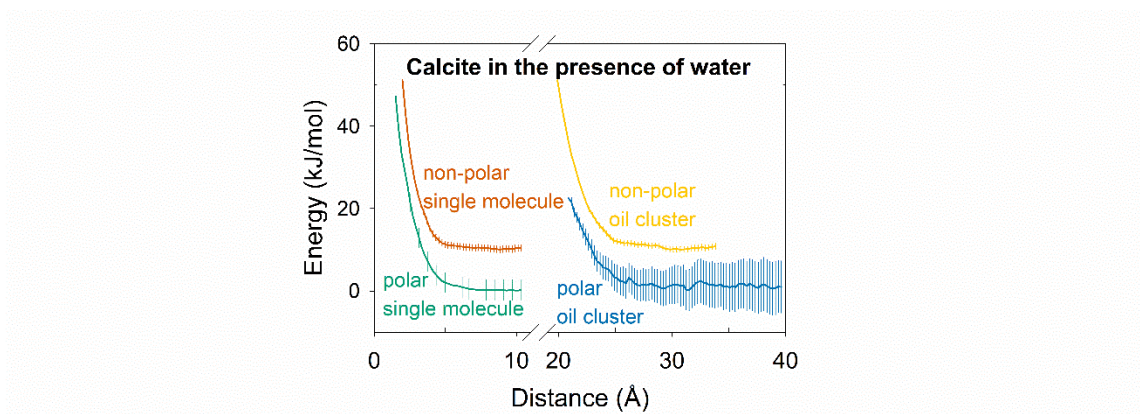
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Table 1. Desorption energy of single molecule oil droplet and 30-molecule oil drop on calcite and kerogen surface under 300 K. The () denotes the errors propagated from the output data of WHAM.

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

640 Supplement Information

641

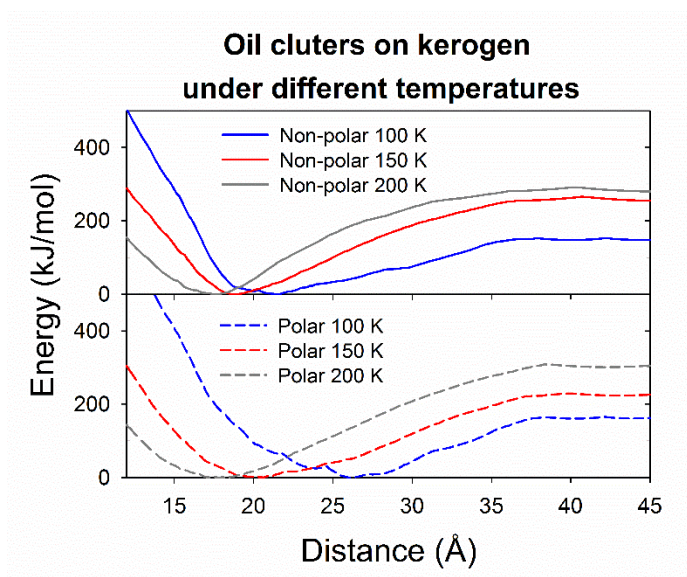


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643 Fig S1. Free energy surfaces of oil drop of polar or non-polar oil on calcite surface with water. The
644 density of displayed data is reduced for visual clarity.

