Oil transport in shale nanopores and micro-fractures: modeling and analysis

Jiangfeng Cui^{a,*}

^a Physical Science and Engineering Division, King Abdullah University of Science and Technology, Jeddah, Saudi Arabia

* Corresponding author. E-mail address: cuijiangfeng_pascal@126.com

Abstract

The mathematical modelling and analysis for the apparent permeability of shale oil with complicated compositions in dual-wettability shales (superior to existing single-component or single-wettability analysis), which is the core of this work, will help understand the detailed contributions of the considered mechanisms. Based on a previously established flow enhancement model, the effects of the mixed wettability and those triggered by asphaltenes, namely, the wettability alteration, the pore radius reduction, and the viscosity increment, are taken into account by respective corrections of the variables in the model. The effect of the mixed wettability is quantified by the water-wet area ratio, while the surface coverage, the adsorption thickness, and the volume fraction in the free phase are utilized to quantify the effects of asphaltenes. The volume fraction of asphaltenes in the free phase is related to that in both phases by the volume conservation equation. The full mathematical model and its several simplifications are achieved. Comprehensive sensitivity analysis and comparisons are carried out to demonstrate the effects of each variable (i.e., the pore radius, the initial water-wet surface ratio, the relative adsorption thickness, and the surface coverage) on: (1) the flow enhancement; (2) the relative importance of all mechanisms; (3) the differences among organic pores/inorganic pores/micro-fractures; and (4)

the overall contribution of asphaltenes. The effect of different adsorption patterns (characterized by the relative adsorption thickness and the surface coverage) is also discussed.

Keywords

Shale oil, asphaltenes, mixed wettability, adsorption, mathematical model

1. Introduction

With the declining production of conventional resources, recently worldwide researchers switched their enthusiasm to enhanced recovery methods of unconventional resources, shale oil reserves for instance. Shale formations are rich in reserve, and even a slight increase in the recovery means a significant increment in the production. However, due to the ultra-low permeability and the poorly connected porosity of shales, the not well-known oil flow mechanisms in shales need more investigation (Bousige et al., 2016; Falk et al., 2015). Shales are featured by the organic matter and nanoscale pores, and some studies have shown the enhancement effect in organic nanopores. On the other hand, different from shale gas, crude oil has complicated compositions (e.g., resins and asphaltenes), and some previous works have targeted at the consequent formation damage. These characteristics should be both considered for a comprehensive research on the oil flow regularities in shale rocks, as such combination will induce some new scientific findings.

Primary MDS (Molecular dynamics simulation) researches by Wang et al. show the static adsorption (Wang et al., 2015b, 2015a) and dynamic flow (Wang et al., 2016a, 2016b) characteristics of shale oil. The concept of the flow enhancement (Strogatz et al., 2005) stemming from the boundary slip (Botan et al., 2011; Ho et al., 2011; Li et al., 2010; Neto et al., 2005; Thomas and McGaughey, 2009; Wang et al., 2010) is used to characterize the deviation from classic fluid dynamics. Results illustrate the distinct flow properties between organic and inorganic nanopores: oil flow in organic pores is much faster. In reality, MDS might not quantitatively describe the interfacial dynamics well (Secchi et al., 2016). Cui et al. (Cui et al., 2017) formulated and analyzed the liquid permeability of nanopores following Mattia's model (Mattia et al., 2015; Mattia and Calabro, 2012; Ritos et al., 2014). The solid-liquid interaction is

incorporated via the adhesion work and the surface diffusion (Park and Aluru, 2010, 2007; Wei et al., 2011). They found that the effect of the physical adsorption on the oil flow is probably negligible. The critical pore radius when the boundary slip comes into play is provided. At the macroscale, researchers (Cui et al., 2018; Javadpour et al., 2015; Zhang et al., 2017) investigated the effects of the organic matter (Xi and Congli, 2015) on the liquid flow in shales in different views. However, at the pore scale, the impact of the prevalent mixed wettability (Habibi et al., 2016; Hu et al., 2014; Lu et al., 2012) has not been discussed. Moreover, light oil is assumed in aforementioned papers. Actually, the wettability alteration (Behbahani et al., 2014) and other mechanisms could result from the adsorption of asphaltenes in shale oil (Qin et al., 2000; Shedid et al., 2006). Nevertheless, there has been no research simultaneously quantifying the impacts of the mixed wettability and asphaltenes in shale oil rocks.

In this paper, the mathematical model incorporating the effects of the originally mixed wettability and the mechanisms triggered by asphaltenes is established. Comprehensive sensitivity analysis and comparisons with simplified models are carried out to demonstrate the crude oil flow mechanisms in shales. On the other hand, the effect of different adsorption patterns is briefly discussed.

2. Mathematical model

Fig. 1. The conceptual model.

In this section, a mathematical model for the apparent permeability of shale oil considering light oil as well as asphaltenes in dual-wettability shales is established. As shown in Fig. 1 (the conceptual model), the two states of asphaltenes, free and deposited, are considered. The free asphaltenes increase the viscosity of shale oil, and the deposited asphaltenes can narrow the flow conduit and change the initial mixed wettability of the substrate. It should be noted that the particles can be asphaltene molecules, nanoaggregates or clusters. On the other hand, the particles can stack several layers (Behbahani et al., 2014; Betancourt et al., 2016; Jafari Behbahani et al., 2013), and only one layer is shown for convenience.

