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Experimental and Molecular Insights on Sieving of Hydrocarbon Mixtures in Niobrara Shale

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Abstract

In nanoporous rocks, potential size/mobility exclusion and fluid-rock interactions in nano-sized pores and pore throats may turn the rock into a semi-permeable membrane, blocking or hindering the passage of certain molecules while allowing other molecules to pass freely. In this work, we conducted several experiments to investigate whether Niobrara samples possess such sieving properties on hydrocarbon molecules. Molecular dynamics simulation of adsorption equilibrium was performed to help understand the trends observed in the experiments. The procedure of the experiments includes pumping of liquid binary hydrocarbon mixtures ($C_{10} C_{17}$) of known compositions into Niobrara samples, collecting of the effluents from the samples, and analysis of the compositions of the effluents. A specialized experimental setup that uses an in-line filter as a mini-core holder was built for this investigation. Niobrara samples were cored and machined into 0.5-inch diameter and 0.7-inch length mini-cores. Hydrocarbon mixtures were injected into the mini-cores and effluents were collected periodically and analyzed using gas chromatography. To understand the potential effects of hydrocarbon-rock interactions on their transport, molecular dynamics simulations were performed to clarify the adsorption of C_{10} and C_{17} molecules on calcite surfaces using all-atom models. Experimental results show that the heavier component (C_{17}) in the injected fluid was noticeably hindered. After the start of the experiment, the fraction of the lighter component (C_{10}) in the produced fluid gradually increased and eventually reached levels that fluctuated within a range above the fraction of C_{10} in the original fluid; besides, the fraction of C_{17} increased in the fluid upstream of the sample. Both observations indicate the presence of membrane properties of the sample to this hydrocarbon mixture. Simulation results suggest that, for a calcite surface in equilibrium with a binary mixture of C_{10} and C_{17} , more C_{17} molecules adsorb on the carbonate surface than C_{10} molecules, providing a mechanism that directly supports the experimental observations. Some experimental observations suggest that size/mobility exclusion should also exist. This experimental study is the first evidence that nanoporous reservoir rocks may possess membrane properties that can filter hydrocarbon molecules. Component separation due to membrane properties has not been considered in any reservoir simulation models. The consequence of this effect and its dependence on the mixture and environmental conditions (surface, pressure, temperature) are worthy of discussions and further investigations.

Introduction

Semi-permeability is generally defined as the ability of semi-permeable membranes, typically natural or synthetic filtering materials, to separate substances according to their physical or chemical properties when a driving force (e.g. chemical potential gradient) is applied across the membrane, allowing certain molecules and ions to pass but restricting the transport of others.

Shale with clastic components is known to possess membrane properties to ionic species within an aqueous phase from electrostatic exclusion. Naturally negatively charged clay platelets tend to attract cations and repel anions to maintain electrical neutrality, thus forming an electrical double layer (EDL) near the clay platelet surface, as shown in figure 1. The EDLs of adjacent clay platelets can get overlapped because of, for instance, overburden pressure during sedimentation, narrowing the electrical neutrality zone in between. Therefore, anions attempting to pass through might be repelled by the negatively charged clay platelets, and their corresponding cations might either remain to maintain the electrical neutrality of the external solution or get attracted by the clay platelets, resulting in the restriction of ion transport to some extent.



Figure 1. (a) electrical charge distribution near clay surface (b) non-overlapped EDLs (c) overlapped EDLs between adjacent clay platelet (Mitchell and Soga 2005, Keijzer 2000)