645

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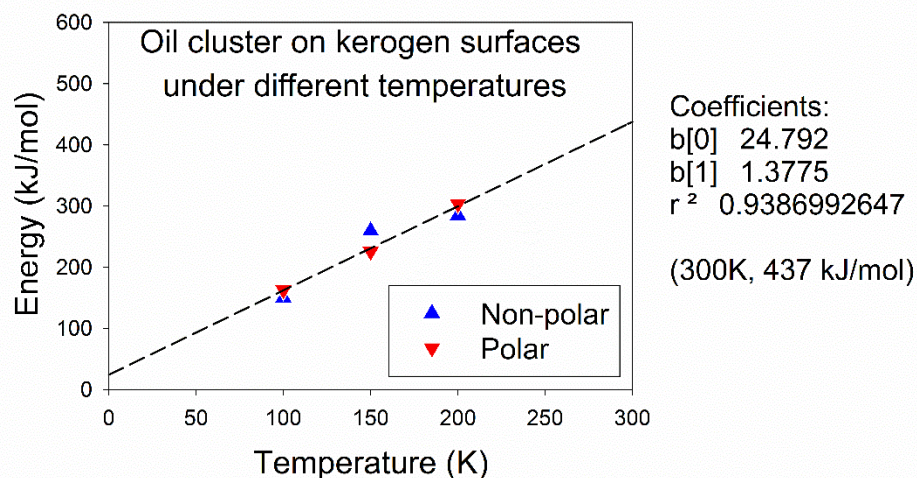


647

648 Fig S2. Free energy surfaces of 30-molecule oil drops interacting with kerogen surface under different
 649 temperatures. According to the data point pattern on this chart, the correlation between desorption energy
 650 and temperature can be formulated using the same equation below for both polar and non-polar oil. The
 651 error bars are smaller than the symbol size.

652

653



654

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

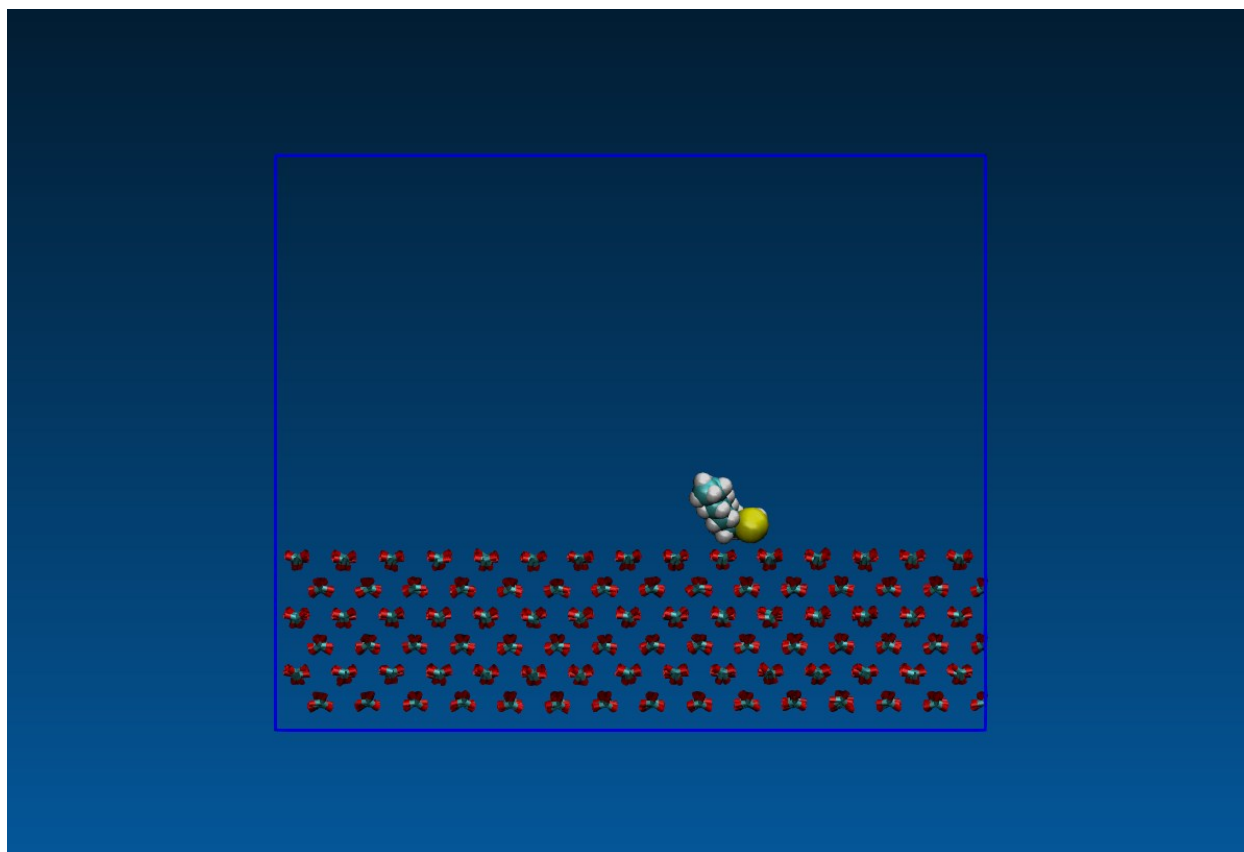
656 The non-polar and polar oil drops exhibit linear relationship between temperature and desorption
 657 energy (with a R-squared value of 0.9387). The non-polar and polar oil drops follow the same
 658 correlation between desorption energy (E_d in kJ/mol) and temperature (T in K):