The mathematical model to be established is based on the flow enhancement λ of a nanopore is (Mattia and Calabro, 2012):

$$\lambda = 1 + \frac{8\mu}{R^2} \frac{D_s L}{W_A} \quad (1)$$

where μ is the viscosity, R is the pore radius, D_s is the surface diffusion, W_A is the adhesion work, and L is the pore length.

2.1 Effect of the mixed wettability

In this work, both organic and inorganic surfaces are considered. To incorporate the mixed wettability property, the equivalent expressions for the surface diffusion and the adhesion work should be obtained. The equivalent adhesion work can be achieved by the arithmetic average:

$$W_A = (1 - \alpha)W_{A,o} + \alpha W_{A,w} \quad (2)$$

where α is the area ratio of the water-wet surface, subscripts o and w stand for oil-wet and water-wet surfaces, respectively. However, the treatment of the equivalent surface diffusion is different. With comparison to the 2D permeability upscaling formula (Naraghi and Javadpour, 2015):

$$k_{LB} = \frac{N_c}{N_r} \sum_{i=1}^{N_r} \frac{1}{\sum_{j=1}^{N_c} \frac{1}{k_{i,j}}} \quad (3)$$

$$k_{UB} = \frac{N_c}{N_r} \frac{1}{\sum_{j=1}^{N_c} \frac{1}{\sum_{i=1}^{N_r} k_{i,j}}} \quad (4)$$

$$k_{eq} = \sqrt{k_{UB} k_{LB}} \quad (5)$$

where subscripts UB and LB stand for the upper bound and the lower bound respectively, k_{eq} is its statistical average, N_c is the number of grids in columns, N_r is the number of grids in rows, $k_{i,j}$ is the permeability of the grid (i, j) . In case that both surfaces are distributed evenly, the equivalent surface diffusion can be calculated as follows:

$$D_{s,UB} = \frac{N_c}{N_r} \sum_{i=1}^{N_r} \frac{1}{\sum_{j=1}^{N_c} \frac{1}{D_{s,i,j}}} = \frac{1}{\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}}} \quad (6)$$

$$D_{s,UB} = \frac{N_c}{N_r} \frac{1}{\sum_{j=1}^{N_c} \frac{1}{\sum_{i=1}^{N_r} D_{s,i,j}}} = \alpha D_{s,w} + (1-\alpha) D_{s,o} \quad (7)$$

$$D_s = \sqrt{D_{s,UB} D_{s,LB}} = \sqrt{\frac{\alpha D_{s,w} + (1-\alpha) D_{s,o}}{\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}}}} \quad (8)$$

where D_s is its statistical average, and $D_{s,i,j}$ is the surface diffusion of the unit (i, j) . α imposes complicated impacts on D_s , and D_s should decrease with enlarging α (Appendix A provides a detailed explanation).

2.2 Effect of asphaltenes

Asphaltenes can influence the hydrocarbon effective mobility mainly by the pore radius reduction, the wettability alteration, and the viscosity increment (Jafari Behbahani et al., 2013). In

this section, their respective modeling methods are discussed. In view of the complexities of the equilibrium and realistic different structures (i.e., molecules, nanoaggregates or clusters) for asphaltenes, the ultimate adsorption thickness and the surface coverage are directly taken for discussions. Actually the referred adsorption also includes the deposition, but for concision, only the adsorption is referred in following discussions. It should be noted that the variation in the oil composition will lead to slightly different physical properties (i.e., the surface diffusion, the adhesion work, and the density), but this deviation is not incorporated in this work for simplicity.

2.2.1 Wettability alteration

In this preliminary investigation, for the pore surface covered by asphaltenes, it is assumed that its property is the same as the originally organic surface. Consequently, the initial water-wet and oil-wet surface ratios should be adjusted according to the surface coverage of adsorbed asphaltenes to determine the flow enhancement accurately. Assuming that adsorbed asphaltenes are randomly distributed (independent of the original wettability), the water-wet area ratio should be corrected as follows:

$$\alpha = \alpha_o \cdot (1 - \gamma) \quad (9)$$

where γ is the surface coverage of asphaltenes. Correspondingly, the oil-wet area ratio changes from $(1 - \alpha_o)$ to $(1 - \alpha)$.

2.2.2 Pore radius reduction

Due to the ultra-low mobility of adsorbed asphaltenes (Pan et al., 2005; Qin et al., 2000), the pore radius should be reduced to represent the resulting reduction in the flow capacity (a detailed derivation is provided in Appendix B):

$$R = R_o - \gamma h \quad (10)$$

where h is the adsorption thickness. The flow enhancement with the corrected pore radius does not accord to the original pore radius. To accurately describe the flow deviation from the original case, the final expression of the flow enhancement should be multiplied by $(1/8R^2)/(1/8R_o^2)=(R/R_o)^2$.

2.2.3 Viscosity increment

Actually, the viscosity of movable oil depends on its containing fraction of asphaltenes, and the classical Einstein's equation is utilized to depict such relationship (Ghanavati et al., 2013):

$$\mu = \mu_o (1 + 2.5\phi) \quad (11)$$

where μ_o is the viscosity of light oil (contains no asphaltenes), and ϕ is the volume fraction of asphaltenes in the free phase. However, it should be noted that the original concept of the flow enhancement is directly related to the "permeability", and does not have a direct relationship with the "viscosity". Therefore, the final flow enhancement should be divided by the viscosity increment factor $(1+2.5\phi)$. The treatments with the viscosity here might seem redundant, but the constant "1" in Eq. (1) makes them plausible. The notation of the flow enhancement in this paper is similar to the "mobility", which is the ratio of the permeability to the viscosity. Actually, the viscosity change will lead to a significant change in the "permeability", but only a slight change in the "flow enhancement/mobility".