Investigations that dedicated to identifying and exploring the membrane properties of shale due to electrostatic exclusion have been carried out in several laboratory studies. Wyllie (1948) measured the electrical potential across a shale which is placed between NaCl solutions with different concentrations on the opposite side, showing that shale can act as a semi-permeable membrane. Buneev et al. (1947) and Lomtadze (1954) experimentally investigated the salt-filtering properties of clavs, which shows the membrane properties of shale directly. Kemper (1961) observed the development of osmotic pressure between two separating solutions with different salt concentrations by shale. Kemper (1960), McKelvey and Milne (1962), Kryukov et al. (1962), Englehardt and Gaida (1963) and Milne et al. (1964) reported that compacted clays can exclude salt ions from experimental results, which again indicates the membrane properties of shale. Young and Low (1965) demonstrated experimentally that certain natural clavey rocks also exclude salt ions and have membrane properties. Not only the results of laboratory studies have revealed the membrane properties of shale, but observations from geological fields also indicate that shale can act as semi-permeable membranes. Berry (1959, 1960) found that the presence of chemical and pressure anomalies is widely distributed in the San Juan Basin of New Mexico and Colorado, which they believe can best be explained by the chemical osmosis or salt filtration caused by membrane properties of shale. Berry and Hanshaw (1960) and Hill et al. (1961) suggested shale acting as a semi-permeable membrane might be the reason for similar chemical and pressure anomalies in Alberta, Canada. Bailey et al. (1961) also reported the existence of salt filtration in Wheeler Ridge anticline of the San Joaquin Valley, California. In recent, Neuzil (2000) showed that water transport between boreholes is interrelated with an applied chemical gradient through a nine-year in-situ field experiment which

measures the fluid pressure and concentration on the Cretaceous Pierre Shale in South Dakota, confirming the significant role of membrane properties in shale.

The abovementioned studies all focused on membrane behavior of shale, or more precisely, clay-rich rocks, to charged components in an aqueous solution due to electrostatic exclusion. To date, few studies have been carried out on membrane behavior of shale to uncharged components such as hydrocarbon molecules, which are of importance to petroleum exploration and production. According to the classification of International Union of Pure and Applied Chemistry (IUPAC), pores with diameters less than 2 nm are micropores, 2-50 nm are mesopores, and greater than 50 nm are macropores. In tight shale, the sizes of micropores and a portion of mesopores, along with connecting pore throats are less than 2-3 nm (Kuila and Prasad 2013), comparable or less than the sizes of certain hydrocarbon molecules (Nelson 2009). Thus, even though hydrocarbon molecules are uncharged, it is possible that size/mobility exclusion can hinder larger / less mobile molecules or even filter them out when flowing through shale, resulting in shale prone to producing lighter and more mobile components. Additionally, mineral surfaces can preferentially adsorb certain components over others (Cheng and Huang 2004; Heller and Zoback 2014; Wang et al. 2015), and such a mechanism could also generate membrane behavior when adsorbing surfaces are unsaturated.

Currently, there is some evidence of membrane behavior of shale for hydrocarbons derived from observed compositional differences between hydrocarbons in the reservoir and its associated source rocks. Hunt and Jameson (1956), Brenneman and Smith (1958), and Hunt (1961) all noted that most of the source oils are composed of more aromatic hydrocarbons when they are compared with their reservoir oils. Additionally, Olsen (1969, 1972) and Kharaka and Smalley (1976) experimentally demonstrated that kaolinite, which essentially is electrically balanced and has no charge layer according to Grim (1968), can still act as a semi-permeable membrane to chloride solutions, proving that the semi-permeability of kaolinite is mainly based on size exclusion. Whitworth (1993) concluded that chalks might be able to act as efficient geological membranes based on size exclusion mechanism by comparing the pore sizes of chalks and commercially uncharged membranes. All these observations point to the notion that some level of sieving for hydrocarbon molecules in shales due to size exclusion should exist. On the other hand, Kang et al. (2011) provided a mechanistic description of CO_2 uptake into shales, suggesting that the nanopores can behave as a molecular sieve in which CO_2 can reside but other molecules cannot due to preferential adsorption. Our study here is the first effort to experimentally probe the sieving effect on hydrocarbon transport in shale. Note that the 'shale' investigated in this paper can be referred to any tight, nanoporous rock that contains flowable hydrocarbons, and does not necessarily require richness in clay content. Such use is common among petroleum engineering literature.

Experimental and Simulation Methodology

First, we performed 'Filtration Test' which essentially is a combination of a mini-scale core flooding test and a compositional analysis using gas chromatography. The objective of this test is to check whether Niobrara shale possesses membrane properties to hydrocarbon mixtures flowing through it and to obtain a preliminary understanding of such properties if they exist.

In the 'Filtration Test', a binary hydrocarbon mixture was pumped from a transfer vessel and injected into a rock sample fixed in a vertically placed mini core-holder. The effluent fluid was collected at the outlet of the core-holder using a collection vial and then sent to gas chromatography for compositional analysis. The schematic diagram of our self-designed mini core flooding setup is shown in figure 2. Note that our setup can conduct tests on multiple rock samples simultaneously by connecting multiple core holders to the transfer vessel in parallel.