659

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

660 The energy required for oil drop desorption from kerogen surface increases when the system
 661 temperature rises. As shown in Fig 9, a close examination on the interface of oil and surface
 662 reveals that molecules of oil drop are strongly attached to the kerogen surface. The same
 663 correlation of energy and temperature suggested that the intermolecular bonding between
 664 kerogen and oil are so strong that the effect of oil polarity is negligible during such interactions.

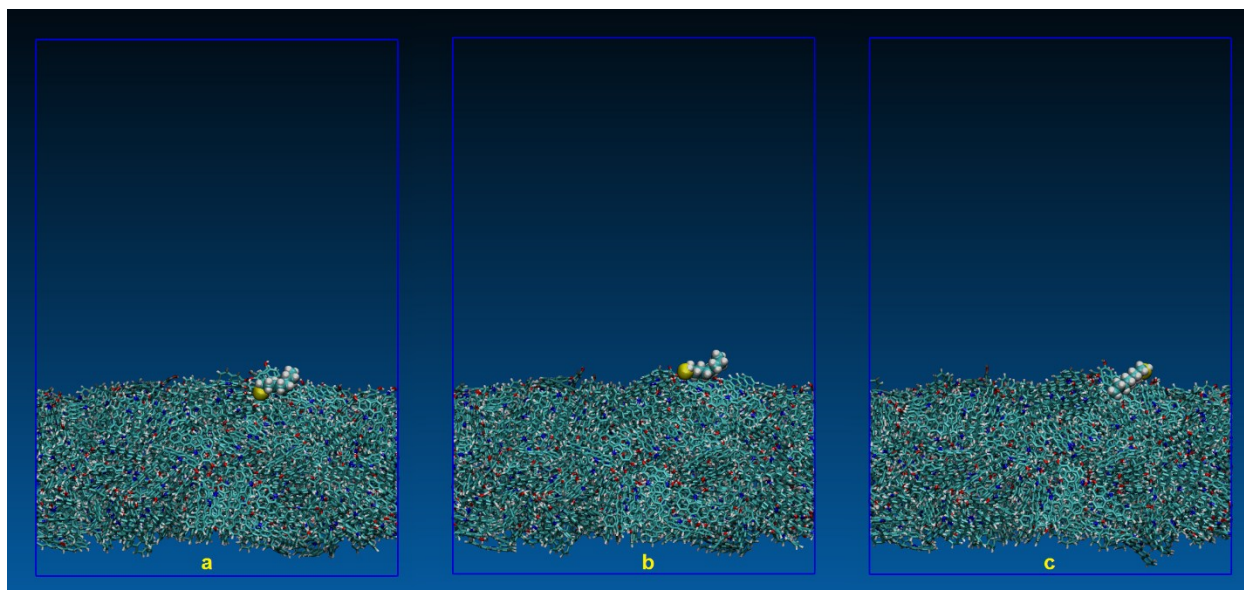
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666

667 Fig S4. Snapshot of the simulation trajectory of calcite surface interaction with polar oil
668 molecule in the absence of water.

669



670

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

676

677 Table S1. Desorption energies of oil drops on kerogen surface under different temperatures in the absence
678 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]

679