Generally, there is an exponential relationship between the oil viscosity and the asphaltene content. Nevertheless, it is well-known that oil is already difficult to move in the ultra-tight shale matrix, and thus shale oil with high asphaltene content would be extremely difficult to be exploited economically. Therefore, low asphaltenes content is assumed in this paper. In other words, the linear relationship between the oil viscosity and asphaltene content holds.

2.2.4 Volume conservation

The pressure/temperature/time changes can lead to the dissolution or deposition of asphaltenes (Wang and Civan, 2005; Zendehboudi et al., 2013), but its total volume fraction β should remain constant:

$$\varphi \cdot \pi R^2 + \pi(R_o^2 - R^2) = \beta \cdot \pi R_o^2 \quad (12)$$

Eq. (12) can be transformed into:

$$\varphi = 1 - (1 - \beta) \left(\frac{R_o}{R} \right)^2 \quad (13)$$

2.3 Mathematical model

From all the above discussions, the full expression for the flow enhancement is reached:

$$\lambda = \left\{ 1 + \frac{8\mu_o \left[3.5 - 2.5(1 - \beta) \left(\frac{R_o}{R_o - \gamma h} \right)^2 \right]}{(R_o - \gamma h)^2} \sqrt{\frac{\alpha_o \cdot (1 - \gamma) D_{s,w} + [1 - \alpha_o \cdot (1 - \gamma)] D_{s,o}}{\frac{\alpha_o \cdot (1 - \gamma)}{D_{s,w}} + \frac{1 - \alpha_o \cdot (1 - \gamma)}{D_{s,o}}}} \frac{L}{[1 - \alpha_o \cdot (1 - \gamma)] W_{A,o} + \alpha_o \cdot (1 - \gamma) W_{A,w}} \right\} \cdot \frac{\left(\frac{R_o - \gamma h}{R_o} \right)^2}{3.5 - 2.5(1 - \beta) \left(\frac{R_o}{R_o - \gamma h} \right)^2} \quad (14)$$

To make the form of Eq. (14) simpler, the concept of the relative adsorption thickness h_r is introduced:

$$h_r = \frac{h}{R_o} \quad (15)$$

Therefore, Eq. (14) is simplified as:

$$\lambda = \left[1 + \frac{8\mu_o \left[3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2 \right]}{R_o^2 (1-\gamma h_r)^2} \sqrt{\frac{\alpha_o \cdot (1-\gamma) D_{s,w} + [1-\alpha_o \cdot (1-\gamma)] D_{s,o}}{\frac{\alpha_o \cdot (1-\gamma)}{D_{s,w}} + \frac{1-\alpha_o \cdot (1-\gamma)}{D_{s,o}}} L} \right] \cdot \frac{(1-\gamma h_r)^2}{3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2}$$

(16)

It is apparent that the relationship between λ and R_o is the same as our previous work (Cui et al., 2017). This phenomena further strengthens the rationale of the introduction of h_r . Practically it is rather difficult to isolate some correction factors and research them in detail: the term $(1-\gamma h_r)^2$ accounts for the effect of the pore radius reduction, but it is contained in the expression of the viscosity increment; $(1-\gamma)$ appears many times in different places in the expressions for the equivalent surface diffusion and adhesion work, and therefore it is not convenient to isolate the impact of the wettability alteration.

To investigate the contributions of each stated mechanism, several simplified expressions of Eq. (16) are listed below for comparisons and analysis.

(1) $\gamma=0, h_r=0, \beta=0$ (only light oil):

$$\lambda = 1 + \frac{8\mu_o}{R_o^2} \sqrt{\frac{\alpha_o D_{s,w} + (1-\alpha_o) D_{s,o}}{\frac{\alpha_o}{D_{s,w}} + \frac{1-\alpha_o}{D_{s,o}}} L} \quad (17)$$

(2) Ignore the wettability alteration expressed in Eq. (9):

$$\lambda = \left\{ 1 + \frac{8\mu_o \left[3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2 \right]}{R_o^2 (1-\gamma h_r)^2} \sqrt{\frac{\alpha_o D_{s,w} + (1-\alpha_o) D_{s,o}}{\frac{\alpha_o}{D_{s,w}} + \frac{1-\alpha_o}{D_{s,o}}}} L \right\} \cdot \frac{(1-\gamma h_r)^2}{3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2} \quad (18)$$

(3) Ignore the pore radius reduction expressed in Eq. (10):

$$\lambda = \left\{ 1 + \frac{8\mu_o \left[3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2 \right]}{R_o^2} \sqrt{\frac{\alpha_o \cdot (1-\gamma) D_{s,w} + [1-\alpha_o \cdot (1-\gamma)] D_{s,o}}{\frac{\alpha_o \cdot (1-\gamma)}{D_{s,w}} + \frac{1-\alpha_o \cdot (1-\gamma)}{D_{s,o}}}} L \right\} \cdot \frac{1}{3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2} \quad (19)$$