Figure 2. Schematic diagram of experimental setup

The mini core-holder was remodeled from an in-line filter manufactured by Swagelok, which has a maximum working pressure of 2500 psi. The core samples drilled perpendicular to lamination were cut into cylinders with a length of around 0.7 inches and a diameter of 0.5 inches (figure 3). They were desiccated in a vacuum oven (12 psi or 24.5 inHg at Golden, Colorado) at 150 °C for 48 hours, coated by a specific type of epoxy (epoxy A) and then placed in the center of the mini core-holder as shown in figure 4. After that, the epoxy-coated rock sample was bonded with the inner wall of the mini core-holder, coated by epoxy A as well, by filling the annulus in between with another type of epoxy (epoxy B), as shown in figure 5. The epoxy that was used to coat the rock sample and the core-holder is specifically designed for bonding rocks and metals, and the epoxy used in between is dedicated for bonding plastics and epoxy. To seal the annulus part between the rock sample and the core-holder so that the injected fluid can only flow through the rock sample, all of the epoxy used in the experiment was water and hydrocarbon resistant and cured under pressure (60 psig) to reduce the volume of pores in the epoxy caused by air bubbles. Additionally, we made several perforated metal gaskets and placed them right before the outlet of the core-holder against the rock sample (figure 4), to provide mechanical support to the rock sample when the sample is under pressure, while still allowing the fluid to be produced from the rock.



Figure 3. Niobrara sample



Figure 4. Schematic diagram of mini core-holder with a rock sample placed inside



Figure 5. Schematic diagram of rock sample bonded to the inner wall of the core holder

For fluid collection, the effluent fluid flowed into a 0.3 ml graduated clear glass V-Vial from the inlet tube and discharged the pre-existing water inside the vial used to prevent hydrocarbon evaporation through the outlet tube of the vial. Over time, the effluent fluid gradually accumulated in the top part of the vial (figure 6). The outlet tube can be controlled by a releasing valve. After collecting a certain amount of effluent, the fluid was transferred to a PTFE vial compatible with our Agilent 7890B Gas Chromatography system for compositional analysis to detect if there is any compositional change between the injected and produced fluid.



Figure 6. Schematic diagram of collecting vial

From our experimental results, as will be presented in the next section, we clearly detected the compositional changes of a binary hydrocarbon fluid mixture after flowing through Niobrara samples. To evaluate the mechanisms that have led to such compositional differences and specifically preferential adsorption, we conducted molecular dynamics simulations of interactions between the binary mixture and calcite surfaces, the method of which is presented below.

Figure 7 shows a snapshot of the molecular dynamics (MD) simulation system. The system consists of a \sim 2 nm-thick model Niobrara substrate and a \sim 8 nm thick binary mixture of linear alkanes of C₁₀ and C₁₇ (molar ratio 4:1). The system is periodic in directions parallel to the calcite slab (x- and y-directions). To effectively remove the periodicity in the direction perpendicular to the substrate (z-direction), a large vacuum space was placed outside of the mixture. The system measures $4.85 \times 3.98 \times 19.00$ nm³ in x-, y-, and z-directions. Both C₁₀ and C₁₇ were described using all atoms models. The optimized parameter set of the original OPLS-AA force fields for hydrocarbons were applied for C₁₀ and C₁₇ (Siu et al. 2012). The

Niobrara substrate was modeled using a calcite slab, given that calcite is the main component of Niobrara shales (Kuila and Prasad 2013). The $\{10\overline{1}4\}$ structure was used for calcite substrate, resulting in the most stable and neutral cleavage plane. The Lennar-Jones (LJ) potential and partial charges of calcite atoms were taken from the re-fitted Dove's potential (Rahaman et al. 2008). During the simulation, calcite atoms were fixed in space. The interatomic potentials between different atoms were obtained using geometric combination rule.



Figure 7. A snapshot of molecular dynamics simulation system. The calcite is shown in small spheres (Calcium: yellow, Carbon: cyan, and Oxygen: red). The hydrocarbons are shown as van der Waals spheres (C_{17} in blue and C_{10} in red). The black dashed box shows the simulation box.