(4) Ignore the viscosity increment expressed in Eq. (11):

$$\lambda = \left\{ 1 + \frac{8\mu_o}{R_o^2 (1-\gamma h_r)^2} \sqrt{\frac{\alpha_o \cdot (1-\gamma) D_{s,w} + [1-\alpha_o \cdot (1-\gamma)] D_{s,o}}{\frac{\alpha_o \cdot (1-\gamma)}{D_{s,w}} + \frac{1-\alpha_o \cdot (1-\gamma)}{D_{s,o}}}} L \right\} \cdot (1-\gamma h_r)^2 \quad (20)$$

(5) Ignore the slip enhancement (micro-fractures, R_o is large enough):

$$\lambda = \frac{(1-\gamma h_r)^2}{3.5 - 2.5(1-\beta) \left(\frac{1}{1-\gamma h_r} \right)^2}$$

For the common scale of micro-fracture apertures, the slip enhancement is negligible (as illustrated in Fig. 2). It should be noted that this paper employs the circular pore model, while

fracture surfaces are usually planar. Nevertheless, the regularities should be similar, and the results should systematically deviate to some extent. The accurate modeling of shale micro-fractures will be discussed in our forthcoming article.

3. Results and discussions

Table 1

Parameters for analysis

Parameter	L	μ_o	β	h_r		
Value	2 μm	0.8 mPa·s	0.5	0.2		
Parameter	γ	$D_{s,w}$	$D_{s,o}$	$W_{A,o}$	$W_{A,w}$	
Value	0.5	$0.3 \times 10^{-9} \text{ m}^2/\text{s}$	$3 \times 10^{-9} \text{ m}^2/\text{s}$	0.1 J/m ²	1 J/m ²	

The basic parameters for sensitivity analysis are set as Table 1. There are significant differences in the size and the wettability between inorganic and organic pores, and these differences probably lead to distinct flow characteristics. Thus, the two pore types are discussed respectively in following discussions. Organic pores dominate in several nanometers and tend to be oil-wet, and $R_o=5$ nm, $\alpha_o=0.2$ are set. The radius of mainly water-wet inorganic pores mostly lies in tens of nanometers, and $R_o=20$ nm and $\alpha_o=0.8$ are set for them. Besides, micro-fractures are prevalent in shale formations, thus $R_o=1000$ nm and $\alpha_o=0.5$ are taken for them. Actually, the aperture of micro-fractures mostly lies between 1 μm and 100 μm . However, the increase of aperture imposes a negligible impact on the respective contributions from each mechanism if the aperture is beyond 1 μm (as illustrated in Fig. 2). On the other hand, the effect of the wettability is negligible at this scale (Cui et al., 2017), and the actual value of α_o will not affect the results.

From Eq. (16), there are altogether 11 variables: μ_o , β , R_o , γ , h_r , α_o , $D_{s,w}$, $D_{s,o}$, $W_{A,o}$, $W_{A,w}$, L .

Among them, $D_{s,w}$, $D_{s,o}$, $W_{A,o}$, $W_{A,w}$, L , and μ_o are of little interest to this work, and can be regarded as constants. Besides, due to the equilibrium of asphaltenes, γ and h_r will change if β changes. Thus, β is regarded as a constant. To conclude, only the four variables, α_o , γ , R_o and h_r , deserve sensitivity analysis: α_o is about the original wettability condition, γ and h_r are about the adsorption pattern of asphaltenes, and R_o is the magnitude of the concerned pore scale. For each variable, the four simplified circumstances mentioned in Sec 2.3 and Eq. (16) are compared to show the respective contributions of each mechanism. Utilizing representative parameters, the differences among organic pores, inorganic pores, and micro-fractures, are also discussed.

3.1 Effect of pore radius (R_o)

Fig. 2. Effect of the pore radius. (a): analysis for organic pores. (b): analysis for inorganic pores. (c): analysis for micro-fractures. It should be noted that R_o is set as full intervals instead of specific values here, as R_o is right the variable for sensitivity analysis. For organic and inorganic pores, the interval is [1 nm, 1000 nm]; for

micro-fractures, the interval is [1 μm , 100 μm]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

From Fig. 2, the flow enhancement of organic pores is very sensitive (decreases rapidly) to the pore radius (mainly several nanometers), and for inorganic pores (mainly tens of nanometers) it is much less sensitive, while for micro-fractures the aperture has no contribution to the flow enhancement.

It is evident that the relative importance of all considered mechanisms will change with the increment of the pore radius for organic and inorganic pores. While for micro-fractures, there is no such change. At the relatively small pore scale, the wettability alteration contributes more than others. As the pore radius increases, the viscosity increment and the pore radius reduction gradually come into stage and contribute more than the wettability alteration. For large enough pores (and micro-fractures), the influence of the wettability alteration is negligible. Therefore, the wettability alteration is only meaningful to the nanoscale oil flow, while the viscosity increment and the pore radius reduction should be concerned for only macroscale applications. This is the fundamental difference among them.

In another view, the addition of asphaltenes will enhance the permeability if the pore radius is below about 10 nm, and impair the flow conductance when the pore radius is beyond about 10 nm. This critical value (10 nm) is slightly larger for organic pores, and for inorganic pores it is slightly smaller, while there is no such critical value for micro-fractures.

3.2 Effect of initial water-wet surface ratio (α_o)

Fig. 3. Effect of the initial water-wet surface ratio. (a): analysis for organic pores. (b): analysis for inorganic pores. (c): analysis for micro-fractures. It should be noted that α_o is set as intervals instead of specific values here, as α_o is right the variable for sensitivity analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 3, the oil flow in shale organic nanopores is very sensitive to the initial wettability condition of the substrate: with the increase of the initial water-wet surface ratio, the flow enhancement decreases rapidly. For inorganic nanopores, the relationship is much less sensitive. As for micro-fractures, there is no such sensitivity.

Apparently, for organic pores, the contribution of the wettability alteration is primary unless the initial water-wet surface ratio is extremely small. In essence, more water-wet surface ratio offers more chances for the wettability alteration to come into play. Comparatively speaking, the

rank for inorganic pores and micro-fractures is totally different. The viscosity increment and the pore radius reduction have greater contributions compared to organic pores.

In another view, the addition of asphaltenes will enhance the permeability of organic pores, while reduce the permeability of inorganic pores and micro-fractures. The contribution of asphaltenes is nearly insensitive to the initial wettability condition (the initial water-wet surface ratio) for inorganic pores. For micro-fractures, such contribution is totally insensitive. While for organic pores, moderate initial water-wet surface ratio is most beneficial for its permeability enhancement.

3.3 Effect of relative adsorption thickness (h_r)

Fig. 4. Effect of the relative adsorption thickness. (a): analysis for organic pores. (b): analysis for inorganic pores.

(c): analysis for micro-fractures. It should be noted that the interval for sensitivity analysis here is not $[0, 1]$,

because the relative adsorption thickness is subject to the total volume fraction β (Eq. (12)). $[0, 0.6]$ is the

maximum rational range after some calculations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As illustrated in Fig. 4, the flow enhancement values of organic and inorganic pores, as well as micro-fractures, are all not sensitive to the adsorption thickness: the change of the permeability of organic pores is not easily observable, while inorganic pores and micro-fractures experience a slight decrease and then a slight increase in the permeability with enlarging adsorption thickness.

With the increase of the adsorption thickness, the three effects also will re-rank. For organic pores, the pore radius reduction starts from no impact and gradually increases, while the impact of the viscosity increment gradually diminishes. At the same time, the influence of the wettability alteration dominates and seems unchanged throughout. Fundamentally speaking, the adsorption region directly narrows the flow conduit and thus weakens the flow capacity. Moreover, more adsorption indicates less dissolved asphaltenes in flowable oil, which is of a smaller viscosity and easier to flow. For inorganic pores and micro-fractures, the regularities are similar. However, the wettability alteration plays a relatively much less important role, while the others are dominant.

In another view, the addition of asphaltenes will enhance the permeability of organic pores, while reduce the permeability of inorganic pores and micro-fractures. The contribution of asphaltenes is seemingly not related to the adsorption thickness.

3.4 Effect of surface coverage (γ)

Fig. 5. Effect of the surface coverage. (a): analysis for organic pores. (b): analysis for inorganic pores. (c): analysis for micro-fractures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5 shows the positive contribution of the surface coverage to the flow enhancement for organic pores, while for inorganic pores this enhancement is only observable at a high surface coverage. Interestingly, the effect on micro-fractures can be slightly negative.

Increasing surface coverage will also lead to the re-rank of the mechanisms. For organic pores, the effect of the pore radius reduction is negligible throughout. Only the viscosity increment plays a role when the surface coverage is relatively low, while the wettability alteration is dominant if the surface coverage is larger. The explanation for this subsection is the most complicated, because all proposed mechanisms are of concern. Firstly, on condition that other variables are not changed, more coverage of asphaltenes implies less free asphaltenes, resulting in a lower oil viscosity and a greater flow speed. Secondly, a larger coverage will result in more oil-wet surface (the wettability alteration), and this contributes to a greater transport velocity. Thirdly, the organic permeability is insensitive to the pore radius (Cui et al., 2017), and therefore the contribution of the pore radius reduction is negligible. Contrary to organic pores, the impact of the pore radius

reduction is observable for inorganic pores and micro-fractures, and the viscosity increment also plays a more important role, while the influence from the wettability alteration is far less important.

In another view, the addition of asphaltenes will enhance the permeability of organic pores unless the surface coverage is small enough, while reduce the permeability of inorganic pores unless the surface coverage is large enough. While for micro-fractures, this contribution is totally negative. Obviously, the contribution of asphaltenes is intimately related to the surface coverage for organic and inorganic pores. As for micro-fractures, there is no such relevance.

3.5 Effect of adsorption pattern (h_r and γ)

In this paper, the adsorption pattern (or the solution of asphaltenes) is characterized and can be fully determined by the relative adsorption thickness and the surface coverage. Based on the results from Sec. 3.3 and Sec 3.4, it can be concluded that for organic and inorganic pores the flow enhancement can vary significantly with different adsorption patterns if the adsorbed amount (or the dissolved amount) keeps constant. However, for micro-fractures, such variance is not obvious. In other words, accurately depicting the adsorption pattern, not just the adsorbed amount (or the dissolved amount), is essential for precisely determining the flow capacity of shale nanopores (except micro-fractures). To be more exact, a flat configuration of adsorbed asphaltenes is favorable for the oil flow capacity of shale nanopores with a fixed amount of adsorbed asphaltenes. Nevertheless, for micro-fractures, there is no such regularity.

4. Conclusions

This work established a mathematical model for the shale oil permeability including the effects of the mixed wettability and asphaltenes. As for asphaltenes, the effects of the wettability

alteration, the pore radius reduction, and the viscosity increment are incorporated. The main findings are summarized as follows:

(1) The sensitivity to each variable. The flow enhancement is not sensitive to the adsorption thickness. As for the initial water-wet surface ratio, the surface coverage, and the pore radius, the flow enhancement of organic pores is more sensitive than inorganic nanopores, and then micro-fractures. The contribution of the surface coverage is positive, while that of the rest two factors is negative.