MD simulations were performed using the 5.1.4 version of Gromacs (Abraham et al. 2015). The density of the 1:4 binary hydrocarbon mixture was first obtained from NPT ensemble at 300 K and 1 bar. Then ~8 nm thick mixture was placed above the calcite surface shown in figure 7. An NVT ensemble with velocity-rescale thermostat and a time constant of 2 ps at 300 K were adopted (Bussi et al. 2007). A global cutoff of 1.2 nm was used for computing the LJ potential, and the particle mesh Ewald (PME) method was used to calculate the electrostatic interactions (Darden et al. 1993). The time step is 2 fs. The simulation ran for 30 ns and data from the last 20 ns was used for analysis.

Experimental and Simulation Results

We performed 'Filtration Test' on six Niobrara samples which were collected from a quarry in Longmont, Colorado. The quarry itself has excellent exposures of the Fort Hays limestone and up to the B Marl of the Smoky Hill chalk member of the Niobrara formation. Other than Niobrara samples, we also tested 3 Berea sandstone samples as a comparison, because theoretically Berea sandstone samples have much larger pore and pore throat sizes than Niobrara samples, and therefore have no membrane properties or sieving effect on the transport of hydrocarbon molecules.

Sample #	Length (in)	Diameter (in)	Pore Volume (cc)
Niobrara Shale #1	0.735	0.5	0.189
Niobrara Shale #2	0.704	0.5	0.181
Niobrara Shale #3	0.741	0.5	0.191
Niobrara Shale #4	0.688	0.5	0.177
Niobrara Shale #5	0.716	0.5	0.184
Niobrara Shale #6	0.731	0.5	0.188
Berea Sandstone #1	0.738	0.5	0.475
Berea Sandstone #2	0.733	0.5	0.472
Berea Sandstone #3	0.705	0.5	0.454

Table 1. Parameters of core samples for filtration test

Table 1 lists the parameters of each core sample used in the 'Filtration Test', including core length, diameter, and pore volume. The pore volume of each sample was calculated based on an estimated porosity of 8% for Niobrara samples and 20% for Berea sandstone samples. The average injection pressure for each Niobrara sample was around 2000 psi, and 4 psig for Berea sandstone samples. Table 2 lists the duration of injection and production for each Niobrara sample, which is typically in tens of days, however, for Berea sandstone samples, the entire test was completed within hours because of their higher permeability.

Sample #	Injection, days	Production, days	
Niobrara Shale #1	81	75	
Niobrara Shale #2	72	66	
Niobrara Shale #3	72	66	
Niobrara Shale #4	33	28	
Niobrara Shale #5	33	26	
Niobrara Shale #6	33	28	

Table 2. Duration of injection and production of each Niobrara sample in the filtration test

Filtration test results of Niobrara samples #1 - #6 are shown in figure 8 - 13, and the results of Berea sandstone samples are shown in figure 14 - 16. In each plot, x-axis is the amount of fluid in terms of pore volume produced from each sample, and y-axis is the fluid composition in terms of mole fraction of C_{10} . The red short line represents the mole fraction of C_{10} in the injected fluid that differed slightly for each sample. Blue short lines represent the mole fraction of C_{10} in the produced fluid, and the orange short line measured at the end of the production represents the mole fraction of C_{10} in the upstream of the core holder or the remaining injection fluid. Each data point (marked by -) is the average of two consecutive GC measurements and the up (\land) and down (\lor) arrows respectively represent the 1^{st} and 2^{nd} GC measurement result for each data point. Additionally, for a comprehensive comparison, we summarized the initial composition of injection fluid, maximum C_{10} mole fraction recorded in the produced fluid and C_{10} mole fraction in the upstream fluid measured at the end of production for each sample fluid.