(2) The essence of mechanisms. The wettability alteration is only meaningful to the nanoscale oil flow (mainly organic pores), and relevant to the initial water-wet surface ratio and the surface coverage. While the viscosity increment and the pore radius reduction should be concerned for only macroscale applications (mainly inorganic pores and micro-fractures), and they are both relevant to the relative adsorption thickness and the surface coverage.

(3) Effect of asphaltenes. Generally, the addition of asphaltenes will enhance the permeability of organic pores, while reduce the permeability of inorganic pores and micro-fractures. The contribution of asphaltenes is not related to the adsorption thickness, but relevant to the surface coverage and the pore radius (except micro-fractures). As for the initial water-wet surface ratio, it differs between organic pores and inorganic pores & micro-fractures.

(4) Effect of the adsorption pattern. A flat configuration of adsorbed asphaltenes is relatively favorable for the oil flow capacity of shale nanopores, while for micro-fractures the configuration makes a negligible contribution.

Nomenclature

MDS Molecular dynamics simulation

1	358	λ	Flow enhancement
2			
3	359	μ	Oil viscosity
4			
5			
6	360	R	Pore radius
7			
8			
9	361	D_s	Surface diffusion
10			
11			
12	362	W_A	Adhesion work
13			
14	363	L	Pore length
15			
16			
17	364	α	Area ratio of the water-wet surface
18			
19			
20	365	k_{eq}	Statistical average of the equivalent permeability
21			
22			
23	366	N_c	Number of grids in columns
24			
25			
26	367	N_r	Number of grids in rows
27			
28	368	$k_{i,j}$	Permeability of the grid (i, j)
29			
30			
31	369	$D_{s,i,j}$	Surface diffusion of the unit (i, j)
32			
33	370		
34		γ	Surface coverage of asphaltenes
35			
36	371	h	Adsorption thickness
37			
38			
39	372	φ	Volume fraction of asphaltenes in the free phase
40			
41			
42	373	β	Total volume fraction of asphaltenes
43			
44			
45	374	h_r	Relative adsorption thickness
46			
47	375	<i>Subscripts</i>	
48			
49			
50	376	o	Oil-wet/original
51			
52			
53	377	w	Water-wet
54			
55			
56	378	UB	Upper bound
57			
58			
59	379	LB	Lower bound
60			
61			
62			
63			
64			
65			

References

- Behbahani, T.J., Ghotbi, C., Taghikhani, V., Shahrabadi, A., 2014. Investigation of asphaltene adsorption in sandstone core sample during CO₂ injection: Experimental and modified modeling. *Fuel* 133, 63–72. <https://doi.org/10.1016/j.fuel.2014.04.079>
- Betancourt, S.S., Ventura, G.T., Pomerantz, A.E., Vilorio, O., Dubost, F.X., Zuo, J., Monson, G., Bustamante, D., Purcell, J.M., Nelson, R.K., Rodgers, R.P., Reddy, C.M., Marshall, A.G., Mullins, O.C., 2016. Nanoaggregates of Asphaltenes in a Reservoir Crude Oil and Reservoir Connectivity $\dagger$. *Energy and Fuels* 1178–1188.
- Botan, A., Rotenberg, B., Marry, V., Turq, P., Noetinger, B., 2011. Hydrodynamics in clay nanopores. *J. Phys. Chem. C* 115, 16109–16115. <https://doi.org/10.1021/jp204772c>
- Bousige, C., Ghimbeu, C.M., Vix-Guterl, C., Pomerantz, A.E., Suleimenova, A., Vaughan, G., Garbarino, G., Feygenson, M., Wildgruber, C., Ulm, F.-J., Pellenq, R.J.-M., Coasne, B., 2016. Realistic molecular model of kerogen's nanostructure. *Nat. Mater.* 15, 576–82. <https://doi.org/10.1038/nmat4541>
- Cui, J., Cheng, L., Li, L., 2018. Apparent permeability and representative size of shale: a numerical study on the effects of organic matter. *Comput. Geosci.* <https://doi.org/10.1007/s10596-018-9739-3>
- Cui, J., Sang, Q., Li, Y., Yin, C., Li, Y., Dong, M., 2017. Liquid permeability of organic nanopores in shale: Calculation and analysis. *Fuel* 202, 426–434. <https://doi.org/10.1016/j.fuel.2017.04.057>
- Falk, K., Coasne, B., Pellenq, R., Ulm, F., Bocquet, L., 2015. Subcontinuum mass transport of condensed hydrocarbons in nanoporous media. *Nat. Commun.* 1–7. <https://doi.org/10.1038/ncomms7949>

- Ghanavati, M., Shojaei, M.J., Ahmad Ramazani, S.A., 2013. Effects of asphaltene content and temperature on viscosity of Iranian heavy crude oil: Experimental and modeling study. *Energy and Fuels* 27, 7217–7232. <https://doi.org/10.1021/ef400776h>
- Habibi, A., Dehghanpour, H., Binazadeh, M., Bryan, D., Uswak, G., 2016. Advances in Understanding Wettability of Tight Oil Formations: A Montney Case Study. *SPE Reserv. Eval. Eng.* 19, 583–603. <https://doi.org/10.2118/175157-PA>
- Ho, A.T., Papavassiliou, D. V, Lee, L.L., Striolo, A., 2011. Liquid water can slip on a hydrophilic surface. *Proc. Natl. Acad. Sci.* 108, 16170–16175. <https://doi.org/10.1073/pnas.1105189108/-/DCSupplemental>. www.pnas.org/cgi/doi/10.1073/pnas.1105189108
- Hu, Y., Devegowda, D., Striolo, A., Phan, A.T. Van, Ho, T.A., Civan, F., Sigal, R., 2014. Microscopic dynamics of water and hydrocarbon in shale-kerogen pores of potentially mixed wettability. *SPE J.* 20, 112–124.
- Jafari Behbahani, T., Ghotbi, C., Taghikhani, V., Shahrabadi, A., 2013. Asphaltene deposition under dynamic conditions in porous media: Theoretical and experimental investigation. *Energy and Fuels* 27, 622–639. <https://doi.org/10.1021/ef3017255>
- Javadpour, F., McClure, M., Naraghi, M.E., 2015. Slip-corrected liquid permeability and its effect on hydraulic fracturing and fluid loss in shale. *Fuel* 160, 549–559. <https://doi.org/10.1016/j.fuel.2015.08.017>
- Li, Y., Xu, J., Li, D., 2010. Molecular dynamics simulation of nanoscale liquid flows. *Microfluid. Nanofluidics* 9, 1011–1031. <https://doi.org/10.1007/s10404-010-0612-5>
- Lu, S., Huang, W., Chen, F., Li, J., Wang, M., Xue, H., Wang, W., Cai, X., 2012. Classification and

424 evaluation criteria of shale oil and gas resources : Discussion and application. *Pet. Explor. Dev.*
 425 39, 268–276. [https://doi.org/10.1016/S1876-3804\(12\)60042-1](https://doi.org/10.1016/S1876-3804(12)60042-1)
 426 Mattia, D., Calabro, F., 2012. Explaining high flow rate of water in carbon nanotubes via solid-liquid
 427 molecular interactions. *Microfluid. Nanofluidics* 13, 125–130.
 428 <https://doi.org/10.1007/s10404-012-0949-z>
 429 Mattia, D., Leese, H., Lee, K.P., 2015. Carbon nanotube membranes: From flow enhancement to
 430 permeability. *J. Memb. Sci.* 475, 266–272. <https://doi.org/10.1016/j.memsci.2014.10.035>
 431 Naraghi, M.E., Javadpour, F., 2015. A stochastic permeability model for the shale-gas systems. *Int. J.*
 432 *Coal Geol.* 140, 111–124. <https://doi.org/10.1016/j.coal.2015.02.004>
 433 Neto, C., Evans, D.R., Bonaccorso, E., Butt, H.-J., Craig, V.S.J., 2005. Boundary slip in Newtonian
 434 liquids: a review of experimental studies. *Reports Prog. Phys.* 68, 2859–2897.
 435 <https://doi.org/10.1088/0034-4885/68/12/R05>
 436 Pan, C., Feng, J., Tian, Y., Yu, L., Luo, X., Sheng, G., Fu, J., 2005. Interaction of oil components and
 437 clay minerals in reservoir sandstones. *Org. Geochem.* 36, 633–654.
 438 <https://doi.org/10.1016/j.orggeochem.2004.10.013>
 439 Park, J.H., Aluru, N.R., 2010. Ordering-induced fast diffusion of nanoscale water film on graphene. *J.*
 440 *Phys. Chem. C* 114, 2595–2599. <https://doi.org/10.1021/jp907512z>
 441 Park, J.H., Aluru, N.R., 2007. Surface diffusion of n-alkanes: Mechanism and anomalous behavior.
 442 *Chem. Phys. Lett.* 447, 310–315. <https://doi.org/10.1016/j.cplett.2007.09.047>
 443 Qin, X., Wang, P., Sepehrnoori, K., Pope, G.A., 2000. Modeling asphaltene precipitation in reservoir
 444 simulation. *Ind. Eng. Chem. Res.* 39, 2644–2654.
 445 Ritos, K., Mattia, D., Calabrò, F., Reese, J.M., 2014. Flow enhancement in nanotubes of different

materials and lengths. *J. Chem. Phys.* 140, 014702. <https://doi.org/10.1063/1.4846300>

Secchi, E., Marbach, S., Niguès, A., Stein, D., Siria, A., Bocquet, L., 2016. Massive radius-dependent flow slippage in carbon nanotubes. *Nature* 537, 210–213. <https://doi.org/10.1038/nature19315>

Shedid, S.A., U, S.C., Zekri, A.Y., U, U.A.E., 2006. Formation Damage Caused by Simultaneous Sulfur and Asphaltene Deposition. *spe Prod. Oper.* 18–20.