From the results, it can be noticed that for all Niobrara samples, C_{10} mole fraction in the produced fluid had various degrees of increase compared with the injection fluid, of which Niobrara samples #1 – #4 changed relatively more significantly, and Niobrara sample #5 and #6 changed relatively mildly. Oppositely, C_{10} mole fraction in the fluid upstream of each Niobrara sample decreases, indicating that the remaining injection fluid became heavier. For Berea sandstone samples, it can be noticed from figure 14 – 16 that all the blue points, which represent C_{10} mole fraction in the produced fluid, are almost at the same level as the injection fluid (red point), indicating there was no compositional change of the fluid flowing through Berea sandstone samples. Noted that perhaps because of the vaporization of C_{10} in the experiment, we observed a tiny amount of decrease of C_{10} in the produced fluid of Berea sandstone samples, but negligible compared to the changes in Niobrara samples. From the comparison between the results of Niobrara and Berea samples, the heavier component (C_{17}) in the injected fluid was noticeably hindered only when flowing through Niobrara samples. The fraction of lighter component (C_{10}) increased in the produced fluid, and the fraction of heavier component (C_{17}) in the upstream fluid increased. Both indicate hindrance of C_{17} transport and the latter specifically suggests size/mobility exclusion as C_{17} was prevented from entering the sample.

rable 5. Summary of field composition					
Sample #	Injection	Production		Upstream	
	C ₁₀ %	Max C ₁₀ %	Change % (vs. Injection)	C ₁₀ %	Change % (vs. Injection)
Niobrara Shale #1	79.41	80.14	0.73↑	79.17	0.24↓
Niobrara Shale #2	79.41	80.43	1.02↑	79.00	0.41↓
Niobrara Shale #3	79.41	80.44	1.03 ↑	78.92	0.49↓
Niobrara Shale #4	80.12	80.56	0.44 ↑	79.92	0.20↓
Niobrara Shale #5	80.12	80.20	0.08 ↑	80.05	0.07↓
Niobrara Shale #6	80.12	80.31	0.19↑	80.03	0.09↓
Berea Sandstone #1	81.32	81.31	0.01↓		
Berea Sandstone #2	77.69	77.67	0.02↓		
Berea Sandstone #3	80.70	80.69	0.01↓		

Table 3. Summary of fluid composition



Figure 8. Filtration test result of Niobrara shale sample #1







Figure 10. Filtration test result of Niobrara shale sample #3







Figure 12. Filtration test result of Niobrara shale sample #5







Figure 14. Filtration test result of Berea sandstone sample #1







Figure 16. Filtration test result of Berea sandstone sample #3

To better understand the mechanisms behind these observations, we performed molecular dynamics simulations. A specific goal of molecular dynamics simulations is to clarify the role of preferential adsorption. It is recognized that, in addition to size/mobility exclusion, preferential adsorption of C_{17} over C_{10} on the calcite surfaces of Niobrara samples may also lead to the increase of C_{10} in the produced fluid simply because more C_{17} were adsorbed. For this reason, molecular dynamics simulation of adsorption equilibrium on calcite surfaces using all-atom models was performed to characterize the preferential adsorption of C_{10} and C_{17} .

Figure 17 shows the density profiles of C_{10} and C_{17} near calcite surface from the carbon atoms (panel a) and from the center of mass (panel b) of hydrocarbon molecules. One can observe that near extended calcite surface both hydrocarbons show distinct layering due to adsorption. Particularly, the first layer was dominated by C_{17} molecules even though the density of C_{17} away from calcite was systematically lower, suggesting preferential adsorption of C_{17} over C_{10} molecules. To quantitatively compare the adsorption of C_{10} and C_{17} , we defined a surface excess as

$$\Gamma_{s} = \int_{0}^{z_{2}} \rho(z) dz - (z_{2} - z_{1}) \rho_{bulk} \dots \dots \dots \dots (1)$$

where $\rho(z)$ is the number density of hydrocarbon as a function of z, ρ_{bulk} is the corresponding number density of the bulk mixture, and z_2 is the position that the density profiles approach bulk values (dashed lines in figure 17).



Figure 17. Density profiles of hydrocarbon mixtures near calcite surface. (a) The density profiles based on carbon atoms of hydrocarbon. z_1 is the position of first adsorption peak. (b) The density profiles based on center of mass position of hydrocarbon molecules.