Strogatz, S.H., Abrams, D.M., McRobie, A., Eckhardt, B., Ott, E., 2005. Enhanced flow in carbon nanotubes. *Nature* 438, 43–44. <https://doi.org/10.1038/43843a>

Thomas, J.A., McGaughey, A.J.H., 2009. Water flow in carbon nanotubes: Transition to subcontinuum transport. *Phys. Rev. Lett.* 102, 184502. <https://doi.org/10.1103/PhysRevLett.102.184502>

Wang, H., Liu, Y., Li, M., Huang, H., Xu, H.M., Hong, R.J., Shen, H., 2010. Water flow enhancement in hydrophilic nanochannels. *Nanoscale* 4, 1166–1169. <https://doi.org/10.1039/b000000x>

Wang, S., Civan, F., 2005. Modeling Formation Damage by Asphaltene Deposition During Primary Oil Recovery. *J. Energy Resour. Technol.* 127, 310. <https://doi.org/10.1115/1.1924465>

Wang, S., Feng, Q., Javadpour, F., Xia, T., Li, Z., 2015a. Oil adsorption in shale nanopores and its effect on recoverable oil-in-place. *Int. J. Coal Geol.* 147–148, 9–24. <https://doi.org/10.1016/j.coal.2015.06.002>

Wang, S., Feng, Q., Zha, M., Lu, S., Qin, Y., Xia, T., Zhang, C., 2015b. Molecular dynamics simulation of liquid alkane occurrence state in pores and slits of shale organic matter. *Pet. Explor. Dev.* 42, 844–851. <https://doi.org/10.11698/PED.2015.06.10>

Wang, S., Javadpour, F., Feng, Q., 2016a. Molecular dynamics simulations of oil transport through inorganic nanopores in shale. *Fuel* 171, 74–86. <https://doi.org/10.1016/j.fuel.2015.12.071>

Wang, S., Javadpour, F., Feng, Q., 2016b. Fast mass transport of oil and supercritical carbon dioxide

through organic nanopores in shale. Fuel 181, 741–758.

<https://doi.org/10.1016/j.fuel.2016.05.057>

Wei, M.J., Zhou, J., Lu, X., Zhu, Y., Liu, W., Lu, L., Zhang, L., 2011. Diffusion of water molecules confined in slits of rutile TiO₂(110) and graphite(0001). Fluid Phase Equilib. 302, 316–320.

<https://doi.org/10.1016/j.fluid.2010.09.044>

Xi, Z., Congli, W., 2015. Analysis of Formation Conditions of Shale Oils in the Changling Depression , Sourthern Songliao Basin 2 Forming Conditions of Shale Oil. Acta Geol. Sin. 89, 332–334.

Zendehboudi, S., Ahmadi, M.A., Mohammadzadeh, O., Bahadori, A., Chatzis, I., 2013. Thermodynamic investigation of asphaltene precipitation during primary oil production: Laboratory and smart technique. Ind. Eng. Chem. Res. 52, 6009–6031.

<https://doi.org/10.1021/ie301949c>

Zhang, Q., Su, Y., Wang, W., Lu, M., Sheng, G., 2017. Apparent permeability for liquid transport in nanopores of shale reservoirs: Coupling flow enhancement and near wall flow. Int. J. Heat Mass Transf. 115, 224–234. <https://doi.org/10.1016/j.ijheatmasstransfer.2017.08.024>

Appendix A. Partial derivative for surface diffusion (D_s)

The expression for the equivalent surface diffusion is simplified by taking its square:

$$D_s^2 = \frac{\alpha D_{s,w} + (1-\alpha) D_{s,o}}{\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}}} \quad (21)$$

The partial derivative of Eq. (21) for α is:

$$\begin{aligned}
\frac{\partial D_s^2}{\partial \alpha} &= \frac{\partial}{\partial \alpha} \left[\frac{\alpha D_{s,w} + (1-\alpha) D_{s,o}}{\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}}} \right] / \frac{\partial}{\partial \alpha} \\
&= \frac{(D_{s,w} - D_{s,o}) \left(\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}} \right) - [\alpha D_{s,w} + (1-\alpha) D_{s,o}] \left(\frac{1}{D_{s,w}} - \frac{1}{D_{s,o}} \right)}{\left(\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}} \right)^2} \quad (22) \\
&= \frac{D_{s,w} - D_{s,o}}{D_{s,w} D_{s,o}} \frac{D_{s,o} + D_{s,w}}{\left(\frac{\alpha}{D_{s,w}} + \frac{1-\alpha}{D_{s,o}} \right)^2} < 0
\end{aligned}$$

Namely, as the water-wet area becomes more significant, the equivalent surface diffusion is reduced. This regularity accords with the common sense.

Appendix B. Derivation for equivalent radius

The exact solution for the equivalent radius is derived at first, and then the rationale of the approximation is explained. The cross-section area belonging to asphaltenes S is:

$$S = \pi[R_o^2 - (R_o - h)^2] \gamma \quad (23)$$

The equivalent radius is deduced from the cross-section area for movable oil:

$$\pi R^2 + S = \pi R_o^2 \quad (24)$$

Based on Eqs. (23) and (24), the ultimate solution for R is:

$$\begin{aligned}
R &= \sqrt{R_o^2 - (2R_o h - h^2) \gamma} = R_o \sqrt{1 - (2h_r - h_r^2) \gamma} \\
&\approx R_o \sqrt{1 - 2\gamma h_r} \approx R_o \left(1 - \frac{2\gamma h_r}{2} \right) = R_o - h\gamma \quad (25)
\end{aligned}$$

Actually, the amount of asphaltenes is not significant in shale oil (h_r is negligible), thus the above approximation holds.

- (1) The effects of mixed wettability and asphaltenes on shale permeability are studied.
- (2) Wettability alteration, pore radius reduction, and viscosity increase are considered.
- (3) The differences among organic pores, inorganic pores and micro-fractures are shown.
- (4) The respective contributions of all mechanisms to flow enhancement are investigated.
- (5) Adsorption detail is important for flow in shale nanopores, not for micro-fractures.