Considering the effective space occupied by the hydrocarbons (figure 17a), we set z_2 to be 8 nm. Consequently, surface excesses were measured to be $\Gamma_s^{C_{10}} = 5.76 \times 10^{-1}$ nm⁻² and $\Gamma_s^{C_{17}} = 3.08$ nm⁻² based on carbon atoms and $\Gamma_s^{C_{10}} = 5.56 \times 10^{-2}$ nm⁻² and $\Gamma_s^{C_{17}} = 1.80 \times 10^{-1}$ nm⁻² based on center of mass of hydrocarbon molecules. These values show that both hydrocarbons were enriched near the calcite surface and the enrichment of C_{17} is more significant. Comparing with the molar ratio (i.e. $\rho_{bulk}^{C_{17}}/\Gamma_{bulk}^{C_{10}} = 0.25$ from hydrocarbon molecules) in bulk mixture, the molar ratio of the enrichment (i.e. $\Gamma_s^{C_{17}}/\Gamma_s^{C_{10}} = 3.24$ from hydrocarbon molecules) is more than 10 times higher, meaning strong preferential adsorption of C_{17} molecules. This preferential adsorption was largely determined by the first adsorption peak. Given such sharp adsorption peaks from both carbon atoms and center of mass of hydrocarbons shown in figure 17 and the snapshot of hydrocarbon near calcite surface shown in figure 7, we concluded that molecular chains of hydrocarbons were aligned well to the calcite surface due to confinement. Presumably, the preferential adsorption of C_{17} within the first peak originates from the better alignment of C_{17} 's longer chain near an atomically smooth solid substrate.

Discussions

From the results of molecular dynamics simulation, Niobrara samples tend to adsorb more C_{17} molecules. This mechanism can definitely decrease the fraction of heavier component (C_{17}) and increase that of lighter component (C_{10}) in the produced fluid.

Some experimental observations, however, suggest that size/mobility exclusion should also exist. If size/mobility exclusion does not exist in Niobrara samples, compositional difference should be entirely due to preferential adsorption. Once the Niobrara sample reaches its adsorption saturation, there should be no more compositional difference between the injected and produced fluid. However, several of our experimental results showed sustained compositional differences between the produced fluid and the injected fluid. Another piece of experimental evidence that supports the existence of size/mobility exclusion is the observed increase of mole fraction of heavier component (C_{17}) in the upstream fluid of each Niobrara sample, represented by orange points in the corresponding plots. Such increases can only be explained, in our opinion, by the exclusion of access of C_{17} into certain pores of the sample.

Analysis of the molecular simulation data, in conjunction with knowledge of the surface area of Niobrara samples, can provide another, and perhaps more quantitative proof that size/mobility exclusion should exist. Unfortunately, currently the result of this analysis is not conclusive. We calculated the extra amount of C_{17} adsorbed ($N_{C_{17} adsorbed}$) due to preferential adsorption in Niobrara sample based on the excess adsorption capacity (E) of C_{17} derived from molecular simulation results (eq. 2-3), as well as the amount of C_{17} missing ($N_{C_{17} missing}$) in the produced fluid relative to the injected fluid, i.e. the cumulative molar difference between C_{10} and C_{17} in the produced fluid, based on the composition of each data point of effluent fluid measured in the experiment (eq. 4). The specific surface area (A_s) of Niobrara samples, which ranges between 3.88 and 14.31 m²/g, was estimated from measured adsorption isotherms using a modified BET theory (Kuila and Prasad 2013). m is the mass of each Niobrara sample. N_A is Avogadro constant. E stands for excess adsorption capacity for C_{17} . $X_{C_{10}}$ and $X_{C_{17}}$ represent the mole fraction of C_{10} and C_{17} in the volume of fluid collected for each data point. The molar volume (V_m) of fluids with different C_{10} and C_{17} compositions were estimated using a mixing rule (eq. 5), where the molar volume of C_{10} is 194.9 cm³/mol and C_{17} is 309.1 cm³/mol.

$$N_{C_{17} adsorbed}(mol) = \frac{A_s \times m}{N_A} \times E \dots (2)$$

$$E (nm^{-2}) = \Gamma_s^{C_{17}} - \Gamma_s^{C_{10}} \times \left(\frac{X_{C_{17}}}{X_{C_{10}}}\right)_{injected} \dots (3)$$

$$N_{C_{17} missing}(mol) = \sum_{effluent \ points} \left\{ \left[\left(\frac{X_{C_{17}}}{V_m}\right)_{injected} - \left(\frac{X_{C_{17}}}{V_m}\right)_{produced} \right] \times V \right\} \dots (4)$$

$$V_m(cm^3/mol) = X_{C_{10}} \times \frac{M_{C_{10}}}{\rho_{C_{10}}} + X_{C_{17}} \times \frac{M_{C_{17}}}{\rho_{C_{17}}} \dots (5)$$

According to mass conservation, if the extra amount of C_{17} adsorbed due to preferential adsorption in Niobrara sample ($N_{C_{17} adsorbed}$) is less than the amount of C_{17} missing in the produced fluid ($N_{C_{17} missing}$), then preferential adsorption alone cannot explain the fate of all missing C_{17} molecules. Size/mobility exclusion thus should exist. On the contrary, if $N_{C_{17} adsorbed}$ is approximate to or more than $N_{C_{17} missing}$, then preferential adsorption can be used to explain all the compositional differences and size/mobility exclusion may or may not exist. Table 4 below presents the range of the extra amount of C_{17} adsorbed due to preferential adsorption, the cumulative molar difference between C_{10} and C_{17} in the produced fluid for each Niobrara sample and the corresponding ratio between these two numbers. For Niobrara samples #1 - 4, $N_{C_{17} missing}$ in the produced fluid are clearly more than $N_{C_{17} adsorbed}$. For sample #5, however, we observed a negative value of $N_{C_{17} missing}$, which means that the cumulatively produced C_{10} is more than

 C_{17} relative to the injected fluid. Early productions from sample #5 had lower fractions of C_{10} , which was also observed in sample #1, #2 and #6, compared with the injected fluid. Since sample #5 produced less fluid and had a relatively shorter production time (table 2), these low fractions of C_{10} at early times of production, the source of which is not clear, affected the cumulative of sample #5. For sample #6, $N_{C_{17} \text{ missing}}$ in the produced fluid lies within the estimated range of $N_{C_{17} \text{ adsorbed}}$.

Sample	Mass (g) \sum_{eff}	volume (cc)	$N_{C_{17} adsorbed} \ (10^{-5} mol)$	$N_{C_{17} \text{ missing}} (10^{-5} \text{ mol})$	N _{C17} missing N _{C17} adsorbed
Niobrara #1	5.52	6.45	0.59 - 2.17	15.33	7.06 - 25.98
Niobrara #2	5.29	3.60	0.56 - 2.08	8.89	4.27 - 15.88
Niobrara #3	5.57	3.50	0.59 - 2.17	10.88	5.01 - 18.44
Niobrara #4	5.17	4.10	0.55 - 2.04	4.84	2.37 - 8.80
Niobrara #5	5.38	1.26	0.58 - 2.12	-0.40	
Niobrara #6	5.49	3.26	0.59 – 2.17	0.81	0.37 - 1.37

Table 4. Mass conservation calculation result

Conclusions

Starting from the conjecture that Niobrara samples might behave as a semi-permeable membrane, which allows the passage of lighter components and hinders the transport of heavier components, we explored the membrane behavior of six Niobrara samples through experiments. From five of the samples, we observed that the heavier component (C_{17}) was clearly hindered or sieved, with a corresponding increase of C_{17} in the upstream fluid and a decrease of C_{17} in the produced fluid. On the contrary, there were no such compositional changes observed for Berea sandstone samples, demonstrating the presence of sieving effect or membrane behavior of Niobrara samples.

Molecular dynamics simulation results indicate heavier component (C_{17}) adsorbs more strongly to the Niobrara sample, proving one mechanism for the observed sieving. Experimental observations of sustained compositional difference and increased fraction of C_{17} upstream of Niobrara samples suggest that size/mobility exclusion should also exist. A material balance calculation performed using molecular simulation data and knowledge of the surface area of the samples did not yield conclusive results. However, four of the six samples had cumulative compositional differences that could not be explained solely by preferential adsorption.

This experimental study is the first evidence that nanoporous reservoir rocks may behave as a semipermeable membrane, hindering the transport of or filtering selected hydrocarbon molecules due to preferential adsorption and size/mobility exclusion. Such componential separation of hydrocarbon mixtures caused by membrane properties of nanoporous rocks has not been considered in any reservoir simulation models. The consequence of this sieving effect and its dependence on the mixture and environmental conditions (surface, pressure, temperature) are worthy of discussions and further investigations.

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